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Chemical and Sensory Characterization of Oxidative Changes in Roasted Almonds Undergoing Accelerated Shelf Life

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Supporting Information

ABSTRACT: In almonds, there is no standard method for detecting oxidative changes and little data correlating consumer perception with chemical markers of rancidity. To address this, we measured peroxide values (PV), free fatty acid values (FFAs), conjugated dienes, tocopherols, headspace volatiles, and consumer hedonic response in light roasted (LR) and dark roasted (DR) almonds stored under conditions that promote rancidity development over 12 months. Results demonstrate that, although rancidity develops at different rates in LR and DR almonds, consumer liking was not significantly different between LR and DR almonds. Average hedonic ratings of almonds were found to fall below a designated acceptable score of 5 ("neither like nor dislike") by 6 months of storage. This did not correspond with recommended industry rejection standard of PV < 5 mequiv peroxide/kg oil and FFA < 1.5% oleic. FFAs remain well below <1.5% oleic during storage, indicating that FFAs are not a good marker of rancidity in roasted almonds stored in low humidity environments. Regression of consumer liking to concentration of rancidity indicators revealed that selected headspace volatiles, including heptanal, octanal, nonanal, 2-octenal, 2-heptanone, 2-pentylfuran, hexanal, and pentanal, had a better correlation with liking than did nonvolatile indicators.

KEYWORDS: *almond, Prunus dulcis, HS-SPME GC/MS, peroxide value, hedonic analysis*

INTRODUCTION

Sweet almonds (*Prunus dulcis*) are considered an excellent source of dietary protein, fiber, and micronutrients such as vitamin E.[1,2] Almonds are also high in unsaturated fatty acids (44−61% fat by weight) and low in moisture (less than 10% moisture w/w) and are subject to lipid oxidation and the development of rancidity during storage.[1−3] These changes can result in objectionable flavor and loss of nutritive quality.[3−6] The two most abundant fatty acids in almonds are oleic acid (18:1, 62−80%) and linoleic acid (18:2, 10−18%).[1] Unshelled raw almonds have a shelf life of approximately 12 months due to relatively high concentrations of naturally occurring tocopherols (~24 mg/100 g).[7] Shelling and processing almonds exposes nutmeats to light, heat, moisture, and oxygen, which can initiate lipid oxidation and shorten shelf life.[5] Although lipid oxidation and the development of rancidity is a persistent problem for processors, there is no completely objective chemical method for determining the onset of rancidity. To date, the industry relies on indirect measures (i.e., peroxide value [PV] and free fatty acids [FFAs]) to estimate lipid oxidation in almonds. Currently, there is no uniform or standard method for detecting oxidative changes in almonds and, more importantly, there is little data correlating consumer perception with these chemical markers of rancidity.[3,8−11]

Rancidity development can occur through hydrothermal or enzymatic hydrolysis of triglycerides (i.e., hydrolytic rancidity) and/or through the direct oxidation of fatty acids and triglycerides (i.e., oxidative rancidity).[4,5] Both processes produce a range of primary lipid oxidation products (e.g., free fatty acids, lipid hydroperoxides, and conjugated dienes and trienes) and secondary lipid breakdown products (e.g., aldehydes, ketones, alcohols, hydrocarbons, oxiranes, and lactones).[4,12] Primary oxidation assessment methods often include measuring PV and conjugated dienes (CD). Peroxide value measures the concentration of lipid peroxide, while CD assess the degree of double bond rearrangement co-occurring with the peroxidation of linoleic acid.[13] Measuring FFAs in conjunction with lipid peroxidation indicates the degree of hydrolytic rancidity. PV is the most common method used by the industry to estimate oxidation in almonds, while methods such as FFA, CD, and tocopherol quantitation are less commonly employed.[3,7,11,14,15]

Because lipid hydroperoxides are themselves imperceptible to humans, measuring peroxidation may not directly correlate with flavor changes in nuts.[12] Quantitation of headspace volatiles associated with rancidity (e.g., hexanal) has been used in many foods to better approximate development of rancid flavor and aroma.[3,5,6,16,17] However, human perception of volatiles can differ based on unique product characteristics such as surface area, moisture content, serving temperature, composition, and

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competing volatiles in the product headspace.[18] Additionally, sensory testing may not indicate whether the product is considered acceptable by the end-user, as trained sensory judges should not answer affective questions.[18] It is therefore prudent to perform hedonic analysis of food products to benchmark chemical measures with changes in consumer acceptance.[6]

A number of studies have assessed consumer acceptance in relation to chemical measures of rancidity in almonds.[3,9−11,15] Most[3,10,11,15] have focused on the effect of packaging type on consumer acceptance (and chemical markers of oxidation) during storage. For example, Mexis and Kontominas measured PV, hexanal, color, fatty acid methyl esters (FAME), and consumer acceptance to study the effects of active packaging, nitrogen flushing, and packaging material on the oxidation of whole, unpeeled raw almonds.[3] Raisi et al. evaluated the impact of packaging on PV, conjugated trienes, and hedonic ratings in ground and whole unpeeled almonds for 10 months of storage under either vacuum, 95% CO_2, or ambient atmosphere.[15] Senesi et al. measured the effect of packaging on oxygen and light permeability, storage atmosphere, and temperature on several aspects of oxidation and sensory quality of peeled whole raw almonds over 546 days of storage.[11] Though a number of studies have evaluated the relationship between packaging type, changes in oxidation indicators, and consumer acceptance, no study directly compares oxidation indictors to each other in their ability to correlate with consumer acceptance of almonds. Additionally, there exists little published literature on the volatile profile of roasted almonds during accelerated storage or the relationship between volatile profile, rancidity indicators, and consumer acceptance.[19]

Herein, we assess common indicators of lipid oxidation in almonds, including PVs, FFAs, and CD, in conjunction with headspace volatile profiles, α-tocopherol concentration, and hedonic analysis of roasted almonds to evaluate how volatile and nonvolatile oxidation indicators correlate with consumer acceptance in roasted almonds. Data from this study will allow processors to understand how well chemical markers of rancidity correlate with consumer liking during rancidity development in roasted almonds. Identifying which indicators optimally correlate with consumer liking will ensure processors do not mischaracterize and discard acceptable samples or fail to identify deteriorated samples.

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-hexanl (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). All other standards, solvents, and reagents were purchased from either Fisher Scientific Company (Fairlawn, NJ, United States) or Sigma-Aldrich Chemical Co. These included the following: HPLC/spectrophotometric grade solvents ethanol, methanol, methyl *tert*-butyl ether, glacial acetic acid, chloroform, and 2,2,4-trimethylpentane; analytical grade sodium hydroxide, hydrochloric acid (ACS certified 36.5−38% w/w), potassium iodide (99.9%), and sodium thiosulfate (99%); and analytical standards of (±)-α-tocopherol, (+)-δ-tocopherol, (+)-γ-tocopherol, volatile compounds (95−99%), and conjugated linoleic acid (99%). Exceptions included 2-(ethylthio)-ethanol (96%) (Alfa Aesar, Ward Hill, MA, United States) and 3-hydroxybutan-2-one (Supelco, Bellefonte, PA, United States).

Roasting and Storage of Samples. A 200 kg sample of dehulled, raw, Nonpareil almond kernels with skin (from the 2014 harvest year) was obtained from Blue Diamond Growers (Sacramento, CA, United States). Almonds were dry roasted in a BCO-E1 electric convection oven (Bakers Pride, Allen, TX, United States). Kernels were roasted under two different conditions: 115 ± 6 °C for 60 min and 152 ± 6 °C for 15 min to produce a "light" and "dark" degree of roast, respectively. Almonds were divided into 480 g samples and placed in a controlled atmosphere chamber (KMF 240 Constant Climate Chamber by Binder Inc. Bohemia, NY, United States). Samples were stored at 15 ± 1% relative humidity (RH) and 39 ± 1 °C for intervals of 1−12 months. Eight samples each of LR and DR almonds were randomly 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, United States) until analyzed.

Sample Preparation for Non-Sensory Analysis. Sample preparation was adapted from the method of Zhang et al.[20] A 300 g sample of LR and DR almonds were thawed and analyzed within 1 week of removing almonds from controlled storage. An approximate 50 g aliquot was removed and ground for nine 1 s pulses (Waring Laboratory Equipment, Torrington, CT, United States). The resulting powder was sieved through a 20 mesh Tyler standard screen (W.S. Tyler Industrial Group, Mentor, OH, United States). The sieved powder was weighed into 20 mL glass headspace vials (Restek Corporation, Bellefonte, PA, United States) to give 5.00 ± 0.02 g aliquots, and vials were capped. Oil was extracted from the remaining almond powder with an oil press (Carver, Inc., Wabash, IN, United States). The resulting oil was collected and transferred to a 40 mL amber borosilicate glass sample vial with a polytetrafluoroethylene (PTFE) lined, rubber faced cap (Fisher Scientific, Pittsburgh, PA, United States), flushed with nitrogen, and stored at −80 °C until analysis.

Peroxide Value, Free Fatty Acids, and Conjugated Dienes. Peroxide value of each sample was determined according to the AOCS Official Method Cd 8-53;[21] the FFA was determined according to the AOCS method Cd 3d-63,[22] and CD was determined according to AOCS method Ti la-64.[13]

Headspace Solid-Phase Microextraction (HS-SPME) GC/MS Detection of Headspace Volatiles. Headspace analysis was adapted from the method of Xiao et al.[23] Almonds were ground and sieved with a 20 Tyler sieve (W.S. Tyler), 5 ± 0.02 g of which was weighed into each 20 mL glass headspace vials (Restek Corporation). Vials were capped and crimped immediately with magnetic caps containing 3 mm PTFE-lined silicone septa (Supelco Co., Bellefonte, PA, United States) and allowed to equilibrate for at least 4 h. This equilibration period was found to produce the least relative standard deviation among native headspace compounds (see Supporting Information). All samples were run in triplicate.

To account for variations in fiber and instrument sensitivity, stable isotope external standards were run on each day of analysis. Standards were run externally (in devolatized almond matrix) rather than

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internally to avoid interference of internal standards with the natural equilibrium between the SPME fiber matrix, headspace volatiles, and volatiles in the sample matrix during extraction. In this way, the potential competition of internal standards with native compounds for adsorption sites on the SPME fiber was also avoided. Responses of external standards were used to normalize the compound peak areas observed in samples on each day of analysis to those of the first day of analysis (for sample calculations, see the Supporting Information).

The external standard was prepared as follows: 5 ± 0.02 g of ground, devolatized[23] almonds were measured into a 20 mL headspace vial into which a 200 μL glass vial insert was placed (Thomas Scientific, Swedesboro, NJ, United States). Devolatized almonds were prepared by holding ground, LR almonds under vacuum (30 mmHg) at 90 °C for at least 3 days to reduce competing native volatile compounds that might influence external standard response, as the external standard was intended to indicate fiber and instrument precision. A 0.5 μL glass capillary tube was filled with a 1000 ppm solution of methylpyrazine-d_6, hexanol-d_{13}, and octanal-d_{16} in methanol. The filled capillary tube was dropped into the 200 μL vial insert, and the headspace vial was capped and allowed to equilibrate for 2 h, which allowed the entire contents of the capillary tube to volatize and equilibrate with ground almonds. The vial was immediately analyzed after this equilibration period.

Volatiles were quantitated by comparing the extracted ion peak areas to those of a relative standard, either methylpyrazine-d_6, hexanol-d_{13}, or octanal-d_{16}. These were chosen to represent the range of structures and polarities of the most highly concentrated native headspace compounds. Relative standard curves were prepared to give final concentrations (μg/kg ground almond) in the expected concentration ranges of the native headspace compounds. A 5 μL capillary tube of methanolic standard mixture was dropped into a preplaced vial insert above 5 g of ground, devolatized roasted almonds within a 20 mL headspace vial; the vial was capped, and the system was left to equilibrate for 4 h before instrument sampling (to reflect sample preparation). The relative standard curve was prepared from the response of hexanol-d_{13} and octanal-d_{16} at concentration levels of 2000, 1000, 500, 200, 100, 40, 20, 10, and 5 μg/kg almond and the response of methylpyrazine-d_6 at 200, 100, 50, 20, 10, 4, 2, 1, and 0.5 μg/kg almond. The limits of detection (LOD) were 0.254, 1.76, and 0.407 μg/kg almond for methylpyrazine-d_6, octanal-d_{16}, and hexanol-d_{13}, respectively, while the limits of quantitation (LOQ) were 0.771, 5.33, and 1.23 μg/kg almond, respectively. These values were calculated according to eq 1:

$$\text{limit of detection or quantitation} = \frac{F\sigma}{\text{slope}} \quad (1)$$

where F is equal to 3.3 for the LOD or 10 for the LOQ, σ is the standard deviation of the y-intercept of the linear regression fitted to the standard curve, and slope is the slope of the linear regression fitted to the standard curve. The calculation for determining the relative concentration of analytes ($RC_{Analyte}$) is given in the Supporting Information

Sample handling and gas chromatography were performed using an Agilent 7890A gas chromatograph (Agilent Technologies, Santa Clara, CA, United States) equipped with a CTC Combi/PAL autosampler (CTC Analytics AG, 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 30/50 μm 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 fiber was then desorbed in a separated helium-flushed needle-heater for 5 min to prevent carryover effects. The headspace volatiles were separated using a 30 m × 0.25 mm × 0.25 μm Agilent DB-Wax column (Agilent Technologies) 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.

Mass spectrometric detection by electron impact ionization was performed by an Agilent 5975C inert XL EI/CI MSD (Agilent Technologies) with a source temperature of 230 °C and quadrupole temperature of 150 °C. 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 of certain compounds were confirmed using retention index calculation and comparison with reference values (Kovat's Index), and retention time confirmation with standards when available (Table 3). Integration was performed using Agilent MassHunter Quantitative Analysis software (v. B.07.00, Agilent Technologies).

Tocopherol Concentration by High-Pressure Liquid Chromatography (HPLC)-Fluorescence. This method was adapted from Puspitasari-Nienaber et al.[24] for the analysis of tocopherol isomers. Samples were prepared by diluting 0.200 ± 0.02 g oil in 5 mL of HPLC-grade 1:1 methanol:methyl *tert*-butyl ether (MTBE) in amber borosilicate glass vials capped with PTFE-lined caps and agitating for 20 s. Samples were filtered with 0.2 μm nylon filters (EMD Millipore, Billerica, MA, United States) prior to injection. Sample injections of 25 μL were separated on a reversed-phase YMC C30 4.6 mm i.d. × 250 mm, 5 μm polymeric column at 25 °C. Injection, solvent delivery, and fluorescence detection were accomplished by an Agilent 1200 HPLC system (Agilent Technologies). The method was optimized for purposes of separating 3 of 4 tocopherol isomers and effectively removing long-chain triglycerides and fatty acids from the column.[24] Solvent A consisted of 100% methanol, while solvent B consisted of 100% MTBE. The solvent program proceeded as follows: a 15 min linear gradient from 100% solvent A to 65:35 solvent A:B, a 3 min linear gradient from 65:35 solvent A:B to 100% solvent B, which was held for 2 min, and finally a 3 min gradient to 100% solvent A which was held for 2 min. Fluorescence detection was accomplished at an excitation and emission wavelengths of 293 and 325 nm, respectively. Pure standards of α-, δ-, and γ-tocopherol were diluted in methanol to a stock concentration of 200 mg/mL. Actual concentration of stock solutions was determined using UV−vis spectrophotometry at an absorption wavelength of 292 nm for α-tocopherol, and 298 nm for δ- and γ-tocopherol, respectively, and extinction coefficients of 75.8, 91.4, and 87.3 $\varepsilon^{1\%}$ 1 cm, respectively.[25] Working standards of 40, 20, 10, 5, 1, 0.5, 0.1, 0.05, and 0.01 ppm were created from stock solution in serial dilution to create the curve for each standard. Standard curves of α- and δ-tocopherol were found to be linear from 0.1 to 40 ppm (r^2 = 0.999), while γ-tocopherol was found to be linear from 0.1 to 10 ppm (r^2 = 0.999). According to eq 1, the LODs of α-, δ-, and γ-tocopherol were 0.025, 0.19, and 0.0038 ppm respectively, while the LOQs were 0.085, 0.063, and 0.013 ppm, respectively.

Consumer Hedonic Analysis. Ninety-nine untrained consumers between the ages of 14 and 80, who were not pregnant and consumed almonds at least once a month, were recruited in the city of Davis, California for hedonic analysis. Consumers were served samples (6−7 almonds), identified by three-digit random numbers, at room temperature. Consumers were asked to taste two almonds at a time and indicate their liking of samples by marking a nine-point hedonic scale.[16,18] Participants were given verbal and written instructions, a tray of samples, a paper ballot, and sat voluntarily at seats separated by dividers at which distilled water, an expectoration cup, and unsalted wheat crackers were provided for palate cleansing. Consumers tasted samples in a random and counterbalanced order to ensure that carry-over effects were minimized.

Statistics. Results from all analyses were analyzed with 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 age as main effects. Where appropriate, a Bonferroni correction was made to the p-value to adjust for multiple iterations of ANOVA. When significant main effects were found, Tukey's honestly significant difference posthoc testing was performed. A correlation matrix was constructed of all chemical measures and average hedonic ratings, and their Pearson's correlation r-value and p-value of correlation were calculated. Statistical analysis was performed primarily using R and R studio software, including base

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statistical analysis packages, as well as SensoMineR, plyr, dplyr, ggplot2, agricolae, and hmisc.[26]

RESULTS AND DISCUSSION

Almonds were roasted under conditions to produce LR or DR almonds and stored at 39 ± 1 °C and 15% relative humidity for 12 months. Temperature conditions were chosen to be high enough to accelerate the development of lipid peroxidation and rancidity over the typical shelf life of roasted almonds[7,27] but not so high as to alter the typical progress of rancidity.[10] Humidity levels were chosen to avoid increasing the moisture content of almonds[28] and thereby altering the texture, as this might produce an unintended negative bias in consumer perception.[29]

Rancidity development was evaluated by measuring PV, FFAs, CDs, total tocopherols, and volatile organic compounds by HS-SPME-GC/MS at 1-month intervals over the 12-month storage period. Consumer hedonic testing was performed on samples to correlate chemical markers of lipid oxidation in almonds with consumer preference.

Consumers (99) performed a hedonic rating of the LR and DR samples at 0 (control), 2, 4, 6, 8, and 10 months. ANOVA demonstrated a significant difference in liking related to the storage time of the sample, but no significant difference was found in liking related to the degree of roasting (i.e., LR or DR). The average hedonic score was highest at time 0 (7.2 ± 1.7 for DR and 7.4 ± 1.4 for LR) and decreased with the time the almonds were stored, reaching a low of 4.2 ± 2.0 and 4.7 ± 2.1 for DR and LR, respectively (Table 1 and 2). Almonds stored for 12 months were noticeably rancid and were not used to perform consumer hedonic rating. Tukey's HSD posthoc analysis revealed that, on average, consumers had a significant difference in liking between samples aged 0, 2, 4, and 6 months, while there was no significant difference found between samples aged 6, 8, and 10 months (Table 1 and 2).

Peroxide value (PV) is commonly used in the industry to indicate almond quality[8,14,15] and, in general, almonds are considered to not have undergone significant lipid oxidation if values are <5 mequiv peroxide/kg oil.[8] Herein, the initial average PV in the DR and LR almonds were 0.61 and 0.58 ± 0.04 mequiv peroxide/kg oil, respectively (Tables 1 and 2). These results are in agreement with results of Mexis et al.[9] for PV of fresh roasted almonds. PVs were found to differ significantly with relation to storage time as well as between roast level, while the correlation of PV with consumer liking had an R^2 of only 0.489 (significant at $p < 0.05$). DR almonds displayed a maximum PV between 8 and 10 months and exceeded 5 mequiv peroxide/kg oil by 5 months of storage (Table 2, Figure 1A). The PVs began to decline after 10 months and reflected expected degradation to secondary oxidation products. In contrast, the LR samples displayed overall PVs lower than those of the DR samples (Tables 1 and 2, Figure 1A), and never exceeded the 5 mequiv industry-recommended limit. Maximum PV in LR almonds was observed between 6 and 8 months (Figure 1A, Table 1). PVs for both types of almond samples had changed significantly by two months of storage.

FFAs, measured as % oleic, in both LR and DR almonds increased over the 12 months of storage (Figure 1B) and were significantly different between LR and DR almonds. Levels of FFAs correlated significantly with liking (R^2 = 0.761) at $p <$ 0.05 and differed significantly from an initial value of 0.20 ± 0.03% oleic by 2 months in DR samples and from an initial

Table 1. Average Values and Standard Deviations Resulting from Chemical Analyses and Consumer Hedonic Analysis of LR Almonds for Even Storage Times and Correlation R^2 Values of Chemical Analysis versus Mean Hedonic Score[a]

	accelerated storage time (months)						
analysis	0	2	4	6	8	10	12	correlation R^2 value
peroxide value (meq peroxide/kg oil)	0.57 ± 0.04 e	1.13 ± 0.14 d	1.38 ± 0.20 d	2.84 ± 0.02 b	2.14 ± 0.18 c	2.70 ± 0.08 b	1.26 ± 0.08 d	0.489
free fatty acid value (% oleic)	0.21 ± 0.00 d	0.25 ± 0.00 cd	0.28 ± 0.00 bc	0.31 ± 0.01 abc	0.32 ± 0.02 ab	0.36 ± 0.03 a	0.36 ± 0.03 a	0.761
conjugated dienes (%)	0.213 ± 0.000 f	0.222 ± 0.000 f	0.255 ± 0.000 cd	0.242 ± 0.003 e	0.261 ± 0.008 bc	0.267 ± 0.002 b	0.302 ± 0.001 a	0.540
α-tocopherol conc (mg/kg oil)	435 ± 4 a	424 ± 16 a	406 ± 1 abc	387 ± 3 bcd	362 ± 4 def	363 ± 32 def	334 ± 11 f	0.814
β- + γ-tocopherol conc (mg/kg)	34.3 ± 0.5 ab	34.0 ± 0.2 ab	34.1 ± 0.3 ab	32.8 ± 0.5 ab	31.9 ± 0.4 ab	33.5 ± 1.0 ab	31.7 ± 0.9 ab	0.721
δ-tocopherol conc (mg/kg)	9.38 ± 0.09 ab	8.35 ± 0.07 bc	8.68 ± 0.10 abc	7.95 ± 0.32 c	8.10 ± 0.10 c	8.61 ± 0.27 bc	8.24 ± 0.30 bc	0.625
mean consumer hedonic score	7.4 ± 1.4 a	6.6 ± 1.5 b	5.8 ± 1.55 c	4.9 ± 1.9 d	4.9 ± 2.0 d	4.7 ± 2.1 d		
mode of consumer hedonic score	8	7	6	4	4	4		

[a]Values followed by the same letter were not found significantly different from other values on the same line by Tukey's HSD testing.

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Table 2. Average Values and Standard Deviations Resulting from Chemical Analyses and Consumer Hedonic Analysis of DR Almonds for Even Storage Times and Correlation R^2 Values of Chemical Analysis versus Mean Hedonic Score[a]

analysis	accelerated storage time (months)							correlation R^2 value
	0	2	4	6	8	10	12	
peroxide value (meq peroxide/kg oil)	0.61 ± 0.04 n	2.21 ± 0.12 m	3.96 ± 0.07 l	11.36 ± 0.23 j	16.07 ± 0.53 g	16.48 ± 0.18 g	13.00 ± 0.03 i	0.489
free fatty acid value (% oleic)	0.20 ± 0.03 j	0.18 ± 0.00 i	0.37 ± 0.01 g	0.36 ± 0.01 e	0.42 ± 0.04 c	0.54 ± 0.04 c	0.57 ± 0.04 a	0.761
conjugated dienes (%)	0.216 ± 0.001 j	0.238 ± 0.001 i	0.286 ± 0.002 g	0.362 ± 0.001 e	0.464 ± 0.003 c	0.464 ± 0.002 c	0.508 ± 0.001 a	0.540
α-tocopherol conc (mg/kg oil)	444 ± 1 a	418 ± 7 ab	396 ± 2 bc	358 ± 8 de	328 ± 8 fg	277 ± 6 h	292 ± 9 h	0.814
β- + γ-tocopherol conc (mg/kg)	35.0 ± 0.1 a	34.0 ± 0.8 abcd	34.4 ± 0.5 ab	32.3 ± 0.3 cdefg	32.0 ± 0.6 efg	31.0 ± 0.1 g	31.2 ± 1.3 fg	0.721
δ-tocopherol conc (mg/kg)	9.05 ± 0.21 a	8.66 ± 0.22 ab	8.33 ± 0.47 bc	7.52 ± 0.30 d	7.98 ± 0.15 cd	8.10 ± 0.04 bcd	8.23 ± 0.20 bc	0.625
mean consumer hedonic score	7.2 ± 1.7 a	6.8 ± 1.4 b	5.8 ± 1.7 c	4.7 ± 2.0 d	4.5 ± 2.0 d	4.2 ± 2.0 d		
mode of consumer hedonic score	8	8	7	4	4	4		

[a]Values followed by the same letter were not found significantly different from other values on the same line by Tukey's HSD testing.

value of 0.21 ± 0.00% oleic by 4 months in LR samples (Tables 1 and 2). By 12 months of storage, levels of FFAs in DR and LR almonds increased to 0.57 ± 0.04 and 0.36 ± 0.03% oleic, respectively, below the industry-recommended maximum value of <1.5% oleic (Tables 1 and 2).[8]

FFA is a measure of hydrolytic rancidity occurring either by enzymatic or spontaneous hydrolysis of triglycerides.[5,14] During almond roasting, naturally occurring lipases and other enzymes that may hydrolyze triglycerides are inactivated.[14] The roasting process also reduces almond moisture content, making it less available for lipolysis, a condition maintained by the low RH of sample storage conditions. The dependence of FFA values on storage RH was demonstrated by Lin et al., who showed that whole blanched almond samples stored at 37.8 °C and 35% RH remained below 0.3% oleic for 8 months of storage, while samples stored at 65% RH had increased to 0.4% oleic, and samples stored at 85% had increased to over 0.8% oleic in the same period.[27] Additionally, unheated samples showedr increases in FFA greate than those in blanched samples, attributed to greater enzyme activity.[27] Enzyme activity and above-average humidity are of little concern if almonds are roasted and packaged under controlled atmosphere, and FFA levels may not exceed 1.5% oleic during extended storage despite increases in PV and other indicators of rancidity[27] (Tables 1 and 2). Our results and those of Lin at al.[27] indicate that the existing limit of <1.5% FFA is a more useful indicator of rancidity development and possibly compromised quality in raw almonds exposed to atmospheric moisture.

Similar to the FFA, relative changes in levels of CD were significant over the 12 months of storage (Tables 1 and 2), and levels were significantly different between roast level. CD correlated significantly with liking (R^2 = 0.540) at $p < 0.01$. Initial levels of CDs in DR and LR almonds were 0.22 ± 0.00 and 0.21 ± 0.00%, respectively. At 12 months of storage, values increased to 0.51 ± 0.00 (DR) and 0.30 ± 0.00 (LR), an increase of 135 and 41.7%, respectively (Tables 1 and 2). Significant increases were first observed at 2 months for the DR samples and at 3 months for LR samples (Tables 1 and 2).[4] CD has been found to be a good correlate of PV and indicator of lipid oxidation in soybean, sunflower, and other oils high in polyunsaturated fatty acids well as frying fats subjected to high heat.[13]

Herein, CD levels in LR and DR almonds displayed a pattern of change similar to that of FFA levels but did not correlate as well with PV (Figure 1C). CDs may not correlate well with PVs in almonds because CDs are developed from polyunsaturated fatty acids, which account for ∼10−20% of fatty acids in almonds, while fatty acid hydroperoxides measured by PV may develop from both mono- and polyunsaturated fatty acids, which together account for ∼90% of the fatty acids in almonds.[1]

Measures such as PV and CD commonly applied to liquid oil may have less predictable values in complex substrates without a continuous lipid fraction such as whole nuts.[630] CD has not been widely employed to indicate rancidity in nuts, and no recommended limit of CD in almonds currently exists. However, the sensitivity of this assay may be limiting for routine screening in an industrial setting.

Tocopherols were resolved as three peaks correlating to α-, δ-, and coeluted β- + γ-tocopherol in almond oil. All isomers were found to vary significantly over storage time, while only α-tocopherol was found to be significantly different between roast levels (Figure 1D). All isomers were found also to correlate

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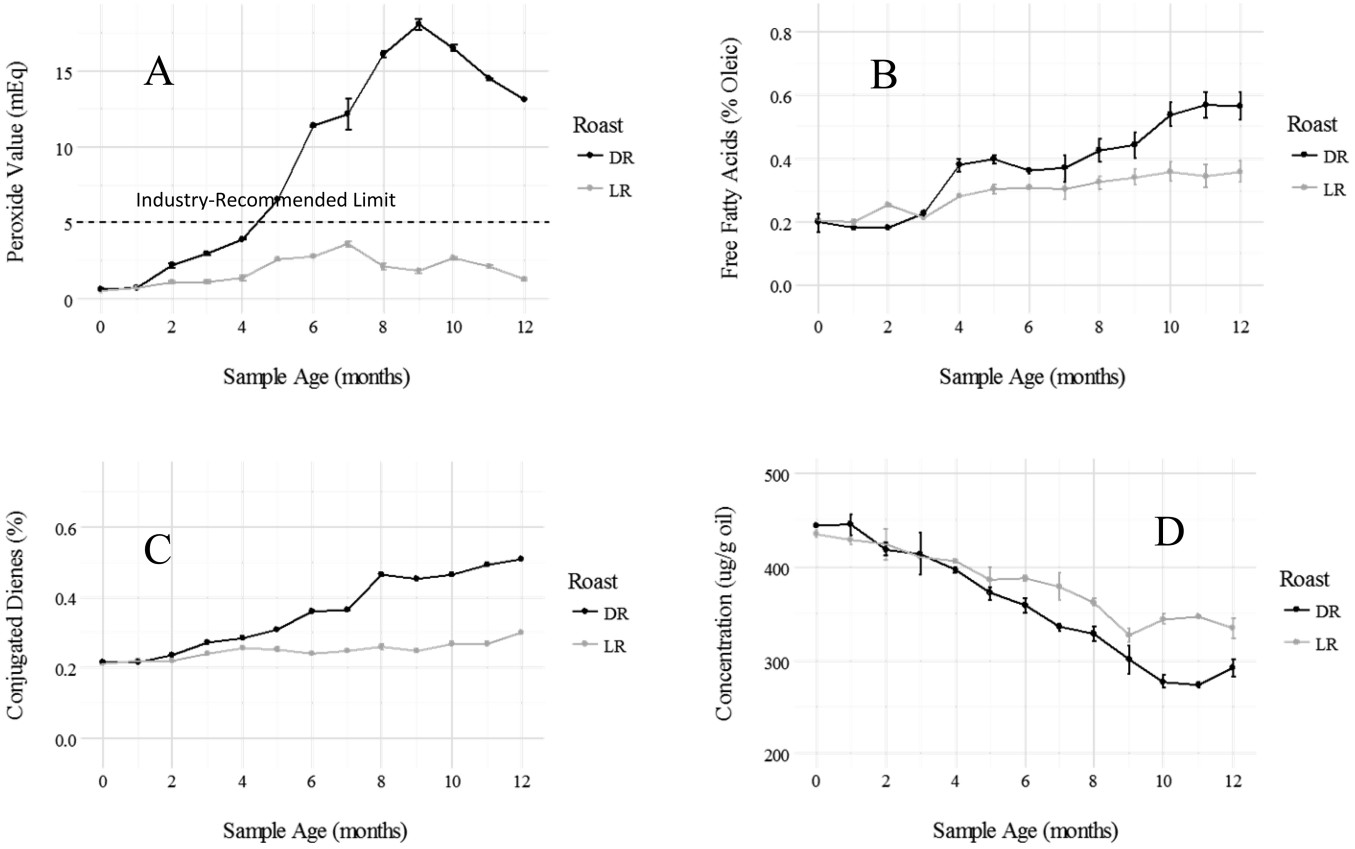

Figure 1. Peroxide value (A), free fatty acid value (B), conjugated diene value (C), and α-tocopherol concentration (D) at each month of storage time. Values for LR almonds are depicted with gray, and DR almonds are depicted with black.

significantly with consumer liking at $p < 0.01$. α-Tocopherol had the highest R^2 value at 0.814, whereas β- + γ- and δ-tocopherol had correlation R^2 values of 0.721 and 0.625, respectively. Initial average levels of α-tocopherol in DR and LR almonds were 444 ± 1 and 435 ± 4 mg/kg oil, respectively (Tables 1 and 2), and these values decreased significantly at 3 months in DR almonds and 5 months in LR almonds. After 12 months of storage, levels of α-tocopherol decreased by 34.3 and 23.2% in DR and LR almonds, respectfully; levels of β- + γ-tocopherol decreased by 7.72−10.5%, and δ-tocopherol decreased by 9.08−12.1% (Table 1 and 2).

A total of 98 volatile compounds were detected in roasted almonds over the 12 months of accelerated storage (Table 3). Fifty compounds were confirmed with authentic standards (Table 3). Tentative identities of the remaining 48 compounds were made by comparing MS spectra with the NIST 14 Library (NIST Library Search program) and calculating Kovat's retention indixes (KI) with literature values of standards chromatographed under comparable conditions.[19,23]

Sample storage time was found to have a significant effect on all volatile compounds, whereas degree of roasting was found to be significant for all but 25 of the compounds (Table 3). In general, levels of organic acids, aldehydes, and alcohols (>4 carbons in length) increased during storage, whereas alcohols with 4 or fewer carbons in length decreased. Pyrazines generally decreased over the 12 months of storage, as did ketones and esters with less than 6 carbons. Ketones and esters with 6 or more carbons increased over the course of 12 months of storage (Figures 2A−P).

Under accelerated storage conditions, heat and atmospheric oxygen promote the peroxidation and decomposition of oleic and linoleic acid.[4,17] Of the volatiles identified, several may result from oleic acid hydroperoxide decomposition, including octanal, heptanal, nonanal, octane, 2-decenal, 2-undecenal, decanal, and heptane (Table 3).[4] Cleavage of linoleic hydroperoxides can result in production of hexanal, pentanal, 1-pentanol, 2-pentylfuran, 2-octenal and 3-octen-2-one, 2-hexenal, 2,4-decadienal, 2,4-nonadienal, 2-heptenal, and 1-octen-3-ol, all of which were identified in LR and DR headspace (Table 3).[4] All volatile products of oleic and linoleic acid were found to increase over the course of storage.

Organic acids such as acetic, pentanoic, and hexanoic acid have been previously identified as possible tertiary products of lipid oxidation.[19,31] Acetic, pentanoic, and hexanoic acid were among the organic acids identified in almond headspace (Table 3). These and other acids found in almond headspace were possibly generated by the oxidation of related saturated aldehydes or autoxidation of unsaturated aldehydes such as 2,4-decadienal.[12,31]

Application of heat in low moisture food systems can instigate complex Maillard reactions which contribute characteristic flavors to many cooked foods, including nuts.[32] A variety of Maillard reaction products were identified in almond headspace, including several pyrazines, pyrroles, furans, 4-hydroxy-2,5-dimethylfuran-3-one, methanethiol, dimethyldisulfide, 2,3-pentanedione, 1-(acetyloxy)-2-propanone, 2-methylpropanal, and 2- and 3-methylbutanal (Table 3).[19,32] During Maillard reactions, 2-methylpropanal, 2- and 3-methylbutanal, and a variety of alkylpyrazines are generated by Strecker

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Table 3. Compounds Tentatively Identified and Quantitated in LR and DR Almond Headspace

compound group	volatile compound	external standard	CAS number	t_R[a] unknown	standard KI[b]	unknown KI[b]	literature KI[b] (NIST)	quant. ion[c]
organic acid	3-methylbutanoic acid[d]	hexanol-d_{13}	503-74-2	23.22	1670	1681	1680	60.1
	acetic acid[di]	hexanol-d_{13}	64-19-7	18.20	1427	1427	1429	60.1
	butanoic acid[d]	hexanol-d_{13}	107-92-6	22.37	1630	1639	1650	60.1
	heptanoic acid[d]	hexanol-d_{13}	111-14-8	28.41	1942	1948	1954	60.1
	hexanoic acid[d]	hexanol-d_{13}	106-70-7	26.39	1842	1842	1849	60.1
	nonanoic acid[d]	hexanol-d_{13}	112-05-0	31.39	2099	2101	2144	60.1
	octanoic acid[d]	hexanol-d_{13}	124-07-2	30.20	2034	2040	2038	60.1
	pentanoic acid[e]	hexanol-d_{13}	109-52-4	24.46		1744	1725	60.1
low mol. wt. alcohol[f]	3-methyl-1-butanol[d]	hexanol-d_{13}	123-51-3	11.31	1212	1212	1209	55.1
	1,2-propanediol[e]	hexanol-d_{13}	627-69-0	21.48		1592	1599	45.1
	2-hydroxypropyl acetate[e]	hexanol-d_{13}	57-55-6	21.08		1571	1579	74.1
	1-butanol[d]	hexanol-d_{13}	71-36-3	9.00	1138	1140	1145	56.1
	2,3-butanediol[dg]	hexanol-d_{13}	513-85-9	20.72	1552	1553	1542	45.1
	2-chloro-1-propanol[e]	hexanol-d_{13}	78-89-7	16.17		1364	1376	57.1
	1-chloro-2-propanol[di]	hexanol-d_{13}	127-00-4	14.68	1316	1317	1314	45.1
	2-methyl-1-propanol[di]	hexanol-d_{13}	78-83-1	7.25	1093	1086	1092	84.1
high mol. wt. alcohol[f]	1-heptanol[d]	hexanol-d_{13}	111-70-6	18.56	1441	1442	1467	70.1
	1-hexanol[d]	hexanol-d_{13}	111-27-3	15.97	1356	1357	1355	56.1
	1-nonanol[d]	hexanol-d_{13}	143-08-8	22.95	1667	1668	1661	56.1
	1-octanol[d]	hexanol-d_{13}	111-87-5	20.86	1559	1560	1553	69.1
	1-octen-3-ol[d]	hexanol-d_{13}	3391-86-4	18.43	1436	1434	1430	57.1
	1-pentanol[d]	hexanol-d_{13}	71-41-0	12.89	1259	1261	1255	55.1
	2-furanmethanol[di]	hexanol-d_{13}	98-00-0	22.83	1668	1661	1660	98.1
	3-heptanol[e]	hexanol-d_{13}	589-82-2	14.35		1307	1306	69.1
low mol. wt. aldehyde[g]	2-methylbutanal[di]	octanal-d_{16}	96-17-3	3.13	902	893	909	57.1
	2-methylpropanal[di]	octanal-d_{16}	78-84-2	2.14	818	821	819	72.1
	3-methylbutanal[di]	octanal-d_{16}	590-86-3	3.19	899	897	925	58.1
	butanal[d]	octanal-d_{16}	123-72-8	2.68	858	860	867	72.1
high mol. wt. aldehyde[g]	(*E*,*E*)-2,4-decadienal[e]	octanal-d_{16}	25152-84-5	25.69		1808	1807	81.1
	(*E*,*E*)-2,4-nonadienal[e]	octanal-d_{16}	5910-87-2	23.63		1702	1701	81.1
	(*Z*)-2-decenal[e]	octanal-d_{16}	2497-25-8	22.54		1645	1644	70.1
	(*Z*)-2-heptenal[e]	octanal-d_{16}	57266-86-1	14.86		1322	1319	83.1
	(*E*)-2-hexenal[d]	octanal-d_{16}	6728-26-3	11.36	1212	1213	1204	69.1
	(*E*)-2-nonenal[d]	octanal-d_{16}	18829-56-6	20.24	1526	1527	1530	83.1
	(*E*)-2-octenal[d]	octanal-d_{16}	2548-87-0	17.73	1411	1412	1412	70.1
	(*E*)-2-undecenal[e]	octanal-d_{16}	53448-07-0	24.63		1754	1722	70.1
	benzaldehyde[d]	octanal-d_{16}	100-52-7	19.81	1505	1507	1502	105
	decanal[d]	octanal-d_{16}	112-31-2	19.44	1487	1488	1484	57.1
	heptanal[d]	octanal-d_{16}	111-71-7	10.26	1177	1179	1174	70.1
	hexanal[di]	octanal-d_{16}	66-25-1	6.85	1068	1074	1084	57.1
	nonanal[d]	octanal-d_{16}	124-19-6	16.90	1385	1386	1380	57.1
	octanal[d]	octanal-d_{16}	124-13-0	13.93	1292	1293	1280	84.1
	pentanal[d]	octanal-d_{16}	110-62-3	4.21	985	973	984	58.1
ester	methyl acetate[di]	octanal-d_{16}	79-20-9	2.27	827	829	828	74.1
	methyl hexanoate[d]	octanal-d_{16}	142-62-1	10.41	1189	1184	1184	74.1
low mol. wt. ketone[h]	1-(acetyloxy)-2-propanone[ei]	octanal-d_{16}	592-20-1	18.50		1442	1469	74
	2,3-pentanedione[ei]	octanal-d_{16}	600-14-6	6.15		1051	1058	100.1
	2-pentanone[d]	octanal-d_{16}	107-87-9	4.21	983	972	981	86.1
	3-hydroxybutan-2-one (acetoin)[di]	octanal-d_{16}	513-86-0	13.61	1289	1283	1284	45.1
	acetone[ei]	octanal-d_{16}	67-64-1	2.16		822	819	58.1
high mol. wt. ketone[h]	2-decanone[e]	octanal-d_{16}	693-54-9	19.34		1482	1482	58.1
	2-heptanone[d]	octanal-d_{16}	110-43-0	10.15	1174	1176	1170	58.1
	2-nonanone[d]	octanal-d_{16}	821-55-6	16.78	1382	1382	1387	58.1
	2-octanone[d]	octanal-d_{16}	111-13-7	13.79	1288	1289	1297	58.1
	3-nonen-2-one[e]	octanal-d_{16}	14309-57-0	19.72		1501	1506	125.1
	3-octen-2-one[e]	octanal-d_{16}	18402-82-9	17.20		1395	1390	111.1
alkane	3-ethyl-2-methyl-1,3-hexadiene[e]	octanal-d_{16}	61142-36-7	17.33		1399	nd	67.1
	heptane[e]	octanal-d_{16}	142-82-5	1.64		684	700	71.1
	octane[e]	octanal-d_{16}	111-65-9	2.07		817	800	85.1
	styrene[i]	octanal-d_{16}	100-42-5	12.71		1255	1261	104
	toluene[i]	octanal-d_{16}	108-88-3	5.52		1032	1042	91.1

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Table 3. continued

compound group	volatile compound	external standard	CAS number	t_R[a] unknown	standard KI[b]	unknown KI[b]	literature KI[b] (NIST)	quant. ion[c]
furan	2-propylfuran[e]	2-methylpyrazine-d_6	4229-91-8	5.41		1028	1027	81.1
	2-butylfuran[d]	2-methylpyrazine-d_6	4466-24-4	8.42	1126	1122	1123	81.1
	2-pentylfuran[e]	2-methylpyrazine-d_6	3777-69-3	12.04		1235	1231	81.1
heterocycle	2-acetylpyridine[ei]	2-methylpyrazine-d_6	1122-62-9	21.59		1598	1597	78.1
	2-acetylpyrrole[d]	2-methylpyrazine-d_6	1072-83-9	28.44	1947	1949	1949	94.1
	4-hydroxy-2,5-dimethylfuran-3-one[d]	2-methylpyrazine-d_6	3658-77-3	29.44	2021	1999	1997	128.1
	furan-2-carbaldehyde (furfural)[d]	2-methylpyrazine-d_6	98-01-1	18.48	1436	1438	1455	96
	1-*H*-pyrrole[di]	2-methylpyrazine-d_6	109-97-7	19.73	1500	1502	1498	67.1
	5-methyl-2-octylfuran-3-one[e]	2-methylpyrazine-d_6	57877-72-2	25.76		1811	nd	98.1
lactone	γ-hexalactone[e]	2-methylpyrazine-d_6	695-06-7	23.55	1696	1698	1703	85.1
	δ-hexalactone[e]	2-methylpyrazine-d_6	823-22-3	25.25		1785	1770	70.1
	γ-octalactone[e]	2-methylpyrazine-d_6	104-50-7	27.51		1901	1901	85.1
	butyrolactone[ei]	2-methylpyrazine-d_6	96-48-0	22.01		1619	1626	86.1
	pantolactone[e]	2-methylpyrazine-d_6	599-04-2	29.39		1998	1998	71.1
oxirane	butyl oxirane[e]	2-methylpyrazine-d_6	1436-34-6	5.51		1031	nd	71.1
	methoxymethyl oxirane[e]	2-methylpyrazine-d_6	930-37-0	15.82		1352	nd	45.1
sulfur-containing	dimethyl disulfide[d]	2-methylpyrazine-d_6	624-92-0	6.38	1058	1058	1077	94.1
	methanethiol[e]	2-methylpyrazine-d_6	74-93-1	1.58	680	665	692	48.1
	1-methylthio-2-propanone[e]	2-methylpyrazine-d_6	14109-72-9	15.07		1328	1293	104
	ethyl 2-(methylthio)-acetate[d]	octanal-d_{16}	4455-13-4	18.16	1424	1425	1450	62.1
	4-mercapto-4-methyl-2-pentanol[e]	hexanol-d_{13}	255391-65-2	20.08	1609	1520	1535	75.1
terpene	3-carene[e]	2-methylpyrazine-d_6	29050-33-7	8.75		1133	1135	44
	α-pinene[d]	2-methylpyrazine-d_6	80-56-8	5.10	1018	1019	1026	93.1
	o-cymene[e]	2-methylpyrazine-d_6	527-84-4	13.21		1271	1272	119.1
pyrazine	2-ethyl-6-methylpyrazine[ei]	2-methylpyrazine-d_6	13925-03-6	16.64		1378	1382	121.1
	2,3-dimethylpyrazine[ei]	2-methylpyrazine-d_6	5910-89-4	15.18	1335	1332	1337	108.1
	2,5-dimethylpyrazine[d]	2-methylpyrazine-d_6	123-32-0	14.84	1320	1322	1320	108.1
	2,6-dimethylpyrazine[ei]	2-methylpyrazine-d_6	108-50-9	15.03	1324	1328	1325	108.1
	2-ethenyl-6-methylpyrazine[ei]	2-methylpyrazine-d_6	13925-09-2	19.30		1480	1488	120.1
	2-ethyl-3,5-dimethylpyrazine[e]	2-methylpyrazine-d_6	13067-27-1	18.58	1441	1443	1444	135.1
	2-ethyl-5-methylpyrazine[e]	2-methylpyrazine-d_6	13360-64-0	17.13		1393	1397	121.1
	3-ethyl-2,5-dimethylpyrazine[e]	2-methylpyrazine-d_6	13360-65-1	18.19	1425	1426	1430	135.1
	2-ethylpyrazine[ei]	2-methylpyrazine-d_6	13925-00-3	15.18	1331	1332	1337	107.1
	2-methylpyrazine[d]	2-methylpyrazine-d_6	109-08-0	13.04	1264	1266	1267	94.1
	pyrazinamide[ei]	2-methylpyrazine-d_6	98-96-4	23.87		1714	1740	80.1

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Table 3. continued

compound group	volatile compound	external standard	CAS number	t_R[a] unknown	standard KI[b]	unknown KI[b]	literature KI[b] (NIST)	quant. ion[c]
	pyrazine[ei]	2-methylpyrazine-d_6	290-37-9	11.12	1204	1206	1204	80.1
	2,3,5-trimethylpyrazine[e]	2-methylpyrazine-d_6	14667-55-1	17.13	1397	1393	1402	122.1

[a]t_R, retention time. [b]KI, Kovat's retention index based on 30m DB-Wax column; literature values were obtained from NIST Chemistry WebBook, http://webbook.nist.gov/chemistry/Quant. [c]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 ≤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 $p < 0.05$.

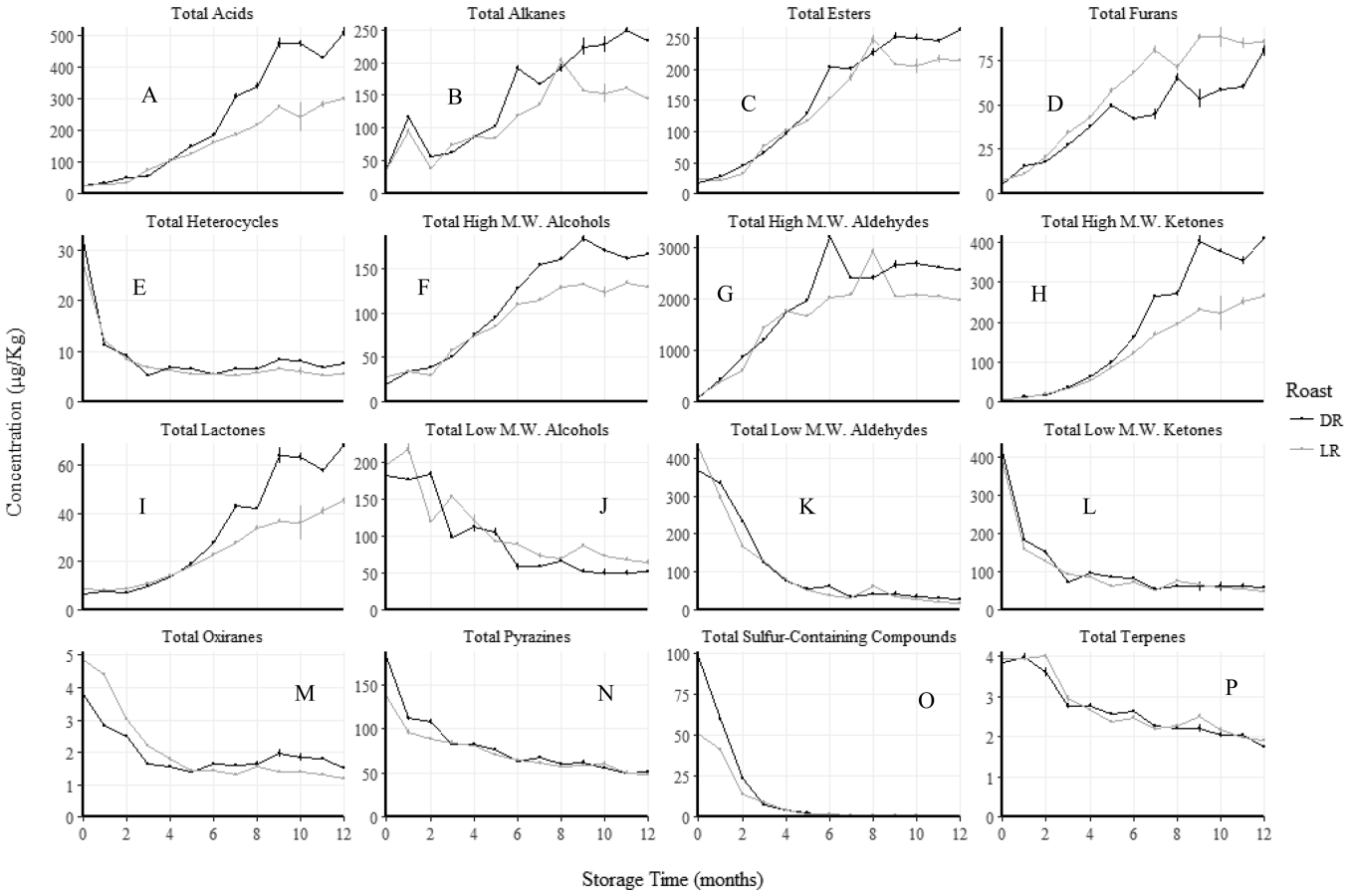

Figure 2. Concentration of summed volatiles in DR and LR almonds (μg/kg) over time, grouped by structural similarity. Compound group membership is displayed in Table 3.

degradation of leucine, isoleucine, and glycine, while furans and furanones originate from cyclization and dehydration of the Amadori compound.[32] Methanethiol and dimethyldisulfide are degradation products of methionine,[33] while both 2,3-pentanedione and 1-(acetyloxy)-2-propanone have been shown to result from heating of Maillard compound 2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one.[34]

The degree of liking of LR and DR almonds changed significantly from the control almonds by 2 months of storage. Volatile compounds for which there was a significant correlation ($p < 0.05$) and a significant positive or negative change in concentration at 2 months are shown in Table 4. Of these 47 compounds, 36 are positively correlated with consumer liking and are primarily Maillard reaction products. These compounds were found in highest concentrations in fresh roasted almonds and decreased significantly by two months of storage (Table 4).

Maillard products 2-methylpropanal and 2,3-methylbutanal have low odor thresholds[33] (Table 5) and contribute a malty, nutty aroma to foods, while alkylpyrazines contribute a roasty, nutty, and earthy aroma to peanuts[35] and have been reported in toasted almonds.[19,23,36] 2,5-Dimethylpyrazine and 2-methylpyrazine were the pyrazines found in highest abundance in fresh roasted almonds (Table 4), but ethylmethylpyrazines are reported to have low sensory thresholds (<1 μg/kg) and may also be important to toasted almond aroma. Furfural and 2-furanmethanol were identified in toasted almonds and have sweet/almond and cooked sugar aromas, respectively, but due to a high sensory threshold (>1 mg/L), furans were reported unlikely to contribute to toasted almond aroma.[36] 1-

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Table 4. Change in Concentration from 0 to 6 Months of Compounds with Significant Correlation ($p < 0.05$) to Consumer Liking[a]

name	Pearson's r value	concentration in DR almonds			concentration in LR almonds		
		0 months	2 months	6 months	0 months	2 months	6 months
positive correlations							
1,2-propanediol	0.940	127 ± 4	124 ± 4	37.4 ± 5.2	128 ± 8	75.8 ± 0.3	67.1 ± 1.4
methoxymethyl oxirane	0.939	3.70 ± 0.00	2.27 ± 0.03	0.604 ± 0.020	4.73 ± 0.25	2.80 ± 0.05	0.744 ± 0.007
2-chloro-1-propanol	0.936	0.601 ± 0.003	0.592 ± 0.007	nd	0.706 ± 0.020	0.399 ± 0.009	nd
1-chloro-2-propanol	0.927	52.1 ± 0.1	47.4 ± 0.2	11.7 ± 0.3	60.0 ± 0.3	31.5 ± 0.2	12.3 ± 0.1
2-ethylpyrazine	0.921	5.56 ± 0.08	3.45 ± 0.09	2.11 ± 0.05	5.11 ± 0.15	3.28 ± 0.04	2.28 ± 0.02
2,3-dimethylpyrazine	0.918	3.67 ± 0.04	2.36 ± 0.11	1.37 ± 0.04	3.22 ± 0.05	2.05 ± 0.02	1.54 ± 0.15
2-ethyl-6-methylpyrazine	0.908	5.41 ± 0.10	3.59 ± 0.10	2.13 ± 0.05	4.24 ± 0.17	3.16 ± 0.06	2.35 ± 0.06
toluene	0.895	4.58 ± 0.10	6.39 ± 0.27	5.32 ± 0.60	6.93 ± 0.08	4.14 ± 0.11	3.75 ± 0.19
2,5-dimethylpyrazine	0.886	80.1 ± 1.4	49.2 ± 1.3	28.8 ± 0.7	60.6 ± 1.5	40.3 ± 0.4	29.8 ± 0.7
3-methylbutanal	0.886	92.9 ± 0.8	64.4 ± 0.9	11.2 ± 0.7	114 ± 1	46.4 ± 1.0	8.28 ± 0.14
2-methylbutanal	0.884	225 ± 3	146 ± 2	23.1 ± 1.8	260 ± 5	106 ± 2	18.8 ± 0.2
3-ethyl-2,5-dimethylpyrazine	0.880	9.22 ± 0.22	7.36 ± 0.43	4.79 ± 0.07	7.06 ± 0.27	6.32 ± 0.18	5.01 ± 0.07
2,6-dimethylpyrazine	0.870	13.7 ± 0.3	8.45 ± 0.23	4.25 ± 0.05	8.7 ± 0.45	6.57 ± 0.36	4.78 ± 0.15
1-methylthio-2-propanone	0.869	2.5 ± 0.1	3.15 ± 0.01	nd	4.37 ± 0.10	5.25 ± 0.09	0.752 ± 0.022
2-furanmethanol	0.866	1.85 ± 0.04	1.34 ± 0.06	0.363 ± 0.010	1.61 ± 0.09	0.672 ± 0.008	0.497 ± 0.033
2-ethyl-5-methylpyrazine	0.861	2.11 ± 0.06	1.35 ± 0.035	0.864 ± 0.009	1.51 ± 0.03	1.18 ± 0.02	0.934 ± 0.012
2-methylpyrazine	0.855	44.6 ± 1.8	21.8 ± 0.5	12.6 ± 0.5	35.5 ± 0.6	17.4 ± 0.2	12.1 ± 0.1
pyrazine	0.842	2.49 ± 0.14	1.19 ± 0.05	0.755 ± 0.020	2.41 ± 0.04	0.984 ± 0.038	0.688 ± 0.013
methyl acetate	0.825	15.4 ± 0.1	9.35 ± 0.31	4.31 ± 0.20	20.2 ± 0.1	5.69 ± 0.19	2.52 ± 0.24
1-(acetyloxy)-2-propanone	0.820	266 ± 17	97.8 ± 3.1	41.2 ± 3.4	211 ± 7	71.7 ± 0.3	45.1 ± 0.1
pyrazinamide	0.812	1.32 ± 0.06	0.417 ± 0.011	nd	0.681 ± 0.032	0.317 ± 0.006	nd
acetoin	0.807	48.9 ± 1.2	11.3 ± 0.2	2.04 ± 0.07	44.8 ± 1.0	11.4 ± 0.2	2.22 ± 0.06
acetone	0.800	55.6 ± 0.8	33.8 ± 0.5	24.9 ± 2.7	96.4 ± 2.1	34.7 ± 1.8	14.9 ± 0.5
furfural	0.794	14.9 ± 0.4	6.43 ± 0.25	3.95 ± 0.12	15.3 ± 0.7	5.63 ± 0.14	3.78 ± 0.04
2-methylpropanal	0.792	48.1 ± 0.8	16.7 ± 0.6	2.94 ± 0.25	57.4 ± 0.8	11.8 ± 0.6	1.83 ± 0.08
methanethiol	0.783	1.32 ± 0.11	0.318 ± 0.008	0.0841 ± 0.0164	1.84 ± 0.08	0.341 ± 0.028	0.146 ± 0.006
trimethylpyrazine	0.760	13.0 ± 0.3	8.17 ± 0.35	4.93 ± 0.08	7.15 ± 0.31	6.24 ± 0.14	5.02 ± 0.08
2-methyl-1-propanol	0.746	0.44 ± 0.02	2.14 ± 0.01	0.832 ± 0.067	1.51 ± 0.02	2.01 ± 0.05	0.797 ± 0.016
pyrrole	0.727	14.0 ± 0.5	1.65 ± 0.03	0.243 ± 0.006	9.47 ± 0.15	1.62 ± 0.05	0.393 ± 0.027
2,3-pentanedione	0.721	28.6 ± 0.6	2.15 ± 0.08	0.409 ± 0.021	25.7 ± 0.7	1.96 ± 0.05	0.449 ± 0.023
4-mercapto-4-methyl-2-pentanol	0.721	5.88 ± 0.15	nd	nd	2.99 ± 0.06	nd	nd
dimethyl disulfide	0.714	0.857 ± 0.002	2.36 ± 0.103	nd	1.78 ± 0.0322	3.91 ± 0.128	0.325 ± 0.012
2-acetylpyrrole	0.713	0.821 ± 0.0168	0.530 ± 0.019	0.405 ± 0.0176	1.02 ± 0.06	0.759 ± 0.017	0.591 ± 0.016
negative correlation							
hexanoic acid	−0.900	1.05 ± 0.06	14.7 ± 3.0	128 ± 4	1.96 ± 0.32	12.3 ± 0.2	106 ± 3
pentanal	−0.902	3.92 ± 0.04	62.8 ± 0.6	241 ± 10	5.5 ± 0.1	41.3 ± 0.8	123 ± 1
hexanal	−0.902	58.0 ± 0.3	716 ± 16	2380 ± 40	77.9 ± 1.8	492 ± 9	1480 ± 10
2-pentylfuran	−0.909	4.86 ± 0.14	13.9 ± 0.2	31.6 ± 0.9	6.48 ± 0.33	16.3 ± 0.4	50.8 ± 0.4
(*E*)-2-hexenal	−0.922	nd	2.93 ± 0.17	9.81 ± 0.29	1.23 ± 0.01	2.67 ± 0.02	5.96 ± 0.11
(*Z*)-2-heptenal	−0.928	0.799 ± 0.034	6.51 ± 0.23	33.4 ± 0.6	nd	5.12 ± 0.07	20.5 ± 0.5
1-butanol	−0.931	0.542 ± 0.033	1.48 ± 0.03	5.15 ± 0.28	0.623 ± 0.006	1.05 ± 0.02	3.87 ± 0.10
3-octen-2-one	−0.934	0.465 ± 0.003	5.58 ± 0.16	30.8 ± 0.7	0.755 ± 0.049	5.6 ± 0.9	26.1 ± 0.5
styrene	−0.943	1.53 ± 0.02	3.85 ± 0.05	6.64 ± 0.44	1.79 ± 0.05	2.47 ± 0.05	5.99 ± 0.09
1-pentanol	−0.946	3.79 ± 0.06	16.8 ± 0.2	66.6 ± 1.5	6.31 ± 0.14	11.7 ± 0.1	49.4 ± 0.5
heptanal	−0.976	2.69 ± 0.06	31.5 ± 0.9	187 ± 3	3.25 ± 0.12	22.5 ± 0.3	137 ± 2

[a]Only compounds which changed significantly between 0 and 2 months of storage in both dark and light roast almonds are displayed. [b]Compound identity was confirmed with an authentic standard.

(Acetyloxy)-2-propanone was found in high abundance in fresh roasted almonds (Table 4), and similar to 2,3-pentanedione can possess a buttery or nutty aroma. The positive aroma attributes associated with these Maillard products and abundance in fresh almonds supports their positive relationship to consumer acceptance and the concurrent significant decrease in both liking and abundance of these products (Tables 1,2 and 4).

Eleven compounds in Table 4 were negatively correlated with liking and increased significantly in concentration by two months. These compounds were primarily products related to lipid oxidation and included hexanoic acid, pentanal, hexanal, 2-pentylfuran, (*E*)-2-hexenal, (*Z*)-2-heptenal, 1-butanol, 3-octen-2-one, styrene, 1-pentanol, and heptanal.[4] Aldehydes typically possess penetrating aroma characters such as grassy, cucumber,

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Table 5. Compounds Found to Have a Significant Correlation with Consumer Liking ($p < 0.05$) and an Absolute Regression Slope of >2 μg/kg Change in Concentration Per Unit Liking with Aroma Characteristics and Concentration in Almonds at 4 and 6 Months[a]

compound name	linear R^2 value	slope of conc (μg/kg) vs liking	aroma quality	aroma threshold (μg/kg)	DR 4 months	DR 6 months	LR 4 months	LR 6 months
heptanal[l,m,p]	0.952	−82.55	fatty, rancid, citrus	50[b,q]	**85.4 ± 2.0**	**187 ± 3**	**87.1 ± 0.9**	**137 ± 2**
1-pentanol[m,p]	0.894	−20.87	pungent, fermented, fruity	470[c,q]	36.9 ± 0.8	66.6 ± 1.5	34.6 ± 0.3	49.4 ± 0.5
octanal[l,p]	0.885	−93.24	citrus-like, soapy, penetrating	55[b,q]	**69.5 ± 1.5**	**158 ± 5**	**69 ± 1**	**127 ± 3**
octane[l]	0.863	−41.20	gasoline	940[d,q]	49.7 ± 1.2	114 ± 1.98	49.7 ± 0.829	69 ± 0.53
nonanal[l,p]	0.856	−72.66	cucumber, lemon peel, fatty	260[b,q]	55.5 ± 1.09	117 ± 3.9	52.5 ± 1.48	95 ± 3.02
1-heptanol[l,p]	0.852	−14.41	musty, herbal, pungent	425[e,r]	9.84 ± 0.301	21.8 ± 0.642	8.73 ± 0.155	17.3 ± 0.251
(*E*)-2-hexenal[l,p]	0.851	−2.81	penetrating, fatty, green banana	250[b,q]	5.13 ± 0.271	9.81 ± 0.292	5.28 ± 0.0326	5.96 ± 0.114
(*E*)-2-octenal[l,m,p]	0.846	−20.11	pungent, cucumber, fatty	50−125[b,q]	25.1 ± 0.36	46.5 ± 1.19	22.4 ± 0.439	29 ± 0.772
2-heptanone[p]	0.846	−68.01	fruity, blue cheese, coconut	140[e,r]	37.1 ± 0.599	107 ± 2.67	31.9 ± 0.226	78.5 ± 0.807
2-pentylfuran[n]	0.826	−19.62	green bean, metallic, vegetable	2000[b,q]	28.8 ± 0.583	31.6 ± 0.883	32.4 ± 0.349	50.8 ± 0.429
γ-hexalactone[l]	0.815	−13.50	coconut, vanilla, cream	1600[f,r]	7.66 ± 0.0919	19.3 ± 0.22	6.9 ± 0.128	14.5 ± 0.235
hexanal[l,m]	0.814	−736.91	fatty, green, grassy	75[b,q]	**1360 ± 15.9**	**2380 ± 34.6**	**1390 ± 8.25**	**1480 ± 6.5**
pentanal[l,m,p]	0.813	−73.57	fermented, bready, fruity	150[b,q]	110 ± 1.26	**241 ± 10.1**	111 ± 0.789	123 ± 0.559
hexanoic acid[p,o]	0.810	−95.96	sweaty, cheesy, goaty	700[j,q]	59.8 ± 2.11	128 ± 4.38	56.3 ± 1.22	106 ± 3.32
heptane[l]	0.769	−11.10	sweet, ethereal	250 000[g,q]	14 ± 0.225	34.2 ± 2.67	15.2 ± 0.669	18.9 ± 0.284
decanal[l,p]	0.756	−5.72	sweet, citrus, floral	75[b,q]	2.44 ± 0.139	6.1 ± 0.367	2.35 ± 0.0381	5.23 ± 0.367
1-octen-3-ol[m,p]	0.753	−11.27	mushroom, earthy, oily	1[e,r]	**7.29 ± 0.237**	**14.9 ± 0.365**	**5.75 ± 0.158**	**10 ± 0.207**
1-octanol[l,p]	0.751	−4.26	green, citrus, rose	190[e,r]	2.14 ± 0.106	4.7 ± 0.243	1.83 ± 0.0628	3.7 ± 0.131
butanal[n,p]	0.746	−7.96	cocoa, musty, malty	25[h,q]	8.59 ± 0.131	24.5 ± 1.36	7.89 ± 0.0648	9.23 ± 0.303
pentanoic acid	0.746	−21.60	sickening, putrid, rancid	280[i,r]	9.43 ± 0.385	23.2 ± 0.574	9.17 ± 0.225	19 ± 0.338
2-octanone[p]	0.695	−13.34	musty, blue cheese, mushroom	190[b,r]	4.08 ± 0.127	11.7 ± 0.0845	3.58 ± 0.114	8.96 ± 0.185
2-butyl furan[n,p]	0.662	−6.24	fruity, wine, sweet	10 000[g,q]	6.9 ± 0.948	8.7 ± 0.418	8.66 ± 0.138	14.5 ± 0.244
benzaldehyde[p,o]	0.586	−2.53	artificial almond, sweet, cherry	350[k,r]	8.79 ± 0.334	10.6 ± 0.568	9.1 ± 0.0877	8.71 ± 0.195
2-nonanone[p]	0.576	−15.57	fruity, soapy, cheese	190[b,r]	2.46 ± 0.147	8.56 ± 0.381	2.13 ± 0.0545	5.79 ± 0.263
heptanoic acid[p]	0.557	−5.96	rancid, cheesy, sweat	100[k,q]	1.13 ± 0.101	3.24 ± 0.229	1.12 ± 0.0574	2.51 ± 0.235
octanoic acid[p]	0.519	−6.68	waxy, rancid, oily	3000[j,q]	0.863 ± 0.0568	2.77 ± 0.498	0.768 ± 0.289	2.07 ± 0.359
pyrrole[p]	0.529	5.37	sweet, nutty	20 000[e,r]	0.448 ± 0.022	0.243 ± 0.006	0.63 ± 0.0117	0.393 ± 0.027
2,3,5-trimethylpyrazine	0.578	2.71	roast, peanut, hazelnut,	90[f,r]	6.42 ± 0.254	4.93 ± 0.0842	6.03 ± 0.156	5.02 ± 0.0826
2-methylpropanal[p]	0.628	20.54	fresh, aldehydic, floral,	3.4[f,q]	4.49 ± 0.0703	2.94 ± 0.247	4.35 ± 0.143	1.83 ± 0.0769
furfural[p]	0.631	4.63	sweet, almond, bread	3000[e,r]	5.2 ± 0.219	3.95 ± 0.12	4.55 ± 0.0394	3.78 ± 0.0424
acetoin[p]	0.652	18.46	sweet, buttery, creamy	800[e,r]	4.25 ± 0.105	2.04 ± 0.066	4.17 ± 0.104	2.22 ± 0.0554
methyl acetate[p]	0.681	5.96	sweet, fruity, rum	nd	4.1 ± 0.107	4.31 ± 0.196	4.3 ± 0.235	2.52 ± 0.237
2-methylpyrazine[p]	0.731	11.34	chocolate, roasty, nutty	60[e,r]	15.8 ± 0.577	12.6 ± 0.479	15.4 ± 0.199	12.1 ± 0.113
2,6-dimethylpyrazine	0.758	2.94	coffee, roasted nuts, cocoa	nd	6.09 ± 0.129	4.25 ± 0.0526	6.1 ± 0.0847	4.78 ± 0.148
2-methylbutanal[p]	0.781	83.19	fruity, chocolate, nut	10[f,q]	**43.7 ± 0.691**	**23.1 ± 1.8**	**47.9 ± 1.17**	**18.8 ± 0.159**
3-methylbutanal[p]	0.785	35.66	chocolate, nutty, malty	5.4[f,q]	**19.6 ± 1.09**	**11.2 ± 0.675**	**20.3 ± 0.63**	**8.28 ± 0.141**

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Table 5. continued

compound name	linear R^2 value	slope of conc (μg/kg) vs liking	aroma quality	aroma threshold (μg/kg)	DR 4 months	DR 6 months	LR 4 months	LR 6 months
2,5-dimethylpyrazine[p]	0.786	16.71	cocoa, roasted nut, roast beef	1700[e,r]	37.1 ± 1.17	28.8 ± 0.705	36.6 ± 0.718	29.8 ± 0.667
1-chloro- 2-propanol[p]	0.860	17.31	nd	nd	20.7 ± 0.448	11.7 ± 0.297	20.7 ± 0.0339	12.3 ± 0.0829

[a]Only compounds confirmed with authentic standards are shown. All aroma descriptors obtained from Good Scents Company (www.thegoodscentscompany.com/).[37] Bold typeface indicates that compound concentration is above the published threshold. [b]Ref 43. [c]Ref 44. [d]Ref 45. [e]Ref 36. [f]Ref 33. [g]Ref 46. [h]Ref 47. [i]Ref 48. [j]Ref 49. [k]Ref 50. [l]Recognized autoxidation product of oleic acid methyl ester, oleic acid hydroperoxide, or triolein.[4,12,43] [m]Recognized autoxidation product of linoleic acid ethyl ester, linoleic acid hydroperoxide, or trilinolein.[4,12,43] [n]Recognized autoxidation product of linolenic acid methyl ester, linolenic acid hydroperoxide, or trilinolenin.[4,12,43] [o]Possible oxidation product from oxidation of 2,4-decadienal.[12,31] [p]Compound identity was confirmed with an authentic standard. [q]Threshold in aliphatic/oil matrix. [r]Threshold in aqueous matrix.

fatty, citrus peel, fruity, and floral (Table 5). Higher alcohols possess fermentative aromas, while 3-octene-2-one contributes a mushroom and earthy character.[37] Organic acids such as hexanoic acid possess penetrating goaty, sweaty, and cheesy aromas, and 2-pentylfuran has a beany and metallic character. At a certain abundance, all of these compounds would contribute non-natural aroma to almonds and are therefore considered deleterious to almond aroma,[5] offering support to the significant negative correlation these compounds have with liking.

The significant decrease in average liking of DR and LR almonds at two months of storage and concurrent change in volatiles may offer insight into the phenomenon termed "flavor fade" in peanuts. Flavor fade is attributed to the decrease in positive sensory attributes related to roasted peanut flavor observed early in storage.[35,38,39] Reed et al.[39] and Powell et al.[35] attributed flavor fade to decreases in concentration from initial values of certain pyrazines, as most pyrazines have an inherent nutty or roasted aroma and have been attributed to the main flavor of peanuts.[35] Warner et al., however, attributed the flavor fade of stored peanuts to a masking effect of increases in lipid oxidation aldehydes such as pentanal, hexanal, heptanal, octanal, and nonanal because pyrazine concentrations were found not to differ significantly during the storage period.[38] Results from our study indicate that flavor fade in almonds, as indicated by consumer liking, may be a combination of decreases in abundance of compounds associated with fresh roasted product such as pyrazines and other Maillard products and concurrent increases in lipid oxidation products.

By 6 months of storage, almonds received average hedonic ratings below 5 ("neither like nor dislike") (Tables 1 and 2). Some groups have used hedonic ratings at or below 5 to create an acceptability limit for product acceptance and chemical indicators of rancidity.[9,40] PVs for dark roasted samples and light roasted samples at 6 months of storage were 11.36 and 2.84 mequiv peroxide/kg oil, respectively. Currently, acceptable limits for PV are <5 mequiv peroxide/kg oil, and unacceptable PV levels in dark roasted samples would have precluded this consumer acceptability limit.[8] In LR almonds, however, PV at 6 months was only 2.84 and remained below the <5 mequiv peroxide/kg oil benchmark for the duration of the study. Raisi et al. also observed PVs below 5 mequiv peroxide/kg oil in whole, raw almonds with consumer hedonic ratings below 5 on a 9-point scale.[15]

Senesi et al. found that acceptance ratings decreased below 5 on a 9-point hedonic scale when PVs ranged from 1.1−1.32 mequiv O_2, and FFA ranged from 4.09−6.70% oleic in whole, peeled almonds stored under vacuum at 20 °C.[11] However, at the point that hedonic scores were below 5 in DR and LR samples, FFAs were only 0.36 and 0.31% oleic, respectively (Tables 1 and 2). Harris et al. observed similar FFA values in diced, roasted almonds at the point that consumer hedonic scores fell below 5 on a 9-point scale (0.30% oleic).[10] The results of our study suggest that the current industry limits of PV < 5 mequiv peroxide/kg oil and FFA < 1.5% oleic do not correspond with consumer liking (average hedonic score below 5 on a 9-point scale).

Concentration of headspace volatiles has been used to more directly assess perceptual changes in flavor and to supplement rancidity indicators such as PV, FFA, and CD.[6,9,41] For example, hexanal is frequently detected in tree-nut products subjected to oxidation and is widely considered a good indicator of oxidation.[3,9,41,42] To examine which headspace

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volatiles may best correlate with consumer liking and therefore serve as an effective indicator of rancidity in accordance with consumer acceptance, average liking was regressed to relative concentrations of confirmed headspace compounds (Table 5). Table 5 indicates that many of the measured headspace compounds are strongly and significantly correlated with liking ($p < 0.05$) and are better correlated with liking than PV, CD, and FFAs. Criteria for choosing an optimal indicator may include: a compound widely detected in almond headspace, a compound for which standards are widely available and affordable, and a compound for which there is a large change in concentration per unit change in degree of liking, as this would allow for changes in concentration to be detected across a range of method precision and sensitivity.

Using this criteria, heptanal, octanal, nonanal, 2-heptanone, hexanal, pentanal, and hexanoic acid, in order of correlation value, are optimal indicators of rancidity. Each of these compounds are widely recognized products of lipid oxidation and display a change of at least 50 μg/kg per unit change in liking (Table 5). Furthermore, heptanal, octanal, nonanal, hexanal, pentanal, and hexanoic acid had similar concentrations in both LR and DR almonds at four months of aging, indicating that these indicators are robust to processing differences during early rancidity development (Table 5). Though heptanal, octanal, and nonanal display a degree of correlation with average consumer liking closer than that of hexanal, hexanal changed by a much greater concentration per unit change in liking (737 μg/kg), making this indicator especially effective in situations where a detection method is less precise and thus less sensitive to changes in headspace volatile concentration over time.

To identify which volatile compounds negatively correlated with consumer liking were responsible for decreases in liking of roasted almonds at four and six months, concentration of volatiles in almond samples were compared to the published sensory threshold (Table 5). Multiple compounds were found at levels above the sensory threshold in LR and DR almonds stored for four months (heptanal, octanal, hexanal, and 1-octen-3-ol) and DR almonds stored for six months (heptanal, octanal, hexanal, 1-octen-3-ol, and pentanal) (Table 5, bold typeface). These compounds have aroma characteristics such as rancid, penetrating, soapy, grassy, fatty, and fungal and are the most plausible contributors to undesirable flavor changes associated with oxidative rancidity and associated decreases in liking of samples.

The results of this study indicate that certain headspace volatiles correlate better with consumer liking than rancidity indicators such as PV, FFA, and CD (Tables 1–4). For PV and FFA, the recommended industry rejection standard of PV < 5 mequiv and FFA < 1.5% oleic were not effective in rejecting our samples before the consumer acceptance scores dropped below 5 in the case of FFA for either light or dark roasted samples and PVs in light-roasted samples. PV in LR almonds never exceeded 4 mequiv peroxide/kg oil for the duration of the study, while PV in DR almonds exceeded 16 mequiv peroxide/kg oil. Therefore, PV rejection thresholds should be refined to reflect differences in development of PVs resulting from differences in almond processing. In addition, the results of this work and other studies indicate that FFAs in heated almond samples remain at low levels during storage in low humidity (Tables 1 and 2).[10,11] The rejection threshold of FFA < 1.5% oleic may be best suited for raw almonds exposed to ambient humidity rather than roasted almonds.

Headspace volatiles such as heptanal, octanal, nonanal, and hexanal displayed good correlation with consumer liking across samples tested and displayed a large degree of concentration change per unit change in hedonic score. Concentration limits for these volatiles are not currently established for almond samples, and limits in acceptable concentration may be unique to individual processing establishments according to desired product characteristics and consumer acceptance. Further investigation should be done to establish whether these indicators correlate well with consumer acceptance under less extreme storage or packaging conditions and across different processing variables.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.6b05357.

Includes preliminary data on headspace volatile equilibration, sample calculations of external standardization, and concentrations of quantitated tentatively identified and verified compounds in all almond samples for each sampling period (PDF)

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■ ABBREVIATIONS USED

PV, peroxide value; FFA, free fatty acid value; CD, conjugated dienes; LR, light roasted; DR, dark roasted; PTFE, polytetrafluoroethylene; MTBE, methyl-*tert*-butyl-ether; HS-SPME, headspace solid-phase microextraction; ANOVA, analysis of variance; MANOVA, multivariate analysis of variance

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