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Effect of Drying Moisture Exposed Almonds on the Development of the Quality Defect Concealed Damage

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ABSTRACT: Concealed damage (CD), is a term used by the nut industry to describe a brown discoloration of kernel nutmeat that becomes visible after moderate heat treatments (e.g., roasting). CD can result in consumer rejection and product loss. Postharvest exposure of almonds to moisture (e.g., rain) is a key factor in the development of CD as it promotes hydrolysis of proteins, carbohydrates, and lipids. The effect of drying moisture-exposed almonds between 45 to 95 °C, prior to roasting was evaluated as a method for controlling CD in roasted almonds. Additionally, moisture-exposed almonds dried at 55 and 75 °C were stored under accelerated shelf life conditions (45 °C/80% RH) and evaluated for headspace volatiles. Results indicate that drying temperatures below 65 °C decreases brown discoloration of nutmeat up to 40% while drying temperatures above 75 °C produce significant increases in brown discoloration and volatiles related to lipid oxidation, and nonsignificant increases in Amadori compounds. Results also demonstrate that raw almonds exposed to moisture and dried at 55 °C prior to roasting, reduce the visual sign of CD and maintain headspace volatiles profiles similar to almonds without moisture damage during accelerated storage.

KEYWORDS: *Prunus dulcis, concealed damage, drying, nonpareil: GC/MS, volatiles, Maillard reaction, Amadori compounds*

INTRODUCTION

California is a world leader in the production of almonds (*Prunus dulcis*), with an estimated annual production of >800 000 ton in 2014−2015.[1] In wet harvest years (i.e., if it rains while almonds are on the ground), a considerable problem for the almond industry is a defect called concealed damage (CD). CD is a brown discoloration of the kernel interior (nutmeat) that appears in some almonds only after moderate to high heat treatment (e.g., blanching, roasting, etc.). Almonds with CD have no visible defects on the exterior of the raw kernel (i.e., surface of whole almond beneath the skin) or on the surface of whole roasted kernel.[2] CD is frequently associated with bitter flavor(s) that can result in immediate consumer rejection.[3]

In previous studies we demonstrated that postharvest kernel moisture ≥8% is a key factor in the development of CD in raw almonds, and is accelerated with increasing storage temperature.[4] In typical commercial practices, if almonds become wet (i.e., while on the ground), they are left in the field to dry in windrows to a kernel moisture content of <6%.[3] Temperatures in windrows can range from ambient to 70 °C.[5] Almonds are then stored in stockpiles until they can be processed.[3] During this stage and especially during a rainy season, almonds may also be exposed to extra moisture. In this case, almonds are typically dried at the hulling/shelling facility using batch dryers. Unhulled almonds are loaded into the batch dryer, and heated air (often 54 °C or higher depending on the processor) is blown upward through the almonds. Depending on the initial moisture content, nuts may remain in the dryer for 6 to 10 h.[3] In extreme cases, wet almonds may be held in the dryer for >24 h.[3]

To date, there is little information available evaluating relationships between initial kernel moisture, drying time, and drying temperature on the incidence of CD in almonds.[6,7] However, almonds exposed to moisture for extended periods of time demonstrate higher levels of reducing sugars, protein degradation, and lipid oxidation.[3,4,6] These chemical changes can increase precursor availability for nonenzymatic or Maillard browning reaction which is thought to cause the discoloration observed in almonds with CD. These chemical changes may also result in reduced stability of almonds during storage by promoting early rancidity development (i.e., the oxidation of lipids).[4] Pearson[6] was the first to recognize that drying wet almonds prior to roasting had the potential to reduce CD by decreasing levels of free reducing sugars. Additionally, Pearson[7] demonstrated that drying temperature could affect the incidence of CD by drying almonds that were soaked in water for either 30 or 60 min. In Pearson's study, almonds were soaked and held at a constant relative humidity of 95% at 22 °C for 12 or 60 h, respectively, and subsequently dried at either 55 or 110 °C. Almonds dried at 110 °C displayed 44% CD, whereas the almonds dried at 55 °C had 1.2% CD. These results suggest that lower drying temperatures may decrease the incidence of CD in almonds exposed to postharvest moisture.

Chemical changes related to moisture exposure in almonds may promote early rancidity development and decreased shelf life.[4] To date, there are no studies evaluating this relationship. Like almonds, pistachio nuts[8] and macadamia nuts[9] contain a

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Table 1. Final Moisture Content, Drying Time, CIELab Color Values, Reducing Sugar Content (g/100 g Almonds Dry wt), Protein Content (g/100 g Almonds Dry wt), Amadori Product Content (ΔOD/g Protein Dry wt), and % Concealed Damage (CD) for Almonds Dried at Different Temperatures[a]

ME almonds	moisture content after drying (%)	drying time (hours)	L[b]	a[b]	b[b]	% concealed damage	reducing sugar (g/100 g almonds dry wt)	Amadori compounds (ΔOD/g protein dry wt)
not dried	9.4(0.4)		67.47(0.23)[b]	5.36(0.83)[a]	22.00(0.53)[a,b]	33(4)[c]	0.346(0.056)[a]	0.825(0.041)[a]
dried @ 45 °C	5.4(0.0)	11.5	72.81(0.28)[a]	4.56(0.40)[a]	19.97(0.34)[c,d]	19(4)[d]	0.443(0.076)[a]	0.582(0.302)[a]
dried @ 55 °C	4.8(0.1)	9	72.61(0.16)[a]	4.75(0.05)[a]	20.21(0.35)[c,d]	21(2)[c,d]	0.398(0.054)[a]	0.945(0.001)[a]
dried @ 65 °C	5.2(0.1)	8	72.73(0.62)[a]	4.51(0.45)[a]	19.15(0.52)[d]	23(1)[c,d]	0.433(0.000)[a]	0.924(0.083)[a]
dried @ 75 °C	4.4(0.0)	7	72.03(0.09)[a]	5.04(0.01)[a]	19.84(0.13)[c,d]	59(6)[a,b]	0.476(0.015)[a]	1.211(0.109)[a]
dried @ 85 °C	5.2(0.2)	4	68.56(0.04)[b]	5.60(0.17)[a]	20.99(0.23)[b,c]	71(2)[a]	0.413(0.060)[a]	1.764(0.804)[a]
dried @ 95 °C	4.8(0.0)	3	68.31(0.63)[b]	5.39(0.35)[a]	22.49(0.13)[a]	54(3)[b]	0.366(0.090)[a]	1.525(0.244)[a]

[a]Values represents mean (± SD) of duplicate samples (note: different letter in the same column means significant difference $p < 0.05$). [b]ME: Almonds were exposed to moisture for 24 h to reach an internal moisture content of ca. 8−9% before drying.

high amount of unsaturated fatty acids making them prone to hydrolytic and oxidative rancidity. The unsaturated fatty acids can experience additional oxidation or secondary reactions resulting in the production of volatile compounds including: aldehydes, ketones, acids, alcohols, hydrocarbons, lactones, and esters. Many of these compounds result in the off-odors associated with rancidity development in nuts[11] which will affect consumer acceptance. It has been proposed that accelerated storage of seeds over several days at high temperature and high humidity is a good predictor for shelf life.[10] Seeds that deteriorate at a high rate in these conditions will do also in long-term storage under normal conditions.

The specific objectives of this study were to determine: (1) if drying wet almonds (i.e., those with an internal kernel moisture content of >8%) to ∼5% moisture, prior to roasting, can aid in controlling CD, and (2) if these almonds experience an increase in lipid oxidation that could compromised shelf life. To achieve this, reducing sugars, Amadori compounds, and headspace volatile compounds were measured in moisture-exposed almonds that were dried over a range of temperatures (45−95 °C) that a processor might use.

MATERIALS AND METHODS

Chemicals and Reagents. All reagents were of analytical grade. Octanal-d_6, 2-methylpyrazine-d_6, and *n*-hexyl-d_{13} alcohol were used as stable-isotope internal standards and were purchased from C/D/N Isotopes Inc. (Quebec, Canada). Saturated alkanes standard (C_7−C_{40}; 1000 μg/mL in hexane) was purchased from Supelco Analytical (Bellefonte, PA, USA). Nitro Blue Tetrazolium, potassium hexacyanoferrate (II), copper sulfate pentahydrate, and albumin (from bovine serum) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Streptomycin sulfate was purchased from Acros (New Yersey, USA). Sodium citrate, sodium carbonate anhydrous, potassium thiocyanate, sodium phosphate dibasic, sodium phosphate monobasic, and ammonium sulfate were purchased from Fisher Scientific (Pittsburgh, PA, USA). HEPES was purchased from USB corporation (Cleveland, OH, USA). Bradford reagent was purchased from Biorad (CA, USA). Authentic standards of 2-methyl-1-propanol, hexanal, heptanal, octanal, nonanal, furfural, decanal, furfuryl alcohol, and 1-nonanol were obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI, USA). Authentic standards of 2-methyl-1-butanol, 3-methyl-1-butanol, 1-hexanol, 1-octen-3-ol, pyrrole, benzaldehyde, benzyl alcohol, 2-phenylehtyl alcohol, and 2,3-butanediol were obtained from Sigma-Aldrich (St. Louis, MO, USA). Authentic standard of 1-butanol was obtained from Acros Organics (Thermo Fisher Scientific Inc., Waltham, MA, USA).

Experimental Design. *Influence of Moisture.* Shelled almonds (i.e., raw almond kernels, 50 lbs var. Nonpareil) were supplied by Baldwin Minkler Farms (Orland, CA) in May 2015. For each drying condition (given below), two vessels (e.g., 500 mL glass jars) containing one hundred kernels each were exposed to moisture. A moisture content inside the vessels of ∼8−9% was achieved by spraying ca. 9 g of water onto the almonds. The vessels were closed and placed under temperature control in incubators (Thermo Scientific, Marietta, OH) at 45 ± 2 °C for 24 h to induce the development of CD.[4] The individual vessels were removed from the oven and subsamples were evaluated to confirm the final moisture content gravimetrically. The remaining kernels were dried at either 45, 55, 65, 75, 85, or 95 °C for different amount of time (see Table 1) until reaching a final moisture of <6% using a convection oven (Thermo Scientific, Marietta, OH). These samples were evaluated for moisture gravimetrically, percentage CD based upon established CIELab color values,[4] reducing sugars, protein content, Amadori compounds, and volatile analysis by HS-SPME GC/MS. In addition, a positive control was prepared which consisted of two vessels each containing one hundred almond kernels which were exposed to moisture in a convection oven for incubation (Thermo Scientific, Marietta, OH) at 45 ± 2 °C for 24 h to induce the development of CD. The positive control corresponded to moisture-exposed almonds without a drying treatment. A negative control included almonds not exposed to moisture and incubated under the same conditions of 45 ± 2 °C for 24 h.

Influence of Storage. Almond kernels were exposed to a moisture content of ∼8−9% in a as described above. Almonds were then dried at 55 or 75 °C to a moisture content of <6%. After drying, 100 kernels were stored under accelerated conditions at 45 °C/80% RH (Constant Climate chamber model KMF240, Binder, NY). After 2, 5, 7, 14, 21, and 28 days of storage, samples corresponding to each drying temperature were randomly selected from the climate chamber and analyzed for volatiles by HS-SPME GC/MS.

Percentage Concealed Damage (Whole Kernel). The percentage CD was measured in almond kernels using a previous reported colorimetric method[4] in which a L color value of <71 is used to classify almonds with CD.

Moisture Determination. The moisture content was determined gravimetrically by drying homogenized[4] almond samples (∼1 g) at 95−105 °C under vacuum for 48 h. Moisture was determined in duplicate, and the results were averaged.

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CIE Lab Color Values. Approximately 3 g of raw ground almond, after moisture exposure and drying, was used to measure the color using a ColorFlex spectrophotometer (HunterLab, Reston, VA). The color values L* (lightness), a* (redness/greenness), and b* (yellowness/blueness), according to the CIE Lab color scale, were recorded using a port size of 1.25 in. with D65 optical sensor and 10° angle of vision. Measurement were done in duplicate.

Measurement of Reducing Sugars. Reducing sugar content was measured using the quantitative Benedict's method.[12] Solution A consisting of sodium citrate (100 g), sodium carbonate anhydrous (32.5 g), and sodium thiocyanate (62.5 g) was dissolved in 400 mL of Milli-Q water (Millipore, USA). Solution B consisting of copper sulfate pentahydrate (9 g) was dissolved in 50 mL of distilled water. Solution A and B were mixed and 0.13 g of potassium hexacyanoferrate (II) was added and then diluted to 500 mL. For colorimetric analysis, 35 mL of this solution was diluted with 100 mL distilled water (diluted QBR). For quantitation of reducing sugars, a standard curve was prepared by mixing 1 mL of glucose (0−1.09 mg/mL) with 1 mL of diluted QBR and placed in boiling water for 5 min. Samples were subsequently filtered through 0.20 μm Nylon membrane (Millex-GN, Merck Millipore, Ireland) and transferred to a 1 mL cuvette and absorbance read at 735 nm (PharmaSpec UV-1700 UV−vis Spectrophotometer, Shimadzu, Japan).

A 1 mL aliquot of hexane was added to a 200−250 mg sample of ground almond in 2 mL centrifuge tube. After vortexing for 30 s and centrifuging at 8000 rpm for 6 min, the hexane layer was removed and 1 mL of distilled water was added. Then, samples were shaken at 300 rpm for 60 min at room temperature, vortexing every 15 min. Next, vials were centrifuged at 8000 rpm for 6 min and supernatant was filtered through glass wool. 200 μL of the filtered solution was diluted to 1 mL with distilled water and 1 mL of diluted QBR was added. Samples were placed in boiling water for 5 min. Samples were next filtered (0.20 μm Nylon membrane, Millex-GN, Merck Millipore, Ireland) and transferred to a 1 mL cuvette and absorbance read at 735 nm. (PharmaSpec UV-1700 UV−vis Spectrophotometer, Shimadzu, Japan). Measurement were performed in duplicate.

Measurement of Protein Content and Amadori Compounds. A 100 mg sample of ground almonds was taken and 1 mL of hexane was added to a 2 mL centrifuge tube. After vortexing for 30 s and centrifuging at 8000 rpm for 6 min, the hexane layer was removed and 1.2 mL of phosphate buffer (50 mM, pH 7.2) was added. Samples were then shaken at 300 rpm for 60 min at room temperature, vortexing every 15 min. Next, 200 μL of 10% streptomycin sulfate (50 mM HEPES, pH 7.2) was added and the vials were centrifuged at 13000 rpm for 15 min and supernatant was filtered through glass wool. Almond protein was precipitated with ammonium sulfate (0.50 g/mL). After centrifuging at 13000 rpm for 15 min, the precipitated proteins were redissolved in 1 mL of phosphate buffer (50 mM, pH 7.2). Extracted proteins were used for the determination of protein content and Amadori compounds.[13]

For protein content, a standard curve using bovine serum albumin (BSA) from 0−20 μg/mL was prepared. A 100 μL aliquot of each standard solution or extracted protein solution was mixed with 5 mL of Bradford[14] reagent and absorbance read at 595 nm (PharmaSpec UV-1700 UV−vis Spectrophotometer, Shimadzu, Japan). Measurements were done in duplicate.

The content of Amadori compounds was measured using the nitro blue tetrazolium (NBT) method.[13] Briefly, a 1 mL aliquot of NBT solution (0.5 mM NBT in 100 mM sodium carbonate pH 10.3) was added to 100 μL of extracted proteins and incubated at 40 °C in a water bath. Absorbance was read at 550 nm after 10 and 20 min of incubation (PharmaSpec UV-1700 UV−vis Spectrophotometer, Shimadzu, Japan). Amadori compounds were expressed as ΔOD/g protein dry basis.[13] Measurements were done in duplicate.

Measurement of Volatile Compound Using HS-SPME GC/MS. Volatiles were analyzed using a previously reported method.[4] Briefly, ground almond (200−250 mg) was added to a 2 mL crimp top vial with 1 μL mixture of internal standard (25.7 μg/mL octanal-d_6, 18.9 μg/mL 2-methylpyrazine-d_6, and 50.6 μg/mL *n*-hexyl-d_{13} alcohol) and sealed with an aluminum seal (PTFE/Silicone liner, Fisherbrand, Fisher Scientific, USA). The samples were incubated for 15 min at room temperature (25 ± 2 °C). Samples were exposed to a previously conditioned 1 cm 50/30 μm DVB/CAR/PDMS solid phase micro extraction (SPME) fiber (Supelco, Inc., Bellefonte, PA) over the headspace (HS) of the sample for 30 min at room temperature (25 ± 2 °C). The SPME fiber was immediately injected for 10 min into a Hewlett-Packard 6890 series gas chromatography (GC) system coupled with HP 5973 mass selective detector (MS; Agilent Technologies, Palo Alto, CA). An Agilent DB-Wax column (30 m length, 0.25 mm ID, 0.25 μm film) was used to separate compounds. The oven temperature program started with an initial setting of 40 °C for 1 min, followed by a ramp of 5 °C/min to 180 °C, then 10 °C/min to 210 °C with a hold time of 3 min. The injector temperature was set at 240 °C. Helium was used as the carrier gas at a flow at 0.7 mL/min. MS transfer line temperature was set at 250 °C. The temperatures of MS quadruple and MS source were 150 and 230 °C respectively. Total ion chromatograms (TICs) were collected scanning from m/z 30 to 180 at a rate of 2.48 scans/sec.

Identification and Relative Quantitation. Volatile compounds were identified by comparing MS spectra and retention times with those of authentic standards when available. Volatile compounds without authentic standards were tentatively identified by comparing the Kovats' retention indexes (K.I.) and/or mass spectrum, with those reported in the NIST Mass Spectral Search Program (version 2.0 a) with >80% as a cutoff to match compounds. The K.I.s were calculated from the retention times of C_7−C_{40} *n*-alkanes.

Relative quantitation of each volatile compound was performed by comparing the total peak area at of each compound to the total peak area of one of three internal standards (i.e., octanal-d_{16}, 2-methylpyrazine-d_6, and *n*-hexyl-d_{13} alcohol, for aldehydes, pyrazines, and alcohols, respectively). Relative concentration was determined using the following equation according to Hopfer et al.[15] and Baek et al.:[16]

$$\text{Relative Concentration}\left(\frac{ng}{g}\right) = \frac{\left(\frac{\text{Peak Area}}{\text{Internal Standard Peak Area}}\right)}{\text{Sample Weight}} \times \text{Internal Standard Added}$$

Statistical Analysis. All statistical analyses were performed using R and R studio (version 0.98.1102). All data sets were tested for significance (p-value <0.05) using Analysis of Variance (ANOVA) with Tukey test as a post hoc analysis.

RESULTS AND DISCUSSION

Previous studies have demonstrated that almonds exposed to >8% moisture prior to roasting have increased levels of CD.[4] Herein, almonds were exposed to moisture to reach an internal average moisture content of ca. 8−9% before drying. Kernels were subsequently dried to ca. 5−6% moisture to determine if drying kernels, prior to roasting, would reduce visual and chemical signs of CD. Almonds with a CIE L color value <71 were classified as having CD as this was found to correlate to visual discoloration over >50% of the kernel surface.[4] In almonds with an internal kernel moisture content of 9.4 ± 0.4% but not dried (moisture exposed [ME] control), 33 ± 4% of the kernels displayed CD (Table 1). ME almonds dried at temperatures of 45, 55, or 65 °C displayed a decrease of 19, 21, and 23% in CD, respectively. Conversely, ME almonds dried at 75, 85, and 95 °C exhibited increases of 59, 71, and 54% in CD, respectively. These results demonstrate that drying ME almonds at or below 65 °C can reduce the visible sign of CD (i.e., brown discoloration) whereas drying above 75 °C will increases the visual signs of CD. Pearson et al.[7] (1998) observed a similar trend in almonds soaked for either 30 or 60 min in water and then held at 95% RH for as long as 60 h to

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induce the development of CD. When these almonds, which achieved a moisture content of 44%, were dried at 110 °C, 44.4% of the almonds developed visible CD whereas when dried at 55 °C, only 1.2% of the almonds developed CD. In these studies, CD was estimated using a photographic method. Similar results were obtained by Prichavudhi et al.[17] for the reduction of internal browning in macadamia nuts exposed to moisture content using lower drying temperatures.

The color values obtained for almonds after ME and subsequently drying at different temperatures is given in Table 1. The ME almonds with no drying present an L* value of 67.47, a* value of 5.36, and a b value of 22.00. The L* values increased significantly (mean 72.72; $p < 0.05$) with drying temperatures between 45−75 °C. The b* values also increased significantly with drying temperatures of 85 and 95 °C ($p < 0.05$) however no significant difference was found for a* color values. At drying temperatures above 85 °C the L*, a*, and b* color values did not differ significantly from the ME control almonds ($p > 0.05$). Changes in the color values L*, a*, and b* are related with the formation of pigments during drying due to nonenzymatic Maillard reactions.[18] In the initial stage of the Maillard reaction, an amino compound reacts through a nucleophilic attack to the carbonyl group of a reducing sugar, leading to the formation of a Schiff's base which further reacts and rearranges to an Amadori compound. Amadori compounds are precursors for flavors and off-flavors formed during thermal processing of food. They have been detected in dehydrated fruits, such as in dried figs, dried apricots, prunes, and dates.[19]

To evaluate the contribution of Maillard reactions in almonds at these drying temperatures, reducing sugars and Amadori compounds were measured. No significant differences ($p > 0.05$) were found in reducing sugars between ME control almonds (0.346 ± 0.056 g/100 g almonds dry wt.) and ME and dried almonds between 45−95 °C (range from 0.366 ± 0.090 to 0.476 ± 0.015 g/100 g almonds dry wt.) (Table 1).

An apparent increase in Amadori compounds was observed in ME almonds that were dried between 55−95 °C (Table 1). The levels of Amadori compounds decreased (29%) in ME almonds dried at 45 °C relative to the ME control almonds. Whereas, drying almonds at 55 and 65 °C resulted in an 15% and 12% increase in Amadori compounds. At the higher drying temperatures of 75, 85, and 95 °C an increase of 47, 114, and 85% was observed, respectively. A similar trend was obtained by Eichner et al.[20] in carrots. For example, drying carrots to a final moisture content of 6% at 60, 90, and 110 °C resulted in an increase in Amadori compounds of 280% (90 °C) and 468% (110 °C) when compared with the concentration obtained at 60 °C. The concomitant increase in Amadori compounds with drying temperature is attributed to the increase in the activation energy of the Maillard reaction due to a decrease in the water content.[20]

To evaluate if sugar hydrolysis contributes to Maillard reactions, a correlation analysis was made between reducing sugar and Amadori compounds (Figure 1). Data indicate that the two parameters are moderately correlated ($r = -0.404$). Similar results were obtained by Murthy et al.[21] where the correlation was less significant between the content of glucose and Amadori products. Zhang et al.[22] (2011) previously reported that the content of reducing sugars (i.e., fructose + glucose) for Nonpareil almonds was 0.355 g/100 g. Considering that the content of reducing sugar did not change significantly during drying results suggest that color changes that occur with drying are not necessarily related to only

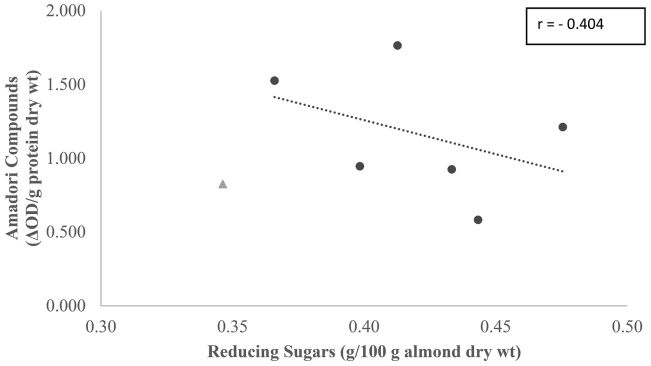

Figure 1. Correlation between reducing sugar and Amadori compounds in almonds dried between 45 and 95 °C (▲: CD).

carbohydrate/protein reactions. An alternative reaction may be happening during drying of ME almonds that leads to the development of the brown pigment after heat treatment. Hidalgo et al.[23] demonstrated that lipid oxidation byproducts, such as carbonyls compounds, mainly aldehydes, may also interact with amino acid residues to produce brown pigments. Almonds are composed of 40−60% lipids,[24] which could oxidize and degrade into multiple carbonyl and dicarbonyl compounds. Therefore, volatile compound profiles were also measured in all samples to identity the role of lipid oxidation in the development of CD in ME almonds.

Using NIST libraries and Kovats index values, 41 volatiles were measured in raw ME almonds and in ME and dried almonds (Table 2). Compounds identified include alcohols (18), aldehydes (9), lactones (2), ketones (5), furan (1), furanone (1), pyrrole (1), sulfur-containing compounds (2), a terpene (1), and an organic acid (1). The volatile compounds identified are similar to the volatiles reported previously for almonds.[4,25,26]

The volatile compounds identified in ME control almonds and in ME and dried almonds (45−95 °C) are summarized in Table 3. Because 40−60% of the almond kernel weight is derived from lipids, primary oleic acid (C18:1, 70−80%) and linoleic acid (C18:2, 20−30%),[24] increases in the decomposition of fatty acids with drying temperature would be expected.[9] The decomposition of fatty acids will result in the generation of alcohols, aldehydes, ketones, and other products.[23] Table 3 shows that, overall, volatile compounds related to fatty acid decomposition increase with drying temperature. For example, levels of short chain alcohols, such as 1-propanol, increase between 45−65 °C and levels of total 2,3-butanediol increases as temperature increases; whereas levels of long chain alcohols (i.e., 2-pentanol, 1-hexanol, heptanol, and 1-nonanol) decrease with temperature. Significant increases were observed for several aldehydes (e.g., hexenal, nonanal); especially at temperatures above 75 °C. Hexanal is a common oxidation product of linoleic acid and it has been related with rancid off-flavors.[27] Increases were observed for the lactones at drying temperatures above 75 °C. Sulfur related compounds increased significantly with drying with all temperature. Drying between 45 and 75 °C decreased levels of acetic acid significantly whereas drying at temperatures above 85 °C produced increases in acetic acid. Acetic acid comprises a secondary product of the oxidation of oleic acid.[25] Significant differences ($p < 0.05$) in 3-hydroxy-2-butanone and 1-hydroxy-2-propanone were observed in samples dried above 85 °C. These ketones are products of lipid oxidation.[28]

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Table 2. HS-SPME-GC/MS Identification of Volatiles in Raw (var. Nonpareil) Before and After Drying

volatile compounds	KI	standard KI	literature KI[a]	internal standard[b]
pinene[e]	1029		1032	hexyl-d_{13} alcohol
1-propanol[e]	1046		1037	hexyl-d_{13} alcohol
hexanal[c]	1081	1086	1084	octanal-d_{16}
2-methyl-1-propanol[c]	1095	1096	1099	hexyl-d_{13} alcohol
3-methoxy-2-butanol[e]	1110			hexyl-d_{13} alcohol
2-pentanol[e]	1122		1118	hexyl-d_{13} alcohol
1-butanol[c]	1145	1147	1145	hexyl-d_{13} alcohol
3-methyl-hexanal[e]	1182			octanal-d_{16}
heptanal[c]	1184	1186	1183	octanal-d_{16}
2-methyl-1-butanol[c]	1208	1209	1208	hexyl-d_{13} alcohol
3-methyl-1-butanol[c]	1210	1210	1205	hexyl-d_{13} alcohol
2-pentyl-furan[e]	1231		1240	octanal-d_{16}
3-methyl-3-buten-1-ol[e]	1249			hexyl-d_{13} alcohol
1-pentanol[e]	1252	1251	1255	hexyl-d_{13} alcohol
dihydro-2-methyl-3(2H)-furanone[e]	1262	-	1260	octanal-d_{16}
3-hydroxy-2-butanone[e]	1284	1281	1287	octanal-d_{16}
octanal[c]	1288	1289	1287	octanal-d_{16}
1-hydroxy-2-propanone[e]	1297		1284	octanal-d_{16}
S-ethyl ethanethioate[e]	1331			hexyl-d_{13} alcohol
6-methyl-5-hepten-2-one[e]	1337		1339	octanal-d_{16}
1-hexanol[c]	1355	1356	1354	hexyl-d_{13} alcohol
2-hydroxy-3-pentanone[e]	1358		1361	octanal-d_{16}
4-hydroxy-4-methyl-2-pentanone[e]	1362		1366	octanal-d_{16}
nonanal[c]	1393	1394	1394	octanal-d_{16}
3-(methylthio)-1-propanol[e]	1452			hexyl-d_{13} alcohol
1-octen-3-ol[c]	1451	1452	1456	hexyl-d_{13} alcohol
heptanol[c]	1457	1458	1453	hexyl-d_{13} alcohol
furfural[c]	1460	1461	1466	octanal-d_{16}
acetic acid[e]	1467		1471	hexyl-d_{13} alcohol
decanal[c]	1498	1499	1495	octanal-d_{16}
pyrrole[c]	1513	1514	1512	2-methylpyrazine-d_6
benzaldehyde[c]	1521	1521	1522	octanal-d_{16}
1-octanol[c]	1560	1560	1565	hexyl-d_{13} alcohol
dihydro-2(3H)-furanone (γ-butyrolactone)[e]	1613		1647	octanal-d_{16}
phenylacetaldehyde[e]	1621		1623	octanal-d_{16}
furfuryl alcohol[c]	1630	1630	1659	hexyl-d_{13} alcohol
1-nonanol[c]	1632	1632	1624	hexyl-d_{13} alcohol
5-ethyldihydro-2(3H)-Furanone (γ-hexalactone)[e]	1651		1694	octanal-d_{16}
benzyl alcohol[c]	1859	1859	1865	hexyl-d_{13} alcohol
2-phenylethyl alcohol[c]	1886	1897	1908	hexyl-d_{13} alcohol
total 2,3-butanediol[c,d]				hexyl-d_{13} alcohol

[a]KI, Kovats' indices. Values were obtained from either http://www.flavornet.org/f_kovats.html, http://www.pherobase.com/database/kovats/kovats-index.php, http://www.odor.org.uk/, or http://webbook.nist.gov/chemistry/name-ser.html. [b]Internal standard used for relative quantitation. [c]Compounds verified with authentic standards. [d]Corresponds to the sum of the two isomers. [e]Compounds "tentatively identified" on the basis of their MS spectra and MS fragmentation pattern.

Results suggest that volatiles related with lipid oxidation increase with drying temperature especially above 75 °C. Pearson[6] reported a similar trend in water soaked almonds and after drying at 55 and 110 °C where the refractive index of almond oil was used as a marker of lipid oxidation. When comparing the refractive index of normal almonds (no moisture exposure, no drying) and water soaked almonds, a significant decrease in oil refractive index was obtained in the soaked almonds indicating that fatty acid oxidation occurred. After drying, the refractive index showed a significantly lower refractive index in almond oil from samples dried at 110 °C as compared with 55 °C, suggesting increased lipid degradation as drying temperature increases.

Pyrrole, phenylacetaldehyde, and furfural were present only in samples dried above 85 °C. Pyrrole and phenylacetaldehyde are produced via the Maillard reaction and Strecker degradation during roasting.[29,30] The thermal degradation of sugars produces furan-containing compounds such as furfural.[29] Our results show that drying temperature above 85 °C promotes the development of Maillard-related compounds as well as lipid oxidation.

To further evaluate if lipid oxidation byproducts contribute to Maillard reactions, a correlation analysis was made between total aldehydes (e.g., hexanal, heptanal, octanal, nonanal, and decanal) and Amadori compounds (Figure 2). Total aldehydes exhibited a strong correlation with the content of Amadori compounds (r = 0.838). Similar results (r = 0.881) were

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Table 3. Effect of Drying at Different Temperatures on Volatile Profiles in Almonds Exposed To Conditions Leading To CD[a]

volatile	drying temperature						
	not dried	45 °C	55 °C	65 °C	75 °C	85 °C	95 °C
Alcohols							
1-propanol	33.1(2.6)^{c}	97.4(11.6)^{a,b}	118.8(22.4)^{a}	116.5(0.5)^{a}	83.4(4.8)^{a,b}	76.4(14.2)^{a,b,c}	64.6(6.4)^{b,c}
2-methyl-1-propanol	39.7(6.2)^{b}	48.2(3.1)^{a,b}	46.8(3.3)^{a,b}	45.9(3.9)^{a,b}	41.6(1.6)^{b}	69.7(8.9)^{a}	62.3(10.8)^{a,b}
3-methoxy-2-butanol	4.9(0.9)^{b}	8.6(0.2)^{a}	7.5(1.3)^{a,b}	6.6(0.8)^{a,b}	4.4(0.2)^{b}	6.3(0.9)^{a,b}	5.1(0.8)^{b}
2-pentanol	7.9(1.6)^{b}	13.5(0.3)^{a}	12.6(0.8)^{a,b}	11.8(1.6)^{a,b}	9.8(0.9)^{a,b}	11.3(2.5)^{a,b}	8.6(0.8)^{a,b}
1-butanol	6.9(0.5)^{c}	12.1(1.1)^{a,b}	11.8(0.5)^{a,b}	11.9(0.1)^{a,b}	14.3(1.8)^{b,c}	9.9(1.5)^{b,c}	8.8(1.0)
2-methyl-1-butanol	29.4(1.2)^{b}	44.5(2.6)^{a}	40.9(1.7)^{a,b}	36.2(4.1)^{a,b}	29.2(2.5)^{b}	42.8(4.1)^{a}	39.6(3.4)^{a,b}
3-methyl-1-butanol	73.0(14.9)^{a}	84.9(8.0)^{a}	82.4(1.3)^{a}	72.6(6.7)^{a}	85.3(14.1)^{a}	95.5(15.6)^{a}	74.8(9.5)^{a}
3-methyl-3-buten-1-ol	3.8(2.6)^{a}	3.0(0.1)^{a}	2.7(0.1)^{a}	2.9(0.2)^{a}	5.4(1.0)^{a}	6.9(0.8)^{a}	5.1(1.0)^{a}
1-pentanol	18.1(0.0)^{a}	16.5(0.4)^{a,b}	16.1(1.4)^{a,b,c}	12.5(1.7)^{c,d}	10.7(0.5)^{d}	14.2(0.9)^{b,c,d}	16.2(0.7)^{a,b,c}
1-hexanol	146.6(17.0)^{a}	94.0(0.8)^{b}	89.8(5.1)^{b}	79.5(4.4)^{b,c}	64.5(2.7)^{b,c}	67.1(7.2)^{b,c}	54.6(0.9)^{c}
1-octen-3-ol	5.1(0.5)^{a}	1.5(0.1)^{b,c}	1.5(0.2)^{b,c}	1.7(0.2)^{b,c}	1.4(0.3)^{c}	1.9(0.1)^{b,c}	3.0(0.8)^{b}
heptanol	4.9(0.5)^{a}	4.0(0.1)^{a,b}	3.8(0.5)^{a,b}	3.4(0.3)^{b,c}	2.3(0.0)^{c}	2.2(0.2)^{c}	2.2(0.0)^{c}
1-octanol	4.2(0.0)^{a}	1.8(0.2)^{b,c}	1.8(0.3)^{b,c}	1.8(0.2)^{b,c}	1.3(0.2)^{c}	1.6(0.0)^{b,c}	2.3(0.4)^{b}
furfuryl alcohol	0.7(0.2)^{c}	0.8(0.0)^{b,c}	0.8(0.1)^{c}	0.7(0.1)^{c}	0.6(0.0)^{c}	1.3(0.3)^{b}	2.0(0.1)^{a}
1-nonanol	9.3(2.8)^{a}	8.0(2.1)^{a}	7.6(1.2)^{a,b}	7.0(0.5)^{a,b,c}	2.0(0.4)^{b,c}	2.2(0.1)^{b,c}	1.6(0.4)^{c}
benzyl alcohol	2.4(0.5)^{a}	2.2(0.2)^{a}	2.3(0.4)^{a}	1.4(0.2)^{a}	1.4(0.2)^{a}	2.0(0.0)^{a}	1.9(0.5)^{a}
2-phenylethyl alcohol	4.3(0.0)^{a,b}	4.4(0.5)^{a}	4.5(0.4)^{a}	2.8(0.1)^{b}	3.4(0.1)^{a,b}	4.5(0.3)^{a}	4.4(0.7)^{a}
total 2,3-butanediol	232.2(59.8)^{b,c}	109.3(17.3)^{c}	131.6(28.6)^{c}	163.2(8.4)^{c}	207.4(46.6)^{c}	397.4(31.7)^{a,b}	429.2(66.7)^{a}
Total Alcohols	**626.5**	**554.7**	**583.3**	**578.4**	**568.4**	**813.2**	**786.3**
Aldehydes							
hexanal	21.1(9.8)^{c}	12.4(1.6)^{c}	14.2(2.9)^{c}	22.9(0.3)^{c}	58.6(22.9)^{b,c}	88.0(16.7)^{a,b}	133.2(24.8)^{a}
3-methyl-hexanal	2.2(1.2)^{c}	1.7(0.8)^{c}	1.7(0.1)^{c}	2.0(0.1)^{c}	4.2(1.2)^{b,c}	6.1(0.8)^{a,b}	8.3(1.5)^{a}
heptanal	1.5(0.9)^{b}	0.0(0.0)^{b}	0.0(0.0)^{b}	0.0(0.0)^{b}	0.0(0.0)^{b}	0.0(0.0)^{b}	4.8(0.9)^{a}
octanal	2.0(0.7)^{a,b,c}	1.5(0.6)^{b,c}	0.8(0.0)^{c}	1.5(0.4)^{b,c}	2.0(0.1)^{a,b,c}	2.8(0.1)^{a,b}	3.7(0.9)^{a}
nonanal	58.8(14.8)^{a,b}	22.0(6.6)^{c}	22.8(0.3)^{c}	26.9(0.4)^{b,c}	33.2(1.7)^{b,c}	53.2(0.3)^{a,b,c}	75.2(17.3)^{a}
furfural	0.0(0.0)^{c}	0.0(0.0)^{c}	0.0(0.0)^{c}	0.0(0.0)^{c}	0.0(0.0)^{c}	0.9(0.0)^{b}	2.7(0.0)^{a}
decanal	3.2(1.2)^{a}	2.1(0.4)^{a}	1.7(0.0)^{a}	2.4(0.3)^{a}	1.6(0.1)^{a}	2.5(0.1)^{a}	3.3(0.9)^{a}
benzaldehyde	1.9(0.7)^{c}	5.4(0.1)^{b,c}	7.0(2.0)^{b}	7.8(1.7)^{a,b}	8.8(1.0)^{a,b}	11.4(0.4)^{a}	6.8(0.2)^{b}
phenylacetaldehyde	0.0(0.0)^{c}	0.0(0.0)^{c}	0.0(0.0)^{c}	0.0(0.0)^{c}	0.0(0.0)^{c}	1.5(0.6)^{b}	3.7(0.1)^{a}
Total Aldehydes	**90.7**	**44.8**	**48.2**	**63.5**	**108.4**	**166.4**	**241.7**
Lactones							
dihydro-2(3H)-furanone (γ-butyrolactone)	15.2(1.3)^{b}	14.4(0.9)^{b}	15.9(0.2)^{b}	14.7(1.7)^{b}	14.7(0.2)^{b}	21.9(3.3)^{a,b}	24.2(3.3)^{a}
5-ethyldihydro-2(3H)-Furanone (γ-hexalactone)	4.8(0.0)^{a}	4.7(0.1)^{a,b}	4.3(0.1)^{a,b}	3.6(0.1)^{b}	3.6(0.4)^{b}	4.2(0.5)^{a,b}	4.3(0.4)^{a,b}
Total Lactones	**20**	**19.1**	**20.2**	**18.3**	**18.3**	**26.1**	**28.5**
Terpene							
pinene	12.0(0.1)^{b,c}	17.5(1.3)^{a}	15.2(1.2)^{a,b}	18.1(1.4)^{a}	14.4(1.4)^{a,b}	11.5(1.0)^{b,c}	9.5(1.3)^{c}
Furan							
2-pentyl-furan	2.7(0.1)^{a}	3.3(0.1)^{a}	2.6(0.1)^{a}	2.9(0.0)^{a}	3.1(0.3)^{a}	3.6(0.6)^{a}	4.0(0.6)^{a}
Furanone							
dihydro-2-methyl-3(2H)-furanone	0.0(0.0)^{b}	0.0(0.0)^{b}	0.0(0.0)^{b}	0.0(0.0)^{b}	0.0(0.0)^{b}	0.0(0.0)^{b}	4.8(0.9)^{a}
Ketones							
3-hydroxy-2-butanone	2.1(0.5)^{b,c}	1.8(0.1)^{c}	2.0(0.3)^{c}	3.4(0.3)^{b,c}	3.9(0.4)^{b,c}	7.4(0.0)^{b}	34.5(3.4)^{a}
1-hydroxy-2-propanone	11.7(2.5)^{b}	11.2(1.2)^{b}	11.6(0.4)^{b}	14.2(0.6)^{b}	10.5(1.8)^{b}	13.6(1.6)^{b}	67.9(5.1)^{a}
6-methyl-5-hepten-2-one	7.8(2.7)^{b}	8.3(0.2)^{b}	9.0(0.2)^{b}	8.8(0.1)^{b}	5.9(1.0)^{b}	12.7(0.3)^{a,b}	18.7(4.6)^{a}
2-hydroxy-3-pentanone	0.0(0.0)^{b}	0.0(0.0)^{b}	0.0(0.0)^{b}	0.0(0.0)^{b}	0.0(0.0)^{b}	0.0(0.0)^{b}	2.5(0.4)^{a}
4-hydroxy-4-methyl-2-pentanone	1.1(0.4)^{a}	4.6(1.1)^{a}	4.6(3.1)^{a}	2.8(1.7)^{a}	8.1(3.2)^{a}	4.7(3.2)^{a}	3.1(1.1)^{a}
Total Ketones	**22.7**	**25.9**	**27.2**	**29.2**	**28.4**	**38.4**	**126.7**
Sulfur							
S-Ethyl ethanethioate	2.2(0.1)^{e}	4.5(0.1)^{d}	5.5(0.1)^{c,d}	6.0(0.7)^{c,d}	7.4(0.4)^{b,c}	8.1(0.9)^{a,b}	10.1(0.6)^{a}
3-(methylthio)-1-propanol	27.3(2.9)^{e}	59.2(5.5)^{d}	74.7(8.5)^{c,d}	80.4(9.1)^{c,d}	89.5(1.5)^{c}	124.6(13.5)^{b}	166.2(2.3)^{a}
Total Sulfur	**29.5**	**63.7**	**80.2**	**86.4**	**96.6**	**132.7**	**176.3**
Organic Acid							
acetic acid	103.6(37.4)^{b,c}	42.7(0.3)^{c}	42.2(3.7)^{c}	43.5(5.5)^{c}	75.0(16.0)^{c}	183.7(35.5)^{a,b}	251.8(26.8)^{a}
Pyrrole							
pyrrole	0.0(0.0)^{c}	0.0(0.0)^{c}	0.0(0.0)^{c}	0.0(0.0)^{c}	0.0(0.0)^{c}	0.5(0.1)^{b}	0.9(0.1)^{a}

[a]Values represent mean (±SD) of duplicate based on dry wt. basis (*different letter in the same row means significant difference $p < 0.05$).

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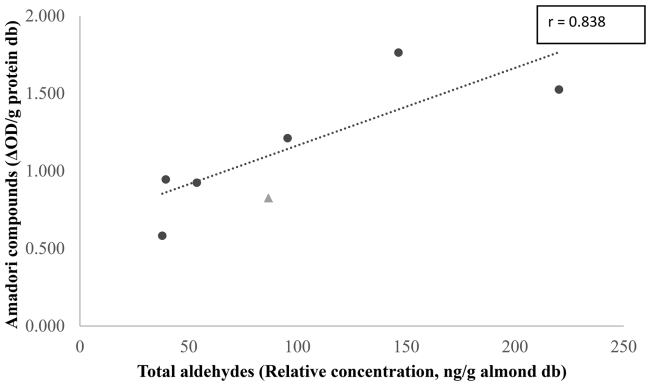

Figure 2. Correlation between total aldehydes and Amadori compounds in almonds dried between 45 and 95 °C (▲: CD).

obtained by Murthy et al.[21] between the content of TBA-reactive products and the content of Amadori products in seed axes of mungbean (*Vigna radiata* Wilczek). A correlation between total ketones and Amadori compounds (data not shown) exhibited a moderate correlation (r = 0.506). The results suggest that the secondary products of lipid oxidation (e.g., aldehydes and other dicarbonyls compounds such as ketones) participate in the formation of Amadori compounds under these conditions. During lipid oxidation hydroperoxides are formed which can be degraded to ketones and aldehydes which will react with amino acids in proteins. Total alcohols and Amadori compounds showed a strong correlation (r = 0.874, data not shown). Alcohols, such as 1-propanol and 1-hexanol, do not directly participate in the Maillard reactions.[18]

Postharvest moisture exposure is known to promote lipid oxidation and consequent formation of lipid oxidation byproducts such as carbonyls compounds.[31] Although drying almonds reduces the visual sign of CD, the oxidative damage is still present. The extent that this may influence shelf life stability and flavor are not known. Therefore, in a preliminary study, ME almonds dried at 55 and 75 °C were stored under accelerated conditions (45 °C, 80% RH) for 28 days. Overall, the volatile profile was characterized by compounds related with lipid oxidation. Similar results were reported by Zacheo at al[31] in almond seed storage at 20 °C/80% RH. Here the lipid content decreased during accelerated aging as well as the content of linoleic and linolenic acids suggesting that fatty acid oxidation had occurred. The seeds also presented high levels of malondialdehyde; a common product of lipid peroxidation of fatty acids.

Figures 3, 4, and 5 show levels of select volatiles during the course of accelerated storage. After 1 week, significant differences ($p < 0.05$) were observed between control (raw almonds, no drying, no moisture exposure with an initial moisture content of 3.9 ± 0.2%) and dried samples in the levels of 3-methyl-1-butanol, acetic acid, and total 2,3-butanediol (Figure 3). Significant differences ($p < 0.05$) were obtained in levels of butyrolactone between almonds dried at 75 °C and control almonds dried at 55 °C after 5 days (Figure 5). After 2 weeks, no significant difference was observed in the level of butyrolactone (Figure 5) between almonds dried at 55 °C and the control. There was no significant difference ($p > 0.05$) in levels of aldehydes (i.e., hexanal, heptanal, octanal, nonanal, and decanal; Figures 3 and 4) between the control and almonds dried at 55 °C after 1 week of storage. In fact, at 2 weeks, the relative concentration of all aldehydes (Figures 3 and 4) in almonds dried at 55 °C were lower than levels found in the control and almonds dried at 75 °C. These results suggest that drying ME almonds at a temperature at or below 55 °C results in volatile profiles similar to almonds not exposed to moisture, with significant reductions in levels of aldehydes associated with

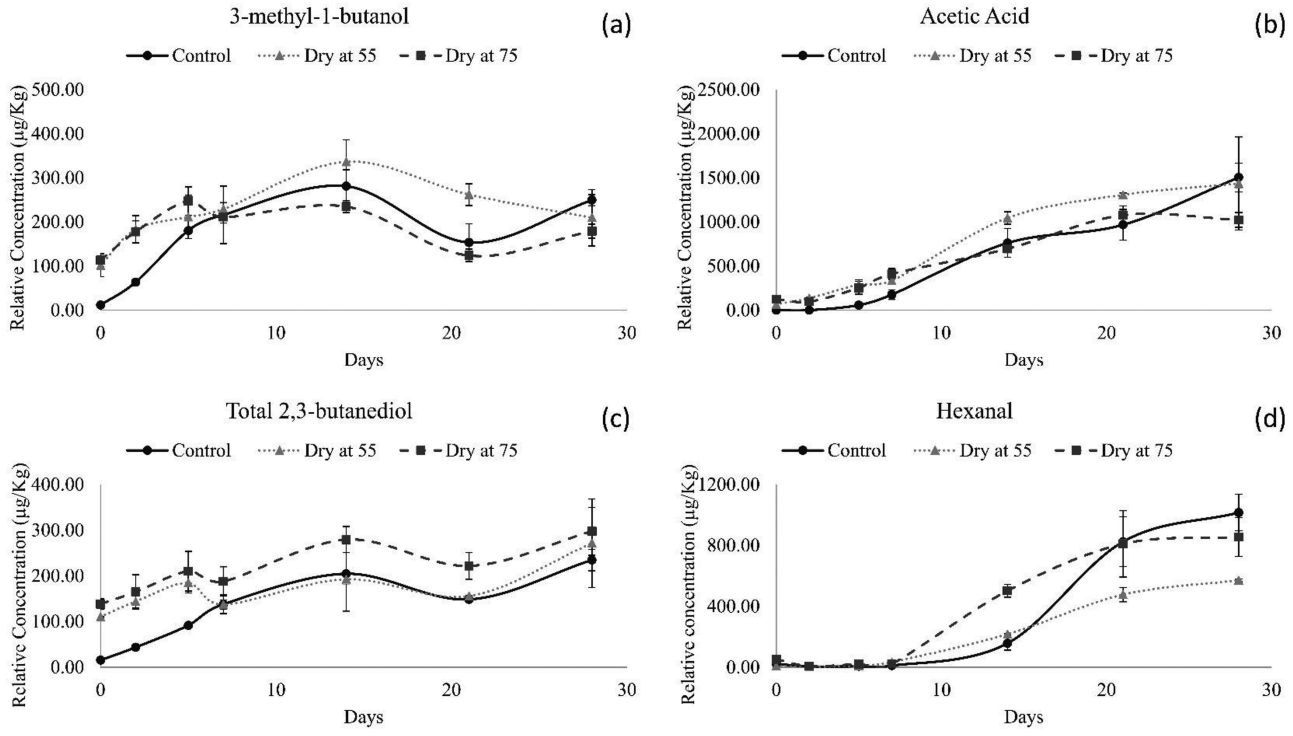

Figure 3. Selected volatile profile in almonds dried at two temperatures and storage in accelerated conditions (40 °C/80% RH). (a) 3-Methyl-1-butanol; (b) acetic acid; (c) total 2,3-butanediol; (d) hexanal.

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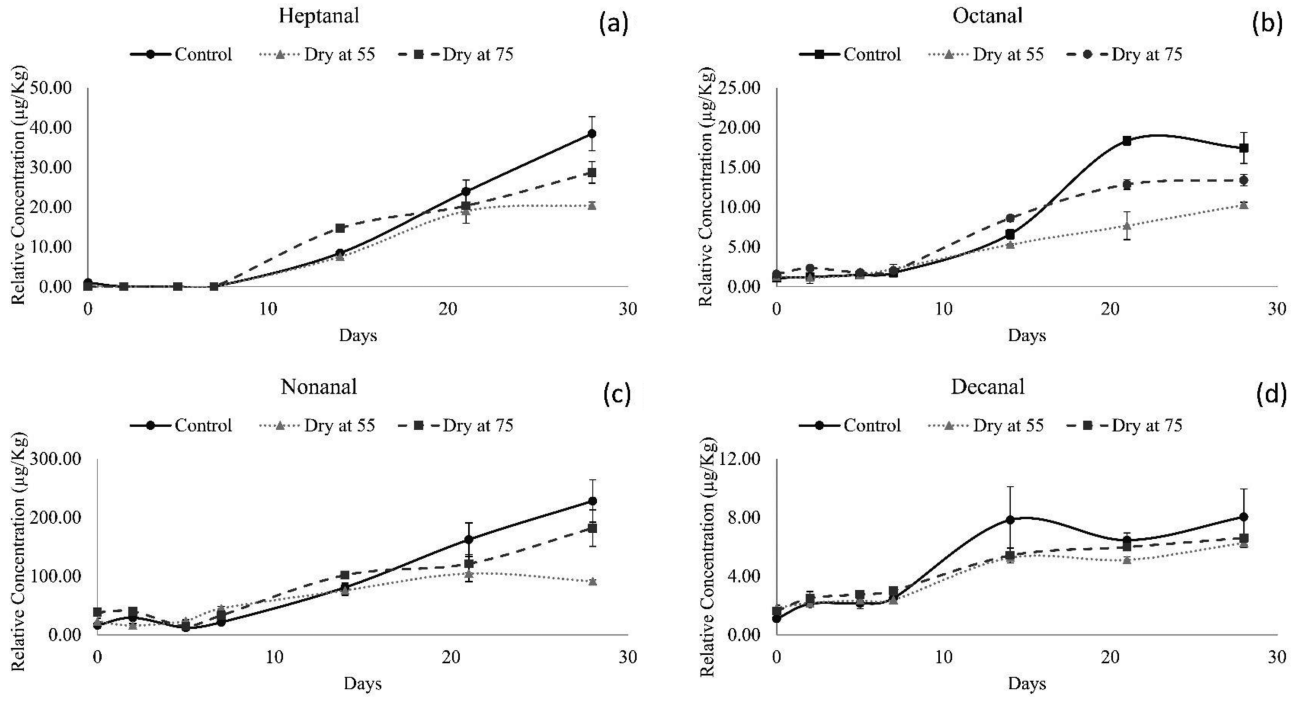

Figure 4. Selected volatile profile in almonds dried at two temperatures and storage in accelerated conditions (40 °C/80% RH). (a) Heptanal; (b) octanal; (c) nonanal; (d) decanal.

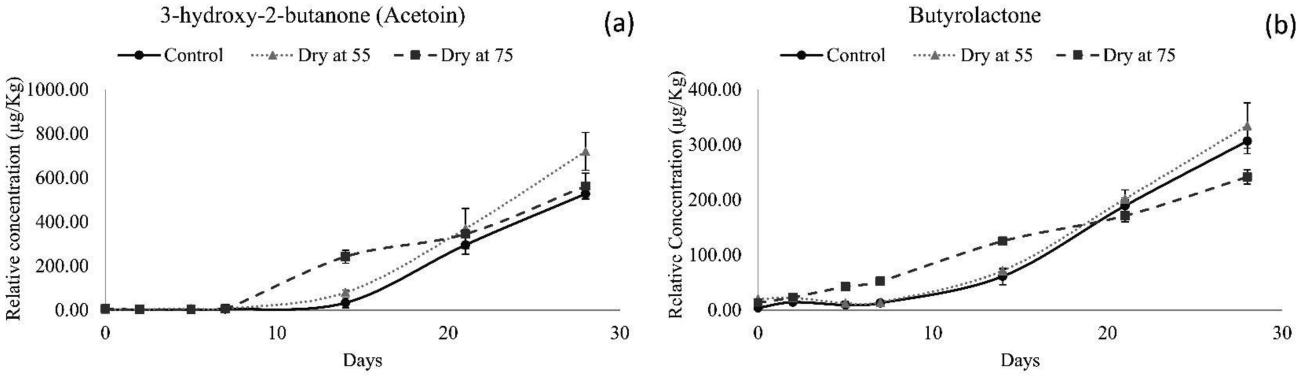

Figure 5. Selected volatile profile in almonds dried at two temperatures and storage in accelerated conditions (40 °C/80% RH). (a) 3-Hydroxy-2-butanone (acetoin); (b) butyrolactone.

lipid oxidation, including: hexanal, heptanal, octanal, nonanal (Figures 3 and 4). Drying almonds at 75 °C results in a lowering of aldehydes related to lipid oxidation and a shelf life similar to control almonds; however, the reduction in aldehydes is less pronounced as compared with almonds dried at 55 °C.

Taken together, these results indicate that drying almonds at or below 65 °C, prior to roasting, can reduce the visible sign of CD (i.e., brown pigmentation) and may help to reduce lipid oxidation during storage. To our knowledge, our results is the first approach. However, further studies evaluating the chemistry, sensory, and textural qualities of ME and dried almonds during storage under less extreme conditions are still needed. These studies will help determine if drying ME almonds before roasting and storage will affect consumer acceptance and shelf life. Moreover, alternative drying protocols and technologies, such as radio frequency or microwave, could be tested to identify the best drying practices for the industry.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS USED

CD, concealed damage; NCD, no concealed damage; db, dry basis; ME, moisture exposed

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