Title

HS-SPME GC/MS characterization of volatiles in raw and dry-roasted almonds (Prunus dulcis)

Authors

Xiao, Lu
Lee, Jihyun
Zhang, Gong
et al.

Publication Date

2014-05-01

DOI

10.1016/j.foodchem.2013.11.052

Peer reviewed

Food Chemistry 151 (2014) 31–39

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

HS-SPME GC/MS characterization of volatiles in raw and dry-roasted almonds (*Prunus dulcis*)

Lu Xiao [a,1], Jihyun Lee [a,1], Gong Zhang [a], Susan E. Ebeler [b], Niramani Wickramasinghe [c], James Seiber [a], Alyson E. Mitchell [a,*]

[a] Department of Food Science and Technology, University of California, Davis, One Shields Avenue, Davis, CA 95616, USA
[b] Department of Viticulture and Enology, University of California, Davis, One Shields Avenue, Davis, CA 95616, USA
[c] Department of Food Science and Technology, Faculty of Agriculture, University of Peradeniya, Peradeniya 20400, Sri Lanka

ARTICLE INFO

Article history:
Received 30 July 2013
Received in revised form 17 September 2013
Accepted 11 November 2013
Available online 18 November 2013

Keywords:
Almond
Raw
Roasted
Volatiles
Profiles
HS-SPME GC/MS

ABSTRACT

A robust HS-SPME and GC/MS method was developed for analyzing the composition of volatiles in raw and dry-roasted almonds. Almonds were analyzed directly as ground almonds extracted at room temperature. In total, 58 volatiles were identified in raw and roasted almonds. Straight chain aldehydes and alcohols demonstrated significant but minimal increases, while the levels of branch-chain aldehydes, alcohols, heterocyclic and sulfur containing compounds increased significantly (500-fold) in response to roasting ($p < 0.05$). Benzaldehyde decreased from 2934.6 ± 272.5 ng/g (raw almonds) to 315.8 ± 70.0 ng/g (averaged across the roasting treatments evaluated i.e. 28, 33 and 38 min at 138 °C) after roasting. Pyrazines were detected in only the roasted almonds, with the exception of 2,5-dimethylpyrazine, which was also found in raw almonds. The concentration of most alcohols increased in the roasted samples with the exception of 2-methyl-1-propanol, 3-methyl-1-butanol and 2-phenylethyl alcohol, which decreased 68%, 80%, and 86%, respectively.

1. Introduction

Tree nuts are used worldwide in confectionary, culinary and bakery food applications due to their desirable flavour attributes and high energy density. Almonds (*Prunus dulcis*, syn *Prunus amygdalus*, *Amygdalus communis* L. and *Amygdalus dulcis* Mill) are one of the most important commercial tree nut crops worldwide. According to the U.S. Department of agriculture, almonds were the top specialty export crop by value in the U.S. in 2010 (Economic research service, 2011). California is the top producer of almonds worldwide, with an estimated annual production of 1 million tons and accounting for 80% of world almond production in 2012–2013 (Almond Board of California., 2012). Almonds kernels are sold raw or roasted and are consumed in a wide variety of foods including baked goods, cereals and confectionaries. Dry roasting (hot air) is a common thermal process used by the almond industry (Almond Board of California., 2007). Common temperatures used for dry roasting range from 130 °C to 150 °C. At 130 °C it takes 40–55 min to obtain a light to medium roast product while at the higher temperature of 150 °C it takes 10–15 min (Almond Board of California, 2007).

Volatile constituents are responsible for the characteristic flavour properties of roasted almonds. To date, there are relatively few studies describing the composition of volatiles in raw, blanched, almond oil and especially roasted almonds (Agila & Barringer, 2012; Beck, Mahoney, Cook, & Gee, 2011; Mexis, Badeka, Chouliara, Riganakos, & Kontominas, 2009; Pićurić-Jovanović & Milovanović, 1993; Sanahuja, Santonja, Teruel, Carratalá, & Selva, 2011; Takei, Shimada, & Watanabe, 1974; Takei & Yamanishi, 1974; Vázquez-Araujo, Enguix, Verdu, García-García, & Carbonell-Barrachina, 2008; Vázquez-Araujo, Verdu, Navarro, Martínez-Sánchez, & Carbonell-Barrachina, 2009). The majority of these studies rely on solvent extraction (Pićurić-Jovanović & Milovanović, 1993; Takei & Yamanishi, 1974; Takei et al., 1974; Vázquez-Araujo et al., 2008; Vázquez-Araujo et al., 2009). For example, Takei et al. (1974) isolated volatiles from roasted almonds using acetone extraction and vacuum carbon dioxide distillation followed by GC/MS. Takei and Yamanishi (1974) used the same approach to evaluate the basic, carbonyl and non-carbonyl fractions of roasted almond. More recent studies have utilised simultaneous steam-distillation with methylene chloride extractions for the analysis of volatiles in toasted Spanish almonds used in manufacturing of

* Corresponding author. Address: Department of Food Science, One Shields Ave, University of California, Davis, CA 95616, USA. Tel.: +1 530 304 6618; fax: +1 530 752 4759.
E-mail address: aemitchell@ucdavis.edu (A.E. Mitchell).
[1] Both authors contributed equally to this work.

0308-8146/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.foodchem.2013.11.052

turrón, an almond based confection (Vázquez-Araujo et al., 2008; Vázquez-Araujo et al., 2009). The composition of volatiles, determined by headspace GC/MS, in enzymatically treated aqueous extracts of almond oil has also been described (Pićurić-Jovanović & Milovanović, 1993). For example, Pićurić-Jovanović and Milovanović (1993) identified ~20 compounds including: alkylfuranones, *n*-alkanes, cyclopentadiene and aromatic compounds such as benzaldehyde, methylphenol, benzyl alcohol and some alkylbenzenes. The predominant volatiles included methylbenzene, benzaldehyde and benzyl alcohol (Pićurić-Jovanović & Milovanović, 1993). More recently, headspace solid phase microextraction gas chromatography/mass spectrometry (HS-SPME GC/MS) has been used to evaluate volatiles in raw and blanched almonds (Beck et al., 2011). Beck et al. (2011) used this approach to evaluate the potential of using volatile profiles to detect aflatoxin infection in almonds. A total of 23 volatiles were identified in raw and blanched almonds. Several volatiles from the blanched almonds, considered fatty acid decomposition products, increases when compared to the emissions of whole almonds and include: hexanal, heptanal, octanal, nonanal, 3-octen-2-one, tetramethylpyrazine and decanal. Mexis et al. (2009) identified 14 volatiles in raw, unpeeled almonds using SPME GC. They also found that aldehydes, ketones and alcohols as secondary oxidation products of almond lipids increased after γ-irradiation (Mexis et al., 2009). Most recently, HS-SPME GC/MS and multivariate statistics were used to discriminate between two Spanish cultivars (Guara and Marcona) and one American almond cultivar (Butte) based upon the volatile profiles of the almond oils (Sanahuja et al., 2011). Selected ion flow tube mass spectrometry (SIFT-MS) was also used to quantify the volatiles in commercially steam-pasteurised raw and roasted sweet almonds (Agila & Barringer, 2012). Using this approach, these authors demonstrated that the majority of volatile compounds in roasted almonds are generated by the Maillard reaction during the roasting process and include numerous pyrazines, furanones and aldehydes. These samples were extracted at 50 °C for 60 min before volatiles were measured which may have resulted in some artifact generation.

Herein, a method was developed to analyse the profile of volatiles in raw and dry roasted almonds using HS-SPME GC/MS. This method offers the advantage of direct extraction of volatiles from the ground almond sample as compared to solvent extraction or analysis of the extracted almond oil (Sanahuja et al., 2011). Moreover, HS-SPME allowed for extractions to occur at ambient temperatures, in contrast to the typical heated extractions, limiting artifact generation and potential changes in the ratio of volatiles in the gas phase. This method was used to evaluate the volatiles profiles in raw and dry-roasted almonds.

2. Materials and methods

2.1. Reagents

Reagents were purchased from either Sigma–Aldrich (St. Louis, MO) or Fisher Scientific (Pittsburgh, PA) and included: C7–C40 saturated alkanes standard (1000 μg/ml in hexane), ethanol (HPLC/Spectrophotometric grade) and 36 other standards (Table 1). The exceptions were decanal (Eastman, Rochester, NY), 2-(ethylthio)-ethanol (Alfa Aesar, Ward Hill, MA), 3-hydroxybutan-2-one (Supelco, Bellefonte, PA) and 1-(methylthio)-2-propanol (Ryan Scientific, Inc., Mount Pleasant, SC). Octanal-d_{16}, 2-methylpyrazine-d_6, and *n*-hexyl-d_{13} alcohol were used as stable-isotope internal standards for three major categories of identified compounds (i.e., aldehydes, pyrazines and alcohols). Stable isotopes were purchased from C/D/N Isotopes Inc. (Quebec, Canada).

2.2. Samples and roasting

Dehulled raw almond kernels with skin (var. Butte/Padre) were obtained from Hughson Nut, Inc. (Hughson, CA) and dry roasted using a Revent Baking rotary roaster by Ready Roast (Madera, CA). The kernels were stored at ambient warehouse temperatures for 7 months prior to roasting. Almond samples for roasting consisted of 4.5–5.4 kg. Almonds were roasted in triplicate batches at 138 °C using different roasting times to achieve light (28 min), medium (33 min) and dark roast (38 min). Volatiles of raw and roasted almonds were analysed immediately after roasting. A 50 g random sample of the almonds was ground using a 51B130 Waring laboratory blender (Waring Laboratory Equipment, Torrington, CT) for 5 s at low speed. These samples were then passed through a 16 mesh Tyler standard screen (W.S. Tyler Industrial Group, Mentor, OH) to generate a uniform powder size, and 5 g (±1%) of this powder was transferred into a 22.5 mm × 75 mm 20-ml glass headspace vial (Sigma–Aldrich, St. Louis, MO) for HS-SPME analysis. Analytical measurements were done in duplicate ($n = 2$).

2.3. Almond moisture

Moisture content of the ground almonds was determined by drying samples (5 g) at 60 °C under vacuum until a constant weight was achieved (Zhang, Huang, Xiao, Seiber, & Mitchell, 2011). Moisture was determined for duplicate samples and the results were averaged.

2.4. HS-SPME sampling

A 1 cm 50/30 μm SPME fibre coated with divinylbenzene/carboxen/polydimethylsiloxane (Supelco, Inc., Bellefonte, PA) was used for headspace analyses of almond sample volatiles. This fibre is commonly used for flavour analysis, and is especially useful for pyrazines (Bail, Stuebiger, Unterweger, Buchbauer, & Krist, 2009; Beltrán, Ramos, Grané, Martín, & Garrigós, 2011; Comuzzo, Tat, Tonizzo, & Battistutta, 2006; Lojzova et al., 2009). In preliminary experiments, the DVB/CAR/PDMS also displayed better sensitivity than the PDMS fibre. The fibre was conditioned in the GC inlet at 270 °C in split mode for 1 h and checked for interference or carryover using the same sample programme before it was used. Volatiles were extracted from 5 g ground almond sample in 20 ml glass sample vials. Internal standards (I.S.; octanal-d_{16}, 2-methylpyrazine-d_6 and *n*-hexyl-d_{13} alcohol) were dissolved in ethanol and then diluted using nanopure water in a cold room (4 °C) to avoid loss of low-boiling point standards. A 100 μl aliquot of the stock internal standard solution was added to each vial and the final internal standard concentration was 10 ng/g. The vials were immediately sealed with an aluminum pressure release seal with a 20-mm PTFE/Silicone liner. After sealing, vials were thermally equilibrated at room temperature for 40 min. This equilibration time was chosen because comparisons of the relative standard deviation indicated that the analysis was highly repeatable at 40 min of equilibrium. The SPME fibre was then exposed over the headspace of the sample to a depth of 30 mm, just above the upper level of sample. Fibres were exposed for 30 min in the headspace of the vials at room temperature (24 ± 1 °C). Extractions lasting 30 min provided the optimum peak area response for most volatile components, while maximizing the number of samples that could be analysed each day. Following headspace extraction, SPME fibres were injected into the GC and remained in the GC inlet for 10 min.

2.5. GC–MS analysis

Volatile analysis was performed on a HP 6890 gas chromatograph coupled to a HP 5973 mass selective detector (Agilent

Table 1
Identified volatiles in raw and freshly roasted almonds (cv. Butte/Padre).[a]

Peak No.	Volatile compounds	T_R[b] of unknown	Standard K.I.[c]	Unknown K.I.	Literature K.I.	Extracted ion[d]	Internal standard
Aldehydes and ketones (19)							
1	Butanal[e]	3.44	784	784	822	72	Octanal-d_{16}
4	2-Methylbutanal	3.91		887	910	57	Octanal-d_{16}
5	3-Methylbutanal	3.97		900	912	44	Octanal-d_{16}
7	2,3-Butanedione[e]	4.94	960	961	970	86	Octanal-d_{16}
8	Pentanal	4.98		963	935	58	Octanal-d_{16}
11	Hexanal[e]	7.13	1073	1073	1084	72	Octanal-d_{16}
15	2-Heptanone[e]	9.72	1189	1179	1170	58	Octanal-d_{16}
16	Heptanal[e]	9.78	1184	1182	1174	70	Octanal-d_{16}
19	2-Hexenal	10.64		1215	1204	69	Octanal-d_{16}
22	2-Methyloxolan-3-one[e]	11.85	1261	1261	1266	43	Octanal-d_{16}
24	3-Hydroxybutan-2-one[e]	12.40	1281	1282	1287	88	Octanal-d_{16}
25	Octanal[e]	12.57	1288	1288	1280	84	Octanal-d_{16}
26	1-Hydroxypropan-2-one	12.76		1295	1291	74	Octanal-d_{16}
28	(*Z*)-2-Heptenal	13.49		1326	1299	83	Octanal-d_{16}
36	Nonanal[e]	15.11	1395	1396	1385	98	Octanal-d_{16}
38	(*E*)-2-Octenal[e]	15.70	1436	1435	1442	83	Octanal-d_{16}
41	Furfural[e]	16.12	1464	1465	1455	96	Octanal-d_{16}
42	Decanal[e]	16.63	1503	1502	1484	82	Octanal-d_{16}
44	Benzaldehyde[e]	16.90	1527	1528	1495	106	Octanal-d_{16}
46	(*Z*)-2-Nonenal[e]	17.01	1537	1539	1510	83	Octanal-d_{16}
50	2-Phenylacetaldehyde[e]	18.04	1639	1640	1640	91	Octanal-d_{16}
Pyrazines (7)							
23	2-Methylpyrazine[e]	11.97	1266	1265	1239	94	2-Methylpyrazine-d_6
29	2,5-Dimethylpyrazine[e]	13.51	1327	1326	1320	108	2-Methylpyrazine-d_6
30	2,6-Dimethylpyrazine	13.66		1334	1308	108	2-Methylpyrazine-d_6
31	2-Ethylpyrazine	13.81		1340	1354	107	2-Methylpyrazine-d_6
32	2,3-Dimethylpyrazine	14.12		1353	1324	108	2-Methylpyrazine-d_6
35	2-Ethyl-6-methylpyrazine	15.00		1391	1381	121	2-Methylpyrazine-d_6
37	Trimethylpyrazine	15.34		1409	1395	122	2-Methylpyrazine-d_6
Alcohols (22)							
56	2-Butanol[e]	5.98	1078	1078	1024	59	Hexyl-d_{13} alcohol
12	2-Methyl-1-propanol[e]	7.54	1096	1092	1099	74	Hexyl-d_{13} alcohol
13	3-Pentanol[e]	7.92	1111	1108	1107	59	Hexyl-d_{13} alcohol
57	2-Propenol	7.98		1111	1136	57	Hexyl-d_{13} alcohol
14	1-Butanol[e]	8.82	1143	1144	1145	56	Hexyl-d_{13} alcohol
18	3-Methyl-1-butanol[e]	10.46	1209	1208	1205	70	Hexyl-d_{13} alcohol
21	1-Pentanol[e]	11.61	1251	1252	1255	70	Hexyl-d_{13} alcohol
27	1-Chloro-2-propanol[e]	13.23	1314	1315		79	Hexyl-d_{13} alcohol
58	3-Methyl-2-butenol[e]	13.48	1325	1325	1313	71	Hexyl-d_{13} alcohol
33	1-Hexanol[e]	14.33	1360	1362	1360	69	Hexyl-d_{13} alcohol
34	2-Chloro-1-propanol	14.54		1371		31	Hexyl-d_{13} alcohol
39	1-(Methylthio)-2-propanol[e]	15.96	1454	1454		106	Hexyl-d_{13} alcohol
40	1-Heptanol[e]	16.09	1467	1463	1467	70	Hexyl-d_{13} alcohol
59	2-Ethyl hexanol[e]	16.52	1493	1494	1487	57	Hexyl-d_{13} alcohol
45	2-(Ethylthio)-ethanol[e]	16.98	1597	1536		75	Hexyl-d_{13} alcohol
47	1-Octanol[e]	17.26	1563	1564	1553	84	Hexyl-d_{13} alcohol
48	1,2-Propanediol	17.54		1591	1603	45	Hexyl-d_{13} alcohol
51	Furfuryl alcohol[e]	18.13	1661	1663	1661	98	Hexyl-d_{13} alcohol
60	Benzyl alcohol	19.67		1855	1865	79	Hexyl-d_{13} alcohol
54	Phenylethyl alcohol[e]	19.90	1929	1930	1925	91	Hexyl-d_{13} alcohol
Additional compounds (10)							
2	Ethyl acetate[e]	3.58	874	876	885	61	2-Methylpyrazine-d_6
9	α-Pinene[e]	5.82	1014	1013	1032	93	2-Methylpyrazine-d_6
10	Methylsulfanylmethane[e]	6.88	1062	1062	1071	94	2-Methylpyrazine-d_6
17	Limonene[e]	10.10	1197	1195	1201	68	2-Methylpyrazine-d_6
20	2-Pentylfuran	11.01		1229	1221	81	2-Methylpyrazine-d_6
43	Pyrrole[e]	16.76	1514	1515	1509	67	Hexyl-d_{13} alcohol
49	γ-Dihydrofuran-2(3H)-one	17.95		1640	1635	86	Hexyl-d_{13} alcohol
52	γ-Oxepan-2-one[e]	18.57	1719	1720	1694	85	Hexyl-d_{13} alcohol
53	Caproic acid[e]	19.47	1859	1857	1829	60	Hexyl-d_{13} alcohol
55	2-Acetylpyrrole	20.24		1991	1950	94	Hexyl-d_{13} alcohol

[a] Volatiles were identified from raw almonds and almonds roasted at 138 °C for 38 min. DB-Wax was used as the analytical column.
[b] T_R stands for retention time.
[c] K.I. stands for Kovats' indices, and values were obtained from http://flavornet.org or www.pherobase.com.
[d] Extracted ion from total ion scan used for quantitation.
[e] Compounds verified with authentic standards.

Technologies, Palo Alto, CA). Compounds were separated on a DB-Wax column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Agilent Technologies). The injection was performed in splitless mode (0.7 mm splitless inlet liner, Supelco) and injector temperature was 220 °C. The purge valve was opened at 0.5 min at a 50 ml/min flow rate. Helium (99.999%) was used as the carrier gas with a constant starting flow rate at 0.7 ml/min. The oven temperature was programmed as follows: 35 °C for 1 min, 5 °C/min to 100 °C,

20 °C/min to a final temperature of 250 °C, with a final holding time of 5 min. The detector was fitted with an electron impact ionization source set at 230 °C. The quadrupole temperature was set to 150 °C and the transfer line temperature was kept at 250 °C. The solvent delay was set to 3 min. Total ion chromatograms were collected scanning from m/z 30 to 150 at a rate of 3.06 scans/s.

2.6. Identification of volatile compounds

Volatile compounds were identified by comparison of their mass spectra and retention times with those of authentic standards, or by comparison of Kovats' retention indexes (K.I.) and mass spectrum, with those reported in the NIST Mass Spectral Search Program (version 2.0a) with <80% as a cutoff to match compounds. The K.I.s were calculated from the retention times of C6–C40 *n*-alkanes.

2.7. Relative quantification of volatile compounds

The whole spectrum was scanned with the total ion chromatogram (TIC) mode. Relative quantification of each volatile compound in raw and dry-roasted almonds was performed using a unique extracted ion peak area at its respective retention time (Table 1) and comparing to the extracted ion 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). The remaining volatiles, (i.e. non aldehydes, pyrazines and alcohols) were quantified by comparisons with the internal standard that eluted closest to each of these compounds (Table 1). Concentration was calculated using the following equation according to Hopfer, Ebeler, and Heymann (2012) and Baek and Cadwallader (1996):

$$\text{Concentration}\left(\frac{\text{ng}}{\text{g}}\right)=\frac{\text{extracted ion peak area}}{\text{extracted ion peak area of I.S.}}\left[\text{I.S.}\left(\frac{10\,\text{ng}}{\text{g}}\right)\right]$$

The peak area of each extracted ion for each analyte was divided by the peak area of extracted ion for the respective internal standard. The area ratio obtained was subsequently converted to relative concentration of the analyte in a 5 g sample based on the concentration of the appropriate I.S. (10 ng I.S./g almond). The obtained relative concentration was used to compare the difference in volatile profiles among raw and roasted almonds. Volatile concentrations were reported on a dry weight basis.

2.8. Recovery and reproducibility

Recovery was measured after addition of hexanal, 2,5-dimethylpyrazine and 1-hexanol into Monterey almond samples (concentrations of 200 ng/g almonds). These volatile were chosen in order to represent the major classes of volatile compounds in almonds (i.e., carbonyls, alcohols and pyrazines). Monterey variety was used because it contained the lowest intensity of volatile compounds. Before adding standards, the almond sample powder was placed in a vacuum oven without heating for 24 h to remove background volatiles. The experiment was done in triplicate. Reproducibility was evaluated by using relative standard deviations (RSD) for the replicate analyses.

2.9. Statistical analysis

Statistical analysis was performed using IBM SPSS statistics software (v. 20.0, SPSS, Inc., Chicago, IL). A multiple comparison procedure for comparing three different roasting conditions (i.e., light, medium and dark roasting) with a control (i.e., raw) was determined using one-way ANOVA followed by the Dunnett's post-test.

3. Results and discussion

3.1. Identification of almond volatiles

The almond moisture levels were 5.05 ± 0.09% (raw), 2.84 ± 0.01% (light), 2.63 ± 0.03% (medium) and 2.38 ± 0.059% (dark roast). A representative GC chromatogram of the volatiles in roasted almonds is demonstrated in Fig. 1. Using NIST libraries and Kovats Index values, 58 compounds in raw and roasted almonds were tentatively identified. These include 19 aldehydes and ketones, 7 pyrazines, 22 alcohols, and 10 additional compounds (Table 1). The identity of 40 of these compounds was confirmed with authentic standards. Peak 39 was a major constituent of roasted almonds (about 23% of the total area). This was identified as 1-(methylthio)-2-propanol since its Kovats Index (I = 1454) and mass spectrum (Fig. 2a) closely matched those of this authentic standard (Fig. 2b). The mass spectrum of this peak demonstrated a molecular ion at m/z 106 and predominant fragment ions were observed at m/z 91, 62 and 45. The structure of 1-methylthio-2-propanol is shown in Fig. 3. To date, 1-(methylthio)-2-propanol has not been reported in raw or roasted almonds (Agila & Barringer, 2012; Beck et al., 2011; Mexis et al., 2009; Pićurić-Jovanović & Milovanović, 1993; Sanahuja et al., 2011; Takei & Yamanishi, 1974; Takei et al., 1974; Vázquez-Araujo et al., 2008; Vázquez-Araujo et al., 2009). Additionally, it has not been found in other roasted nuts including: peanuts, walnuts, cashew nuts, pecans, pistachios, hazel nuts or potato chips and sunflowers. 1-(Methylthio)-2-propanol was detected in a ripening cheese model medium, containing a culture of *Microbacterium foliorum* and *Debaryomyces hansenii* 304, after 41 days of incubation (Deetae, Spinnler, Bonnarme, & Helinck, 2009). It was also reported as a novel volatile in the kraft pulping process in wood liquor treatments at elevated temperatures (Niemela, 2001). As there are no previous reports of 1-(methylthio)-2-propanol in roasted nut, there is a possibility that this compound is an artifact. Herein, 1-(methylthio)-2-propanol was found in both raw and roasted almonds. 1-(Methylthio)-2-propanol was also found in raw almonds purchased from a local grocery store (7.6 ± 0.4 mg/kg). Interestingly, levels were significantly elevated (247.2–325 ng/g) in roasted almonds as compared with the raw almonds (12.8 ± 1.3 ng/g) ($p < 0.01$). The source of the 1-(methylthio)-2-propanol is unclear, however, it is a sulfur-containing compound, and therefore its formation may be associated with levels of free cysteine and methionine, which are typically 0.189 g and 0.151 g per 100 g almonds, respectively (Nutrient Data Laboratory, 2011).

3.2. Recovery and reproducibility

Over-night vacuum-treatment was used to reduce and/or remove volatiles in order to create a sample matrix sample appropriate for spiking. After vacuum-treatment, almonds contained 21.2 ng/g hexanal, 7.2 ng/g 2,5-dimethylpyrazine and 24.3 ng/g 1-hexanol. Authentic standards were spiked into these almond samples (200 ng/g almond). The average recoveries of hexanal, 2,5-dimethylpyrazine, and 1-hexanol were 92%, 97% and 96%, respectively. Relative standard deviation (% RSD) of hexanal, 2,5-dimethylpyrazine and 1-hexanol were 2.1%, 5.1% and 6.1%, respectively.

3.3. Volatile composition of raw almonds

In total, 41 volatiles were identified in raw almonds and include: 13 carbonyls, 1 pyrazine, 20 alcohols and 7 additional

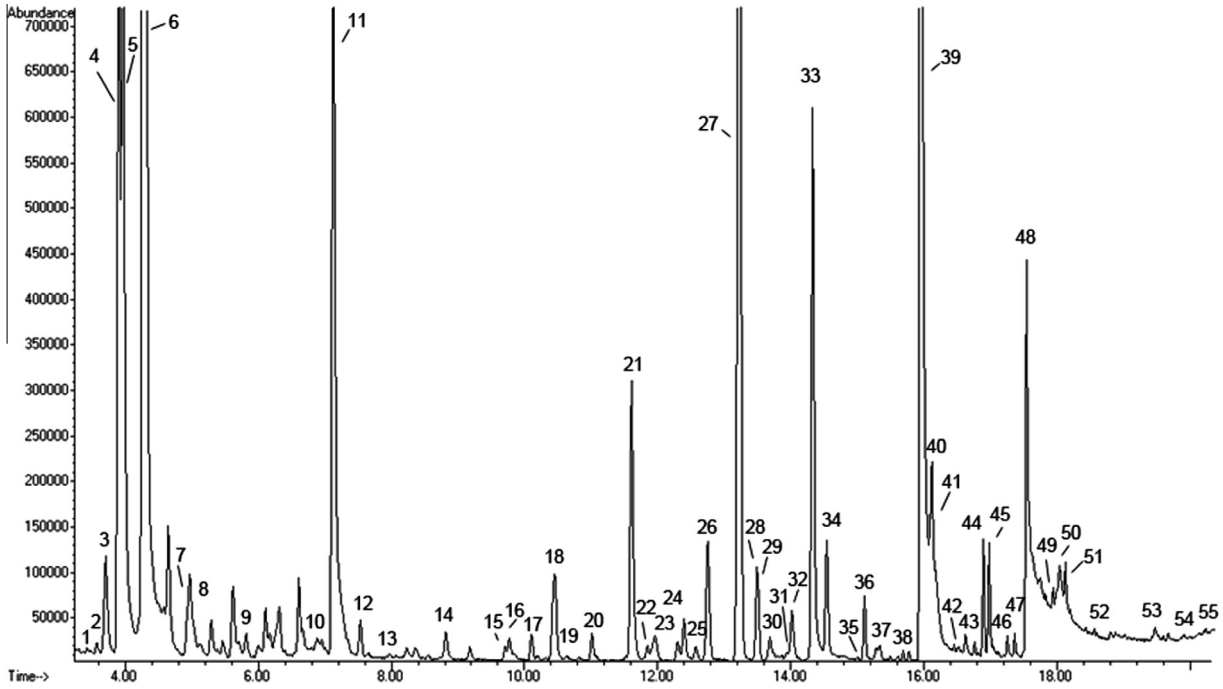

Fig. 1. Representative GC chromatogram of fresh roasted almonds roasted at 138 °C/38 min. 1, Butanal; 2, ethyl acetate; 3, methanol; 4, 2-methylbutanal; 5, 3-methylbutanal; 6, ethanol; 7, 2,3-butanedione; 8, pentanal; 9, α-pinene; 10, methylsulfanylmethane; 11, hexanal; 12, 2-methyl-1-propanol; 13, 3-pentanol; 14, butanol; 15, 2-heptanone; 16, heptanal; 17, limonene; 18, 3-methyl-1-butanol; 19, 2-hexenal; 20, 2-pentylfuran; 21, pentanol; 22, 2-methyloxolan-3-one; 23, 2-methylpyrazine; 24, 3-hydroxybutan-2-one; 25, octanal; 26, 1-hydroxypropan-2-one; 27, 1-chloro-2-propanol; 28, (*Z*)-2-heptenal; 29, 2,5-dimethylpyrazine; 30, 2,6-dimethylpyrazine; 31, 2-ethylpyrazine; 32, 2,3-dimethylpyrazine; 33, 1-hexanol; 34, 2-chloro-1-propanol; 35, 2-ethyl-6-methylpyrazine; 36, nonanal; 37, trimethylpyrazine; 38, (*E*)-2-octenal; 39, 1-(methylthio)-2-propanol; 40, heptanol; 41, furfural; 42, decanal; 43, pyrrole; 44, benzaldehyde; 45, 2-(ethylthio)-ethanol; 46, (*Z*)-2-nonenal; 47, octanol; 48, 1,2-propanediol; 49, γ-dihydrofuran-2(3H)-one; 50, 2-phenylacetaldehyde; 51, furfuryl alcohol; 52, γ-oxepan-2-one; 53, caproic acid; 54, phenylethyl alcohol; 55, 2-acetylpyrrole.

volatiles (Table 2). Benzaldehyde, which is a breakdown product of amygdalin, was the predominant volatile present in raw almonds (2,934.6 ± 272.5 ng/g). This is similar to results reported by Mexis et al. (2009). Hexanal levels in raw almonds were 422.6 ± 97.9 ng/g. Hexanal levels, reported in previous studies on different nuts, ranged from 10 ng/g to over 1000 ng/g (Alasalvar, Odabasi, & Cadwallarder, 2004; Mexis et al., 2009). More than 10 branched-chain alcohols and 2-phenylethanol were found in the raw almonds. 2-Methyl-1-propanol, 3-methyl-1-butanol and 2-phenylethanol are common in plant materials resulting from enzymatic deamination and decarboxylation of amino acids (Fugelsang & Edwards, 2007; Tieman et al., 2006).

Two terpenes, α-pinene and limonene were detected in the raw almonds at <17 ng/g levels. In other reports on raw almonds, terpenes were either not detected or detected at trace levels (Beltrán, Ramos et al., 2011; Beltrán, Santonja, & Garrigós, 2011; Pićurić-Jovanović & Milovanović, 1993).

The concentration of 1,2-propanediol (propylene glycol) was relatively high in raw almonds. This compound may arise from almond processing. Propylene oxide fumigation is a primary almond pasteurisation method and is degraded into 1,2-propanediol (Isikber, Navarro, Finkelman, Rindner, & Dias, 2007).

3.4. Changes in volatile compounds during roasting

Numerous volatile compounds are generated through the Maillard reaction and via lipid oxidation during roasting (Vázquez-Araujo et al., 2008; Vázquez-Araujo et al., 2009). Pyrazines, furans and pyrroles are key components of toasted almond aroma (Vázquez-Araujo et al., 2008). Pyrazines, which have nutty and roasted aromas, are formed during heating via Maillard sugar-amine reactions and Strecker degradation (Alasalvar, Shahidi, & Cadwallader, 2003). The thermal degradation of sugars, such as fructose and glucose, produces furan-containing compounds (e.g. furfural) (Vázquez-Araujo et al., 2008). Almonds are sensitive to lipid oxidation because 48–67% of the almond kernel is oil composed of 63–78% oleic, 12–27% linoleic, 5% palmitic and 1% myristic acid (Mandalari & Faulks, 2008). Linoleic acid is a precursor to many aldehydes and alcohols (Perez, Sanz, Olias, & Olias, 1999) including (*E*)-2-heptenal and nonanal (Min & Smouse, 1985).

HS-SPME GC/MS indicated that a range of 17 ketones, aldehydes, pyrazines, alcohols, aromatic hydrocarbons, furans and pyrroles were formed upon roasting the almonds (Table 2). Increases in the aldehydes and ketones were similar to increases reported for roasted hazel nuts (Alasalvar et al., 2003). The straight chain aldehydes and 2-heptanone, demonstrated significant ($p < 0.05$) but small increases in response to roasting. 2-Heptanone was the only straight chain ketone identified as previously reported (Vázquez-Araujo et al., 2008). Vejaphan and Hsieh (1988) described the formation of C4–C8 aliphatic ketones from lipid degradation during heating.

The concentration of the branched chain and heterocyclic carbonyls increased significantly with roasting time (Table 2); most of these carbonyls may result from Maillard reactions (Pripis-Nicolau, Bertrand, & Maujean, 2000). For example, Pripis-Nicolau and co-workers (2000) described the formation of 2-methyl- and 3-methylbutanal, and phenylacetaldehyde from the Maillard and Strecker reactions. 3-Methylbutanal forms via the Strecker reaction even at low temperatures (Bi & Ma, 2006). Herein, we found 3-hydroxy-2-butanone and 2-methyloxolan-3-one in only the roasted almonds. Levels of 2,3-butanedione also increased in response to roasting. Again, these compounds result from the Maillard reaction (Coghe, Gheeraert, Michiels, & Delvaux, 2006).

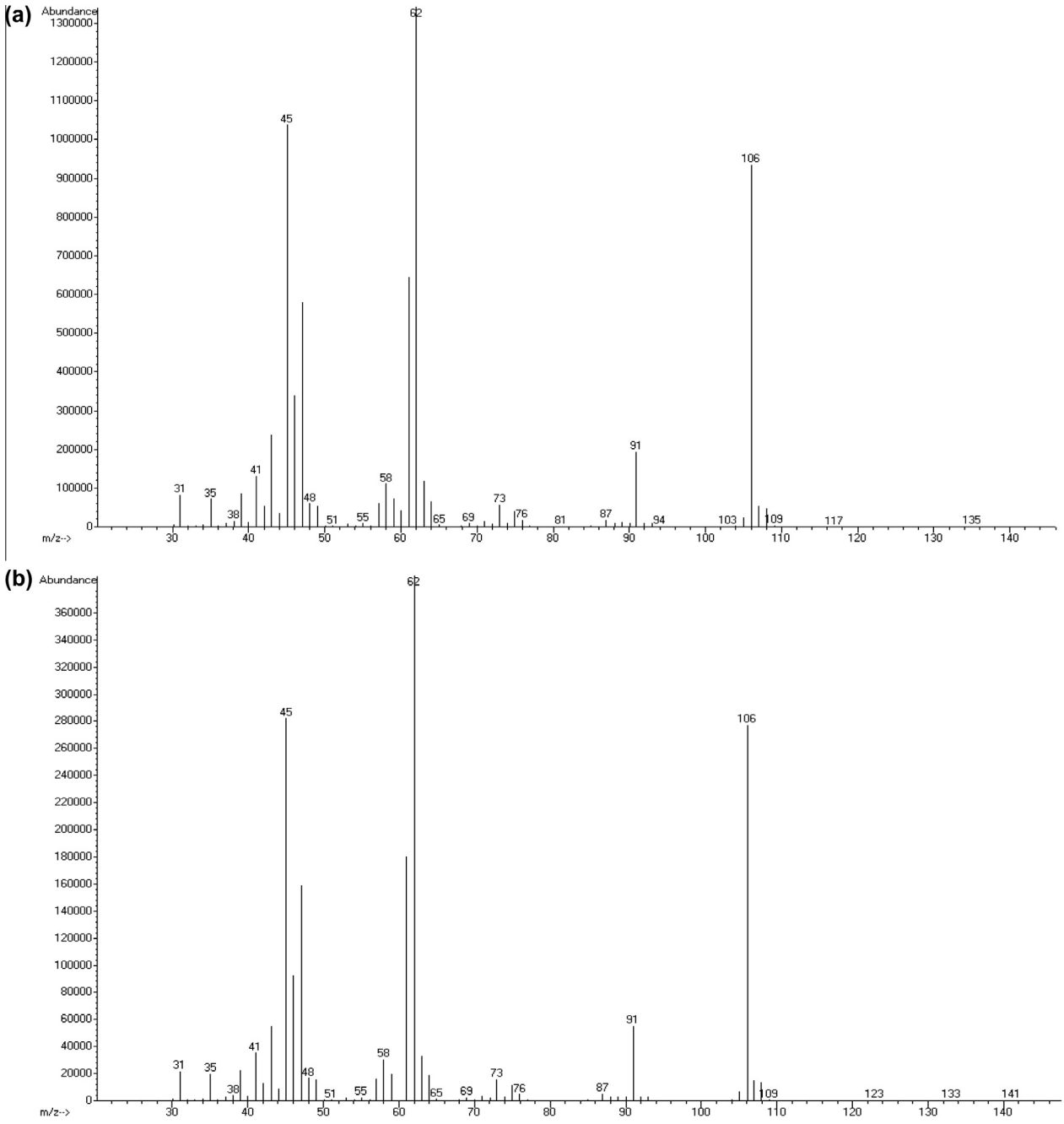

Fig. 2. (a) Mass spectrum of 1-(methylthio)-2-propanol in roasted almond sample; (b) mass spectrum of 1-(methylthio)-2-propanol authentic standard.

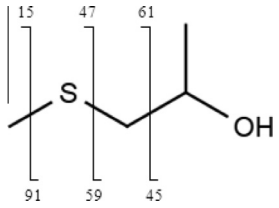

Fig. 3. Chemical structure of 1-(methylthio)-2-propanol.

Benzaldehyde is an aromatic aldehyde with a pleasant almond-like aroma and is essential to almond flavour. It arises from the enzymatic breakdown of the diglucoside amygdalin when almond kernel tissues are disrupted (Sanchez-Perez, Jorgensen, Olsen, Dicenta, & Moller, 2008). Herein, the levels of benzaldehyde decreased upon roasting from 2934.6 ± 272.5 ng/g to an average value of 315.8 ± 70.0 ng/g (averaged across the roasting treatments evaluated i.e. 28, 33 and 38 min at 138 °C). Losses in benzaldehyde result in a reduction of marzipan-related almond flavour.

Free amino acids and monosaccharides give rise to pyrazines via Maillard sugar-amine-type reactions (Coghe et al., 2006). Pyrazines were detected in only the roasted almonds, with the exception of low levels of 2,5-dimethylpyrazine (11.4 ± 0.5 ng/g), which was also found in raw almonds. Low levels of pyrazines may have occurred during nonenzymatic browning during normal almond drying. 2,5-Dimethylpyrazine, 2-methylpyrazine and trimethylpyrazine were previously reported in almonds dry roasted at 177 °C for 5 min (Agila & Barringer, 2012). Herein, 2-methylpyrazine and 2,5-dimethylpyrazine were formed in almonds roasted for 28 min (light roast), while the other pyrazines were only found

Table 2
Volatiles and their concentrations (ng/g) in raw and roasted almonds (dry weight basis).[a]

Possible compounds	Roasting time				Increase[b] (%)
	Raw	28 min	33 min	38 min	
Aldehydes and ketones					
Butanal	19.6 ± 2.7	27.6 ± 1.5*	29.3 ± 0.6*	40.8 ± 2.1***	67
2-Methylbutanal	14.3 ± 0.3	1468.6 ± 25.7**	5000.3 ± 241.1***	6573.7 ± 275.0***	30,216
3-Methylbutanal	32.4 ± 0.5	911.4 ± 50.9*	2867.4 ± 71.1***	4268.9 ± 381.8***	8167
2,3-Butanedione	8.0 ± 0.3	100.3 ± 0.8***	163.7 ± 1.3***	226.3 ± 13.7***	1940
Pentanal	50.4 ± 5.7	223.0 ± 8.6***	169.0 ± 5.1***	264.1 ± 15.9***	334
Hexanal	422.6 ± 97.9	983.0 ± 133.7**	689.0 ± 78.1	1140.8 ± 3.8**	122
2-Heptanone	50.0 ± 4.7	72.0 ± 7.3*	71.0 ± 6.3*	123.6 ± 3.0***	78
Heptanal	40.5 ± 8.9	75.2 ± 16.2*	57.1 ± 4.0	114.8 ± 3.0**	103
2-Hexenal	ND[c]	14.6 ± 2.7**	11.3 ± 2.2*	14.1 ± 2.7**	New
2-Methyloxolan-3-one	ND	15.4 ± 1.3	86.3 ± 4.2***	128.1 ± 11.0***	New
3-Hydroxybutan-2-one	ND	2.2 ± 0.2**	3.0 ± 0.1***	3.8 ± 0.6***	New
Octanal	25.2 ± 4.7	31.1 ± 7.3	18.5 ± 6.3	42.0 ± 3.0	21
1-Hydroxypropan-2-one	1.3 ± 0.0	9.0 ± 0.9*	11.0 ± 0.0**	13.7 ± 3.0**	771
(*Z*)-2-Heptenal	19.1 ± 0.9	65.6 ± 13.2**	36.5 ± 4.6	61.9 ± 1.6**	186
Nonanal	36.6 ± 4.9	55.9 ± 13.3	34.6 ± 4.0	70.5 ± 18.9	47
(*E*)-2-Octenal	7.3 ± 0.9	12.5 ± 2.1	8.3 ± 0.1	15.9 ± 2.0*	67
Furfural	ND	103.2 ± 8.7**	366.1 ± 13.2***	460.0 ± 21.4***	New
Decanal	ND	6.9 ± 2.3*	5.0 ± 1.6	4.6 ± 1.0	New
Benzaldehyde	2934.6 ± 272.5	368.8 ± 41.2***	246.7 ± 53.0***	331.9 ± 65.4***	−89
(*Z*)-2-Nonenal	ND	ND	ND	5.3 ± 1.7**	New
2-Phenylacetaldehyde	ND	107.5 ± 20.3*	284.0 ± 22***	491.3 ± 45.4***	New
Pyrazines					
2-Methylpyrazine	ND	4.1 ± 0.3*	21.5 ± 0.6***	26.5 ± 1.8***	New
2,5-Dimethylpyrazine	11.4 ± 0.5	16.2 ± 0.6***	53.3 ± 0.3***	66.5 ± 0.4***	298
2,6-Dimethylpyrazine	ND	ND	2.8 ± 0.4**	4.2 ± 0.6***	New
2-Ethylpyrazine	ND	ND	2.6 ± 0.1***	3.2 ± 0.1***	New
2,3-Dimethylpyrazine	ND	ND	1.0 ± 0.1***	1.4 ± 0.1***	New
2-Ethyl-6-methylpyrazine	ND	ND	1.7 ± 0.1***	2.2 ± 0.0***	New
Trimethylpyrazine	ND	ND	4.5 ± 0.3***	6.1 ± 0.2***	New
Alcohols					
2-Butanol	2.9 ± 0.4	ND	ND	ND	ND
2-Methyl-1-propanol	3.6 ± 0.3	1.3 ± 0.1***	1.1 ± 0.0***	1.1 ± 0.1***	−68
3-Pentanol	ND	0.8 ± 0.1*	2.4 ± 0.1***	2.7 ± 0.3***	New
2-Propenol	ND	2.0 ± 0.0***	2.0 ± 0.1***	2.2 ± 0.1***	New
1-Butanol	8.4 ± 2.3	11.2 ± 1.1	7.2 ± 0.0	10.7 ± 0.4	15
3-Methyl-butanol	86.4 ± 3.3	19.1 ± 0.3***	15.3 ± 1.0***	17.2 ± 0.6***	−80
1-Pentanol	30.3 ± 4.4	45.6 ± 2.9*	37.7 ± 3.0	54.3 ± 1.3***	51
1-Chloro-2-propanol	106.2 ± 5.4	161.9 ± 2.8***	111.8 ± 2.2	149.6 ± 7.6**	33
3-Methyl-2-butenol	17.3 ± 0.9	ND	ND	ND	ND
1-Hexanol	47.0 ± 1.1	53.1 ± 5.5	42.2 ± 4.7	70.1 ± 0.7**	17
2-Chloro-1-propanol	41.9 ± 3.5	59.5 ± 0.3**	40.9 ± 0.8	53.4 ± 2.2*	22
1-(Methylthio)-2-propanol	12.8 ± 1.3	247.2 ± 23.9**	307.0 ± 27.9**	325.0 ± 53.1***	2190
1-Heptanol	3.2 ± 0.4	3.8 ± 1.0	3.0 ± 0.1	6.0 ± 0.4*	32
2-Ethyl hexanol	2.4 ± 0.1	ND	ND	ND	ND
2-(Ethylthio)-ethanol	1.0 ± 0.0	20.5 ± 3.1**	24.3 ± 1.8**	29.2 ± 3.9***	2321
1-Octanol	0.8 ± 0.0	1.2 ± 0.2	0.9 ± 0.0	1.6 ± 0.1**	45
1,2-Propanediol	269.1 ± 2.5	789.4 ± 72.3***	510.0 ± 16.1*	647.0 ± 73.8**	141
Furfuryl alcohol	0.6 ± 0.0	1.2 ± 0.1***	4.4 ± 0.3***	5.2 ± 0.4***	491
Benzyl alcohol	3.9 ± 0.0	ND	ND	ND	ND
2-Phenylethyl alcohol	6.2 ± 0.6	0.9 ± 0.0***	0.7 ± 0.0***	0.9 ± 0.2***	−86
Additional volatiles					
Ethyl acetate	ND	12.0 ± 1.2***	3.8 ± 0.6*	9.9 ± 0.8***	New
α-Pinene	15.0 ± 0.1	16.5 ± 1.5	11.4 ± 0.2***	14.6 ± 0.9	−5
Methylsulfanylmethane	ND	4.5 ± 0.7	7.8 ± 1.9*	6.1 ± 2.0*	New
Limonene	16.6 ± 0.5	14.5 ± 1.4	7.1 ± 0.2***	13.0 ± 0.5*	−31
2-Pentylfuran	2.4 ± 0.8	16.6 ± 1.2***	25.2 ± 0.6***	30.0 ± 0.2***	905
Pyrrole	ND	0.6 ± 0.1*	2.7 ± 0.1***	2.1 ± 0.3***	New
γ-Dihydrofuran-2(3H)-one	0.7 ± 0.0	1.8 ± 0.2***	2.0 ± 0.0***	2.2 ± 0.1***	179
γ-Oxepan-2-one	1.2 ± 0.3	1.6 ± 0.2	1.4 ± 0.1	2.4 ± 0.3*	49
Caproic acid	1.8 ± 0.6	5.7 ± 1.3*	4.0 ± 0.7	6.7 ± 0.1**	207
2-Acetylpyrrole	ND	0.2 ± 0.0*	0.6 ± 0.0***	0.7 ± 0.1***	New
Total	4355.3 ± 117.5	6167.0 ± 293.2*	11422.4 ± 519.3***	15969.9 ± 680.5***	

[a] Almonds were roasted at 138 °C for 28 (light roast), 33 (medium roast) and 38 min (dark roast). Values are mean ± SD. Volatile concentrations were corrected in moisture content and reported as dry weight basis.

[b] Increase % = %[(average concentrations across the roasting treatments evaluated i.e. 28, 33, and 38 min at 138 °C) − (average concentration in raw almonds)]/(average concentration in raw almonds).

[c] ND stands for not detected.

* $p < 0.05$ For raw (control) vs. corresponding roasting condition.

** $p < 0.01$ For raw (control) vs. corresponding roasting condition.

*** $p < 0.001$ For raw (control) vs. corresponding roasting condition.

in almonds roasted for at least 33 min (medium roast) (Table 2). Seven pyrazines were found in dark roasted almonds (i.e., 38 min roasting time). Generally, longer roasting time at 138 °C generated higher pyrazine concentrations than those in raw almonds. The concentration of most alcohols increased significantly in the roasted samples with the exception of 2-methyl-1-propanol, 3-methyl-1-butanol and 2-phenylethanol, which decreased 68%, 80% and 86%, respectively. Aliphatic alcohols are generated through lipid oxidation; for example, 1-octen-3-ol arises from the thermal decomposition of methyl linoleate hydroperoxide, and 1-butanol is formed from decomposition of linolenic acid (Min et al., 1985). Significant increases as a result of roasting were noted for two sulfur-containing volatiles (1-(methylthio)-2-propanol and 2-(ethylthio)-ethanol), furfuryl alcohol and two branched chain ketone (1-hydroxypropan-2-one and 3-hydroxybutan-2-one) ($p < 0.05$) (Table 2). Furfuryl alcohol, 1-hydroxypropan-2-one and 3-hydroxybutan-2-one are all products from Maillard reactions (Belitz, Grosch, & Schieberle, 2009; O'Brien, 2009). The concentration of most other identified volatiles also increased after roasting (Table 2). Pyrrole and 2-acetylpyrrole were formed during roasting. Levels of caproic acid (hexanoic acid) increased about 200 times relative to the raw almonds. Caproic acid is found naturally in almonds and various nut oils, such as walnut, beechnut and hazelnut oil (Bail et al., 2009) and its increased level may be the result of oxidation of hexanal during heat processing (Reiser, Murty, & Rakoff, 1962). Levels of 2-pentylfuran correlated most strongly with increased roasting time (Table 2). The levels of limonene and α-pinene were found to decrease after roasting.

4. Conclusion

With the exception of decreases in benzaldehyde, 2-methyl-1-propanol, 3-methyl butanol, 2-phenylethyl alcohol, α-pinene and methylsulfanylmethane, all volatiles increased upon roasting; however, the degree by which individual compounds increased or decreased differed. The straight chain aldehydes and alcohols demonstrated significant ($p < 0.05$) but only minimal increases, while the levels of branched-chain aldehydes, alcohols, sulfur-containing compounds and heterocyclic compounds increased to a much greater extent. This difference may be related to the formation mechanisms of these two groups of compounds. Small increases in straight chain volatiles reflect heat-induced oxidation during roasting. The more significant increases in branched chain aldehydes, alcohols, sulfur-containing and heterocyclic compounds reflect Maillard reaction chemistry and the development of roasted almond flavour.

Acknowledgements

We thank the Almond Board of California for financial support and especially Guangwei Huang for his thoughtful input to this study.

References

Agila, A., & Barringer, S. (2012). Effect of roasting conditions on color and volatile profile including HMF level in sweet almonds (*Prunus dulcis*). *Journal of Food Science, 77*, C461–C468.

Alasalvar, C., Odabasi, A. Z., & Cadwallarder, K. R. (2004). Volatiles and flavor of five Turkish hazelnut varieties as evaluated by descriptive sensory analysis, electronic nose, and dynamic headspace analysis/GC–MS. *Journal of Food Science, 69*, SNQ99–SNQ106.

Alasalvar, C., Shahidi, F., & Cadwallader, K. R. (2003). Comparison of natural and roasted Turkish Tombul hazelnut (*Corylus avellana* L.) volatiles and flavor by DHA/GC/MS and descriptive sensory analysis. *Journal of Agricultural and Food Chemistry, 51*, 5067–5072.

Almond Board of California. (2007). *Guidelines for validation of dry roasting processes.*

Almond Board of California. (2012). Almond Almanac.

Baek, H. H., & Cadwallader, K. R. (1996). Volatile compounds in flavor concentrates produced from crayfish-processing byproducts with and without protease treatment. *Journal of Agricultural and Food Chemistry, 44*, 3262–3267.

Bail, S., Stuebiger, G., Unterweger, H., Buchbauer, G., & Krist, S. (2009). Characterization of volatile compounds and triacylglycerol profiles of nut oils using SPME-GC–MS and MALDI-TOF-MS. *European Journal of Lipid Science and Technology, 111*, 170–182.

Beck, J. J., Mahoney, N. E., Cook, D., & Gee, W. S. (2011). Volatile analysis of ground almonds contaminated with naturally occurring fungi. *Journal of Agricultural and Food Chemistry, 59*, 6180–6187.

Belitz, H.-D., Grosch, W., & Schieberle, P. (2009). Aroma compounds. In *Food chemistry*, pp. 340–402). Berlin, Germany: Springer.

Beltrán, A., Ramos, M., Grané, N., Martín, M. L., & Garrigós, M. C. (2011). Monitoring the oxidation of almond oils by HS-SPME-GC–MS and ATR-FTIR: Application of volatile compounds determination to cultivar authenticity. *Food Chemistry, 126*, 603–609.

Beltrán, A., Santonja, M., & Garrigós, M. C. (2011). Classification of almond cultivars using oil volatile compound determination by HS-SPME/GC–MS. *Journal of the American Oil Chemists' Society, 88*, 329–336.

Bi, H. X., & Ma, C. W. (2006). Synthesis of 3-methylbutanal by Strecker reaction at unelevated temperature and in acidic systems. *Chinese Chemical Letters, 17*, 1041–1044.

Coghe, S., Gheeraert, B., Michiels, A., & Delvaux, F. R. (2006). Development of Maillard reaction related characteristics during malt roasting. *Journal of the Institute of Brewing, 112*, 148–156.

Comuzzo, P., Tat, L., Tonizzo, A., & Battistutta, F. (2006). Yeast derivatives (extracts and autolysates) in winemaking: Release of volatile compounds and effects on wine aroma volatility. *Food Chemistry, 99*, 217–230.

Deetae, P., Spinnler, H. E., Bonnarme, P., & Helinck, S. (2009). Growth and aroma contribution of *Microbacterium foliorum, Proteus vulgaris* and *Psychrobacter* sp. during ripening in a cheese model medium. *Applied Microbiology and Biotechnology, 82*, 167–177.

Economic research service, U.S. Department of Agriculture. (2011). *Fruit and tree nut yearbook*.

Fugelsang, K. C., & Edwards, C. G. (2007). *Wine microbiology: Practical applications and procedures* (2nd ed.). New York, NY: Springer.

Hopfer, H., Ebeler, S. E., & Heymann, H. (2012). The combined effects of storage temperature and packaging type on the sensory and chemical properties of Chardonnay. *Journal of Agricultural and Food Chemistry, 60*, 10743–10754.

Isikber, A. A., Navarro, S., Finkelman, S., Rindner, M., & Dias, R. (2007). Propylene oxide as an alternative to methyl bromide for quarantine purposes. In E. J. Donahaye, S. Navarro, C. Bell, D. Jayas, R. Noyes, & T. W. Phillips (Eds.), *Proceedings of international conference on controlled atmosphere and fumigation in stored products, Gold-Coast, Australia, 8–13th August 2004* (pp. 185–191). Israel: FTIC Ltd. Publishing.

Lojzova, L., Riddellova, K., Hajslova, J., Zrostlikova, J., Schurek, J., & Cajka, T. (2009). Alternative GC–MS approaches in the analysis of substituted pyrazines and other volatile aromatic compounds formed during Maillard reaction in potato chips. *Analytica Chimica Acta, 641*, 101–109.

Mandalari, G., & Faulks, R. (2008). Release of protein, lipid, and vitamin E from almond seeds during digestion. *Journal of Agricultural and Food Chemistry, 56*, 3409–3416.

Mexis, S. F., Badeka, A. V., Chouliara, E., Riganakos, K. A., & Kontominas, M. G. (2009). Effect of γ-irradiation on the physicochemical and sensory properties of raw unpeeled almond kernels (*Prunus dulcis*). *Innovative Food Science and Emerging Technologies, 10*, 87–92.

Min, D. B., & Smouse, T. H. (1985). *Flavor chemistry of fats and oils*. Washington, DC: American Chemical Society.

Niemela, K. (2001). Identification of novel volatile sulfur and nitrogen compounds in kraft pulping process streams. In 11*th International symposium on wood and pulping chemistry, Nice, France 11–14th June 2001* (pp. 125–128).

Nutrient Data Laboratory. (2011). *Nutrient data for 12061, nuts, almonds* (*Prunus dulcis*). URL <http://ndb.nal.usda.gov/ndb/foods> Accessed 15.05.12.

O'Brien, J. (2009). Non-enzymatic degradation pathways of lactose and their significance in dairy products. In P. L. H. McSweeney & P. F. Fox (Eds.). *Advanced dairy chemistry: Lactose, water, salts and minor constituents* (Vol. 3, pp. 231–294). New York, NY: Springer.

Perez, A. G., Sanz, C., Olias, R., & Olias, J. M. (1999). Lipoxygenase and hydroperoxide lyase activities in ripening strawberry fruits. *Journal of Agricultural and Food Chemistry, 47*, 249–253.

Pićurić-Jovanović, K., & Milovanović, M. (1993). Analysis of volatile compounds in almond and plum kernel oils. *Journal of the American Oil Chemists' Society, 70*, 1101–1104.

Pripis-Nicolau, L., Bertrand, A., & Maujean, A. (2000). Formation of flavor components by the reaction of amino acid and carbonyl compounds in mild conditions. *Journal of Agricultural and Food Chemistry, 48*, 3761–3766.

Reiser, R., Murty, N. L., & Rakoff, H. (1962). Biosynthesis of linoleic acid from 1-C^{14}-*cis*-2-octenoic acid by the laying hen. *The Journal of Lipid Research, 3*, 56–59.

Sanahuja, A. B., Santonja, M. R., Teruel, N. G., Carratalá, M. L. M., & Selva, M. C. G. (2011). Classification of almond cultivars using oil volatile compounds determination by HS-SPME-GC–MS. *Journal of the American Oil Chemists' Society, 88*, 329–336.

Sanchez-Perez, R., Jorgensen, K., Olsen, C. E., Dicenta, F., & Moller, B. L. (2008). Bitterness in almonds. *Plant Physiology, 146*, 1040–1052.

Takei, Y., Shimada, K., & Watanabe, S. (1974). Volatile components of roasted almonds: Basic fraction. *Agricultural and Biological Chemistry, 38*, 645–648.

Takei, Y., & Yamanishi, T. (1974). Flavor components of roasted almond. *Agricultural and Biological Chemistry, 38*, 2329–2336.

Tieman, D., Taylor, M., Schauer, N., Fernie, A. R., Hanson, A. D., & Klee, H. J. (2006). Tomato aromatic amino acid decarboxylases participate in synthesis of the flavor volatiles 2-phenylethanol and 2-phenylacetaldehyde. *Proceedings of the National Academy of Sciences, 103*, 8287–8292.

Vázquez-Araujo, L., Enguix, L., Verdu, A., García-García, E., & Carbonell-Barrachina, A. A. (2008). Investigation of aromatic compounds in toasted almonds used for the manufacture of turrón. *European Food Research and Technology, 227*, 243–254.

Vázquez-Araujo, L., Verdu, A., Navarro, P., Martínez-Sánchez, F., & Carbonell-Barrachina, A. A. (2009). Changes in volatile compounds and sensory quality during toasting of Spanish almonds. *International Journal of Food Science & Technology, 44*, 2225–2233.

Vejaphan, W., & Hsieh, T. C. (1988). Volatile flavor components from boiled crayfish (*Procambarus clarkii*) tail meat. *Journal of Food Science, 53*, 1666–1670.

Zhang, G., Huang, G., Xiao, L., Seiber, J., & Mitchell, A. E. (2011). Acrylamide formation in almonds (*Prunus dulcis*): Influences of roasting time and temperature, precursors, varietal selection, and storage. *Journal of Agricultural and Food Chemistry, 59*, 8225–8232.