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Influence of Storage on Volatile Profiles in Roasted Almonds (*Prunus dulcis*)

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ABSTRACT: Hexanal, peroxide value, and lipid hydroperoxides are common indicators of lipid oxidation in food products. However, these markers are not always reliable as levels are dynamic and often can be detected only after significant oxidation has occurred. Changes in the volatile composition of light- and dark-roast almonds were evaluated during storage over 24 weeks at 25 or 35 °C using headspace solid phase microextraction (HS-SPME) gas chromatography−mass spectrometry (GC-MS). Several volatile changes were identified in association with early oxidation events in roasted almonds. Hexenal decreased significantly during the first 6 weeks of storage and did not increase above initial levels until 20−24 weeks of storage depending upon the degree of roast. In contrast, levels of 1-heptanol and 1-octanol increased at 16−20 weeks, depending upon the degree of roast, and no initial losses were observed. Seventeen new compounds, absent in raw and freshly roasted almonds but detectable after 6 weeks of storage, were identified. Of these, 2-octanone, 2-nonanone, 3-octen-2-one, 2-decanone, (*E*)-2-decenal, 2,4-nonadienal, pentyl oxirane, and especially acetic acid increased significantly (that is, >10 ng/g). The degree of roasting did not correlate with the levels of these compounds. Significant decreases in roasting-related aroma volatiles such as 2-methylbutanal, 3-methylbutanal, furfural, 2-phenylacetaldehyde, 2,3-butanedione, 2-methylpyrazine, and 1-methylthio-2-propanol were observed by 4 weeks of storage independent of the degree of roast or storage conditions.

KEYWORDS: *almonds, roast, storage, volatiles, headspace solid phase microextraction, HS-SPME, GC-MS, Prunus dulcis, oxidation*

INTRODUCTION

California is the top producer of almonds (*Prunus dulcis*) worldwide, with an estimated annual production of 1 million tons and accounting for 80% of world almond production in 2012−2013.[1] Almonds are typically dried to a moisture content of 5−8% in the field and then transported to a hulling/shelling facility, where they are cleaned, hulled, shelled, and crated for storage. Almonds left in the shell at ambient temperature do not show significant chemical and biochemical changes for 1 year.[2] Shelled almonds can undergo faster deteriorative changes, which lead to shorter shelf life. The most important deteriorative change that occurs during storage is the development of lipid oxidation and the production of off-aromas associated with rancidity. Ideal warehouse storage conditions for raw almonds are 2−7 °C at a relative humidity of 55−65%;[3] however, almonds are also commonly stored at ambient temperatures (~24 °C).

Dry (hot air) roasting is a common thermal process used in the production of a wide array of almond products.[4] Common temperatures used for dry-roasting almonds range from 130 to 155 °C.[4] At lower temperatures, 40−55 min is required to obtain a light to medium roast, whereas at higher temperatures 10−15 min is required to achieve a medium roast.[4] Although roasting is critical to the development of flavor compounds in almonds (e.g., pyrazines and furans), it also promotes reactions that lead to rancidity. Almonds are sensitive to lipid oxidation as 48−67% of the almond kernel dry weight is oil, depending upon the cultivar and growing conditions.[5,6] Almond oil is composed of ~63−79% oleic acid, 12−27% linoleic acid, 5−7% palmitic acid, and 0.3−0.8% palmitoleic acid, and 1−2.8% steric acid.[6] Factors that influence the rate of lipid oxidation in almonds include the composition of fatty acids,[7] the age of the product prior to roasting, roasting conditions, exposure to oxygen, exposure to light, preblanching, moisture content, storage temperature, and exposure to metals prior to roasting.[8−12] Markers of early rancidity development in roasted almonds would be beneficial to better predict shelf life and improve quality control.

Oxidative rancidity in almonds occurs in three phases. During the initial phase, reactive oxygen species combine with unsaturated fatty acids to produce hydroperoxides and free radicals.[12] This is followed by the autoxidation phase in which these unstable products react with additional lipid molecules to form further reactive species.[12] In the terminal phase, relatively unreactive volatile compounds are formed including hydrocarbons, aldehydes, and ketones. Although rancidity is one of the most pressing problems confronting food processors, there is no completely objective chemical method for measuring rancidity. Quality control laboratories currently rely on indirect measures of lipid oxidation such as peroxide values, free fatty acids, thiobarbituric acid (TBA), and conjugated dienes.[12] These measurements are difficult to use as accurate predictors of oxidation as they fluctuate with the various stages of lipid oxidation and during storage. For example, the peroxide value (PV), measures the initial stages of oxidation (i.e., lipid hydroperoxides). However, lipid hydroperoxides have short half-lives and degrade to form other products. Peroxide values

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Table 1. Identified Volatiles in Raw, Freshly Roasted, or Stored Roasted Almonds (cv. Butte/Padre)[a]

PCA code	volatile compound	t_R[b] of unknown	standard KI	unknown KI	literature KI[c]	extracted ion[d]	internal standard	compounds newly produced during storage
	aldehydes and ketones (28)							
X1	butanal[e]	3.44	784	784	822	72	octanal-d_{16}	
X2	2-methylbutanal	3.91		887	910	57	octanal-d_{16}	
X3	3-methylbutanal	3.97		900	912	44	octanal-d_{16}	
X4	2,3-butanedione[e]	4.94	960	961	970	86	octanal-d_{16}	
X5	pentanal	4.98		963	935	58	octanal-d_{16}	
X6	hexanal[e]	7.13	1073	1073	1084	72	octanal-d_{16}	
X7	2-heptanone[e]	9.72	1189	1179	1170	58	octanal-d_{16}	
X8	heptanal[e]	9.78	1184	1182	1174	70	octanal-d_{16}	
X9	2-hexenal	10.64		1215	1204	69	octanal-d_{16}	
X10	2-methyloxolan-3-one[e]	11.85	1261	1261	1266	43	octanal-d_{16}	
X11	3-hydroxybutan-2-one[e]	12.40	1281	1282	1287	88	octanal-d_{16}	
X12	2-octanone	12.41			1285	58	octanal-d_{16}	new
X13	octanal[e]	12.57	1288	1288	1280	84	octanal-d_{16}	
X14	1-hydroxypropan-2-one	12.76		1295	1291	74	octanal-d_{16}	
X15	(*Z*)-2-heptenal	13.49		1326	1299	83	octanal-d_{16}	
X16	2-nonanone	14.98			1388	58	octanal-d_{16}	new
X17	nonanal[e]	15.11	1395	1396	1385	98	octanal-d_{16}	
X18	3-octen-2-one	15.30			1323	111	octanal-d_{16}	new
X19	(*E*)-2-octenal[e]	15.70	1436	1435	1442	83	octanal-d_{16}	
X20	furfural[e]	16.12	1464	1465	1455	96	octanal-d_{16}	
X21	2-decanone	16.47			1484	58	octanal-d_{16}	new
X22	decanal[e]	16.63	1503	1502	1484	82	octanal-d_{16}	
X23	benzaldehyde[e]	16.90	1527	1528	1495	106	octanal-d_{16}	
X24	(*Z*)-2-nonenal[e]	17.01	1537	1539	1510	83	octanal-d_{16}	
X25	2-phenylacetaldehyde[e]	18.04	1639	1640	1640	91	octanal-d_{16}	
X26	(*E*)-2-decenal	18.11			1760	41	octanal-d_{16}	new
X27	2,4-nonadienal	18.50			1709	81	octanal-d_{16}	new
X28	2-undecenal	18.86			1712	83	octanal-d_{16}	new
	pyrazines (7)							
X29	2-methylpyrazine[e]	11.97	1266	1265	1239	94	2-methylpyrazine-d_6	
X30	2,5-dimethylpyrazine[e]	13.51	1327	1326	1320	108	2-methylpyrazine-d_6	
X31	2,6-dimethylpyrazine	13.66		1334	1308	108	2-methylpyrazine-d_6	
X32	2-ethylpyrazine	13.81		1340	1354	107	2-methylpyrazine-d_6	
X33	2,3-dimethylpyrazine	14.12		1353	1324	108	2-methylpyrazine-d_6	
X34	2-ethyl-6-methylpyrazine	15.00		1391	1381	121	2-methylpyrazine-d_6	
X35	trimethylpyrazine	15.34		1409	1395	122	2-methylpyrazine-d_6	
	alcohols (18)							
X36	2-methyl-1-propanol[e]	7.54	1096	1092	1099	74	hexyl-d_{13} alcohol	
X37	3-pentanol[e]	7.92	1111	1108	1107	59	hexyl-d_{13} alcohol	
X38	2-propenol[e]	7.98		1111	1136	57	hexyl-d_{13} alcohol	
X39	1-butanol[e]	8.82	1143	1144	1145	56	hexyl-d_{13} alcohol	
X40	3-methyl-1-butanol[e]	10.46	1209	1208	1205	70	hexyl-d_{13} alcohol	
X41	1-pentanol[e]	11.61	1251	1252	1255	70	hexyl-d_{13} alcohol	
X42	1-chloro-2-propanol[e]	13.23	1314	1315		79	hexyl-d_{13} alcohol	
X43	1-hexanol[e]	14.33	1360	1362	1360	69	hexyl-d_{13} alcohol	
X44	2-chloro-1-propanol	14.54		1371		31	hexyl-d_{13} alcohol	
X45	1-octen-3-ol	15.95			1395	57	hexyl-d_{13} alcohol	new
X46	1-methylthio-2-propanol[e]	15.96	1454	1454		106	hexyl-d_{13} alcohol	
X47	1-heptanol[e]	16.09	1467	1463	1467	70	hexyl-d_{13} alcohol	
X48	2-ethylthioethanol[e]	16.98	1597	1536		75	hexyl-d_{13} alcohol	
X49	1-octanol[e]	17.26	1563	1564	1553	84	hexyl-d_{13} alcohol	
X50	1,2-propanediol	17.54		1591	1603	45	hexyl-d_{13} alcohol	
X51	nonanol	18.11			1619	56	hexyl-d_{13} alcohol	new
X52	furfuryl alcohol[e]	18.13	1661	1663	1661	98	hexyl-d_{13} alcohol	
X53	2-phenylethyl alcohol[e]	19.90	1929	1930	1925	91	hexyl-d_{13} alcohol	
	additional compounds (18)							
X54	ethyl acetate[e]	3.58	874	876	885	61	2-methylpyrazine-d_6	
X55	α-pinene[e]	5.82	1014	1013	1032	93	2-methylpyrazine-d_6	
X56	methylsulfanylmethane[e]	6.88	1062	1062	1071	94	2-methylpyrazine-d_6	

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Table 1. continued

PCA code	volatile compound	t_R[b] of unknown	standard KI	unknown KI	literature KI[c]	extracted ion[d]	internal standard	compounds newly produced during storage
X57	pentyl oxirane	8.66				71	octanal-d_{16}	new
X58	hexyl oxirane	11.54				71	octanal-d_{16}	new
X59	limonene[e]	10.10	1197	1195	1201	68	2-methylpyrazine-d_6	
X60	2-pentylfuran	11.01		1229	1221	81	2-methylpyrazine-d_6	
X61	acetic acid	15.91			1450	43	hexyl-d_{13} alcohol	new
X62	pyrrole[e]	16.76	1514	1515	1509	67	hexyl-d_{13} alcohol	
X63	γ-dihydrofuran-2(3*H*)-one	17.95		1640	1635	86	hexyl-d_{13} alcohol	
X64	vinyl hexanoate	18.16				99	hexyl-d_{13} alcohol	new
X65	γ-oxepan-2-one[e]	18.57	1719	1720	1694	85	hexyl-d_{13} alcohol	
X66	pentanoic acid	18.77			1720	60	hexyl-d_{13} alcohol	new
X67	caproic acid[e]	19.47	1859	1857	1829	60	hexyl-d_{13} alcohol	
X68	heptanoic acid	20.08			1990	60	hexyl-d_{13} alcohol	new
X69	2-acetylpyrrole	20.24		1991	1950	94	hexyl-d_{13} alcohol	
X70	octanoic acid	20.66			2083	60	hexyl-d_{13} alcohol	new
X71	nonanoic acid	21.23			2202	60	hexyl-d_{13} alcohol	new

[a]Volatiles were identified in freshly roasted almonds and in stored almonds after roasting. DB-Wax was used as the analytical column. [b]t_R, retention time. [c]KI, Kovats' index; 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.

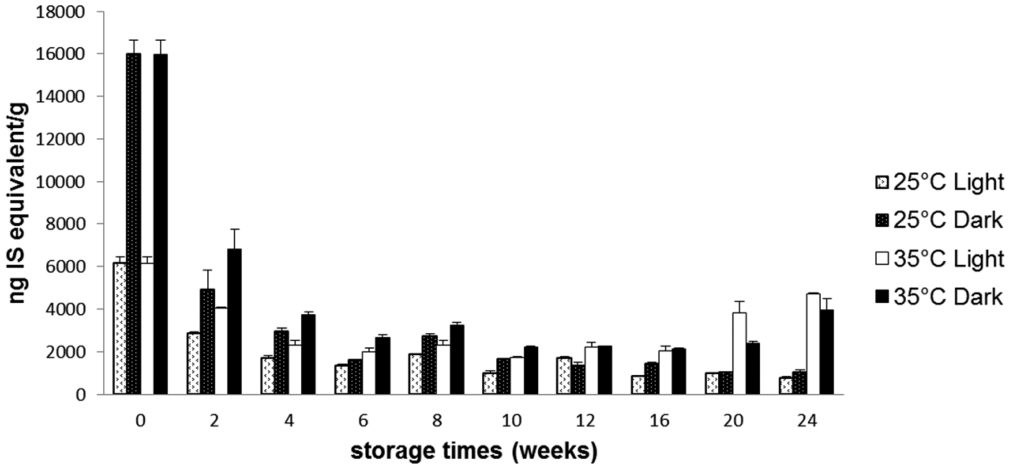

Figure 1. Sum of almond volatile compounds for different roastings, storage temperatures, and storage times.

are not static, and moderate values may reflect depletion rather than low levels of oxidation. The TBA assay can be used to monitor the formation of malondialdehyde, a product of lipid oxidation.[13] However, low TBA values are not absolute indicators of oxidation as malondialdehyde may not be a good marker for other lipid-derived aldehydes and artifacts can easily form during the analysis procedure.[13] Hexanal, the most commonly used marker of lipid oxidation, exists in raw almonds and is generated during heat processing.[14,15] During the initial stages of storage, the hexanal, formed during thermal processing, volatilizes, and levels decrease.[16] As lipids oxidize during storage, the levels of hexanal increase.[17]

Numerous volatile compounds are generated through the Maillard reaction and via lipid oxidation during roasting and are important to flavor.[18,19] These include ketones, aldehydes, pyrazines, alcohols, aromatic hydrocarbons, furans, and pyrroles. Pyrazines, furans, and pyrroles are key components of toasted almond aroma.[18] Pyrazines, which have nutty and roasted aromas, are formed during heating via Maillard sugar–amine reactions and Strecker degradation.[20] The thermal degradation of sugars such as fructose and glucose produce furan-containing compounds (e.g., furfural).[18] Linoleic acid is a precursor to many aldehydes and alcohols[21] including (*E*)-2-heptenal and nonanal.[22] (*E*)-2-Heptenal is responsible for pungent and green aromas,[18] and nonanal is responsible for tallow and fruity aromas.[23] Thermal decomposition of methyl linoleate hydroperoxide generates 1-octen-3-ol,[22] which contributes to an herbaceous aroma in almonds.[18] The oxidation of linolenic acid produces (*Z*)-3-hexen-1-ol (a green leaf aroma)[24] and 1-butanol (an unripe apple aroma).[22,25] Other lipid oxidation volatiles such as lactones, including butyrolactone, contribute to milky and creamy aromas in foods[26]

Roasted almonds often display inconsistent shelf life stability and can develop rancidity during storage, which is usually detected only after nuts develop considerable off-flavors. The inconsistent identification of the presence and extent of rancidity leads to considerable product loss. At the same time, the levels of the desirable aromas that arise from roasting tend to decrease during storage. To address this, we used HS-SPME GC-MS to (1) evaluate changes in volatile profiles of roasted almonds during 6 months of storage, (2) identify possible early markers of rancidity development in roasted almonds, and (3) gain a better understanding of the time line

Table 2. Volatiles Detected in Almond Samples: Raw, Freshly Roasted, or Stored Roasted at 35 °C for 24 Weeks (Nanograms per Gram)

		light roast (28 min at 138 °C)			dark roast (38 min at 138 °C)		
volatile compound	raw	0 weeks	10 weeks	24 weeks	0 weeks	10 weeks	24 weeks
aldehydes and ketones							
butanal	19.6 ± 2.7	27.6 ± 1.5	ND[a]	12.6 ± 1.2	40.8 ± 2.1	ND	25.4 ± 2.3
2-methylbutanal	14.3 ± 0.3	1468.6 ± 25.7	119.9 ± 3.4	76.6 ± 0.4	6573.7 ± 275.0	325.1 ± 58.1	137.6 ± 17.3
3-methylbutanal	32.4 ± 0.5	911.4 ± 50.9	146.8 ± 3.6	89.0 ± 0.9	4268.9 ± 381.8	231.6 ± 45.2	117.3 ± 10.3
2,3-butanedione	8.0 ± 0.3	100.3 ± 0.8	3.4 ± 4.8	10.6 ± 1.3	226.3 ± 13.7	7.3 ± 0.3	16.8 ± 1.7
pentanal	50.4 ± 5.7	223.0 ± 8.6	44.7 ± 1.2	221.8 ± 15.6	264.1 ± 15.9	33.2 ± 4.2	369.3 ± 53.6
hexanal	422.6 ± 97.9	983.0 ± 133.7	441.4 ± 1.9	1631.8 ± 75.1	1140.8 ± 3.8	377.8 ± 45.8	1565.4 ± 251.2
2-heptanone	50.0 ± 4.7	72.0 ± 7.3	65.7 ± 1.6	237.3 ± 0.9	123.6 ± 3.0	40.1 ± 2.6	351.7 ± 38.6
heptanal	40.5 ± 8.9	75.2 ± 16.2	90.0 ± 1.4	306.0 ± 3.9	114.8 ± 3.0	60.6 ± 2.8	214.6 ± 33.0
2-hexenal	ND	14.6 ± 2.7	ND	5.1 ± 0.3	14.1 ± 2.7	ND	4.1 ± 0.0
2-methyloxolan-3-one	ND	15.4 ± 1.3	24.4 ± 1.5	8.7 ± 0.9	128.1 ± 11.0	57.9 ± 6.8	25.1 ± 2.5
3-hydroxybutan-2-one	ND	2.2 ± 0.2	ND	ND	3.8 ± 0.6	0.3 ± 0.1	ND
2-octanone	ND	ND	ND	33.3 ± 0.1	ND	ND	34.2 ± 4.0
octanal	25.2 ± 4.7	31.1 ± 7.3	53.5 ± 1.5	265.1 ± 6.2	42.0 ± 3.0	36.2 ± 2.0	155.6 ± 27.5
1-hydroxypropan-2-one	1.3 ± 0.0	9.0 ± 0.9	0.4 ± 0.0	0.2 ± 0.0	13.7 ± 3.0	0.8 ± 0.1	0.5 ± 0.1
(*Z*)-2-heptenal	19.1 ± 0.9	65.6 ± 13.2	9.7 ± 0.2	43.9 ± 0.6	61.9 ± 1.6	9.5 ± 0.5	32.1 ± 4.4
2-nonanone	ND	ND	ND	31.2 ± 0.2	ND	ND	28.6 ± 4.3
nonanal	36.6 ± 4.9	55.9 ± 13.3	46.1 ± 0.3	112.5 ± 8.1	70.5 ± 18.9	50.6 ± 2.5	59.9 ± 10.3
3-octen-2-one	ND	ND	ND	45.4 ± 0.9	ND	ND	33.6 ± 4.5
(*E*)-2-octenal	7.3 ± 0.9	12.5 ± 2.1	5.7 ± 0.1	42.0 ± 0.3	15.9 ± 2.0	6.8 ± 0.6	34.5 ± 5.3
furfural	ND	103.2 ± 8.7	11.2 ± 1.0	4.9 ± 0.1	460.0 ± 21.4	31.5 ± 2.0	8.9 ± 0.8
2-decanone	ND	ND	ND	10.3 ± 0.4	ND	ND	7.6 ± 1.3
decanal	ND	6.9 ± 2.3	2.5 ± 0.4	8.3 ± 0.6	4.6 ± 1.0	2.4 ± 0.3	3.8 ± 0.5
benzaldehyde	2934.6 ± 272.5	368.8 ± 41.2	431.7 ± 20.5	1048.6 ± 81.5	331.9 ± 65.4	724.8 ± 173.5	180.3 ± 5.8
(*Z*)-2-nonenal	ND	ND	ND	5.7 ± 0.5	5.3 ± 1.7	ND	2.9 ± 0.3
2-phenylacetaldehyde	ND	107.5 ± 20.3	20.2 ± 0.8	14.2 ± 0.8	491.3 ± 45.4	27.0 ± 3.6	8.8 ± 1.7
(*E*)-2-decenal	ND	ND	ND	10.9 ± 0.9	ND	ND	6.6 ± 1.4
2,4-nonadienal	ND	ND	ND	15.4 ± 1.1	ND	ND	10.4 ± 1.6
2-undecenal	ND	ND	ND	3.4 ± 0.3	ND	ND	1.8 ± 0.3
pyrazines							
2-methylpyrazine	ND	4.1 ± 0.3	4.1 ± 0.2	2.6 ± 0.2	26.5 ± 1.8	9.1 ± 0.8	7.3 ± 0.7
2,5-dimethylpyrazine	11.4 ± 0.5	16.2 ± 0.6	21.0 ± 1.5	7.3 ± 0.6	66.5 ± 0.4	47.5 ± 2.0	28.2 ± 2.2
2,6-dimethylpyrazine	ND	ND	1.3 ± 0.1	0.8 ± 0.1	4.2 ± 0.6	4.0 ± 0.2	2.9 ± 0.3
2-ethylpyrazine	ND	ND	ND	ND	3.2 ± 0.1	1.8 ± 0.1	1.4 ± 0.1
2,3-dimethylpyrazine	ND	ND	ND	ND	1.4 ± 0.1	0.8 ± 0.0	0.6 ± 0.0
2-ethyl-6-methylpyrazine	ND	ND	0.6 ± 0.1	0.6 ± 0.1	2.2 ± 0.0	2.2 ± 0.0	2.2 ± 0.2
trimethylpyrazine	ND	ND	1.8 ± 0.1	1.0 ± 0.0	6.1 ± 0.2	6.5 ± 0.1	5.3 ± 0.6
alcohols							
2-methyl-1-propanol	3.6 ± 0.3	1.3 ± 0.1	0.5 ± 0.0	0.4 ± 0.0	1.1 ± 0.1	0.3 ± 0.0	0.3 ± 0.0
3-pentanol	ND	0.8 ± 0.1	ND	ND	2.7 ± 0.3	0.6 ± 0.0	ND
2-propenol	ND	2.0 ± 0.0	ND	ND	2.2 ± 0.1	ND	0.1 ± 0.1
1-butanol	8.4 ± 2.3	11.2 ± 1.1	5.1 ± 1.9	4.5 ± 0.1	10.7 ± 0.4	4.3 ± 0.3	11.6 ± 1.3
3-methyl-1-butanol	86.4 ± 3.3	19.1 ± 0.3	13.7 ± 0.6	15.0 ± 1.0	17.2 ± 0.6	10.6 ± 0.7	8.1 ± 0.6
1-pentanol	30.3 ± 4.4	45.6 ± 2.9	29.3 ± 1.2	52.1 ± 0.0	54.3 ± 1.3	14.4 ± 1.8	101.1 ± 11.2
1-chloro-2-propanol	106.2 ± 5.4	161.9 ± 2.8	12.9 ± 0.8	1.6 ± 0.0	149.6 ± 7.6	11.3 ± 1.2	2.0 ± 0.3
1-hexanol	47.0 ± 1.1	53.1 ± 5.5	50.6 ± 2.1	48.0 ± 1.1	70.1 ± 0.7	21.8 ± 1.2	23.1 ± 2.3
2-chloro-1-propanol	41.9 ± 3.5	59.5 ± 0.3	5.9 ± 0.2	1.1 ± 0.3	53.4 ± 2.2	5.5 ± 0.3	1.1 ± 0.2
1-octen-3-ol	ND	ND	ND	6.9 ± 0.1	ND	ND	8.9 ± 1.3
1-methylthio-2-propanol	12.8 ± 1.3	247.2 ± 23.9	38.9 ± 2.4	7.2 ± 0.8	325.0 ± 53.1	19.4 ± 1.5	4.5 ± 0.8
1-heptanol	3.2 ± 0.4	3.8 ± 1.0	8.7 ± 0.5	36.7 ± 1.1	6.0 ± 0.4	5.0 ± 0.1	33.5 ± 4.6
2-ethyl thioethanol	1.0 ± 0.0	20.5 ± 3.1	4.7 ± 0.3	1.1 ± 0.0	29.2 ± 3.9	3.0 ± 0.2	0.9 ± 0.1
1-octanol	0.8 ± 0.0	1.2 ± 0.2	2.0 ± 0.1	7.6 ± 0.2	1.6 ± 0.1	1.2 ± 0.0	5.9 ± 1.0
1,2-propanediol	269.1 ± 2.5	789.4 ± 72.3	210.6 ± 5.5	139.3 ± 3.5	647.0 ± 73.8	208.4 ± 35.2	258.5 ± 51.1
nonanol	ND	ND	ND	2.0 ± 0.1	ND	ND	1.0 ± 0.1
furfuryl alcohol	0.6 ± 0.0	1.2 ± 0.1	0.8 ± 0.1	0.6 ± 0.0	5.2 ± 0.4	1.1 ± 0.1	0.4 ± 0.0
2-phenylethyl alcohol	6.2 ± 0.6	0.9 ± 0.0	1.5 ± 0.1	1.9 ± 0.1	0.9 ± 0.2	1.5 ± 0.0	1.6 ± 0.1
additional compounds							
ethyl acetate	ND	12.0 ± 1.2	ND	ND	9.9 ± 0.8	ND	ND

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Table 2. continued

		light roast (28 min at 138 °C)			dark roast (38 min at 138 °C)		
volatile compound	raw	0 weeks	10 weeks	24 weeks	0 weeks	10 weeks	24 weeks
α-pinene	15.0 ± 0.1	16.5 ± 1.5	5.3 ± 0.4	2.3 ± 0.2	14.6 ± 0.9	5.1 ± 0.3	2.8 ± 0.5
methylsulfanylmethane	ND	4.5 ± 0.7	ND	ND	6.1 ± 2.0	ND	ND
pentyl oxirane	ND	ND	ND	27.8 ± 0.9	ND	ND	97.5 ± 9.3
hexyl oxirane	ND	ND	ND	42.1 ± 0.2	ND	ND	2.9 ± 0.3
limonene	16.6 ± 0.5	14.5 ± 1.4	6.5 ± 0.2	3.3 ± 0.2	13.0 ± 0.5	5.1 ± 0.1	3.0 ± 0.2
2-pentylfuran	2.4 ± 0.8	16.6 ± 1.2	12.8 ± 0.8	49.8 ± 3.1	30.0 ± 0.2	14.7 ± 0.2	27.2 ± 1.0
acetic acid	ND	ND	ND	45.2 ± 2.3	ND	ND	60.2 ± 16.1
pyrrole	ND	0.6 ± 0.1	0.2 ± 0.0	0.4 ± 0.0	2.1 ± 0.3	0.2 ± 0.0	0.4 ± 0.1
γ-dihydrofuran-2(3*H*)-one	0.7 ± 0.0	1.8 ± 0.2	0.9 ± 0.1	0.9 ± 0.1	2.2 ± 0.1	0.9 ± 0.1	1.1 ± 0.2
vinyl hexanoate	ND	ND	ND	4.9 ± 0.2	ND	ND	8.1 ± 1.3
γ-oxepan-2-one	1.2 ± 0.3	1.6 ± 0.2	2.8 ± 0.1	8.0 ± 0.1	2.4 ± 0.3	1.7 ± 0.1	7.1 ± 1.0
pentanoic acid	ND	ND	ND	2.5 ± 0.2	ND	ND	5.9 ± 1.9
caproic acid	1.8 ± 0.6	5.7 ± 1.3	9.2 ± 0.6	42.4 ± 4.3	6.7 ± 0.1	10.7 ± 0.7	52.0 ± 15.8
heptanoic acid	ND	ND	ND	4.6 ± 0.4	ND	ND	2.7 ± 0.6
2-acetylpyrrole	ND	0.2 ± 0.0	0.4 ± 0.0	0.5 ± 0.0	0.7 ± 0.1	0.7 ± 0.0	0.8 ± 0.1
octanoic acid	ND	ND	ND	5.1 ± 0.7	ND	ND	2.0 ± 0.3
nonanoic acid	ND	ND	ND	2.5 ± 0.2	ND	ND	0.4 ± 0.0

[a]ND, not detected.

for fading of aromas and the point when oxidation products start to dominate volatile profiles.

MATERIALS AND METHODS

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

Almond Samples and Roasting. Raw almond kernels (cv. Butte/Padre) were obtained from Hughson Nut Co. (Hughson, CA, USA) and had been in storage at ambient warehouse temperatures for 7 months since harvest. Kernels were commercially dry roasted using a Revent baking rotary roaster (Ready Roast, Madera, CA, USA). Almonds were roasted in triplicate batches (4.5−5.4 kg each) at 138 °C using different roasting times to achieve light (28 min) and dark roast (38 min). The almonds were stored in two E7/2 Conviron chambers (Manitoba, Canada) with controlled environments of 25 or 35 °C and at 65% relative humidity. The almonds were placed in a single layer on trays in the dark by covering the trays with aluminum foil to simulate dark storage. All almonds were evaluated at 0, 2, 4, 6, 8, 10, 12, 16, 20, and 24 weeks of storage.

To prepare samples for analysis, a random 50 g sample was removed from each tray and ground for 5 s at low speed with a Waring laboratory blender (Torrington, CT, USA). The ground samples were passed through a Tyler standard sieve (16 mesh; Mentor, OH, USA) to collect almond powder of a uniform particle size. For HS-SPME analysis, 5 g (±1%) of the powder was transferred into a 22.5 × 75 mm (20 mL) glass headspace vial (Sigma-Aldrich). Samples were prepared in duplicate (n = 2).

HS-SPME Sampling and Gas Chromatography Analysis. Volatile extraction was carried out as described previously.[27] Briefly, a 1 cm 50/30 μm SPME fiber assembly coated with divinylbenzene/carboxen/polydimethylsiloxane (Supelco, Inc.) was used for headspace analyses of almond sample volatiles. A mixed internal standard solution (octanal-d_{16}, 2-methylpyrazine-d_6, and *n*-hexyl-d_{13} alcohol) was added to each headspace vial containing a 5 g sample of ground almond (10 ng/g). Equilibration time was 40 min, and the SPME fiber extraction time was 30 min in the headspace of the vials at room temperature (24 ± 1 °C). Following headspace extraction, SPME fibers were injected into the GC and remained in the GC inlet for 10 min.

GC-MS Analysis. Volatile analysis was determined using GC-MS analysis on an HP 6890 coupled to an Agilent 5973 mass selective detector (Agilent, Palo Alto, CA, USA) as previously described.[27] Compounds were separated on a DB-Wax column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Agilent Technologies) by applying 35 °C for 1 min, 5 °C/min to 100 °C, and 20 °C/min to a final temperature of 250 °C, with a final holding time of 5 min. The injection was performed in splitless mode (0.7 mm splitless inlet liner, Supelco), and the injector temperature was 220 °C. The purge valve was opened at 0.5 min at a 50 mL/min flow rate. Carrier gas was helium (99.999%) with a constant starting flow rate at 0.7 mL/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 by scanning from m/z 30 to 150 at a rate of 3.06 scans/s.

Identification and Relative Quantification of Volatile Compounds. Volatile compounds were identified by comparison of their mass spectra and retention times with those of authentic standards. Volatile compounds without authentic standards were tentatively identified by comparing the Kovats' retention indices (KI) 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 KIs were calculated from the retention times of C_6−C_{40} *n*-alkanes.

The full spectrum was scanned in total ion chromatogram (TIC) mode. Relative quantification of each volatile compound was performed using a unique extracted ion peak area at its respective retention time 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) as described previously.[27] Concentration was calculated using the following equation according to Baek and Cadwallader:[28]

$$\text{concentration}\left(\frac{\text{ng}}{\text{g}}\right) = \frac{\text{extracted ion peak area}}{\text{extracted ion peak area of IS}} \times \left(\text{IS} \times \frac{10\ \text{ng}}{\text{g}}\right)$$

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

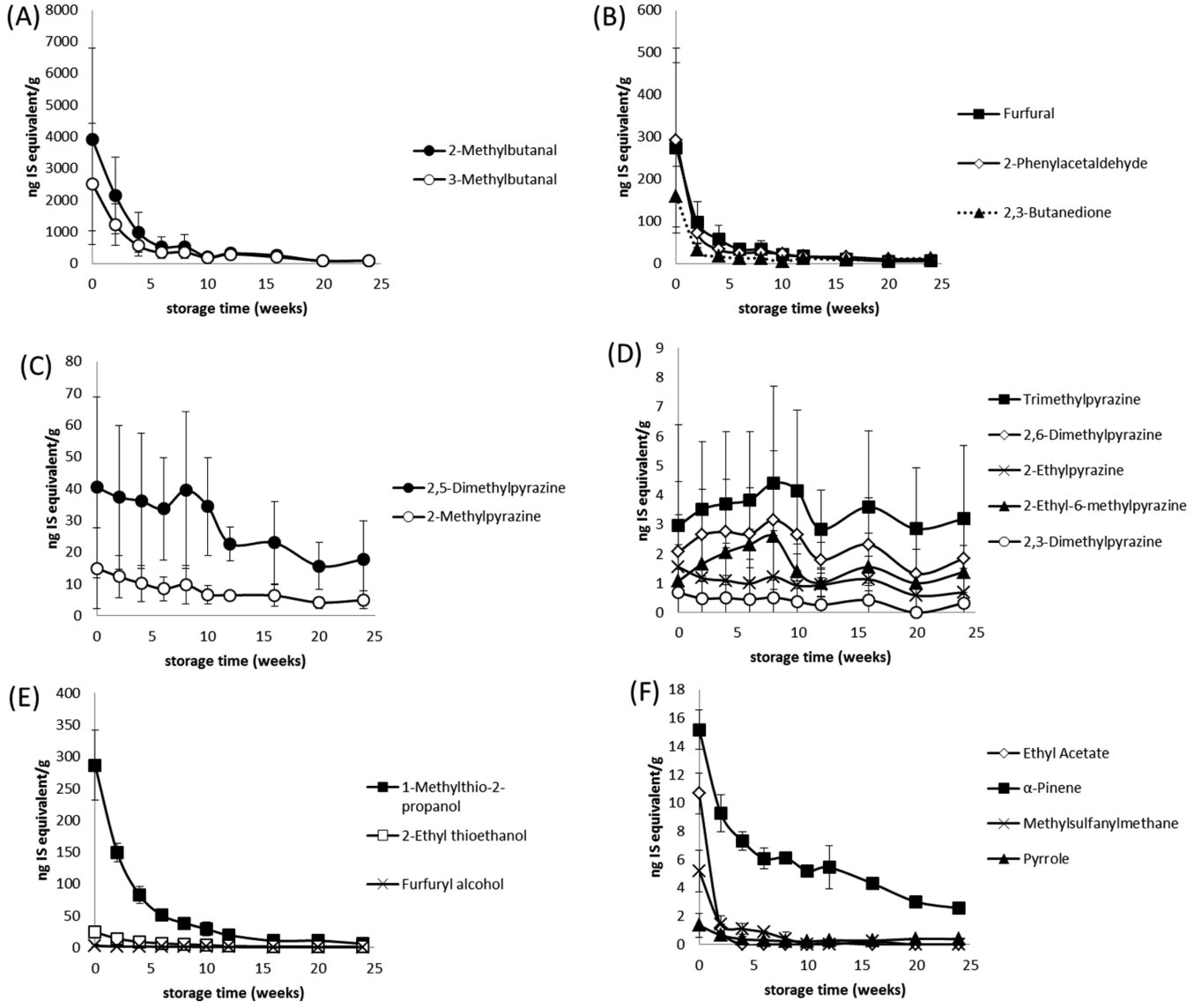

Figure 2. Roasted almond volatile compounds that decreased during almond storage: (A, B) carbonyls; (C, D) pyrazines; (E) alcohols; (F) additional volatiles. Concentrations are the average concentrations across the roasting treatments evaluated (i.e., light- and dark-roasted samples) and stored at 35 °C over 24 weeks.

concentration of the analyte in a 5 g sample based on the concentration of the appropriate IS (10 ng IS/g almond). The obtained relative concentration was used to compare the difference in volatile profiles among raw and roasted almonds.

Statistical Analysis. Principal component analysis (PCA) was performed to visualize clustering formation of different conditions (roasting time and storage time) and the relationship between volatile compounds and samples. Before PCA was performed, a one-way analysis of variance (ANOVA) was used to determine the volatile compounds significantly different in volatile concentrations across the whole data set. XLSTAT (version 2013.05.06) was employed for this analysis. The data were then normalized by log transformation for normal distribution and autoscaling for unit scaling. MetaboAnalyst (www.metaboanalyst.ca) was used for PCA.

■ RESULTS AND DISCUSSION

Seventy-one volatile compounds were identified using NIST libraries and the Kovats index, in freshly roasted and roasted stored almonds.[27] These include 28 aldehydes and ketones, 7 pyrazines, 18 alcohols, and 18 additional compounds (Table 1). The identities of 38 of these compounds were confirmed with authentic standards. Raw almonds contained the fewest volatiles, whereas levels increased in freshly roasted and roasted stored almonds. Some volatiles were specifically unique to the raw,[27] roasted, or roasted stored almonds (Table 1). Seventeen new volatiles were formed during storage and include ketones (2-octanone, 2-nonanone, 3-octen-2-one, and 2-decanone), aldehydes ((*E*)-2-decenal, 2,4-nonadienal, and 2-undecenal), alcohols (1-octen-3-ol and nonanol), oxiranes (pentyl oxirane and hexyl oxirane), and short-chain acids (acetic acid, pentanoic acid, heptanoic acid, and octanoic acid). Higher levels of 1-octen-3-ol, acetic acid, and pentanoic acid were found in the dark-roast almonds as compared to the light-roast almonds. Lower levels of 3-oceten-2-one, 2-decanone, (*E*)-2-decenal, 2,4-nonadienal, and 2-undecenal were found in the dark-roast almonds as compared to the light-roast almonds.

The roasted almonds were stored in dark controlled environments at 25 or 35 °C with 65% relative humidity. Storage studies evaluated the influence of storage temperature and storage time on total volatile compounds in light- and dark-roast almonds over 24 weeks. The dark-roast almonds had

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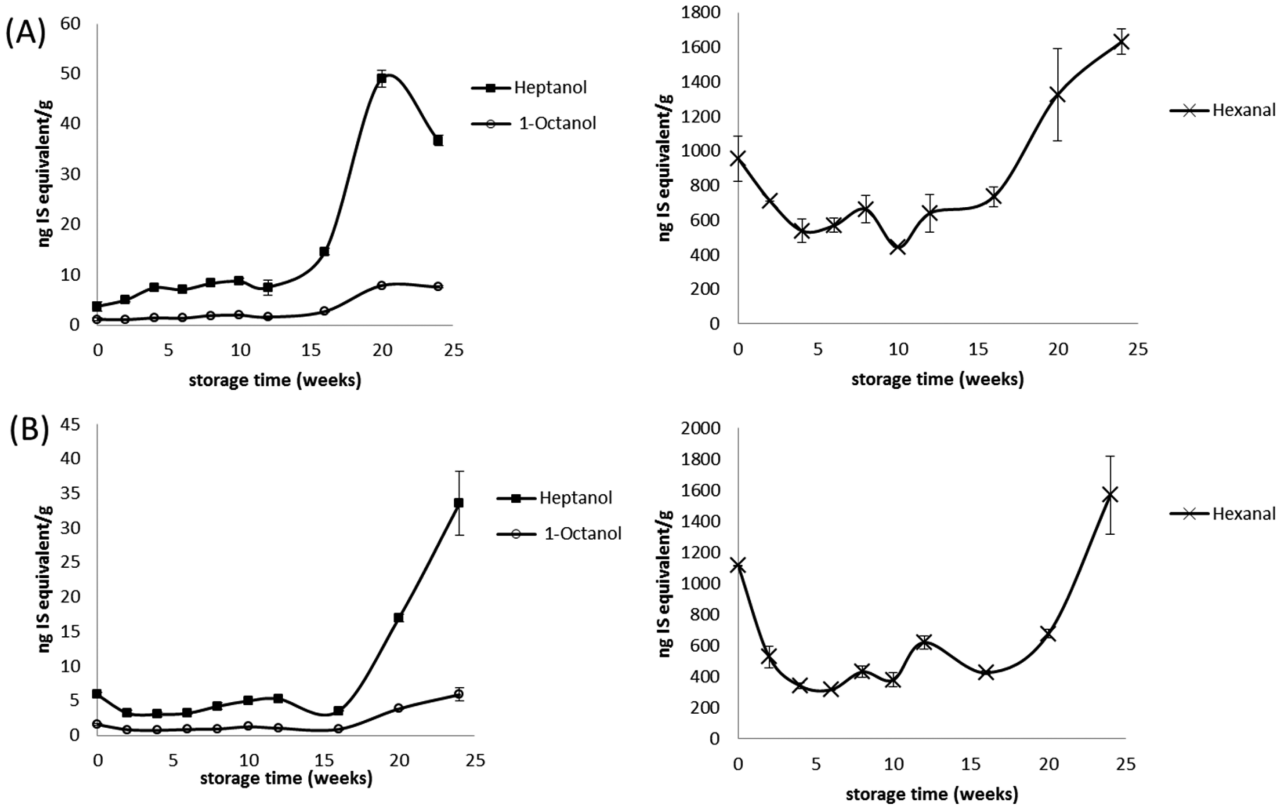

Figure 3. Roasted almond volatile compounds that increased with storage time: 1-heptanol, 1-octanol, and hexanal (a traditional indicator for oxidation in almonds) in (A) light-roasted and (B) dark-roasted samples stored at 35 °C over 24 weeks.

Table 3. Volatiles Formed during the Storage of Almonds at 35°C (Nanograms per Gram)

	light roast (28 min at 138 °C)			dark roast (38 min at 138 °C)		
volatile compound	16 weeks	20 weeks	24 weeks	16 weeks	20 weeks	24 weeks
2-octanone	13.4 ± 1.4	52.3 ± 2.9	33.3 ± 0.1	6.4 ± 0.2	15.4 ± 0.9	34.2 ± 4.0
2-nonanone	9.8 ± 1.4	47.5 ± 0.9	31.2 ± 0.2	4.8 ± 0.3	16.4 ± 0.4	28.6 ± 4.3
3-octen-2-one	18.1 ± 1.8	41.1 ± 2.0	45.4 ± 0.9	9.1 ± 0.4	19.7 ± 0.6	33.6 ± 4.5
2-decanone	2.8 ± 0.2	13.4 ± 0.2	10.3 ± 0.4	ND[a]	7.2 ± 1.4	7.6 ± 1.3
(*E*)-2-decenal	2.9 ± 0.1	7.1 ± 1.1	10.9 ± 0.9	2.4 ± 0.8	5.6 ± 0.4	6.6 ± 1.4
2,4-nonadienal	10.5 ± 0.9	14.2 ± 1.2	15.4 ± 1.1	7.5 ± 0.1	10.9 ± 0.5	10.4 ± 1.6
2-undecenal	ND	2.1 ± 0.7	3.4 ± 0.3	ND	1.5 ± 0.1	1.8 ± 0.3
1-octen-3-ol	2.2 ± 0.2	7.4 ± 0.4	6.9 ± 0.1	1.4 ± 0.0	4.1 ± 0.0	8.9 ± 1.3
nonanol	0.8 ± 0.1	2.2 ± 0.1	2.0 ± 0.1	0.5 ± 0.1	1.1 ± 0.3	1.0 ± 0.1
pentyl oxirane	9.9 ± 0.8	55.8 ± 11.1	27.8 ± 0.9	5.0 ± 0.8	9.5 ± 0.4	97.5 ± 9.3
hexyl oxirane	31.0 ± 3.1	1.7 ± 0.7	42.1 ± 0.2	9.7 ± 1.5	12.2 ± 0.6	2.9 ± 0.3
acetic acid	35.8 ± 2.7	60.8 ± 3.0	45.2 ± 2.3	43.5 ± 5.4	57.9 ± 1.5	60.2 ± 16.1
vinyl hexanoate	1.5 ± 0.2	6.8 ± 0.1	4.9 ± 0.2	1.2 ± 0.0	4.1 ± 0.4	8.1 ± 1.3
pentanoic acid	0.9 ± 0.1	6.1 ± 0.2	2.5 ± 0.2	0.5 ± 0.1	3.3 ± 0.0	5.9 ± 1.9
heptanoic acid	0.6 ± 0.0	5.4 ± 2.3	4.6 ± 0.4	0.5 ± 0.1	4.1 ± 0.7	2.7 ± 0.6
octanoic acid	0.4 ± 0.1	5.2 ± 2.3	5.1 ± 0.7	0.2 ± 0.0	3.6 ± 0.7	2.0 ± 0.3
nonanoic acid	ND	1.3 ± 0.8	2.5 ± 0.2	ND	0.6 ± 0.2	0.4 ± 0.0

[a]ND, not detected.

higher levels of total volatiles as compared to the light-roast almonds (Figure 1). Regardless of the degree of roasting or storage temperature, total volatiles decreased significantly during the first 4 weeks of storage. Volatiles continued to decrease at a slower rate between 6 and 24 weeks. The decrease in total volatiles was due to the loss of volatile compounds that were formed during the roasting process (Table 2). The almonds stored at 35 °C demonstrated increases in total volatiles after 20 weeks of storage, whereas no increases were observed in almonds stored at 25 °C.

The decreases in volatile compounds in the light- and dark-roast almonds stored at 25 or 35 °C were similar. In general, roasting increases the concentration of branch-chain aldehydes, alcohols, pyrazines, heterocyclic, and sulfur-containing compounds.[27] Herein, we found that the majority of these compounds decreased significantly with storage and could not be detected after 8−10 weeks of storage.

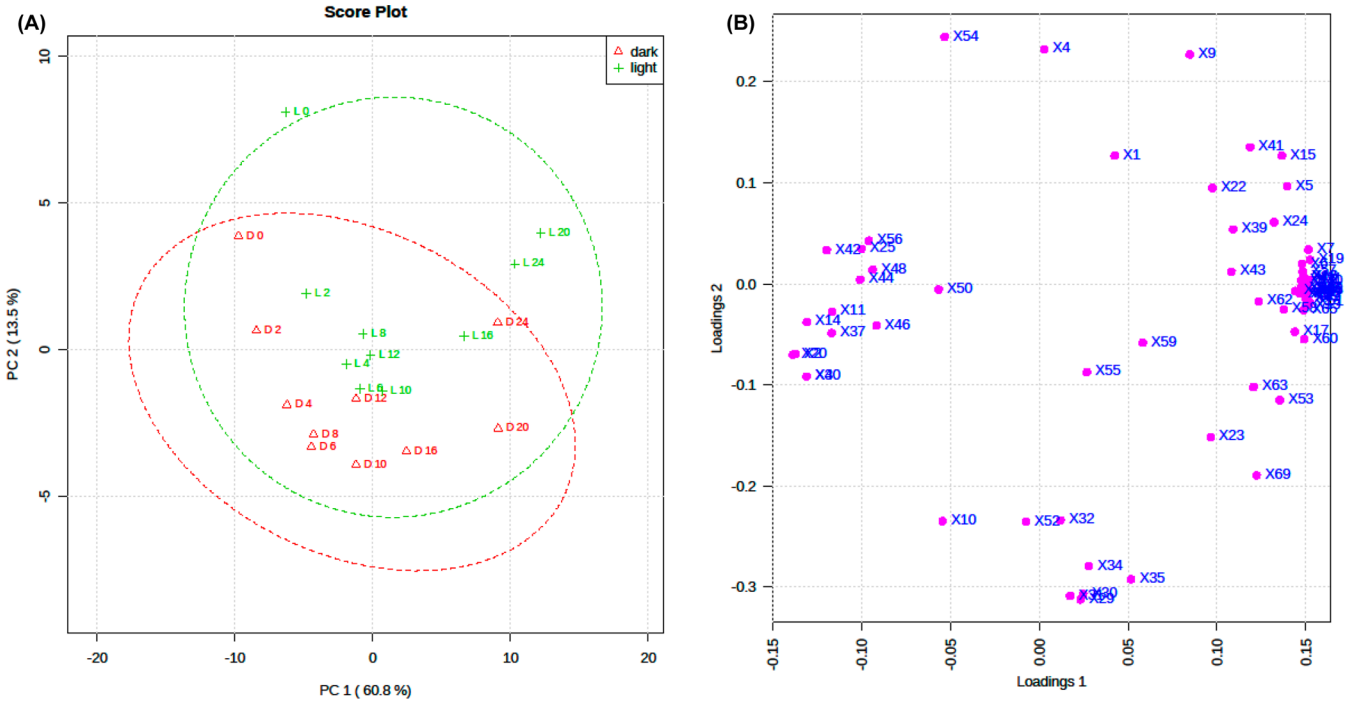

Figure 4. Principal component analysis on 68 volatile compounds determined by HS-SPME-GC-MS for different roasting and storage times: (A) PCA score plot with sample labeling; (B) PCA loading plot with compound codes. Compound codes are explained in Table 1.

The volatile carbonyl compounds detected in roasted almonds include 2-methylbutanal, 3-methylbutanal (Figure 2A), 2,3-butanedione, furfural, and 2-phenylacetaladehyde (Figure 2B). The concentrations of these volatiles decreased by 75−89% in the first month of storage and remained low through the remainder of the 6 month study. 2-Methylbutanal and 2-phenylacetaldehyde are produced through the Strecker reaction.[29] The concentration of these compounds decreased by 45−75% in the first 2 weeks of storage and remained low through the remainder of the 24 week study.

Pyrazines are key components of toasted almond aroma[18] and are formed in almonds during roasting.[27] Herein, most pyrazines did not show significant decrease during storage ($p < 0.05$) (Figure 2C,D). This result is consistent with Warner et al.'s study on roasted peanuts.[30] By 24 weeks of storage the concentrations of trimethylpyrazine and 2,6-dimethylpyrazine remained at initial levels (Figure 2D).

Roasting promoted the formation of Maillard reaction products including furfuryl alcohol and two branched-chain ketones (1-hydroxypropan-2-one and 3-hydroxybutan-2-one). These volatiles decreased significantly (>90%) by 10 weeks of storage regardless of the degree of roast (Table 2). The two sulfur-containing volatiles (1-methylthio-2-propanol and 2-ethylthio-ethanol) formed during roasting decreased significantly with storage time (Figure 2E). The majority of additional volatiles that were detected, such as ethyl acetate, α-pinene, methylsulfanylmethane, and pyrrole, also decreased during storage (Figure 2F).

Levels of straight-chain aldehydes (e.g., butanal, pentanal, hexanal, heptanal, octanal, and nonanal) were significantly higher in the roasted almonds immediately after roasting. Straight-chain aldehydes and alcohols are products of lipid oxidation, generated in response to thermal processing.[18,27] The levels of straight-chain aldehydes decreased over the first 6−10 weeks of storage. After 20 weeks of storage, the levels of these aldehydes increased again, reflecting lipid oxidation (Table 2). The levels of heptanal increased 2−4-fold as compared to its original concentration after 24 weeks of storage. Heptanal is a common oxidation product of oleic acid.[31] The levels of caproic acid (hexanoic acid) began to increase at ∼16 weeks, increasing by 7-fold at 24 weeks. Caporic acid can be generated by the oxidation of lipids.[32]

Hexanal is commonly used as a volatile marker of oxidation in foods.[12] Hexanal is an abundant oxidation product and therefore is more easily detected than are other oxidation products.[12] However, the concentration of hexanal in nuts is affected by numerous factors including kernel maturity,[33] roasting conditions,[15] fat content,[12] and variety.[8] Significant oxidation has generally occurred when substantial increases in hexanal are measurable, and the quality of the almonds may no longer be acceptable.

During initial stages of storage, we found that the levels of hexanal decreased. Levels then increased at ∼20−24 weeks of storage regardless of the degree of roasting (Figure 3A,B). This is similar to results shown by García-Llatas et al.[16] The levels of 1-heptanol increased more significantly between 16 and 20 weeks of storage regardless of the degree of roast (Figure 3A,B), and the response was more sensitive than the response of hexanal. Additionally, unlike hexanal, the levels of 1-heptanol did not show a decrease during the initial 16 weeks of storage. A similar trend was observed for 1-octanol; however, the response of 1-octanol was not as sensitive as that of 1-heptanol.

Additional potential markers of oxidative events include compounds that were initially absent in the roasted almonds but detectable ∼16−20 weeks of storage (i.e., 2-octanone, 2-nonanone, 3-octen-2-one, 2-decanone, (*E*)-2-decenal, 2,4-nonadienal, 2-undecenal, 1-octen-3-ol, nonanol, pentyl oxirane, hexyl oxirane, acetic acid, vinyl hexanoate, pentanoic acid, heptanoic acid, octanoic acid, and nonanoic acid). At 16 weeks of storage, the levels of 2-octanone, 3-octen-2-one, and acetic

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acid showed significant increases (Table 3), whereas hexanal levels (the traditional marker) were not significantly increased. At 24 weeks of storage, 2-octanone, 3-octen-2-one, and acetic acid levels increased between 1.2- and 5.3-fold as compared with their levels at 16 weeks. Thus, 2-octanone, 3-octen-2-one, and acetic acid may be more sensitive indicators of early oxidation development in roasted almonds than hexanal.

A PCA was performed on the data. ANOVA indicated that 2,3-dimethylpyrazine, 2-methyl-1-propanol, and 2-propenol were not significant compounds ($p < 0.001$), and so these compounds were excluded from the PCA. In the PCA score plot, 74.3% of the variance could be explained within the first two dimensions (Figure 4A). Almond samples were separated on the basis of storage periods; volatile profiles in late storage periods (16−24 weeks) separated from volitle profiles from early storage periods (0−12 weeks). PC1 explains 60.8% of the total variance. Along the PC1, early storage periods clustered on the left side, whereas late storage periods clustered on the right side. PC2 explains 13.5% of the total variance. Light-roast samples clustered in the bottom right quadrant, whereas dark-roast samples clustered in the top right.

The PCA loading plot (Figure 4B) indicates that compounds formed during storage drive the separation (i.e., 2-octanone (X12), 2-nonanone (X16), 3-octen-2-one (X18), 2-decanone (X21), (*E*)-2-decenal (X26), 2,4-nonadienal (X27), 2-undecenal (X28), 1-octen-3-ol (X45), nonanol (X51), pentyl oxirane (X57), hexyl oxirane (X58), acetic acid (X61), vinyl hexanoate (X64), pentanoic acid (X66), heptanoic acid (X68), octanoic acid (X70), and nonanoic acid (X71)).

In conclusion, improved sensitivity of oxidation may be achieved by evaluating the levels of two groups of volatile compounds. The first are those that are absent from raw and freshly roasted almonds but detectable around 16 weeks of storage and include certain oxiranes, carbonyls, and short-chain acids. The second includes heptanol and 1-octanol as these correlate to early stages of oxidation and are observed before hexanal levels rise. Together these markers can be used to probe early changes in product quality, improve the sensitivity of detection for oxidation, and help to prevent the loss from significant oxidation in almonds at later stages.

In addition, we found significant decreases in roasting-related aroma volatiles at 4 weeks of storage, independent of the degree of roast or storage temperature. In general, a low volatile stage occurs around the fourth week of storage. This is followed by increasing levels of volatiles associated with lipid oxidation. At a storage temperature of 35 °C, oxidation-related volatiles begin to dominate the volatile profile at 20 weeks.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS USED

HS, headspace; SPME, solid phase microextraction; GC-MS, gas chromatography−mass spectrometry; TBA, thiobarbituric acid; PV, peroxide value; KI, Kovats' retention index; TIC, total ion chromatogram

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