Understanding the Chemistry of Almond Flavor

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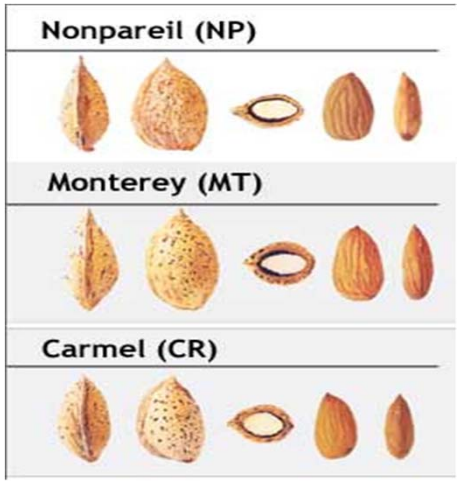
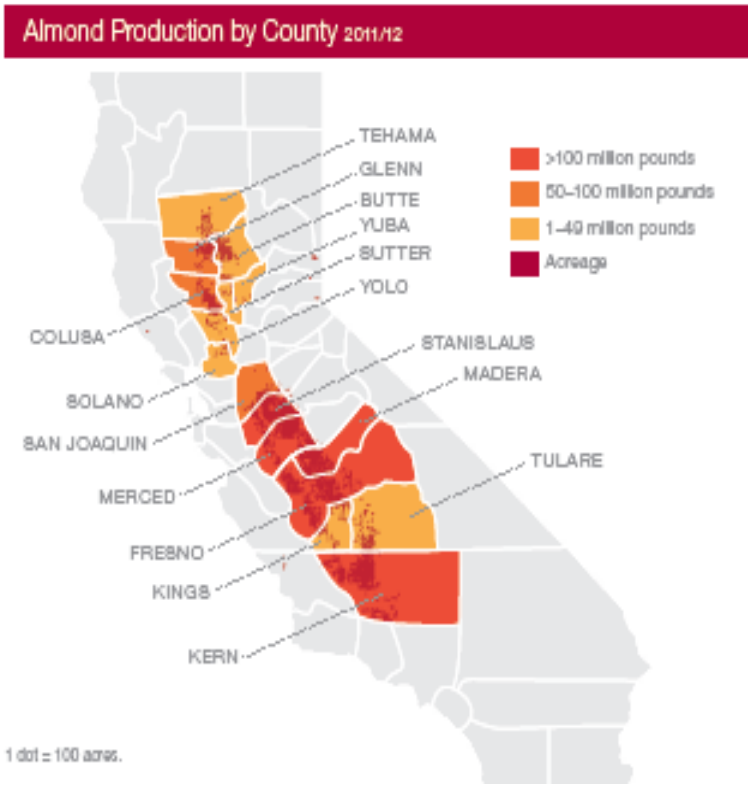
Almonds (*Prunus dulcis*)

- Botanically, the seed (fruit) of a drupe
  - Not a true nut
- A member of the rose family and is related to peaches, plums, apricots and cherries
- Native to the Middle East and South Asia
  - Consumed since the Early Bronze Age (3000-2000 BCE)
- Convenient, dense source of energy that naturally stores well
  - Excellent source of Vitamin E (alpha tocopherol), high value protein, essential minerals and monounsaturated fats
- Consumption is associated with lowering LDL and a reduced risk of heart disease
  - Jenkins et al., *Circulation. 2002; 106(11):1327-1332*

California Almonds

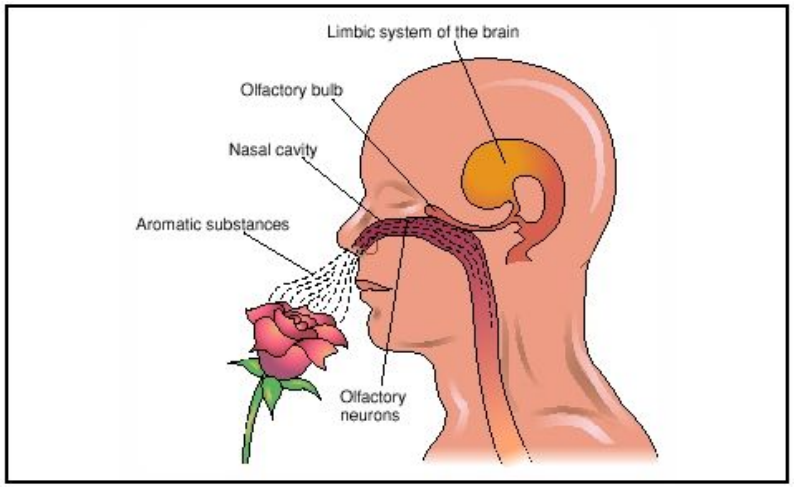
- California grows about 30 varieties of almonds
  - 80% of world almond production in 2015
- The three top almond varieties
  - Nonpareil (39%)
  - Monterey (12%)
  - Carmel (9%)





Flavor

- Flavor is the sensory impression of a food
- Composite quality involving the sensations of aroma, taste, chemical irritation, as well as temperature, texture and sound
- Taste: Humans can distinguish 5 basic flavors
  - Sweet, sour, salty, bitter, and savory (umami)
  - Reactions with taste receptors on the tongue
- Aroma: Involves the interaction of volatile molecules with olfactory receptor neurons located in the nasal passageways



Raw Almonds

Raw Almond Taste

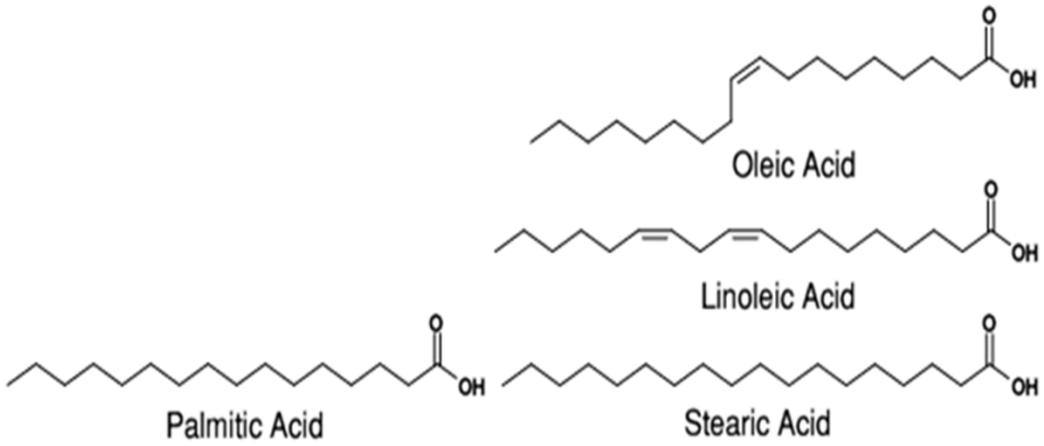
- Primary drivers of almond *taste are* fat, starch and sugars, and amygdalin
- Fat creates a rich taste
- Lack of acid enhances sweetness of starch and sugar
- Bitterness is derived from amygdalin
- Astringency from tannins (skin)

Macronutrient	Range in CA-grown almonds (% g/g almond)
Lipids	35-66
Protein	16-23
Sugars	2.1-7.4
Fiber	11-14

Lipid Composition of Almonds

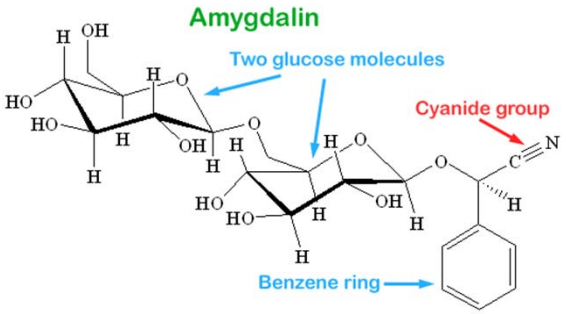
- The primary fatty acids in almonds are *"Heathy fats"*
- Oleic (18:1, 62–80%) and linoleic acid (18:2, 10–18%)

Name	Number of Carbons:Double bonds	Percent in Almond Oil
Oleic	18:1	60-80%
Linoleic	18:2	10-18%
Palmitic	16:0	0.5-8%
Stearic	18:0	1-3%



Almond Phenotypes

- Non-bitter (Sweet)
  - Sweet snacking almonds (creamy nutty flavor)
- Semi-bitter
  - Often used in processing for their “marzipan-like taste”

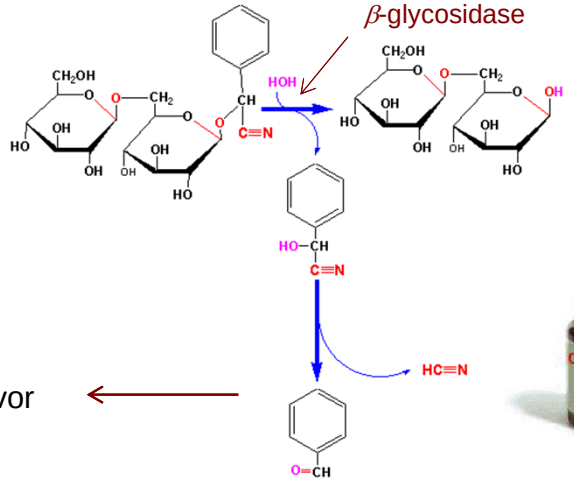


- Bitter
  - Middle East and Asia
  - Oils and flavorings
  - Contain amygdalin (3-5%) and develop a cyanide aroma when moistened (chewed)
  - Can be toxic

Amygdalin

- A diglycoside
- The disruption of almond tissue (e.g. chewing) enables amygdalin to come into contact with enzymes (*b*-glycosidase) and form benzaldehyde and trace levels of HCN

Amygladin = bitter



Benzaldehyde = amaretto flavor

Chemical defense for the plant

Amygdalin in California Almonds

- Developed a sensitive method (UHPLC (ESI)-MS/MS) to measure amygdalin in almonds
  - Understand levels in CA varieties and breeding stocks
- Commercial non-bitter (sweet) varieties
  - Average amygdalin content 63.13 ± 57.54 mg/kg
- Semi-bitter (UCD)
  - Average amygdalin 992.24 ± 513.04 mg/Kg
- Bitter (UCD)
  - Average amygdalin 40,060.34 ± 7,855.26 mg/kg
- Additional applications alcoholic bitters
- USDA recall of almonds

Lee et al., J. Agric. Food Chem. 2013, 61, 7754−7759

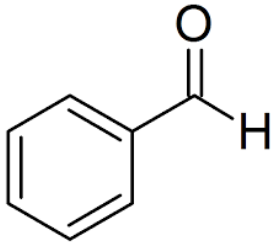
Amygdalin in California Almond Varieties

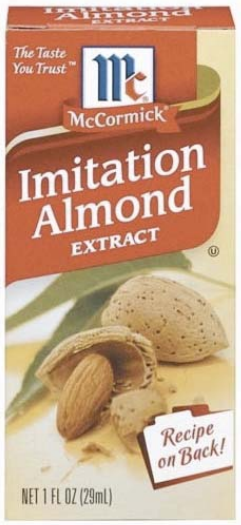
Flavor	Variety	Amygdalin (mg/kg)				
Non-bitter		Growing Region				Mean Concentration
		Colusa	Fresno	Kern	Stanislaus	
	Butte	3.47 ± 0.17*	0.85 ± 0.65			2.16 ± 1.25
	Price	7.49 ± 0.06 d	2.49 ± 0.30 b	1.43 ± 0.05 a	5.85 ± 0.38 c	4.32 ± 2.45
	Sonora	1.83 ± 0.18 a	7.08 ± 1.26 b	5.17 ± 0.51 b	16.95 ± 0.37 c	7.76 ± 6.04
	Nonpareil	7.05 ± 0.56 a	12.92 ± 0.57 b		16.72 ± 1.26 c	12.23 ± 4.41
	Monterey	108.75 ± 1.20 c	44.87 ± 1.12 a	62.17 ± 6.55 b	34.08 ± 10.13 a	62.47 ± 27.19
	Wood Colony	78.25 ± 8.70 c	81.20 ± 3.71 c	63.68 ± 1.22 a	76.99 ± 1.46 ab	75.03 ± 8.07
	Carmel	75.04 ± 5.89 ab	94.72 ± 5.32 b	74.19 ± 19.52 ab	63.94 ± 5.06 a	76.97 ± 15.22
	Mission	72.47 ± 8.84 a	138.11 ± 6.06 b	68.75 ± 26.97 a	79.07 ± 6.11 a	89.60 ± 32.34
	Fritz	133.62 ± 8.37 a	130.05 ± 3.38 a	114.91 ± 16.67 a	200.90 ± 28.82 b	144.87 ± 36.44
	Aldrich	90.06 ± 5.01 a	214.87 ± 11.65 c	194.49 ± 1.55 c	130.34 ± 19.25 b	157.44 ± 54.01
	All Varieties					63.13 ± 57.54

Lee, et al., J. Agric. Food Chem., ***2013****, 61 (32), pp 7754–7759*

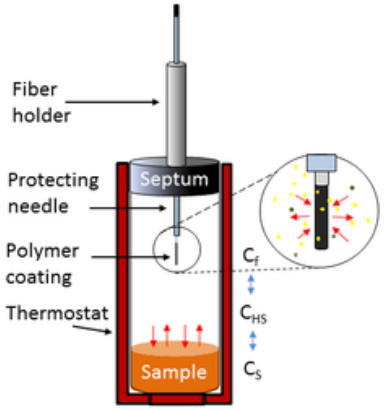
Raw Almond Aroma

- Volatile molecules are responsible for the aroma of almonds
- The predominant almond aroma compound is benzaldehyde
  - Cherry, almond flavor
  - Artificial almond aroma
- Comes from the breakdown of amygdalin





Measuring Volatile Aroma Compounds in Almonds
HS-SPME GC/MS

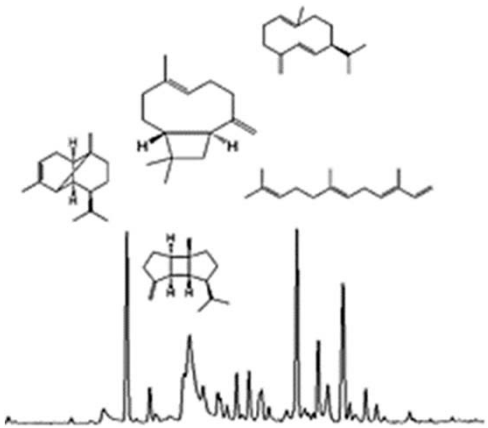


Headspace Solid-Phase Microextraction

5 g sample is placed in a 20-mL SPME vial

Gas Chromatography

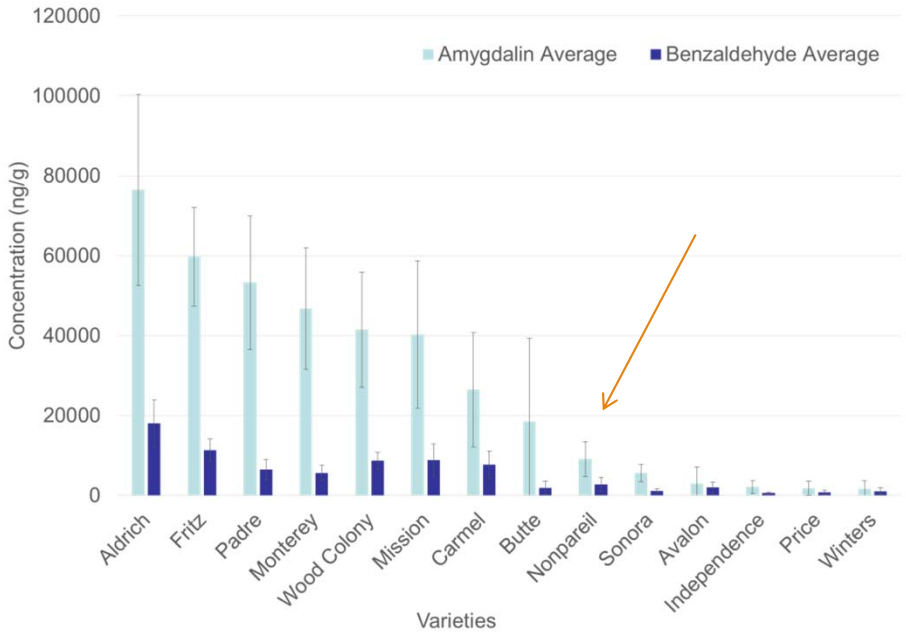
Samples are agitated at 500 rpm and pre-equilibrated at 40ºC for 45 min, after which they were extracted with a 1 cm 30/50um StableFlex DVB/CAR/PDMS fiber exposed for 45 mins at 250 RPM

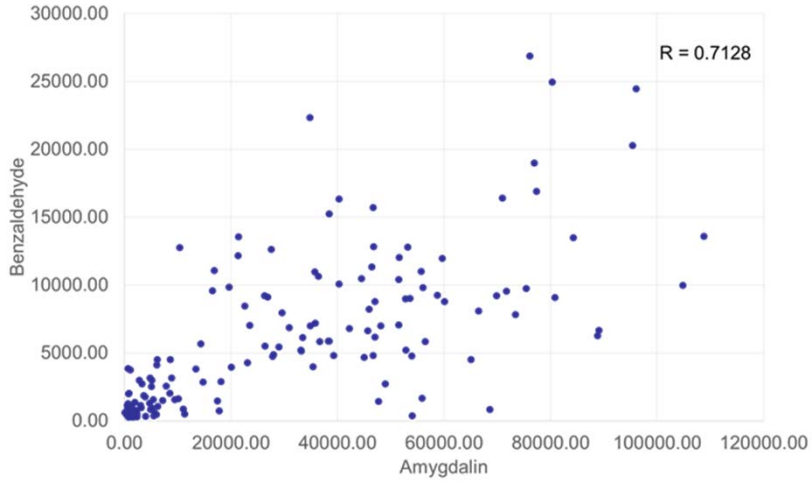


Chromatogram

Amygdalin and Benzaldehyde in California Almonds

- Strong correlation between amygdalin levels and benzaldehyde levels





In preparation K. Lau

Flavor and Variety

- Benzaldhyde ranges between 0.587-17.995 mg/kg in commercial almonds

Variety	Classification type	Average amygdalin (mg/kg)	Average benzaldehyde (mg/kg)
Aldrich	California	76.50 ± 23.99 a	17.995 ± 5886.7 a
Fritz	California, Mission	59.71 ± 12.37 ab	11.315 ± 2795.5 b
Padre	California, Mission	53.24 ± 16.74 bc	8.806.8 ± 4101.5 bc
Monterey	California	46.76 ± 15.21 bc	8.654.3 ± 2137.3 bc
Wood Colony	California	41.49 ± 14.41 bcd	7.703.4 ± 3394.5 bc
Mission	Mission	40.24 ± 18.40 cd	6.489 ± 2503.4 cd
Carmel	California	26.42 ± 14.30 de	5.656.9 ± 1845.3 cde
Butte	California	18.56 ± 20.77 ef	2.768.3 ± 1783.2 def
Nonpareil	Nonpareil	9.11 ± 4.42 ef	1.939.5 ± 1318.9 ef
Sonora	California	5.56 ± 2.20 f	1.936.4 ± 1602.1 ef
Avalon		3.00 ± 4.17 f	1.179.6 ± 488.1 f
Independence		2.07 ± 1.66 f	1.062 ± 871.4 f
Winters	California	1.62 ± 2.10 f	0.730.6 ± 633.3 f
Price	California	1.77 ± 1.74 f	0.587.7 ± 272.9 f

Raw Almond Aroma

literature review

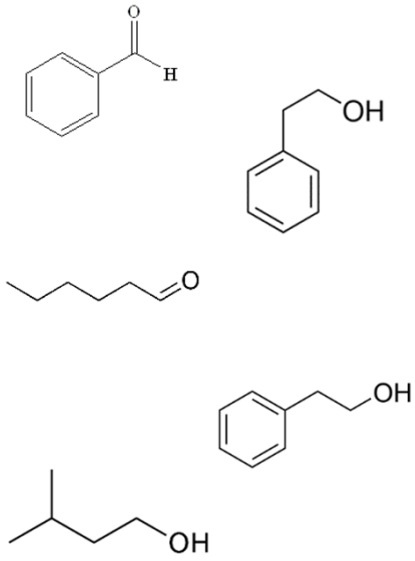
- Volatile compounds identified in raw almonds and reported in 2+ studies
- Benzaldehyde, benzyl alcohol and hexanal are the most widely detected volatiles in raw almonds
- Other key volatiles include: pentanol, hexanol, 2-phenylethanol, 3-methyl-1-butanol, 3-methyl-2-buten-1-ol, and nonenal

Type	Compound	Aroma[a]	Source[b]
Alcohol	1,2-propanediol	nd	2, 3
	1-butanol	medicine, fruit, wine	2, 3, 4
	1-heptanol	herb	2, 7
	1-hexanol	resin, flower, green	1, 2, 3, 7, 4
	1-Nonanol	aldehydic, waxy, citrus	7, 3
	1-octanol	chemical, metal, burnt	2, 3, 7, 4
	1-pentanol	fruity	1, 2, 3, 5, 6
	2-ethyl-1-hexanol	sweet, floral, oily	1, 3,
	2-heptanone	cheesy, banana, fruity	1, 2
	2-methyl-1-propanol	wine, whisky	2, 3, 7
	Benzyl alcohol	floral, phenolic	1, 3, 4, 5, 6, 7
	2-phenylethanol	floral, hyacinth/gardenia	5, 7, 6, 1, 3
	3-methyl-1-butanol	malt	2, 3, 7
	3-methyl-2-Buten-1-ol	fruity, alcoholic, green	5, 7, 6 ,3
	3-Methyl-3-Buten-1-ol	nd	3, 5, 6
Pyrazine	2-Methylpyrazine	roasted	1, 4
Acids	Acetic acid	sour	8, 3
	hexanoic acid	sweaty, rancid	2, 3
Terpenes	alpha-pinene	piny	7, 2
	limonene	orange peel	2, 7
Aldehydes	Benzaldehyde	sweet, marzipan	1, 3, 2, 7, 5, 6, 4
	heptanal	ranid, pungent	1, 2, 7, 4
	Hexanal	grassy, fatty, rancid	1, 8, 2, 3, 5, 7, 6
	Nonanal	soapy, fatty, rancid	8, 2, 3, 7, 4
	Octanal	soapy, fatty, rancid	8, 2, 7
	pentanal	almond, malt, pungent	1, 2
Lactone	butyrolactonec	creamy, oily, fatty	2, 3
Alkane	Toluene	painty	4, 7, 5, 6
Sulfur-containing	Methional	cooked potato	8, 4

Raw Almond Aroma

- Butte/Padre almonds (7 months in storage)
- Raw almond aroma intensity is low with exception of benzaldehyde
- Identified (41): 13 carbonyls, 1 pyrazine, 20 alcohols, and 7 additional volatiles

Compound	Content PPB	Aroma
Benzaldehyde	2,934.6 ± 272.5	sweet, marzipan
3-Methyl-butanal	86.4 ± 3.3	alcoholic, fruity, whiskey, banana
3-Methyl-2-butenol	17.3 ± 0.9	fruity, green, lavender
Benzyl alcohol	3.9 ± 0.0	floral, phenolic
Hexanal	422.6 ± 97.9	grassy, fatty, rancid



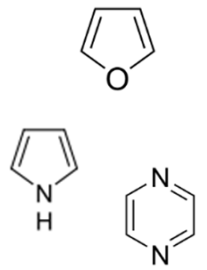
Roasted Almonds

Roasted Almond Flavor

Roasting = Flavor Development

- When almonds are roasted they undergo chemical reactions that lead to the creation and release of volatile compounds
- Heating generates new volatiles through lipid oxidation, sugar pyrolysis, and the Maillard reaction
  - Malty, roasted, chocolate, nutty flavors
- Range and levels of volatiles formed will depend upon the roasting conditions
- Common temperatures used for dry roasting range from 130°C to 150°C

Volatiles in Roasted Almonds

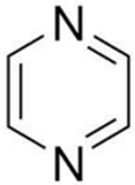


- We roasted almonds under controlled conditions of 138 °C for 38 min
- 17 Additional volatile compounds were identified
  - pyrazines, furans, alcohols, pyrroles, ketones, aldehydes, and aromatic hydrocarbons
- Pyrazines, furans and alcohols are key components of roasted almond flavor
  - Pyrazines: Maillard sugar-amine reactions and Strecker degradation
  - Furan-containing compounds: thermal degradation of sugars
  - Alcohols and aldehydes: lipid oxidation

Xiao et al., J. Food Chemistry 151 (2014) 31-39

Changes in Volatile Pyrazines

Roasted Nutty Aromas



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		
Pyrazines						
2-Methylpyrazine	ND	4.1 ± 0.3*	21.5 ± 0.6***	26.5 ± 1.8***	New	chocolate; meaty; nutty; green
2,5-Dimethylpyrazine	11.4 ± 0.5	16.2 ± 0.6***	53.3 ± 0.3***	66.5 ± 0.4***	298	musty, potato, cocoa, nutty
2,6-Dimethylpyrazine	ND	ND	2.8 ± 0.4**	4.2 ± 0.6***	New	meaty; nutty; medicinal; woody
2-Ethylpyrazine	ND	ND	2.6 ± 0.1***	3.2 ± 0.1***	New	butter; musty; woody; nutty
2,3-Dimethylpyrazine	ND	ND	1.0 ± 0.1***	1.4 ± 0.1***	New	almond; green; meaty; coffee
2-Ethyl-6-methylpyrazine	ND	ND	1.7 ± 0.1***	2.2 ± 0.0***	New	chocolate; meaty; nutty; green
Trimethylpyrazine	ND	ND	4.5 ± 0.3***	6.1 ± 0.2***	New	peanut

Changes in Volatile Aldehydes and Keytones

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	[chocolate/nutty]	14.3 ± 0.3	1468.6 ± 25.7**	5000.3 ± 241.1***	6573.7 ± 275.0***	30,216
3-Methylbutanal	[chocolate]	32.4 ± 0.5	911.4 ± 50.9*	2867.4 ± 71.1***	4268.9 ± 381.8***	8167
2,3-Butanedione	[sweet/butter]	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	[almond/green leaf]	ND[c]	14.6 ± 2.7**	11.3 ± 2.2*	14.1 ± 2.7**	New
2-Methyloxolan-3-one	[rummy/nut]	ND	15.4 ± 1.3	86.3 ± 4.2***	128.1 ± 11.0***	New
3-Hydroxybutan-2-one	[buttery]	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	[brown/caramel]	ND	103.2 ± 8.7**	366.1 ± 13.2***	460.0 ± 21.4***	New
Decanal	[aldehydic]	ND	6.9 ± 2.3*	5.0 ± 1.6	4.6 ± 1.0	New
Benzaldehyde	[almond/marzipan]	2934.6 ± 272.5	368.8 ± 41.2***	246.7 ± 53.0***	331.9 ± 65.4***	−89
(*Z*)-2-Nonenal	[green]	ND	ND	ND	5.3 ± 1.7**	New
2-Phenylacetaldehyde	[honey/floral]	ND	107.5 ± 20.3*	284.0 ± 22***	491.3 ± 45.4***	New

Xiao et al., J. Food Chemistry 151 (2014) 31-39

Changes in Volatile Alcohols

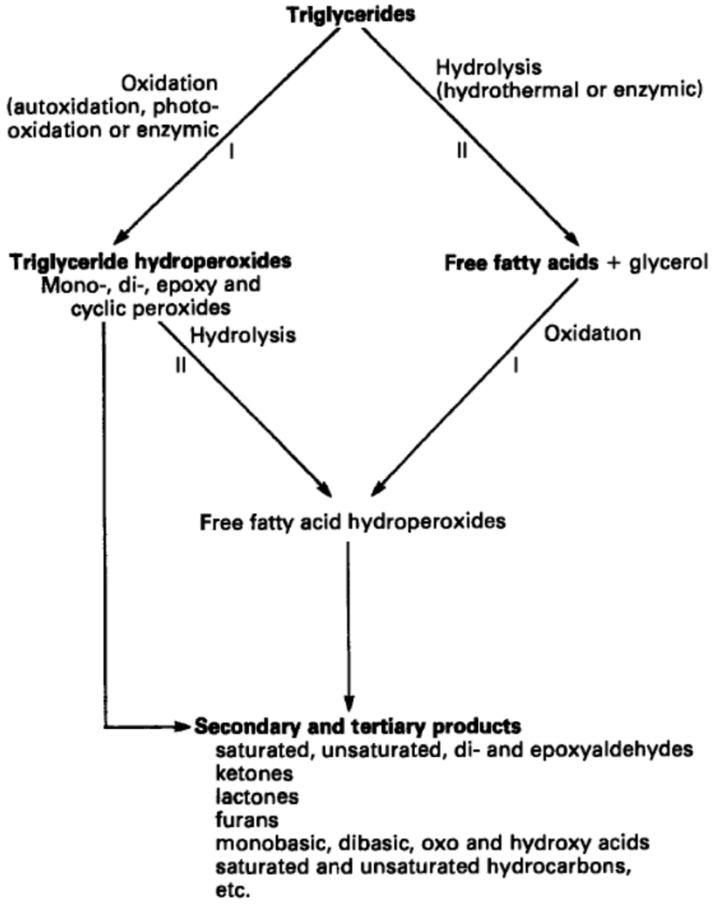
Table 2
Volatiles and their concentrations (ng/g) in raw and roasted almonds (dry weight basis).[a]

Possible compounds	Roasting time				Increase[b] (%)
	Raw	28 min	33 min	38 min	
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

Rancidity in Almonds

Rancidity

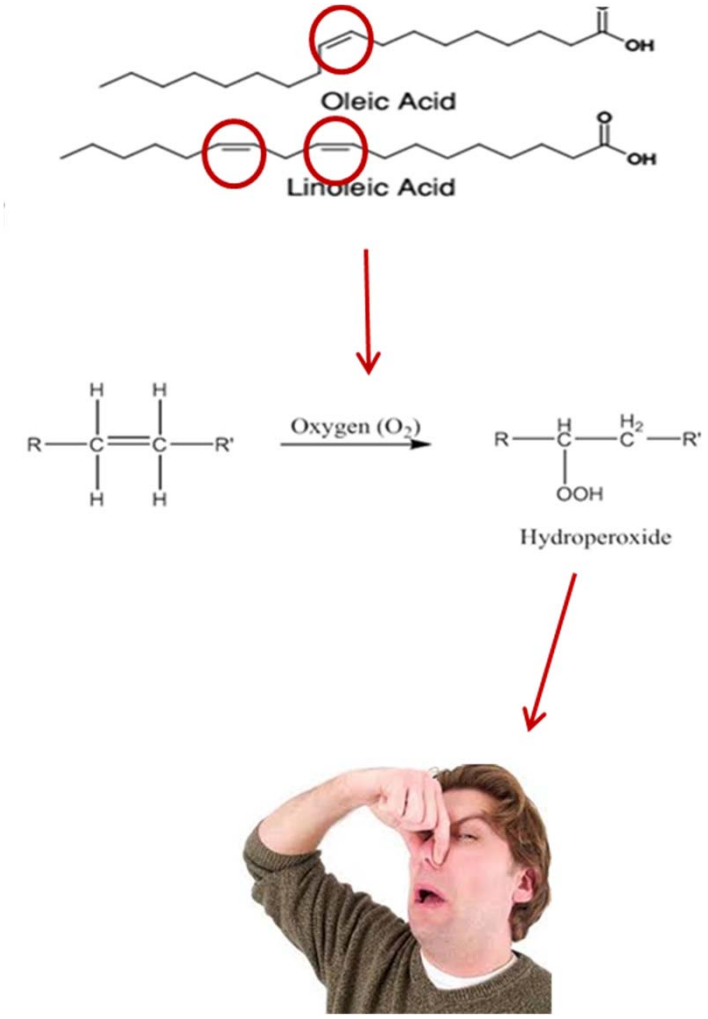
- Rancidity is the unpalatable odor and flavor of deteriorating edible fats and oils in foods
- Rancidity occurs via two chemical reactions:
- Oxidation
  - Oxygen attack of the triglycerides
- Hydrolysis
  - Addition of *water* across triglycerides and release of Fatty acids (FFAs)



Scheme 1. Over-all reaction scheme for (I) oxidative and (II) hydrolytic rancidity

Robards et al., Analyst, 1988 v 113

Rancidity in Almonds



- Rancidity in almonds occurs primarily via the oxidation of oleic [18:1] and linoleic [18:2] acids
  - Initiated by exposure to heat (e.g. pasteurization, blanching, roasting, etc.,), moisture and/or oxygen (e.g. during storage)
- A problem associated with storage and humidity
- Occurs in raw and roasted almonds

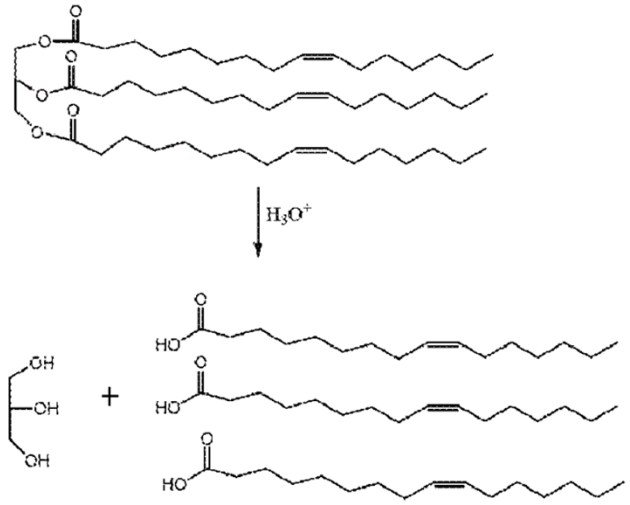
Measuring Rancidity in Almonds

- Although rancidity is a real problem confronting processors, there is no completely objective chemical method for determining rancidity
  - Industry relies on several methods for routine estimates of oxidation however, there is no uniform or standard method for detecting oxidative changes
- Challenges:
  - Lipid oxidation is a dynamic process and levels of chemical markers of lipid oxidation change throughout the lipid oxidation process
  - Little is known regarding correlations between chemical measures of rancidity and consumer acceptance/perception of almonds

Chemical Measures

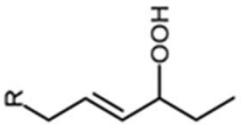
moving analytical targets

- Free Fatty Acids (FFA):
  - Measures the hydrolytic or enzymatic release of FFAs
    - FFAs are more susceptible to oxidation
  - Industry standard is < 1.5% FFAs
- Found to correlate with sensory evaluation in butter
  - No studies in almonds



Chemical Measures

moving analytical targets



Peroxide Value (PV)

- Lipid peroxides are the first product of lipid oxidation and are used as an indicator of early oxidative changes
- Almonds PV < 5 meq/Kg is considered the benchmark

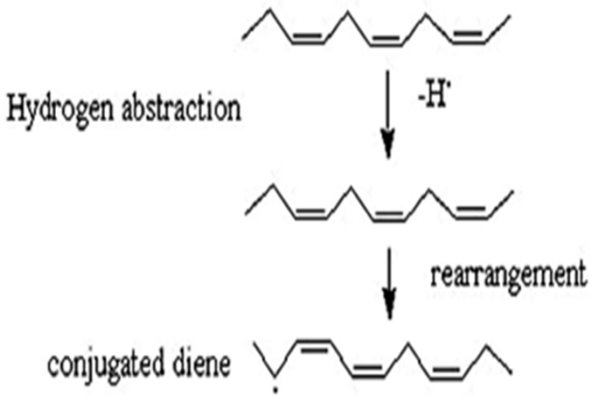
However:

- PV levels decrease as oxidation progresses and lipid peroxides break down
- Low levels can be present when there is extensive lipid oxidation

Chemical Measures

moving analytical targets

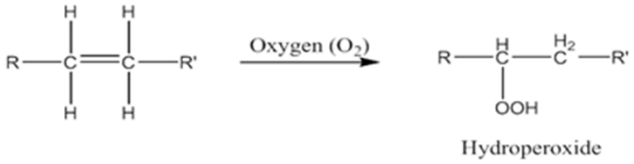
- Conjugated Dienes (CDs)
  - Measures initial stages of rancidity
    - Oxidized linoleic acid rearranges to form a CD
    - CDs absorb UV light at 232–234 nm which can be measured
- However:
  - CD levels can decompose as oxidation progresses
  - No industry values for CDs for almonds



Chemical Measures

moving analytical targets

- Head Space Volatiles
  - Measures the later stages of oxidation
  - After lipid hydroperoxides breakdown
- Hexanal
  - Most commonly measured
  - No industry standard for hexanal in almonds
  - A wide range of volatile compounds exist in raw, roasted, and stored almonds



Linking Rancidity with Consumer Linking

- Monitor these markers of lipid oxidation and volatile aroma profiles in light and dark roasted almonds undergoing accelerated shelf-life conditions that promote rancidity development over 12 months

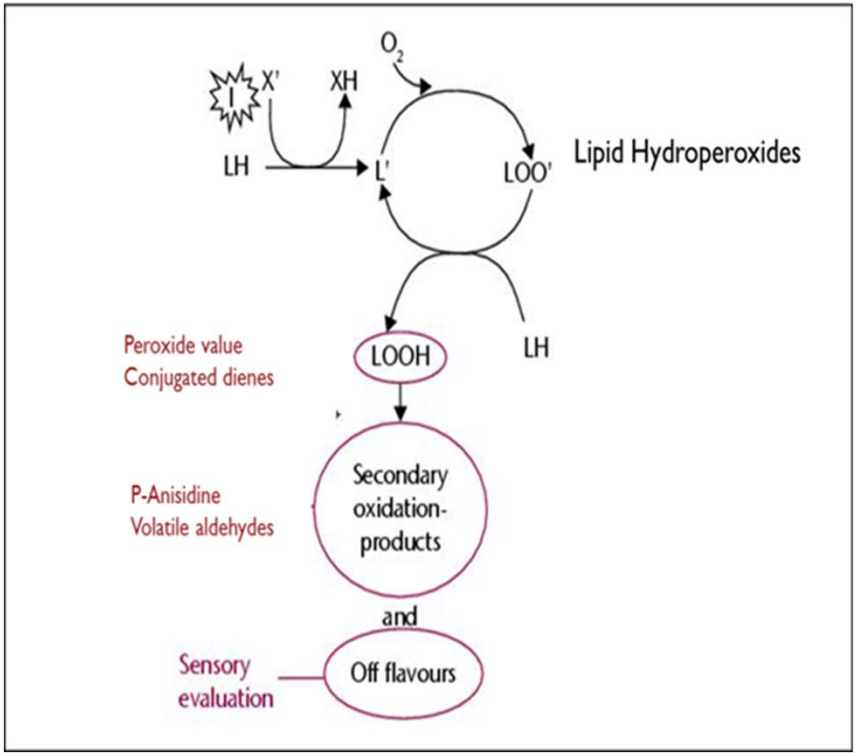
- Measured the consumer hedonic response (degree of liking) of these almonds to determine how consumer liking correlates with the chemical measures during rancidity development during accelerated shelf-life storage

Samples

- De-hulled, raw Nonpareil almonds (2014 Harvest year)
- Almonds were dry roasted at
  - 115 ± 6ºC for 60 min to achieve a light roast
  - 152 ± 6ºC for 15 min to achieve a dark roast
- Almonds were stored at 39 ±1ºC and RH of 15% ±1 for 12 months
- Almonds were randomized and stored in open bags to maximize oxygen exposure during storage
- Almonds were sampled every month (30 days)

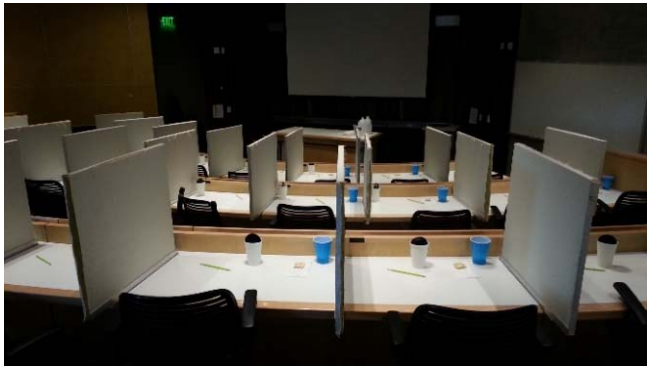
Analytical Correlations

- Hydrolytic Rancidity
  - Free Fatty Acids (FFA)
- Primary Oxidation Products
  - Peroxide Value (PV)
  - Conjugated Dienes (CD)
- Vitamin E
  - Tocopherols (α, $\beta + \gamma$ and δ)
- Volatiles by SPME-HS GC/MS
- Sensory Measures
  - Consumer Hedonic Analysis



Consumer Hedonic Analysis

- Untrained consumers (99) between 14 and 80 and who consumed almonds at least once a month (not pregnant)
- Consumers were served samples of 6-7 almonds coded with randomly generated 3-digit numbers as sample identifiers
- Consumers indicate their liking of samples by marking a 9-pt hedonic scale with accompanying phrases as anchors



How much do you like this sample overall?

☐	☐	☐	☐	☐	☐	☐	☐	☐
Dislike Extremely	Dislike Very Much	Dislike Moderately	Dislike Slightly	Neither Like Nor Dislike	Like Slightly	Like Moderately	Like Very Much	Like Extremely

Hedonic Ratings

- Significant differences in liking related to the storage time
  - Consumers had a significant difference in liking between samples aged 0, 2, 4, and 6 months, while there was no significant difference found between samples aged 6, 8, and 10 months
- No significant difference was found in liking related to roast level

	Storage Time					
Analysis	**0 months**	**2 months**	**4 months**	**6 months**	**8 months**	**10 months**
Light Roast	7.4 ± 1.4 a	6.6 ± 1.5 b	5.8 ± 1.55 c	4.9 ± 1.9 d	4.9 ± 2.0 d	4.7 ± 2.1 d
Dark Roast	7.2 ± 1.7 a	6.8 ± 1.4 b	5.8 ± 1.7 c	4.7 ± 2.0 d	4.5 ± 2.0 d	4.2 ± 2.0 d

*A rating of 5 indicates that the consumer is indifferent to the product and below this begins to dislike the product

Correlation with Measures of Lipid Oxidation

Light Roast Almonds

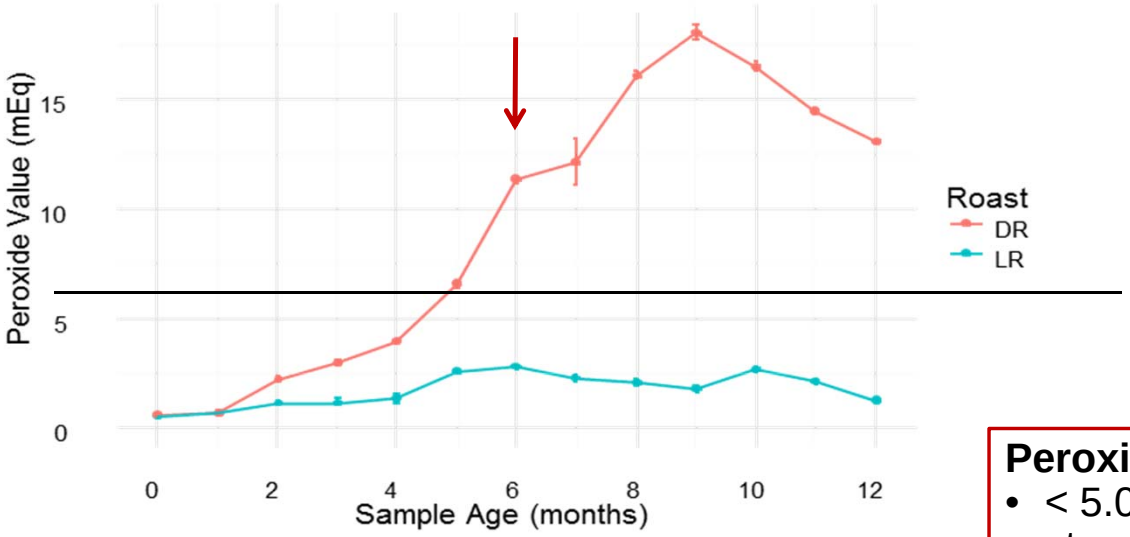
Analysis	Storage Time						
	0 months	**2 months**	**4 months**	**6 months**	**8 months**	**10 months**	**12 months**
Peroxide Value (mEq/g oil)	0.57 ± 0.04 e	1.13 ± 0.14 d	1.38 ± 0.20 d	**2.84 ± 0.02 b**	2.14 ± 0.18 c	2.70 ± 0.08 b	1.26 ± 0.08 d
Free Fatty Acid Value (% oleic)	0.21 ± 0.00 d	0.25 ± 0.00 cd	0.28 ± 0.00 bc	**0.31 ± 0.01 abc**	0.32 ± 0.02 ab	0.36 ± 0.03 a	0.36 ± 0.03 a
Conjugated Dienes (%)	0.213 ± 0.000 f	0.222 ± 0.00 f	0.255 ± 0.000 cd	**0.242 ± 0.003 e**	0.261 ± 0.008 bc	0.267 ± 0.002 b	0.302 ± 0.001 a
Alpha Tocopherol Conc. (mg/kg oil)	435 ± 4 a	424 ± 16 a	406 ± 1 abc	**387 ± 3 bcd**	362 ± 4 def	363 ± 32 def	334 ± 11 f
Beta + Gamma tocopherol Conc. (mg/kg)	34.3 ± 0.5 ab	34.0 ± 0.2 ab	34.1 ± 0.3 ab	**32.8 ± 0.5 ab**	31.9 ± 0.4 ab	33.5 ± 1.0 ab	31.7 ± 0.9 ab
Mean Consumer Hedonic Score	7.4 ± 1.4 a	6.6 ± 1.5 b	5.8 ± 1.55 c	**4.9 ± 1.9 d**	4.9 ± 2.0 d	4.7 ± 2.1 d	

Correlation with Measures of Lipid Oxidation

Dark Roast Almonds

Analysis	Storage Time						
	0 months	**2 months**	**4 months**	**6 months**	**8 months**	**10 months**	**12 months**
Peroxide Value (mEq/g oil)	0.61 ± 0.04 n	2.21 ± 0.12 m	3.96 ± 0.07 l	**11.36 ± 0.23 j**	16.07 ± 0.53 g	16.48 ± 0.18 g	13.00 ± 0.03 i
Free Fatty Acid Value (% oleic)	0.20 ± 0.03 j	0.18 ± 0.00 i	0.37 ± 0.01 g	**0.36 ± 0.01 e**	0.42 ± 0.04 c	0.54 ± 0.04 c	0.57 ± 0.04 a
Conjugated Dienes (%)	0.216 ± 0.001 j	0.238 ± 0.001 i	0.286 ± 0.002 g	**0.362 ± 0.001 e**	0.464 ± 0.003 c	0.464 ± 0.002 c	0.508 ± 0.001 a
Alpha Tocopherol Conc. (mg/kg oil)	444 ± 1 a	418 ± 7 ab	396 ± 2 bc	**358 ± 8 de**	328 ± 8 fg	277 ± 6 h	292 ± 9 h
Beta + Gamma tocopherol Conc. (mg/kg)	35.0 ± 0.1 a	34.0 ± 0.8 abcd	34.4 ± 0.5 ab	**32.3 ± 0.3 cdefg**	32.0 ± 0.6 efg	31.0 ± 0.1 g	31.2 ± 1.3 fg
Mean Consumer Hedonic Score	7.2 ± 1.7 a	6.8 ± 1.4 b	5.8 ± 1.7 c	**4.7 ± 2.0 d**	4.5 ± 2.0 d	4.2 ± 2.0 d	

Peroxide Value

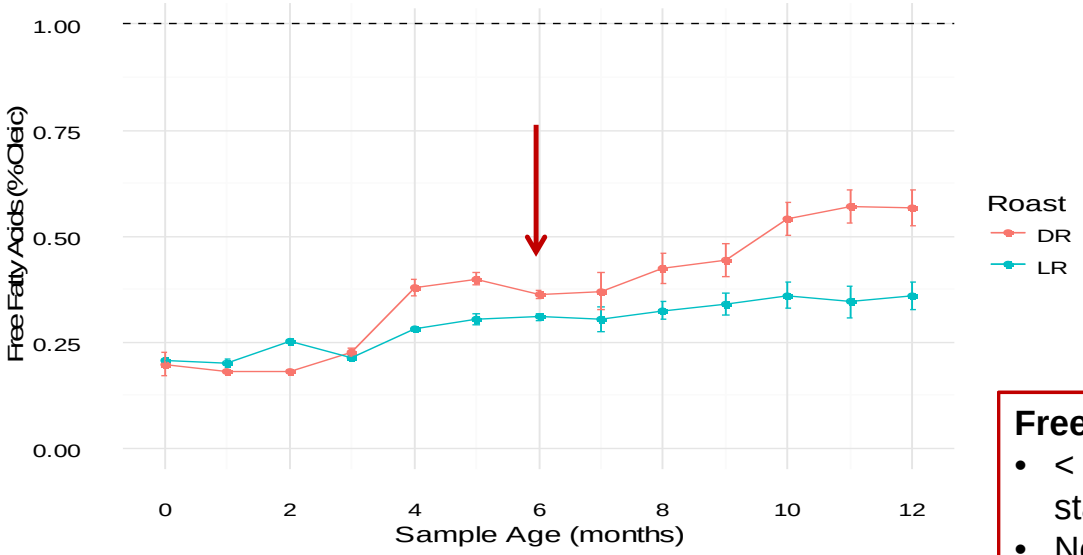


Peroxide Value:

- < 5.0 is a recommended industry rejection standard.
- None of the light roast samples were greater than 5.0, despite consumer indifference/dislike
- Doesn't correlate with consumer liking

Franklin et al., J. Agric. Food Chem. DOI: 10.1021/acs.jafc.6b05357- 2017

Free Fatty Acids

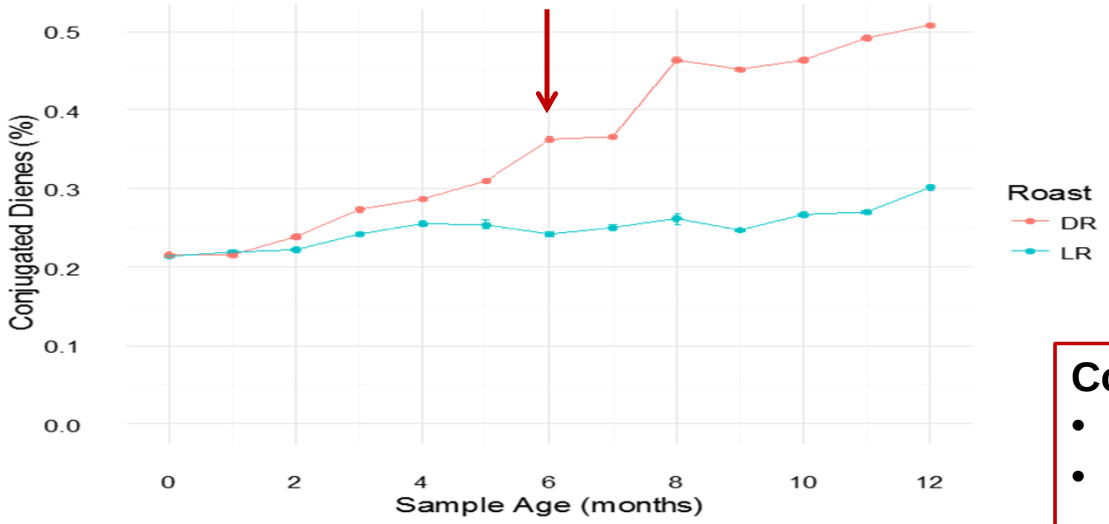


Free Fatty Acids:

- < 1.5% Oleic is a recommended industry rejection standard.
- No samples were greater than 1.5% Oleic, despite being consumer indifference/dislike
- However roasting would inactivate lipase enzymes

Franklin et al., J. Agric. Food Chem. DOI: 10.1021/acs.jafc.6b05357- 2017

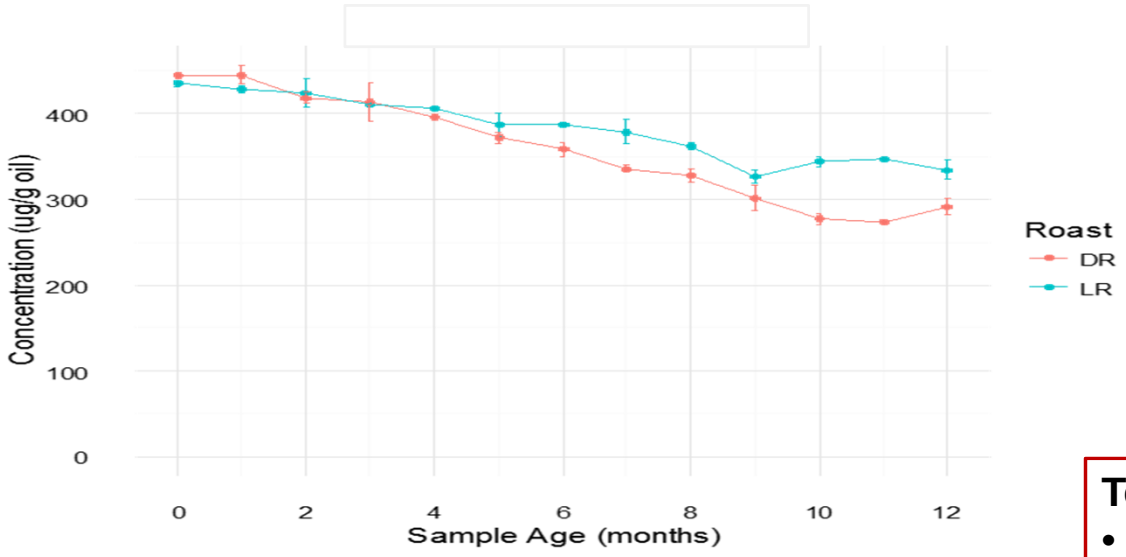
Conjugated Dienes



Conjugated Dienes:

- No industry standard currently exists for CD.
- There was very little change in light roast samples, despite consumer indifference/dislike at 6 months
- Correlates with consumer liking however sensitivity is low

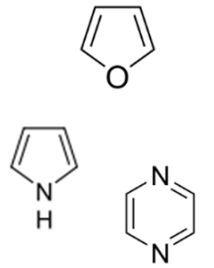
Alpha Tocopherol (Vitamin E)



Tocopherols:

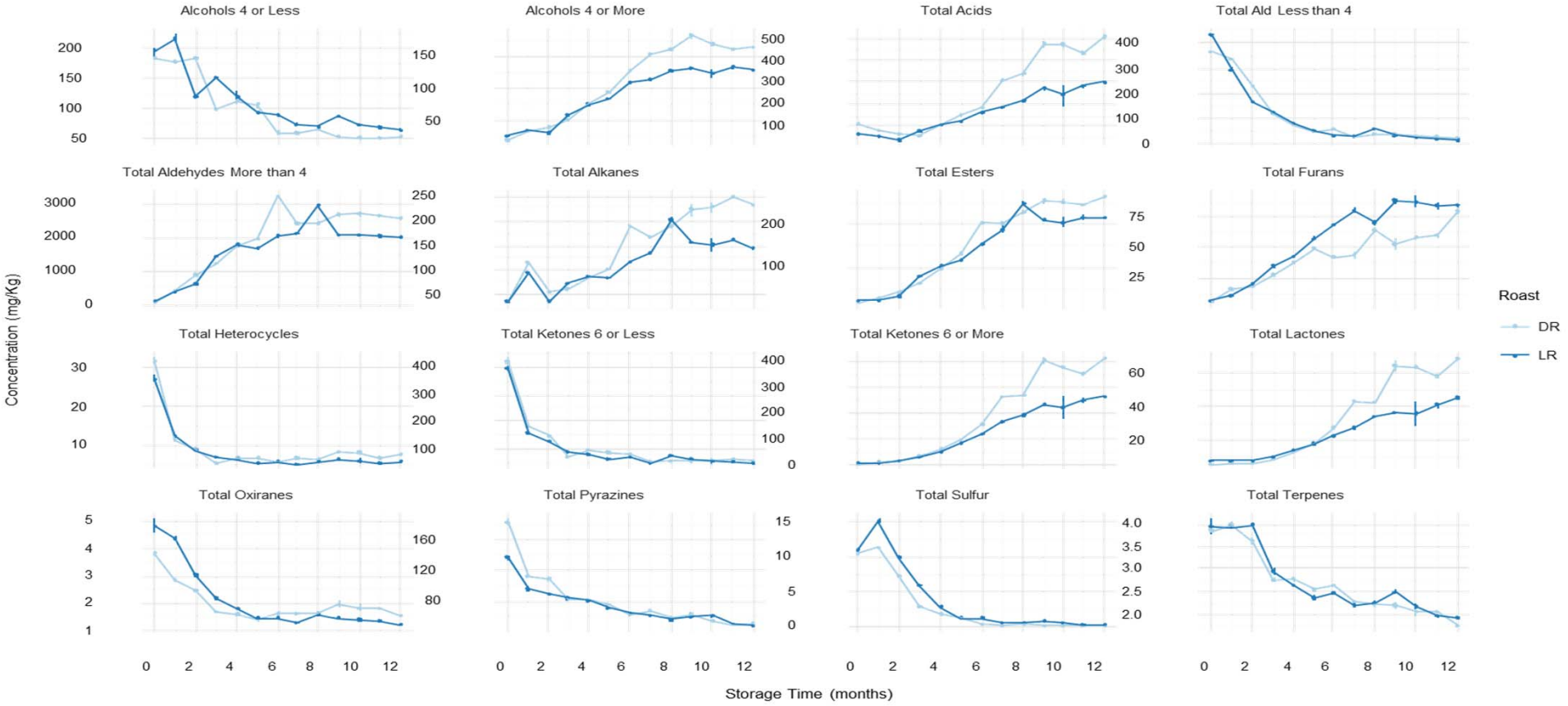
- alpha tocopherol decreased by 34.3 % (DR) and 23.2% in LR almonds
- Undergoing oxidation

Volatile Compounds



- A total of 99 volatile compounds were identified in roasted almonds over the 12 months of storage
- Compounds include: 8 acids, 17 alcohols, 19 aldehydes, 5 alkanes, 4 esters, 11 ketones, 13 pyrazines, 3 terpenes and 20 other compounds
- Authentic standards were available to confirm identifies of 63 compounds
- Tentative identities of the remaining 36 compounds were made by comparing MS spectra with the NIST Library and calculated Kovat's retention indices (KI) with literature values of standards chromatographed under comparable conditions

Trends in Total Volatiles by Class



Flavor fade and lipid oxidation are observed at 6 month

Select compounds that decrease with significant correlation ($r^2 > 8.4$) and correspond with consumer liking

Name	Correlation Value	Concentration in DR			Concentration in LR		
		0 Months	2 Months	4 months	0 Months	2 Months	4 months
Positive Correlations							
methoxymethyl oxirane	0.939	3.7 ± 0.0	2.27 ± 0.03	1.18 ± 0.04	4.73 ± 0.25	2.80 ± 0.05	1.33 ± 0.03
ethylpyrazine	0.921	5.56 ± 0.08	3.45 ± 0.09	2.79 ± 0.10	5.11 ± 0.15	3.28 ± 0.04	2.87 ± 0.05
2,3-dimethylpyrazine	0.918	3.67 ± 0.04	2.36 ± 0.11	1.77 ± 0.02	3.22 ± 0.04	2.05 ± 0.21	1.87 ± 0.08
2-ethyl-6-methylpyrazine	0.908	5.41 ± 0.10	3.59 ± 0.10	2.97 ± 0.13	4.24 ± 0.17	3.16 ± 0.06	2.93 ± 0.04
2,5-dimethylpyrazine	0.886	80.1 ± 1.4	49.2 ± 1.29	37.1 ± 1.17	60.6 ± 1.49	40.3 ± 0.43	36.6 ± 0.72
3-methylbutanal	0.886	92.9 ± 0.8	64.4 ± 0.89	19.6 ± 1.09	114 ± 1.19	46.4 ± 1.04	20.3 ± 0.63
2-methylbutanal	0.884	225 ± 3	146 ± 2.37	43.7 ± 0.691	260 ± 4.84	106 ± 1.82	47.9 ± 1.17
2,6-dimethylpyrazine	0.870	13.7 ± 0.31	8.45 ± 0.23	6.09 ± 0.13	8.7 ± 0.45	6.57 ± 0.36	6.1 ± 0.085
2-ethyl-5-methylpyrazine	0.861	2.11 ± 0.06	1.35 ± 0.03	1.12 ± 0.04	1.51 ± 0.03	1.18 ± 0.024	1.12 ± 0.01
methylpyrazine	0.855	44.6 ± 1.78	21.8 ± 0.48	15.8 ± 0.58	35.5 ± 0.57	17.4 ± 0.25	15.4 ± 0.20
pyrazine	0.842	2.49 ± 0.14	1.19 ± 0.04	0.917 ± 0.03	2.41 ± 0.04	0.984 ± 0.04	0.833 ± 0.01

Select compounds that increase with significant correlation ($r^2 > 9.4$) and correspond with consumer liking

		Concentration in DR			Concentration in LR		
Name	**Correlation Value**	**0 Months**	**2 Months**	**4 months**	**0 Months**	**2 Months**	**4 months**
Negative correlations							
hexanoic acid	-0.900	1.05 ± 0.06	14.7 ± 3.00	59.8 ± 2.11	1.96 ± 0.32	12.3 ± 0.15	56.3 ± 1.22
pentanal	-0.902	3.92 ± 0.04	62.8 ± 0.59	110 ± 1.26	5.5 ± 0.06	41.3 ± 0.84	111 ± 0.79
hexanal	-0.902	58 ± 0.34	716 ± 16.30	1360 ± 15.9	77.9 ± 1.8	492 ± 9.25	1390 ± 8.25
2-pentylfuran	-0.909	4.86 ± 0.14	13.9 ± 0.23	28.8 ± 0.58	6.48 ± 0.33	16.3 ± 0.42	32.4 ± 0.35
2-hexenal	-0.922	0.393 ± 0.01	2.93 ± 0.17	5.13 ± 0.27	1.23 ± 0.01	2.67 ± 0.02	5.28 ± 0.03
2-heptenal	-0.928	0.799 ± 0.03	6.51 ± 0.23	17.6 ± 0.32	1.1 ± 0.057	5.12 ± 0.07	19.2 ± 0.34
1-butanol	-0.931	0.542 ± 0.03	1.48 ± 0.03	2.78 ± 0.07	0.623 ± 0.01	1.05 ± 0.02	2.62 ± 0.02
3-octen-2-one	-0.934	0.465 ± 0.01	5.58 ± 0.15	17.2 ± 0.34	0.755 ± 0.05	5.6 ± 0.09	14 ± 0.35
styrene	-0.943	1.53 ± 0.02	3.85 ± 0.05	5.02 ± 0.17	1.79 ± 0.05	2.47 ± 0.05	5.28 ± 0.02
1-pentanol	-0.946	3.79 ± 0.06	16.8 ± 0.22	36.9 ± 0.81	6.31 ± 0.14	11.7 ± 0.13	34.6 ± 0.27

Compounds with significant correlation with consumer liking ($p < 0.05$) and an absolute regression slope of >2 µg/kg change in concentration per unit liking

Compound Name	Linear R^2 value	Slope of Conc. (µg/kg) vs. liking	Aroma Quality	Aroma Threshold (µg/kg)	DR 4 month	DR 6 month	LR 4 month	LR 6 month
heptanal	0.952	-82.55	fatty, oily, powerful, rancid, citrus, sharp	50[1,O]	**85.4 ± 2.0**	**187 ± 3**	**87.1 ± 0.9**	**137 ± 2**
octanal	0.885	-93.24	citrus-like, soapy, penetrating	55[1,O]	**69.5 ± 1.5**	**158 ± 5**	**69 ± 1**	**127 ± 3**
hexanal	0.814	-736.91	fatty, green, grassy	75[1,O]	**1360 ± 15.9**	**2380 ± 34.6**	**1390 ± 8.25**	**1480 ± 6.5**
1-octen-3-ol	0.753	-11.27	mushroom, earthy, green, oily, fungal	1[4,W]	**7.29 ± 0.237**	**14.9 ± 0.365**	**5.75 ± 0.158**	**10 ± 0.207**
benzaldehyde	0.586	2.53	artificial almond, sweet, cherry	350[W]	8.79 ± 0.334	10.6 ± 0.568	9.1 ± 0.0877	8.71 ± 0.195
furfural	0.631	4.63	sweet, woody, almond, bread	3,000[4,W]	5.2 ± 0.219	3.95 ± 0.12	4.55 ± 0.0394	3.78 ± 0.0424
2-methylbutanal	0.781	83.19	fruity, dry, slightly green, chocolate, nut	10[5,O]	**43.7 ± 0.691**	**23.1 ± 1.8**	**47.9 ± 1.17**	**18.8 ± 0.159**
3-methylbutanal	0.785	35.66	musty, chocolate, nutty, malty	5.4[5,O]	**19.6 ± 1.09**	**11.2 ± 0.675**	**20.3 ± 0.63**	**8.28 ± 0.141**

Conclusions

- Raw almond flavor is dominated by amygdalin and benzaldehyde
- Attributes of roasted almond flavor include: pyrazines, furans and alcohols, furfural, and especially 2-methylbutanal and 3-methylbutanal
- In stored roasted almonds the PV does not relate to consumer liking and 5 mEq/kg is not a good measure of rancidity development or consumer acceptance
- FFA remain below recommended 1.5% oleic indicating this is not a good measure of rancidity development or consumer acceptance of roasted almonds
- Consumer liking was not different based on roast level
  - Consumers changed liking significantly by 2 months, by 4-5 months consumers neither liked nor disliked the almonds
  - Consumers disliked almonds on average by 6 months for both LR and DR
- At 2 months, significantly decreases were observed in compounds related to roasted flavor (pyrazines) indicating that flavor fade occurs rapidly
- At 6 months significant increases in aldehydes were observed with the strong correlations with heptanal, octanal and hexanal

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