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Volatile Compound Profiles of Raw and Roasted Peanut Seeds of the Runner and Virginia Market-types

Jacy R. Weissburg[1], Suzanne D. Johanningsmeier[2] & Lisa L. Dean[2]

[1] Department of Food, Bioprocessing and Nutrition Sciences, North Carolina State University, Raleigh, NC, USA

[2] Food Science and Market Quality and Handling Research Unit, USDA, ARS, SEA, Raleigh, NC, USA

Correspondence: Lisa L. Dean, Food Science and Market Quality and Handling Research Unit, USDA, ARS, SEA, PO Box 7624, NCSU, Raleigh, NC, 2769-7624, USA. Tel: 1-919-515-9110. E-mail: Lisa.Dean@usda.gov

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Abstract

The unique flavor of peanuts that develops during roasting is the primary driving force for the consumption of peanut products. Although rarely consumed raw, the raw state of the peanut contains the precursors involved in the transformations that lead to the distinct flavor development in roasted peanuts. Volatile compounds extracted from the headspace above raw and roasted peanut samples of the runner and virginia market types by solid phase microextraction were characterized using two-dimensional gas chromatography coupled with time-of-flight mass spectrometry. The roasting treatment and peanut market-type each had a significant impact on the types and concentrations of small molecular weight compounds found. Among 361 sample components detected, 290 compounds were found to be significantly different between the raw and roasted treatments ($p < 0.05$). The roasted samples contained pyrazines, pyrroles, thiazoles, and furans. Alcohols were the primary compounds found in the raw peanut samples. Additionally, 107 compounds were found to differ significantly between roasted runner and virginia-type peanuts. Virginia-type peanuts contained higher levels of linoleic acid oxidation products, such as 2-octenal, hexanal, and 1-octen-3-one. More significant distinctions in volatile compounds were recognized between runner and virginia market types than previously observed. In total, this study reported 119 volatile compounds that have not previously been reported in roasted peanuts, including 11 furans, seven pyrroles, five pyridines, and 12 pyrazines.

Keywords: peanuts, *Arachis hypogaea* L., thermal processing, flavor development, roasting

1. Introduction

The unique roasted flavor of peanuts is the basis of most consumer purchases of products containing them (Buckholz, 1981; Sanders et al., 1989). It is well established that the composition and concentration of volatile compounds produced during thermal processing are largely responsible for the characteristic flavor and aroma of roasted peanuts (Coleman et al., 1994; Sanders et al., 1997; Neta et al., 2010). During roasting, the precursor compounds present in the raw peanut participate in reactions that produce the volatiles known to impact the perception of roast peanut flavor (Hodge, 1953; Coleman et al., 1994; Ku et al., 1998). The predominant pathways for formation of volatile compounds in roasted peanuts are through the Maillard reaction, lipid oxidation, and caramelization (Coleman et al., 1994). Heterocyclic nitrogen-containing compounds produced by the Maillard reaction are recognized to be the prime contributors to peanut flavor, specifically pyrazines (Mason et al., 1967; Newell et al., 1967; Walradt et al., 1971; Buckholz et al., 1980; Baker et al., 2003). However, the determination of the specific compounds responsible for roasted peanut flavor has been difficult. Analysis of volatile compounds from roasted peanuts to date typically results in several hundreds of compounds identified and complex chromatograms (Brown et al., 1968; Walradt et al., 1971; Ho et al., 1981; Oupadissakoon & Young, 1984; Braddock et al., 1995; Warner et al. 1996; Baker, 2003; Schirack et al., 2006; Chetschik et al., 2008; Greene et al., 2008; Neta et al., 2010). In the last 50 years, more than 300 volatile compounds have been associated with roasted peanuts (Chetschik et al., 2008; Neta et al., 2010; Zhang et al., 2023). However, no single class of volatile compounds, including pyrazines, independently forms the flavor of roasted peanuts (Schirack et al., 2006). Some other volatile compound classes have been found essential for roasted flavors, include aldehydes, ketones, alcohols, certain hydrocarbons, and phenolic and furan derivatives (Manzano et al., 2013). Understanding the essential volatile compounds and the mechanisms that produce them could allow for

replication of the natural flavor, along with maximizing the intensity of roasted peanut flavor in peanuts (Newell et al., 1967; Pattee et al., 1991).

Virginia and runner-type peanuts comprise 95% of the total peanut market in the United States (American Peanut Council, 2018). Although the two market types differ in various ways such as kernel size, grading factors, optimum growing environment, etc., few differences have been distinguished between their volatile profiles in previous studies (Balota & Phipps, 2013; Ng & Dunford, 2009; Wang et al., 2017). Despite the long list of volatile compounds previously reported in peanuts, research has shown that only a small number of the many compounds in food are significant in estabilishing the flavor (Grosch, 1993). It is difficult to determine which compound(s) potentially relate to flavor as the presence of a compound is not always indicative of the contribution to a particular flavor (Greene et al., 2008). The previous studies investigating volatile compounds in peanuts focused on the peaks with the greatest abundances, drawing correlations with sensory data (Ng & Dunford, 2009; Wang et al., 2017). Despite this, relative concentration and relative flavor, and/or odor activity are not correlated across chemical compounds (Grosch, 1993). To achieve greater detection and discrimination of volatile compounds in peanuts, two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GCxGC-TOFMS) analysis was employed on raw and roasted peanuts virginia and runner-market type peanuts. Two-dimensional gas chromatography (GCxGC) includes two columns connected in series with different separation mechanisms. This technology coupled with time-of-flight mass spectrometry (GCxGC-ToFMS) has been found to result in improved mass spectral matches and detection of more components, compared to the technology with a single column (Adahchour et al., 2005).

This non-targeted, discovery-based approach has provided new insights into the diverse volatile compound profile of peanuts. While previous work focused on the most abundant volatile organic components (VOCs), this study investigated and compared all VOCs present in raw and roasted, runner and virginia-type peanut seeds. Through a nontargeted approach with the use of two-dimensional GC analysis, greater detection and discrimination of volatile characteristics was achieved. This consequential data provides new insights and a more comprehensive view of the compounds developed from roasting, along with differences between the top two market-types. Compounds present in raw peanuts, but absent in the roasted form, could be essential precursors in the thermal reactions along with inactivation of certain enzymes, producing the attributes of a roasted peanut. This knowledge will allow for a targeted breeding approach to improve peanut flavor quality.

2. Method

Chemicals

The internal standards pyrazine-d4 (98%) and pyrrole-d5 (98%) were obtained from CDN Isotopes Inc. (Quebec Canada). Sodium chloride (99.9%) was obtained from Sigma-Aldrich (St. Louis, MO, USA).

2.1 Sampling Procedure

Raw, shelled peanuts of the runner and virginia market types were collected from six different warehouse locations. Each warehouse contributed five individual 4.54 kg samples, each from a distinct commercial lot. The sample size was n=15 for each market type. The runner type peanuts were obtained from 3 different warehouses located in the southern part of the state of Georgia, USA. The virginia type peanut samples were collected from 2 different warehouses in the eastern part of the state of North Carolina, USA and one from the eastern part of the state of Virginia, USA.The utilization of multiple warehouse and commercial lots was done to obtain a representative sample from USA crop for a single growing season. NIST Standard Reference Material® 2387 (Peanut Butter) (National Institute of Standards & Technology, Gaithersburg, MD, USA) was purchased to serve as the control sample for the analysis (NIST QC).

2.2 Internal Standard Preparation

Internal standards, pyrazine-d4 and pyrrole-d5 (CDN Isotopes, Inc., Quebec, Canada) were incorporated into samples at 100 ppb. Solid pyrazine-d4 (0.05 g) was added to 10 mL of HPLC grade water to create a stock solution of 5000 µg/mL concentration. Stock solution (10 µL) was added to 10 mL of HPLC grade water to create a working solution of 5 µg/mL. Working solution (30 µL) was added to each sample vial so it was 100 ppb in the sample for analysis. The same procedure was used for the liquid pyrrole-d5 internal standard.

2.3 Sample Preparation

The peanut samples were subdivided into 2.27 kg aliquots for raw and roasted treatments. The 2.27 kg subsamples from each commercial lot (n=30) for testing in the raw state was blanched. The blanching process was done to remove the skins, so that only seed tissue was included in the samples for analysis. Peanut skin removal prevents interference from compounds, such as proanthocyanidins (Bansode et al., 2015). The peanuts

were blanched with a convection oven (Despatch, Minneapolis, MN, USA) heated to 92 ℃ for one hour, followed by forced air cooling and physical removal of the skins using a model EX whole nut blancher (Ashton Food Machinery, Newark, NJ, USA). After blanching, the samples were stored as 0.45 kg aliquots in vacuum-sealed mylar bags at -80 ℃ until analysis (Klevorn & Dean, 2018).

For the roasted treatment, the 2.27 kg samples of runner (n=15) and virginia-type (n=15) peanuts were dry roasted to a Hunter L-value = 48 ± 1. Colors were verified using a Hunter Model Colorimeter (Hunter Labs, Reston, VA, USA). The samples were roasted as previously described by Poirier et al. (2014) using an Aerolab T-8 lab scale batch roaster (Buhler Aeroglide, Cary, NC, USA). Samples were roasted in removable square product trays that were uniformly perforated, with dimensions of 20 cm x 20 cm, and a depth of 7.62 cm. The temperature of the roaster was set to 177 ℃ and had an air flow rate of 1 m/s. To simulate industry roasting parameters, the airflow switched from up-flow to down-flow halfway through the roast. Immediately after roasting, peanuts were cooled to ambient temperature (~25 ℃) using forced air. The skins were manually removed during the cooling. When the peanuts were cool, the samples were stored in vacuum-sealed mylar bags as 0.45 kg aliquots in a -80 ℃ freezer until analysis (Klevorn & Dean, 2018).

Peanuts were removed from the -80 ℃ freezer immediately before pasting. Each individual 453-gram sample of frozen peanuts was processed into a paste with a Blixer-3 food processor (Robot Coupe, Jackson, MS, USA). Pasted peanut samples were weighed (0.075 g) directly into 10 mL clear screw cap vials (Microliter Analytical Supplies Inc. Suwanee, GA, USA). Next, 0.6 grams of NaCl (Sigma Chemical Corp., St. Louis, MO, USA) was added to each vial to "salt out" volatile components from the samples. Internal standards, pyrazine-d4 and pyrrole-d5, were then added to each vial at a concentration of 100 μg/L. Lastly, 933 mL of HPLC grade water was added to each vial to give it a final sample volume equal to 1.5 mL. Capped sample vials were vortexed for 1 min to ensure adequate mixing. NIST samples were acquired already pasted; and otherwise prepared with the same procedure. Blank samples without addition of peanut paste were prepared the same as the samples. An n-alkane series (Sigma Chemical Corp.) of alkane standards, octane through icosane (C8-C20) and henicosane through tetracontane (C21-C40), was used for retention index calculations (Van den Dool & Kratz, 1963). The alkane standards were prepared per run by pipetting 3 μL of a mix of alkanes: henicosane through tretacontane (C21-C40) into one clear screw cap vial, and then 1 μL of a mix of alkanes: octane through icosane (C8-C20) into another vial.

2.4 Sampling Design

Samples were grouped by commercial lots (1 lot for each market type and warehouse per batch for analysis) and randomized for analysis order with an online randomizer (random.com). Samples were placed in the temperature-controlled sample tray at 2 ℃. Five batches of 33 samples were utilized to complete this study. One raw and one roasted peanut seed paste from each warehouse was tested in every batch (n=6 raw, n=6 roasted) along with the NIST quality control samples (n=3), alkane standards (n=2), and blank samples between runs to minimize carryover (n=16). In each run, the alkane standards were sampled first and last, and the NIST QC were sampled 9th, 19th, and 27th.

2.5 Solid-Phase Microextraction (SPME) of Volatile Components

Peanuts volatile compounds were captured using headspace solid-phase microextraction (HS-SPME) and a CTC Analytics combiPAL autosampler (CTC Analytics, Zwingen, Switzerland). The volatile compounds were sampled using a 1 cm SPME fiber with three-phases divinylbenzene/carbonex/polydimethylsiloxane (DVB/CAR/PDMS) (Supelco Corp., Bellefonte, PA, USA) and a coating thickness of 50/30 μm. The samples were equilibrated at 40 ℃ for 15 minutes with agitation at 500 rpm. The SPME fibers were incorporated through the vial septa at a depth of 12 mm and exposed to the headspace above the sample. The SPME fibers then equilibrated with the sample headspace for 40 minutes at 40 ℃ with agitation at 100 rpm to extract the sample volatiles. The fiber desorbed into the GCxGC-TOFMS instrument for 15 minutes (Neta, 2010).

2.6 Comprehensive Two-Dimensional Gas Chromatography-Time-of-Flight Mass Spectrometry (GCxGC-ToFMS) Analysis

The peanut volatile compounds were profiled using a LECO Pegasus III two-dimensional gas chromatograph (GCxGC) coupled with time-of-flight mass spectrometer (ToFMS) (Model #614-100-700, Leco Corporation, St. Joseph, MI, USA). The instrument was connected to an Agilent GC (Model# 6890 N, Agilent Technologies; Santa Clara, CA, USA) fitted with a secondary oven. The system was assisted by a thermal modulator that was cooled with liquid nitrogen at a modulation time set to 1.75 sec and a hot jet pulse time of 0.35 sec. The cool time between stages was 0.53 sec. Separation of components was conducted using a polyethylene glycol column (SolGel-Wax^{TM}, 30 m x 0.25 mm ID x 0.25 μm df)(SGE, Austin, TX, USA) as the first dimension column, and a

14% cyanopropylphenyl – 86% dimethyl polysiloxane column (RTX 17-01, 1 m x 0.1 mm ID x 0.1 μm df) (Restek, Bellefonte, PA, USA as the second dimension column. Helium was utilized as the carrier gas at a constant flow rate of 1.3 mL/ min. The transfer line was set as 250 ℃ and operated in pulsed splitless mode with a pulse pressure of 37 psi for 1 min, and the split vent was opened 2 min after injection. The primary oven temperature was set to 40 ℃, and programmed to increase to 140 ℃ at a rate of 5 ℃/min, then 10 ℃/min to 250 ℃ with an initial hold of 2 min, and a final hold of 3 min. The secondary oven temperature increased from 55 ℃ to 155 ℃ at 5 ℃/min then 10 ℃/min to 250 ℃ with an initial hold of 2 min, and a final hold of 4 min. The ToFMS detector was operated at -70 eV and an ion source temperature of 200 ℃. Masses within the range of 25-500 m/z were collected. The detector voltage was 1500 V, with a scan rate of 200 spectra/sec (Neta, 2010).

2.7 GCxGC–ToFMS Data Processing

ChromaTOF® software version 4.33 (Leco Corporation, St. Joseph, MI, USA) data processing methods were employed to detect and quantify peaks established on unique masses as set by the deconvolution algorithm. Prior to processing the data, the retention times of the alkane standard peaks were identified to create a retention index table. The NIST/EPA/NIH Mass Spectral Library (National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA, 2005) was utilized for tentative identification of deconvoluted chromatographic peaks for the compounds. Chemical names were attached to peaks that had at least a mass spectral similarity ≥ 750, where 1000 is an exact match. The peak area calculations utilized the unique mass (U) for every peak, as assigned by the ChromaTOF® deconvolution algorithm. In StatCompare® in ChromaTOF®, samples were assigned to their corresponding class including blanks, samples, and quality control (QC) samples. Compounds across all samples were then aligned using the software algorithm and mass spectral similarity match ≥ 600. Tentative identification of volatile compounds in peanuts was performed by comparison of volatile compounds mass spectra and retention times to those reported in the literature, utilizing the National Institute of Standards and Technology (NIST) Chemistry Webbook (https://webbook.nist.gov/chemistry/) (last accessed April 20, 2023). Confirmed identifications were made for those components that matched an authenic standard run on the same instrument under the same conditions.

2.8 Statistical Analysis

The aligned chromatographic data was exported to Microsoft Excel 2016 (Microsoft Corporation, Redmond, WA, USA) for data compilation. A new column that combined peak number and peak name was incorporated to give each peak a unique indentifier for statistical analysis. Missing value replacement was performed in Excel with the "randbetween" function to provide substitution data that reflected possible responses below the detection limit of the method for undetected components (Johanningsmeier & McFeeters, 2011). Analysis of variance (ANOVA) and hierarchical cluster analysis (HCA) were performed in JMP Genomics version 9.4 (SAS Institute, Cary NC, USA). To normalize the peak area variances prior to statistical analysis, a log2 transformation was utilized. An ANOVA was run on the log2 peak areas to detect differences in the compounds among the treatments. To check for instrumental drift, batch variation, and sample variation, the responses in quality control samples were observed for similar resolution of chromatographic peaks. Additionally, to ensure the variation in sample responses was due to the roast level and market-type, the weighted average proportion of variance across principal components was observed among the sample variables, the run order, the batch, and the residual variation. Metabolite peaks with significant differences ($p < 0.05$) among treatment groups were incorporated into hierarchical clustering analysis (HCA) utilizing the Fast Ward method as the clustering process (Johanningsmeier & McFeeters, 2011). The results were displayed in heat maps and were examined for relevant trends. Clusters of metabolites that were present in select treatment groups were selected for further investigation (Johanningsmeier & McFeeters, 2011). Components that existed only in roasted peanut samples were presumed to have been formed due to chemical changes that occurred during the roasting process. Further statistical analysis was performed using XLStat version 9.4 for Windows™ (Addinsoft, Paris, France). Principal component analysis (PCA) was employed as a non-supervised data reduction technique to visualize the relationships in the overall VOC profiles among roast treatments and market-types.

3. Results

3.1 Identification and Quantification of Selected Volatile Compounds in Peanuts

Approximately 515 peaks with a signal to noise ratio (S/N) ≥ 20 were detected among the peanut samples. Manual inspection of the chromatograms and peak table data for chromatograms for the peanut samples compared to blanks containing sodium chloride in water established that 361 of the volatile compounds were assigned to the peanut samples. The 154 artifact peaks included system contaminants such as formaldehyde, were attributed to column bleed at the high end of the temperature program. The polar-semipolar two-column

combination enables isolation of these artifacts from sample volatile components. Unlike one-dimensional GC, this makes it possible to identify and quantify low-level volatile metabolites despite system contaminants (O'Hagan et al., 2007; Johanningsmeier & McFeeters., 2011).

Of the 361 compounds detected in the peanut samples, 274 (75.9%) were tentatively identified by ChromaTOF® data processing with the use of the best spectral match to the NIST library with similarity ≥ 750. The 87 other compounds were unidentified. Comparisons to retention indices reported in the literature resulted in the presumptive identification of 155 volatile compounds in roasted and raw virginia and runner-type peanuts (**Table 1**). Published retention indices were not found or did not match for the other 119 compounds. Authentic standards of 57 compounds were individually chromatographed to confirm the quality of the tentative identifications, and 54 were found to be positively identified by comparisons of the volatile compound's retention index and mass spectra. Metabolites that did not match literature values were further investigated, and either concluded to be left as a mass spectral match or an unknown. Compounds matched to multiple peaks were visually investigated using the chromatographs and mass spectra to further determine the identity. The volatile compounds identified in the raw and roasted virginia and runner-type peanuts included 74 nitrogen containing compounds of which there were 28 pyrazines, 23 furans, six pyridines, and 17 pyrroles. In addition, 19 ketones, six diketones, seven esters, three ethers, 17 sulfur containing compounds, 27 alcohols, 25 aldehydes, and 40 hydrocarbons were identified.

Table 1. Volatile compounds in roasted and raw peanuts of runner and virginia market types detected using SPME GCxGC-ToFMS

Primary Class	Compound	CAS[2] registry #	Method of idenification[3]	Similarity	RI $_{Calc}$[4]	RI$_{Lit}$[5]	Unique mass[6]	HCA Group[7]
Alcohol	Methyl Alcohol	67-56-1	MS, RI, ST	915	869	905	31	1
Alcohol	2-Propen-1-ol*	107-18-6	MS, RI	867	1088	1124	57	1
Alcohol	2-Methyl-5-hexen-3-ol*	32815-70-6	MS	788	1232	Nf	55	1
Alcohol	2-Chloro-2-propen-1-ol*	5976-47-6	MS	763	1547	Nf	57	1
Alcohol	2-Methoxyphenol	90-05-1	MS, RI	818	1820	1855	81	1
Alcohol	Benzyl alcohol	100-51-6	MS, ST	865	1836	Nf	79	1
Alcohol	2-Methoxy-4-vinylphenol	7786-61-0	MS, RI	909	2134	2190	135	1
Alcohol	4-Ethylcyclohexanol*	4534-74-1	MS	809	1509	Nf	58	2
Alcohol	1-Butanol	71-36-3	MS, RI, ST	898	1120	1142	31	4
Alcohol	1-Octen-3-ol	3391-86-4	MS, RI, ST	868	1418	1444	57	5
Alcohol	Isopropyl Alcohol	67-63-0	MS, RI, ST	877	903	905	45	6
Alcohol	1-Propanol	71-23-8	MS, RI, ST	802	1012	1032	31	6
Alcohol	2-Methyl-1-propanol	78-83-1	MS, RI, ST	900	1069	1090	41	6
Alcohol	3-Pentanol*	584-02-1	MS, RI, ST	792	1084	1111	59	6
Alcohol	(S)-(+)-2-Pentanol	26184-62-3	MS	869	1096	Nf	45	6
Alcohol	1-Penten-3-ol	616-25-1	MS, RI, ST	852	1132	1166	57	6
Alcohol	1-Pentanol	71-41-0	MS, RI, ST	901	1222	1246	42	6
Alcohol	(Z)-2-Penten-1-ol*	1576-95-0	MS, ST	877	1289	1323	57	6
Alcohol	(S)-2-Heptanol*	6033-23-4	MS	787	1291	Nf	45	6
Alcohol	1-Hexanol	111-27-3	MS, RI	891	1325	1355	56	6
Alcohol	1-Nonanol*	143-08-8	MS, RI	882	1630	1647	41	6
Alcohol	Phenylethyl Alcohol	60-12-8	MS, RI, ST	896	1875	1904	91	6
Alcohol	(R)-2-Butanol*	14898-79-4	MS	849	998	Nf	45	
Alcohol	3-Methyl-4-penten-1-ol*	51174-44-8	MS	755	1059	Nf	65	
Alcohol	(S)-2-Methylbutan-1-ol *	1565-80-6	MS	862	1179	Nf	41	
Alcohol	(S)-2-Hexanol	52019-78-0	MS	856	1192	Nf	45	
Alcohol	(E)-1,3-Butandien-1-ol*	70411-98-2	MS	776	1236	Nf	70	
Aldehyde	2-Methylpropanal	78-84-2	MS, RI, ST	788	801	817	72	1
Aldehyde	Butanal	123-72-8	MS, RI, ST	855	854	872	27	1
Aldehyde	2-Methylbutanal	96-17-3	MS, RI, ST	887	894	905	41	1
Aldehyde	3-Methylpentanal*	15877-57-3	MS, RI	865	1012	1032	56	1
Aldehyde	Heptanal	111-71-7	MS, RI, ST	873	1161	1185	41	1
Aldehyde	Benzaldehyde	100-52-7	MS, RI	893	1492	1518	77	1
Aldehyde	a-Methylbenzeneacetaldehyde*	93-53-8	MS	751	1607	Nf	105	1
Aldehyde	Benzeneacetaldehyde	122-78-1	MS	904	1609	Nf	91	1
Aldehyde	2-Methyl-3-phenyl-2-propenal*	101-39-3	MS, RI, ST	820	1897	1992	115	1
Aldehyde	3-Methylbutanal	590-86-3	MS, RI, ST	841	898	921	41	3
Aldehyde	O-Methyloxime butanal*	31376-98-4	MS	761	861	Nf	70	5
Aldehyde	Pentanal	110-62-3	MS, RI, ST	849	957	970	44	5
Aldehyde	Hexanal	66-25-1	MS, RI, ST	896	1059	1079	41	6
Aldehyde	Acetaldehyde	75-07-0	MS, RI, ST	765	712	714	29	1

Aldehyde	(Z)-2-Butenal	15798-64-8	MS, RI	925	1016	1035	70	1
Aldehyde	(E)-2-Methyl-2-butenal	497-03-0	MS, RI, ST	940	1070	1087	55	1
Aldehyde	2-Ethyl-trans-2-butenal*	63883-69-2	MS, ST	850	1135	Nf	41	1
Aldehyde	2-Methyl-2-hexenal*	28467-88-1	MS	846	1156	Nf	41	1
Aldehyde	(Z)-2-Heptenal	57266-86-1	MS, RI, ST	905	1299	1310	41	2
Aldehyde	2,4-Decadienal	2363-88-4	MS, RI	860	1778	1794	81	2
Aldehyde	(E)-2-Octenal	2548-87-0	MS, RI, ST	852	1401	1430	41	5
Aldehyde	2-Hexenal	505-57-7	MS, RI	876	1192	1213	41	6
Carboxylic acid	Methyl ester acetic acid*	79-20-9	MS, RI, ST	906	811	819	43	1
Carboxylic acid	Methyl ester-2-propenoic acid*	96-33-3	MS, RI	870	918	938	55	1
Carboxylic acid	Acetic acid	64-19-7	MS, RI, ST	849	1421	1446	45	1
Carboxylic Acid	l-Pantoyl lactone	599-04-2	MS, RI	815	1988	1998	71	1
Carboxylic Acid	Pentanoic acid	109-52-4	MS, RI	873	1806	1728	60	6
Chlorobenze	Benzyl chloride*	100-44-7	MS, RI	852	1486	1488	91	1
Diketone	2,3-Butanedione	431-03-8 (or 625-34-3) cis/trans	MS, RI	863	952	970	43	1
Diketone	2,3-Pentanedione	600-14-6	MS, RI, ST	883	1034	1060	43	1
Diketone	2,3-Hexanedione*	3848-24-6	MS, RI	781	1106	1136	43	1
Diketone	3,4-Hexanedione*	4437-51-8	MS, RI	809	1115	1163	57	1
Diketone	Acetyl valeryl*	96-04-8	MS, RI	818	1127	1146	43	1
Diketone	1,4-Cyclohex-2-enedione*	4505-38-8	MS	821	1698	Nf	54	1
Ester	Methyl formate	107-31-3	MS, RI, ST	866	721	768	31	1
Ester	Methyl propionate*	554-12-1	MS, RI, ST	869	886	889	57	1
Ester	Methyl methacrylate*	80-62-6	MS, RI	818	988	1005	55	1
Ester	2-Methylallyl methacrylate*	816-74-0	MS	755	1247	Nf	69	1
Ester	Tetrahydro-2H-pyran-2-one*	542-28-9	MS	816	1580	Nf	42	1
Ester	n-Caproic acid vinyl ester	3050-69-9	MS	801	1625	Nf	43	6
Ether	Trimethylene oxide*	503-30-0	MS, ST	843	759	Nf	29	1
Ether	(Methoxymethyl)oxirane*	930-37-0	MS	754	1328	Nf	45	1
Ether	Eucalyptol*	470-82-6	MS, RI, ST	819	1190	1215	43	5
Furan	Furan*	110-00-9	MS, RI	860	775	814	39	1
Furan	3-Methylfuran	930-27-8	MS, RI	862	851	867	82	1
Furan	2,4-Dimethylfuran*	3710-43-8	MS, RI	863	947	962	67	1
Furan	2,3-Dihydro-3-methylfuran*	1708-27-6	MS	776	1085	1392	69	1
Furan	2-(2-Propenyl)-furan*	75135-41-0	MS, RI	844	1183	1204	79	1
Furan	2-Methyltetrahydrofuran-3-one	3188-00-9	MS	813	1236	Nf	43	1
Furan	Tetrahydrofuran-2-carbonyl chloride*	52449-98-6	MS	799	1328	Nf	43	1
Furan	2-Furancarbonitrile*	617-90-3	MS	869	1360	Nf	93	1
Furan	Furfural	98-01-1	MS, RI, ST	872	1429	1457	39	1
Furan	1-(2-Furanyl)-ethanone	1192-62-7	MS, RI	894	1470	1500	95	1
Furan	Acetate-2-furanmethanol*	623-17-6	MS, RI	814	1503	1542	81	1
Furan	Dihydro-3-(2H)-thiophenone	1003-04-9	MS, RI	837	1530	1563	46	1
Furan	5-Methyl-2-furancarboxaldehyde	620-02-0	MS, RI	884	1538	1571	110	1
Furan	2-Furanmethanol	98-00-0	MS, RI	929	1619	1655	41	1
Furan	5-Methyl-2-furanmethanol	3857-25-8	MS, RI	840	1682	1724	95	1
Furan	2(5H)-Furanone	497-23-4	MS, RI	851	1714	1740	55	1
Furan	3-phenylfuran	13679-41-9	MS, RI	855	1820	1855	115	1
Furan	2,5-Dimethylfuran-3,4(2H,5H)-dione*	68755-49-7	MS	777	1987	Nf	43	1
Furan	2-Pentylfuran	3777-69-3	MS, RI, ST	858	1211	1229	81	2
Furan	Tetrahydrofuran*	109-99-9	MS, RI	811	870	864	42	3
Furan	2-Ethylfuran*	3208-16-0	MS, RI, ST	808	935	953	81	3
Furan	2-Vinylfuran*	1487-18-9	MS, RI	853	1050	1074	65	
Hydrocarbon	Heptane	142-82-5	MS	870	694	Nf	43	1
Hydrocarbon	(Z),(Z)-2,4-Hexadiene*	6108-61-8	MS	916	765	Nf	67	1
Hydrocarbon	Octane	111-65-9	MS, ST	864	801	Nf	70	1
Hydrocarbon	2,4-Dimethylhexane*	589-43-5	MS	839	900	Nf	57	1
Hydrocarbon	(2-Methylpropyl)-cyclopentane	3788-32-7	MS	852	972	Nf	41	1
Hydrocarbon	3-Ethyl-1-pentene*	4038-04-4	MS	767	1129	Nf	41	1
Hydrocarbon	Trans-1,2-dimethyl-cyclopropane*	2402-06-4	MS	764	1325	Nf	70	1
Hydrocarbon	Acetophenone	98-86-2	MS, RI, ST	830	1617	1647	77	1
Hydrocarbon	1-Nitro-1-phenylpropane*	5279-14-1	MS	796	1669	Nf	91	1
Hydrocarbon	(Ethenyloxy)-benzene*	766-94-9	MS	832	2279	Nf	120	1
Hydrocarbon	2-Octene*	111-67-1	MS, RI	846	851	862	55	2
Hydrocarbon	3-Ethyl-2,5-dimethylhexane*	52897-04-8	MS	804	932	Nf	57	2
Hydrocarbon	Decane*	124-18-5	MS, ST	855	999	Nf	43	2
Hydrocarbon	(E)-1,3-Nonadiene*	56700-77-7	MS, RI	824	1039	1046	54	2
Hydrocarbon	1-Butyl-2-ethyl-cyclopropene*	Nf	MS	787	1389	Nf	67	2

Hydrocarbon	Benzene	71-43-2	MS, ST	933	922	Nf	78	3
Hydrocarbon	Toluene	108-88-3	MS, RI, ST	914	1020	1038	91	3
Hydrocarbon	Ethylbenzene	100-41-4	MS, RI	877	1106	1133	91	3
Hydrocarbon	1,3-Dimethylbenzene	108-38-3	MS, RI	904	1120	1140	91	3
Hydrocarbon	7-Ethyl-1,3,5-cycloheptatriene*	17634-51-4	MS	818	1188	Nf	91	3
Hydrocarbon	Styrene	100-42-5	MS, RI	921	1232	1253	104	3
Hydrocarbon	Tridecane	629-50-5	MS, ST	821	1301	Nf	57	3
Hydrocarbon	2,2,4-Trimethylpentane*	540-84-1	MS, RI	795	646	708	57	4
Hydrocarbon	4-Methylheptane*	589-53-7	MS, RI	840	751	790	43	4
Hydrocarbon	o-Xylene	95-47-6	MS, RI	855	1128	1180	91	4
Hydrocarbon	Trans-1,2-bis(1-methylethenyl) -cyclobutane*	19465-02-2	MS, RI	853	1182	1238	68	4
Hydrocarbon	1,2,3-Trimethylbenzene*	526-73-8	MS	873	1261	Nf	105	4
Hydrocarbon	Pentane	109-66-0	MS	884	575	Nf	43	5
Hydrocarbon	Cyclohexane*	110-82-7	MS, RI, ST	807	705	739	28	5
Hydrocarbon	α-Pinene*	80-56-8	MS, RI, ST	893	1013	1025	93	5
Hydrocarbon	β-Pinene	127-91-3	MS, RI	877	1091	1101	93	5
Hydrocarbon	3-Methylundecane*	1002-43-3	MS	764	1165	Nf	57	5
Hydrocarbon	Cis-1,2-dimethyl-cyclopropane*	930-18-7	MS	797	593	Nf	55	6
Hydrocarbon	1,4-Pentadiene*	591-93-5	MS, RI, ST	854	627	646	67	
Hydrocarbon	2-Methylbutane	78-78-4	MS	829	810	Nf	58	
Hydrocarbon	(Z)-3-Methyl-2-pentene*	922-62-3	MS	757	838	Nf	69	
Hydrocarbon	3-Ethylhexane*	619-99-8	MS	841	855	Nf	43	
Hydrocarbon	3-Methylnonane	5911-04-6	MS, RI	796	964	967	57	
Hydrocarbon	2,2-Dimethyldecane*	17302-37-3	MS	781	991	Nf	57	
Hydrocarbon	4-Ethyl-2-methylhexane*	3074-75-7	MS	827	1096	Nf	43	
Hydrocarbon	Dodecane*	112-40-3	MS, ST	869	1197	Nf	57	
Ketone	Acetone	67-64-1	MS, RI, ST	935	801	826	43	1
Ketone	2-Butanone	78-93-3	MS, RI	855	878	910	43	1
Ketone	2,4-Dimethylpentanal*	27944-79-2	MS	820	1029	Nf	58	1
Ketone	(E)-3-Penten-2-one	3102-33-8	MS, ST	830	1102	1100	69	1
Ketone	3-Hexen-2-one	763-93-9	MS, RI	852	1109	1210	55	1
Ketone	Cyclopentanone	120-92-3	MS, RI	859	1158	1172	55	1
Ketone	2-Heptanone	110-43-0	MS, RI, ST	831	1159	1184	43	1
Ketone	3-Methyl-3-penten-2-one*	565-62-8	MS, ST	769	1172	Nf	55	1
Ketone	Acetoin	513-86-0	MS, RI, ST	833	1255	1281	45	1
Ketone	1-Hydroxy-2-propanone *	116-09-6	MS, RI	883	1269	1304	43	1
Ketone	1-Octen-3-one	4312-99-6	MS, RI, ST	822	1277	1304	55	1
Ketone	2-Cyclopenten-1-one*	930-30-3	MS, RI	767	1325	1349	82	1
Ketone	4-Methyl-2-hexanone*	105-42-0	MS	802	1365	Nf	43	1
Ketone	1-(Acetyloxy)-2-propanone	592-20-1	MS, RI	872	1427	1475	43	1
Ketone	4-Cyclopentene-1,3-dione	930-60-9	MS, RI	843	1550	1542	42	1
Ketone	Butyrolactone	96-48-0	MS, RI	924	1590	1635	42	1
Ketone	6-Oxa-bicyclo[3.1.0]hexan-3-one*	74017-10-0	MS	824	1726	Nf	55	1
Ketone	2-Pentanone	107-87-9	MS, RI	855	954	983	43	3
Ketone	3-Methyl-2-butenal*	107-86-8	MS, RI, ST	803	1106	1216	55	
Ketone	(E,E)-2,4-Heptadienal	4313-03-5	MS, RI	825	1463	1492	81	
Nitrogen Containing	N,N-Dimethyl-methylamine*	75-50-3	MS, RI	756	625	558	58	1
Nitrogen Containing	2-Propenenitrile*	107-13-1	MS, RI	895	966	1002	53	1
Nitrogen Containing	1-Methyl-2-methyleneaziridine*	25012-55-9	MS	759	1109	Nf	42	1
Nitrogen Containing	Trimethyloxazole	20662-84-4	MS, RI	844	1166	1202	43	1
Nitrogen Containing	Methyl 2-oxopropanoate	600-22-6	MS, RI	797	1207	1199	43	1
Nitrogen Containing	2,3,4,5-Tetrahydropyridazine*	113375-01-2	MS	773	1217	Nf	84	1
Nitrogen Containing	3,3-Dimethyl-cyclobutanecarbonitrile*	53783-86-1	MS	798	1226	Nf	56	1
Nitrogen Containing	2,3-Dihydro-1H-indole*	496-15-1	MS	756	1613	Nf	118	1
Nitrogen Containing	5H-1-Pyrindine*	270-21-7	MS	856	2326	Nf	117	1
Nitrogen Containing	4,5-Dimethyl-2-isopropyloxazole	19519-45-0	MS, RI	779	1238	1261	43	2
Nitrogen Containing	Butyl isocyanatoacetate*	17046-22-9	MS	803	674	Nf	42	5
Nitrogen Containing	Isobutyronitrile*	78-82-0	MS, RI	786	978	1010	42	5
Nitrogen Containing	Bis(1,1-dimethylethyl)-nitroxide*	2406-25-9	MS	786	1188	Nf	41	5
Nitrogen Containing	Methallyl cyanide*	4786-19-0	MS	829	1193	Nf	41	5
Nitrogen Containing	Nitromethane*	75-52-5	MS, RI	836	1127	1177	30	6
Nitrogen Containing	1-Nitrohexane	646-14-0	MS	783	1475	Nf	41	6
Pyrazine	Methylpyrazine	109-08-0	MS, RI	888	1236	1272	94	1
Pyrazine	2,6-Dimethylpyrazine	108-50-9	MS, RI	938	1299	1331	108	1
Pyrazine	Ethylpyrazine	13925-00-3	MS, RI	894	1304	1342	107	1
Pyrazine	2,3-Dimethylpyrazine	5910-89-4	MS, RI	910	1315	1346	67	1

Pyrazine	2-Isopropylpyrazine*	9820-90-0	MS	774	1325	Nf	107	1
Pyrazine	2-Ethyl-5-methylpyrazine	13360-64-0	MS, RI	861	1362	1385	39	1
Pyrazine	Trimethylpyrazine	14667-55-1	MS, RI	816	1373	1402	122	1
Pyrazine	n-Pentylpyrazine*	6303-75-9	MS	837	1388	1575	94	1
Pyrazine	Ethenylpyrazine*	4177-16-6	MS, RI	876	1403	1430	106	1
Pyrazine	2,6-Diethylpyrazine	13067-27-1	MS, RI	854	1405	1452	135	1
Pyrazine	3-Ethyl-2,5-dimethylpyrazine	13360-65-1	MS, RI	886	1415	1444	42	1
Pyrazine	2,3-Diethylpyrazine	15707-24-1	MS, RI	896	1425	1449	121	1
Pyrazine	2-Methyl-6-propylpyrazine*	29444-46-0	MS	807	1435	Nf	108	1
Pyrazine	Tetramethylpyrazine*	1124-11-4	MS, RI	849	1443	1462	54	1
Pyrazine	2-Methyl-5-propylpyrazine*	29461-03-8	MS, RI	866	1447	1458	108	1
Pyrazine	2-Ethenyl-6-methylpyrazine	13925-09-2	MS, RI	755	1457	1493	52	1
Pyrazine	2-Isobutyl-3-methylpyrazine*	13925-06-9	MS, RI	806	1460	1490	108	1
Pyrazine	(1-Methylethenyl)pyrazine*	38713-41-6	MS	780	1463	Nf	52	1
Pyrazine	3,5-Diethyl-2-methylpyrazine	18138-05-1	MS, RI	854	1466	1495	149	1
Pyrazine	2,3,5-Trimethyl-6-ethylpyrazine	17398-16-2	MS, RI	786	1484	1506	149	1
Pyrazine	2,5-Dimethyl-3-isobutylpyrazine*	32736-94-0	MS, RI	797	1497	1514	122	1
Pyrazine	2,3-dimethyl-5-(2-propenyl)-pyrazine*	Nf	MS	751	1559	Nf	147	1
Pyrazine	5H-5-Methyl-6,7-dihydrocyclopentapyrazine	23747-48-0	MS, RI	844	1588	1631	119	1
Pyrazine	2-(3-Methylbutyl)-3,5-dimethylpyrazine*	111150-30-2	MS, RI	824	1628	1530	122	1
Pyrazine	2,5-Dimethyl-6,7-dihydro-(5H)-cyclopentapyrazine	38917-61-2	MS, RI	831	1641	1672	133	1
Pyrazine	2-Acetyl-3-methylpyrazine	23787-80-6	MS, RI	789	1657	1628	43	1
Pyrazine	(E)-2-Methyl-5-(1-propenyl)-pyrazine	18217-82-8	MS, RI	774	1679	1635	134	1
Pyrazine	2-Butyl-3-methylpyrazine*	15987-00-5	MS, RI	851	1471	1459	108	
Pyridine	Pyridine*	110-86-1	MS, RI	874	1152	1188	52	1
Pyridine	2-Methylpyridine*	109-06-8	MS, RI	852	1186	1212	93	1
Pyridine	3-Ethenylpyridine*	1121-55-7	MS	865	1475	Nf	104	1
Pyridine	2-Acetylpyridine	1122-62-9	MS, RI	833	1569	1591	79	1
Pyridine	Methyl nicotinate*	93-60-7	MS, RI	841	1739	1766	78	1
Pyridine	1-Acetyl-1,2,3,4-tetrahydropyridine*	19615-27-1	MS	775	1775	Nf	82	1
Pyrrole	1-Methyl-1H-pyrrole	96-54-8	MS, RI	871	1117	1154	81	1
Pyrrole	1-Ethyl-1H-pyrrole	617-92-5	MS, RI	919	1158	1177	80	1
Pyrrole	3-Ethyl-1H-pyrrole	1551-16-2	MS	872	1158	Nf	80	1
Pyrrole	1-Butyl-1H-pyrrole*	589-33-3	MS	769	1237	Nf	80	1
Pyrrole	2-Acetyl-1-pyrroline	85213-22-5	MS, RI	790	1309	1347	43	1
Pyrrole	2-Methyl-1H-pyrrole	636-41-9	MS, RI	882	1519	1559	80	1
Pyrrole	3-Methyl-1H-pyrrole	616-43-3	MS, RI	907	1538	1601	80	1
Pyrrole	1-Ethyl-1H-pyrrole-2-carboxaldehyde*	2167-14-8	MS, RI	809	1576	1564	94	1
Pyrrole	1-Methylpyrrole-2-carboxaldehyde	1192-58-1	MS, RI	876	1586	1622	109	1
Pyrrole	2,5-Dimethyl-1H-pyrrole*	625-84-3	MS, RI	868	1614	1601	94	1
Pyrrole	1-(1-Methylpyrrol-2-yl)-ethanone*	932-16-1	MS, RI	755	1620	1639	108	1
Pyrrole	Methyl 1-methylpyrrole-2-carboxylate*	37619-24-2	MS	867	1665	Nf	108	1
Pyrrole	2-Ethyl-4-methyl-1H-pyrrole	69687-77-0	MS	761	1676	Nf	94	1
Pyrrole	1-(2-Furanylmethyl)-1H-pyrrole	1438-94-4	MS, RI	825	1791	1838	81	1
Pyrrole	3-Acetylpyrrole*	1072-82-8	MS	875	1926	Nf	94	1
Pyrrole	1H-Pyrrole-2-carboxaldehyde	1003-29-8	MS, RI	856	1980	2023	95	1
Pyrrole	4-Pyridinemethanol*	323355-16-6	MS	834	2051	Nf	109	
Sulfur Compounds	Methanethiol	74-93-1	MS, RI	869	644	671	47	1
Sulfur Compounds	Thiophene*	110-02-1	MS, RI	933	1001	1018	84	1
Sulfur Compounds	Methyl thiolacetate*	1534-08-3	MS, RI	908	1026	1055	43	1
Sulfur Compounds	3-Methylthiophene	616-44-4	MS, RI, ST	918	1098	1116	97	1
Sulfur Compounds	2-Ethylthiophene	872-55-9	MS, RI	818	1150	1177	97	1
Sulfur Compounds	2-Methylthiazole	3581-87-1	MS, RI	790	1208	1240	58	1
Sulfur Compounds	Thiazole	288-47-1	MS, RI	885	1218	1250	58	1
Sulfur Compounds	4-Methylthiazole	693-95-8	MS, RI	855	1250	1289	71	1
Sulfur Compounds	Methylthio-2-propanone*	14109-72-9	MS	853	1306	Nf	61	1
Sulfur Compounds	4-Methyl-2-(1-methylethyl)-thiazole*	15679-13-7	MS, RI	823	1325	1339	126	1
Sulfur Compounds	4,5-Dimethylthiazole*	3581-91-7	MS, RI	804	1343	1361	71	1
Sulfur Compounds	Dimethyl trisulfide	3658-80-8	MS, RI, ST	903	1356	1379	45	1
Sulfur Compounds	Methional	3268-49-3	MS, RI	758	1423	1457	48	1
Sulfur Compounds	Dihydro-2-methyl-3(2H)-thiophenone	13679-85-1	MS, RI	814	1497	1537	60	1
Sulfur Compounds	2-Thiophenecarboxaldehyde*	98-03-3	MS, RI	863	1657	1707	111	1
Sulfur Compounds	1-(2-Thienyl)-ethanone	88-15-3	MS, RI	830	1739	1744	111	1
Sulfur Compounds	n-Hexanesulphonylacetonitrile*	203310-42-3	MS	809	833	Nf	41	3

[1] Compounds not reported previously in peanuts are designated with an *

[2] Chemical Abstracts Service registry number

[3] MS: identification based on mass spectral match to the NIST 05 library with >750 similarity, RI: comparison with published retention indices on polyethylene glycol column phase, ST: mass spectral and retention index match to an authentic standard.

[4] Retention indices based on first dimension retention of components on a SOL-GEL-WAX (polyethylene glycol) column using SPME GCxGC-ToFMS

[5] Retention indices reported in the literature (Nf = not found); References available at the NIST Chemistry WebBook database, http://webbook.nist.gov

[6] Unique mass for each component was used for the peak area calculation.

[7] HCA Group # refers to **Figure 3**

The roasted peanut samples contained a higher number of peaks and peaks in greater abundances than raw peanuts in both the runner-type and virginia-type peanut samples, as visualized in the chromatograms in **Figures 1A and 1B**. Between the raw and roasted peanut samples, a total of 252 volatile compounds were found to be significantly different ($p < 0.05$). Of these, 96 compounds were significantly different ($p < 0.05$) between the two market-types. For further investigation of trends in the data, hierarchical cluster analysis and principal component analysis were utilized.

This study reported 119 volatile compounds that have not previously been reported in peanuts, including 11 furans, seven pyrroles, five pyridines, and 12 pyrazines. Additionally, more volatile compound differences were identified between runner and virginia market types than previously reported where no differences ($p < 0.05$) between virginia and runner-type peanuts in their concentrations of total alcohols, aldehydes, alkanes, pyrroles, ketones, pyrazines, and furan derivatives were found (Wang et al., 2017).

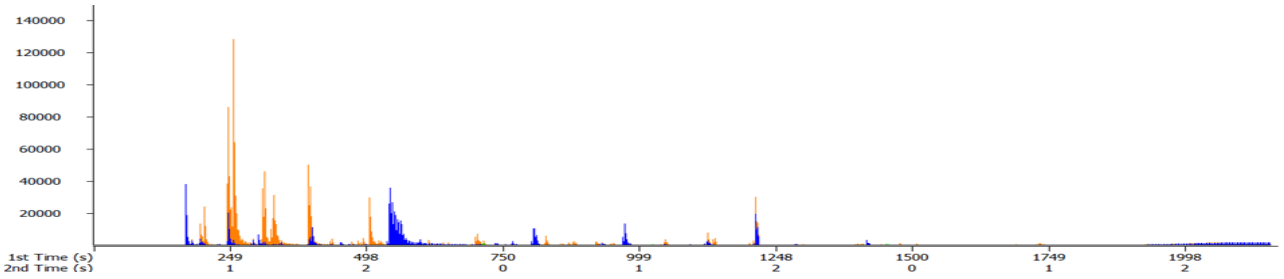


Figure 1A. GCxGC-ToF-MS chromatogram of roasted (orange) and raw (blue) runner- type peanuts

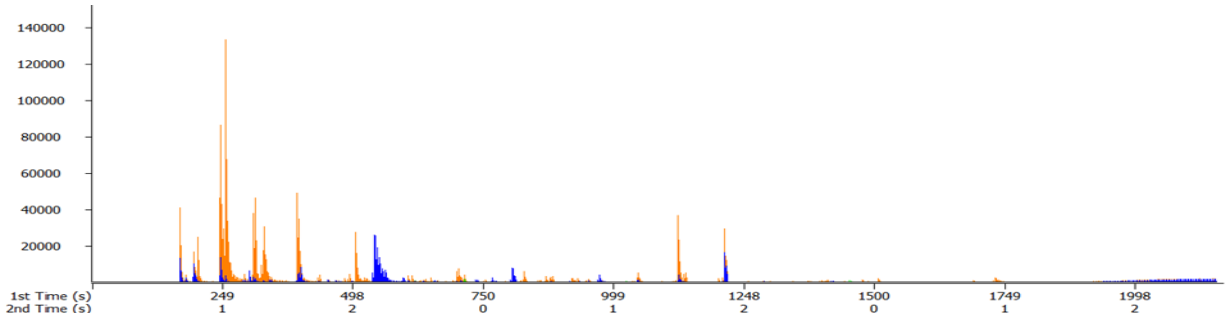


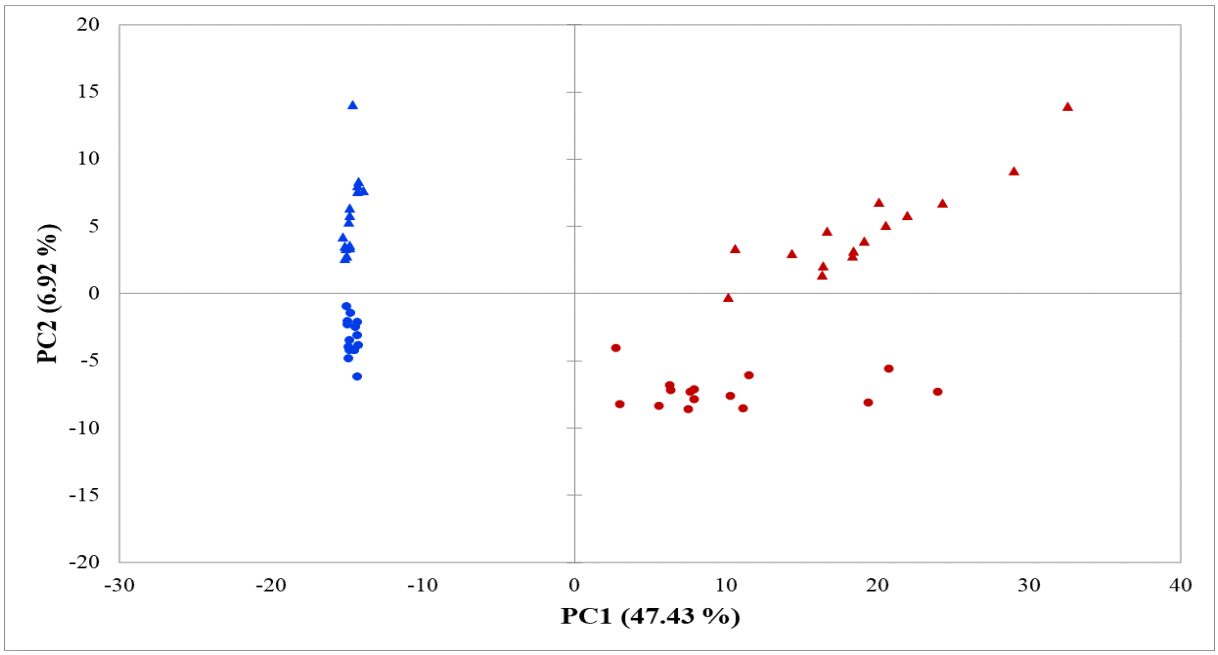
Figure 1B. GCxGC-ToF-MS chromatogram of roasted (orange) and raw (blue) virginia-type peanuts

3.2 Principal Component Analysis

Principal component analysis (PCA) was performed to evaluate the grouping of the peanut samples based on the overall volatile compound composition (**Figure 2**). Principal components (PC) 1 and 2 accounted for a total of 71.6% of the variance in the VOC profiles, with PC1 covering 63.7% and PC2 accounting for 7.2%. The roasted peanut samples loaded positively on PC1, and raw peanut samples loaded negatively on PC1. Several alcohols, such as 1-nonanol, 1-propanol, 2-methyl-1-propanol, (S)-2-heptanol, 3-methyl-4-penten-1-ol, ethanol, (Z)-2-penten-1-ol, and 1-hexanol loaded negatively on PC1 and were strongly associated with the raw samples (data not shown). Numerous aldehydes, such as hexanal, were also correlated with the raw peanuts. Alcohols have been reported to serve as precursors for lipoxygenase-mediated reactions in raw peanuts (Singleton et al., 1976).

In the opposite direction of PC1, the quantity of compounds loaded in the positive direction were so numerous that they are difficult to depict in graphical form, so factor loading charts were investigated (Figure not shown). This group including many pyrazines, such as 3-ethyl-2,5-dimethylpyrazine, 2-ethenyl-6-methylpyrazine,

2-methyl-5-propylpyrazine, trimethylpyrazine, 2,3-dimethylpyrazine, and n-pentylpyrazine. Ketones, pyrroline, oxazole, thiophene, furan, pyridine, and thiazole compounds also had strong associations in the positive direction of PC1.



▲=Raw virginia, ▲=Roasted virginia, ●=Raw runner, ●=Roasted runner.

Figure 2. Principal component analysis (PC1 vs. PC2) of raw and roasted virginia and runner-type peanuts samples

3.3 Hierarchical Cluster Analysis

Hierarchical cluster analysis (HCA) was employed to further visualize the 361 VOCs that were significantly different among treatment groups ($p < 0.05$) The resulting heat map was evaluated for trends, and six distinct clusters were evident (**Figure 3**). The groups represented compounds present in greater concentrations due to the raw or roasted state and/or market-type. From top to bottom, the six groups represent components present in significantly greater concentration in 1(dark blue): roasted virginia and runner, 2(orange): roasted virginia, 3(teal): roasted runner, 4(tan): raw and roasted virginia, 5(green): raw and roasted runner, and 6(light blue): raw virginia and runner. The majority of differentiating volatile compounds clustered together in Group 1 (**Figure 3**) and represented the volatile compounds generated in roasted peanuts from both market types. These 252 compounds included a wide variety of compound classes, comprised of 21 aldehydes, 28 pyrazines, 18 furans, 18 pyrroles, 20 sulfur-containing compounds, along with 61 unknown analytes. Group 2 shows 14 compounds that are predominantly present in roasted virginia peanuts. These compounds included hydrocarbons, aldehydes, a furan, and an oxazole. The 19 compounds in Group 3 were differentiated based on their more prevalent concentration in roasted runner peanuts. These compounds included hydrocarbons, aldehydes, two furans, a ketone, and a sulfonyl compound. The compounds in Group 2 and Group 3 were also the compounds that loaded in PC2 as discussed in the previous section. In Group 4, nine compounds differentiated the raw and roasted runner peanut samples, including six hydrocarbons, one alcohol, and two unknowns., where as Group 5 is comprised of 29 compounds that were dominant in the raw and roasted virginia-type peanut samples. Several nitrogen-containing compounds are present in this group, along with hydrocarbons, alcohols, aldehydes, and 13 unknowns. Finally, Group 6 contains the volatile compounds that were in higher abundance in the raw peanuts from both market types, represented by 21 compounds, including 12 alcohols, hexanal and 2-hexenal, along with n-caproic acid vinyl ester, pentanoic acid, 1-nitrohexane, and nitromethane.

The majority of differentiating volatile compounds clustered together in Group 1 (**Figure 3**) and represented the volatile compounds generated in roasted peanuts from both market types in the HCA. These 252 compounds included a wide variety of compound classes, comprised of 21 aldehydes, 28 pyrazines, 18 furans, 18 pyrroles, 20 sulfur-containing compounds, along with 61 unknown analytes. Group 2 was comprised of 14 compounds

that were predominantly present in the roasted virginia peanut samples. These compounds included hydrocarbons, aldehydes, a furan and an oxazole compound. The 19 compounds in Group 3 were differentiated based on their more prevalent concentration in the roasted runner peanut samples. These compounds included hydrocarbons, aldehydes, two furans, a ketone, and one sulfonyl compound. In Group 4, nine compounds differentiated the raw and roasted runner peanut samples, including six hydrocarbons, one alcohol, and two unknowns. Group 5 was comprised of 29 compounds that were dominant in the raw and roasted virginia-type peanut samples. Several nitrogen-containing compounds are present in this group, along with hydrocarbons, alcohols, aldehydes, and 13 unknowns. Finally, Group 6 contained the volatile compounds predominantlyfound in the raw peanut samples from both market types, represented by 21 compounds, including 12 alcohols, hexanal and 2-hexenal, along with n-caproic acid vinyl ester, pentanoic acid, 1-nitrohexane, and nitromethane.

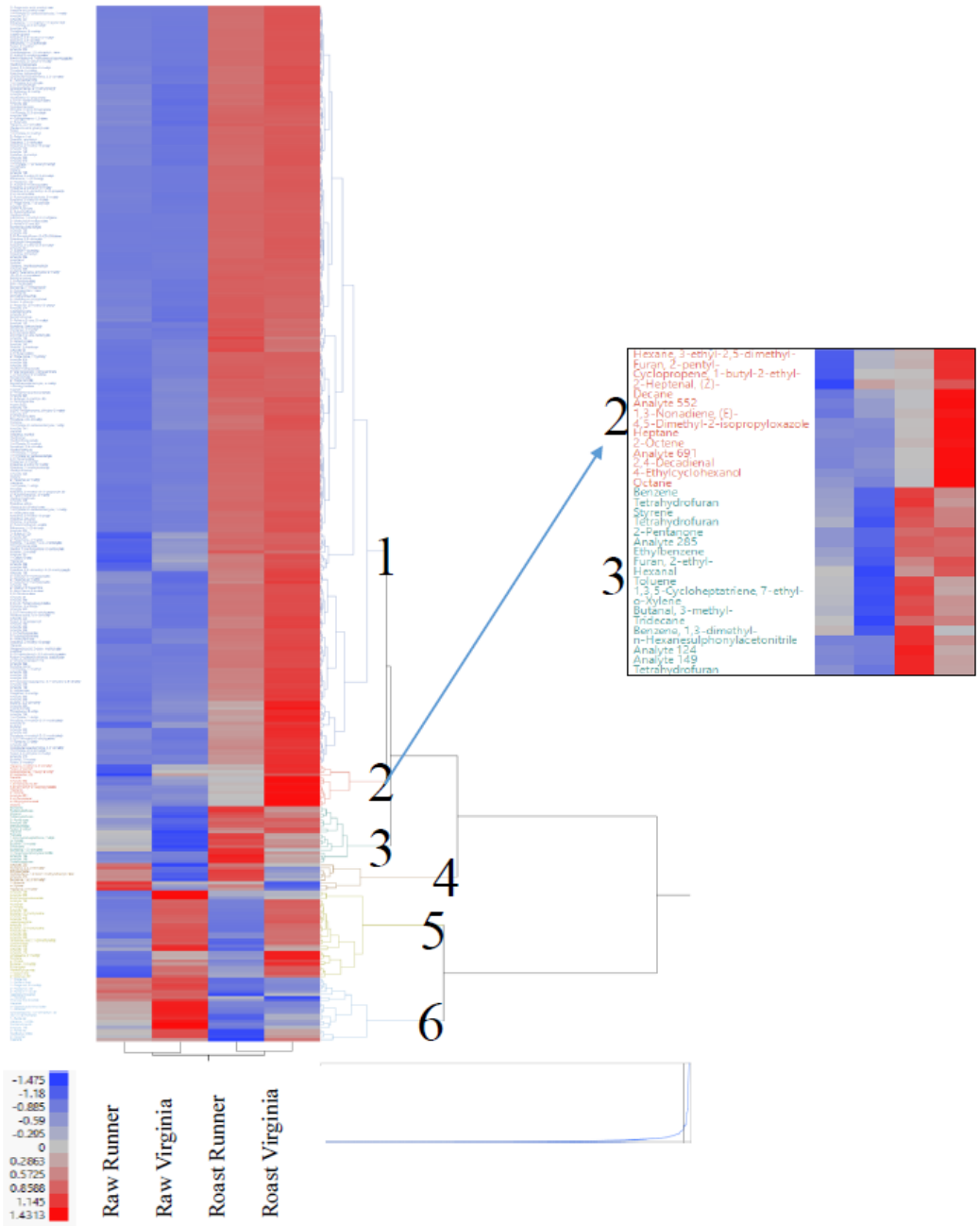


Figure 3. Hierarchical clustering of volatile organic compounds in peanuts that differed in roast treatment and/or market-type

(*fdr* p < 0 .05).

4. Discussion

4.1 Pathways to the Formation of Volatile Compounds

Among the hundreds of VOCs detected in this study, a variety of components from various compound classes were identified. In peanuts, aroma active compounds are generated through chemical reactions induced by heat treatment, including the Maillard reaction, Strecker degradation, thermal degradation of sugars, and lipid oxidation (Neta et al., 2010; Lykomitros et al., 2016b).

The Maillard reaction involves reducing sugars and amino compounds as reactants and yields heterocyclic nitrogen compounds including furans, thiazoles, thiophenes, oxazoles, pyrroles, imidazoles, pyridines, and pyrazines (Hodge, 1953; Milic and Piletic, 1983; Amrani-Hemaimi et al., 1995; Adams et al., 2008; Neta, 2010; Lykomitros et al., 2016a; 2016b). Many of these compounds were identified in the roasted peanut samples, which also underwent the Strecker degradation, where α-amino acids are converted by reductones (α-dicarbonyls) into aldehydes containing a side chain with an imine intermediate. These products can condense to form alkylpyrazines (Sanders et al., 1995; Fennema, 1996; Davies and Labuza, 1997; Manzocco et al., 2000; Purlis, 2010). Aldehydes, which were found in abundance in the raw peanut samples, are important due to their ability to form Schiff base adducts with amino groups (Pattee et al., 1983). This leads to the formation of the ring strucures that can become pyrazines (Guerra & Yaylayan, 2012).

Caramelization, also known as the thermal degradation of sugars, yields low molecular weight open-chain oxygen containing products and heterocyclic oxygen-containing compounds including furan derivatives (Coleman et al., 1994). As expected, the roasted peanut samples contained significantly more ($p < 0.05$) furans than the raw samples.

Lipids are also an important source of flavor compounds. While they do contribute flavors of their own, their primary importance is as precursors to volatile compounds that produce flavors in foods (Forss, 1969; Pattee et al., 1983). Lipids with more than ten carbons are insoluble in water, have low volatility, and do not participate in basic taste (Pattee et al., 1983). Foods with polyunsaturated fatty acids are known to be highly susceptible to lipid oxidation, which leads to the formation of oxygen containing compounds including aliphatic aldehydes, acids, ketones, and alcohols (Coleman et al., 1994; St. Angelo et al., 1996; Warner et al., 1996). Each of these compound classes was detected in the virginia and runner type peanut samples. Oil composes up to 50% of a peanut seed, of which about 50% is oleic (18:1) and 30% is linoleic (18:2) in normal oleic peanuts (St. Angelo et al., 1996; Davis & Dean, 2016). Heat damage to the cell structure can augment the transfer of oxygen to peanut tissues by the release of substances from cell compartments. Due to this, lipid oxidation can potentially be accelerated by roasting (Perren & Escher, 2013). Long chain unsaturated fatty acids in peanuts have little participation in basic tastes but are easily oxidized. The presence of the double bonds enables free radicals to stabilize through the delocalizing of unpaired electrons. This leads to hydroperoxide formation, which is unstable and quickly decomposes into secondary reaction products (St. Angelo et al., 1996; Warner et al., 1996). Products of oxidation, including some alcohols, aldehydes, and furans were detected in greater abundance ($p < 0.05$) in the roasted peanut samples. Several of these pathways are discussed in section 4.2 below.

The conversion of alcohols, which were significantly more abundant in the raw peanut samples ($p < 0.05$), to corresponding aldehydes homologs, which were more abundant in the roasted peanut samples is likely related to enzymatic reactions (Singleton et al., 1976). Previously, the volatile flavor profiles of raw peanuts have been correlated to enzyme activity across stages of peanut seed maturation (Pattee et al., 1970). Singleton et al. (1976) observed n-propanol and n-hexanol were converted to their respective aldehydes when raw peanut extracts were treated with lipoxygenase. Pattee et al. (1970) found that the predominating volatile compounds in raw peanuts were: acetaldehyde, methanol, pentane, ethanol, and hexanal, which were also detected in this study with the exception of ethanol. Those authors speculated that these compounds, aside from hexanal, were produced via lipoxidase and alcohol dehydrogenase (ADH) in peanut seeds. Lovegren et al. (1982) found that methanol, acetaldehyde, ethanol, and an acetone group totaled approximately 80% of the total volatile peaks in raw virginia-type peanuts. The volatile compound data collected in this study includes those previously found and shows a much wider array of compounds that contribute to the volatile profiles of the raw peanut samples.

The runner peanut samples were most differentiated by compounds: 2,2,4-trimethylpentane, 1,3-dimethylbenzene, ethylbenzene, 3-methylpentanal, 3-methylbutanal, benzaldehyde, tetrahydrofuran, 2,3,6-trimethylpyridine, and 2,3-pentadedione in the HCA. Brown et al. (1972) found 3-methylbutanal to be a predominant compound distinguishing between raw and roasted runner-type peanuts. Those authors found that this branched chain aldehyde in large concentrations resulted in the harsh aroma of roasted peanuts. In other studies, 3-methylbutanal has been found to have a malty/chocolate aroma (Matsui et al., 1998; Greene et al.,

2008). Low molecular weight aldehydes in general have also been reported to be responsible for a harsh aroma note in peanuts (Mason et al., 1967). They are formed during roasting as a product of Strecker degradations (Mason et al. 1967; Smit et al. 2008). For example, leucine can form 3-methylbutanal through deamination followed by decarboxylation. Both leucine and 3-methylbutanal were more abundant in virginia-type peanuts (Klevorn et al., 2019). Aldehydes were the most common functional class of the compounds in Group 5, followed by alcohols. These compounds were detected in greater abundance in the raw and roasted virginia-type peanut samples, which may be more susceptible to lipid oxidation.

4.2 Lipid Oxidation Products

Volatile products of autoxidation of fatty acids are significant for the aroma of foods due to their low threshold concentrations for aroma and flavor (Schieberle & Grosch, 1981). The mechanism of autoxidation of linoleic acid (C 18:2) involves removal of a hydrogen atom from the methylene group adjacent to the double bond on carbon-11 producing a pentadienyl radical. Oxygen molecules then attack from both end positions to create an equal combination of conjugated 9- and 13-hydroperoxide isomers (Frankel, 1984). These conjugated isomers are typical, however, 10- and 12-hydroperoxide isomers also exist. These compounds can undergo additional reactions that lead to a number of compounds (Kolchar, 1996), several of which were found in the study reported here.

Methyl linoleate 9- and 13-hydroperoxide isomers can react into three monohydroperoxides, which then decompose into 2-octenal, hexanal, and 2,4-decadienal, which were found in HCA Groups 5, 6, and 2, respectively (Forss, 1969; Schieberle & Grosch, 1981). Formation of 2,4-decadienal is derived from the 9-hydroperoxide isomers, with a beta scission. This product can undergo further oxidation, where a peroxy radical attacks the double bond on carbon-8 and forms 2-octenal (Schieberle & Grosch 1981; Kochlar, 1996). (E)-2-octenal was more abundant in raw (four-fold) and roasted (two-fold) virginia peanuts than raw and roasted runner-type peanuts. Roasted virginia-type peanuts also contained two-fold more 2,4-decadienal than runner-type peanuts.

While 2,4-decadienal can only be formed from 9-hydroperoxide isomers, hexanal can arise from 9- or 13-hydroperoxide isomers. Thus, hexanal is the most abundant aldehyde product of linoleic acid oxidation (Schieberle & Grosch 1981). This was observed in the volatile compound data, as hexanal had the highest relative abundance of the oxidation products for roasted virginia-type peanuts and the highest relative abundance of all compounds for raw virginia-type peanuts. Hexanal was four times more abundant in the raw treatments than the roasted samples, two times more abundant in raw virginia peanut samples than the raw runner-type samples, and three times more abundant in roasted virginia samples than roasted runner-type ($p < 0.05$).

Heptanal can be formed from 2-octenal by autoxidation into a radical acid intermediate. This peroxyacid then decomposes with carbon dioxide as a byproduct, which allows the enol to rearrange into heptanal (Schieberle and Grosch, 1981). Heptanal was found in greater abundance in the roasted peanut samples of both market-types (Group 1) than of the raw samples. The virginia-type peanut samples experienced a two-fold increase, and runner-type samples saw a five-fold increase after roasting.

The 12-hydroperoxide isomer has been detected in vegetable oils and can lead to the formation of aldehydes (Kochlar, 1996). The decomposition mechanism of linoleate 12-hydroperoxide into 2-heptenal involves an alpha scission. A vinyl radical reacts with oxygen to produce vinyl hydroperoxide, which then interacts with other lipid molecules to form 2-heptenal. Additional beta scission pathways modify the stuctures (Kochlar, 1996), which could have produced several of the unsaturated aldehydes found in this study, including, 2-methyl-2-hexenal, 2-ethyl-trans-2-butenal, and 2-butenal. 2-heptenal was significantly more abundant in the roasted virginia peanut samples (Group 2) than the other groups.

The formation of volatile aldehydes, including for nonanal, octanal, decanal, heptanal, and hexanal has been associated with off flavors in the late stages of lipid oxidation (Warner et al., 1996). Hexanal has been found to have a green/cut grass aroma, which is characteristic of raw peanuts of both market-types (Schieberle & Grosch, 1985; Didzbalis et al. 2004; Greene et al., 2008; Erten & Cadwallader, 2017). 2-octenal was associated with virginia-type peanut samples both raw and roasted (Group 5) and has been found to have citrus-like (Didzbalis et al., 2004;), pungent/orange (Erten & Cadwallader, 2017), and fatty (Matsui et al., 1998) aroma qualities. 2,4-decadienal, which was associated with roasted virginia peanuts, and has been found to have a fatty, fried aroma (Schirack et al., 2006; Matsui et al., 1998; Erten & Cadwallader, 2017). (Z)-2-heptenal was significantly associated with virginia-type roasted peanut samples (Group 2) and has been found to have a green or fatty aroma (Schieberle & Grosch, 1985). Heptanal was present in the roasted peanut samples of both market-types (Group 1) and heptanal has been associated with “fatty” odor (Schirack et al. 2006).

Another compound that significantly increased (five-fold) after roasting was 1-octen-3-one is (Group 1). This ketone has been found to be a primary contributor to metallic tastes in fatty foods (Forss, 1969; Pattee et al., 1983; Greene et al., 2008) and to contribute to a mushroom-like flavor in peanuts (Kaneko et al., 2013; Erten & Cadwallader, 2017; Greene et al., 2008). The metal flavor may be attributed to the presence of inorganic salts of copper and iron, which are responsible for the lipid oxidation due to catalyzing the break-down and formation of 1-octen-3-one (Forss, 1969). Roasted peanuts are a good dietary source of each of these microminerals (Davis & Dean 2016). The alcohol homolog, 1-octen-3-ol, was in significantly higher concentrations ($p < 0.05$) in the virginia-type peanuts. This unsaturated alcohol is a major product of autoxidation of linoleic acid, and has been commonly found in meat volatiles, with a mushroom-like odor (Bleicher et al., 2022). Autoxidation of arachidonic acid is another mechanism to produce 1-octen-3-one and 1-octen-3-ol. Linoleic acid has been noted as a precursor of arachidonic acid in peanut oil (Truswell et al., 1994).

Furans can also be derived from oxidized linoleic acid. The proposed mechanism for formation involves linoleate 9-hydroperoxide decomposing to form 2-pentylfuran. This compound was found most abundant in the roasted virginia peanut samples (Group 2), which was two-fold more abundant than in both the raw virginias and roasted runner-type peanut samples. Along with several furan derivatives, 2-pentylfuran is responsible for flavor defects in reverted soybean oil, including metallic and grassy flavors (Kochlar, 1996). At concentrations between 1-10 ppm in refined, bleached, and deodorized cottonseed oil, 2-pentylfuran emits a beany odor, although the effluent of 2-pentylfuran from gas chromatograph has a licorice, and not beany odor (Krishnamurthy et al., 1967). Furan compounds can also be derived from the thermal degradation of glucose (Zhang & Ho, 1991), and through the Maillard browning reaction (Mottram, 1993). Certain furans have been found to have caramel-like, sweet, roasty, burnt, fruity, and pungent aromas characteristic of thermally processed foods (van Boekel 2006; Liu et al., 2011; Kaneko et al., 2013). Food flavor development has been associated with increases in furan levels (Tai & Ho, 1998). Of the 23 furans reported in this study, 18 were more abundant in the roasted peanut samples (Group 1), indicating that the development of most of the compounds in this group was related to thermal processing. However, 2-ethylfuran and 2-vinylfuran were most abundant in the raw virginia-type samples.

4.3 Products of the Maillard Reaction

Groups 1, 2, and 3 contained compounds that were present in roasted peanut samples at levels significantly higher than the raw counterparts. Many compounds associated with thermal processing and browning flavors are heterocylic (Fennema, 1996). These compounds commonly include nitrogen, sulfur, and oxygen substituents, and have been known to contribute general nutty, roasted, toasted, caramel, meaty, burnt, floral, and plant odors (Fennema 1996). **Figure 4** displays the chemical structure of several of such compounds that were detected in this study in roasted peanut samples including pyrazines, pyridines, thiophenes, furans, thiazoles, pyrroles, and oxazoles. Many of these heterocyclic compounds are formed via the Maillard browning reaction, which utilizes amino groups and reducing sugars (Koehler et al., 1969; Koehler et al., 1970), or lipid-derived carbonyls that can also react with amino acids (Zamora & Hidalgo, 2011).

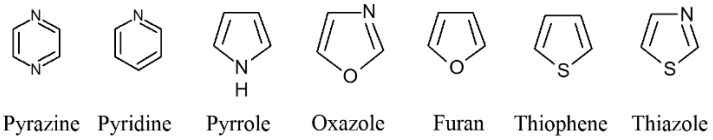


Figure 4. Skeletons of heterocyclic compounds commonly associated with flavor in thermally processed or browned flavors

Pyrazines have been found to be important contributors to flavors in many foods (Mottram, 1994). The 28 pyrazines detected in this study may have formed through several mechanisms. One pathway for pyrazine formation utilizes a reaction between amino acids in the peanut and α-dicarbonyl compounds, which are intermediates in Maillard reactions. This reaction is carried out via the Strecker degradation, where α-amino carbonyls are produced and then condensed into alkylpyrazines (Fennema, 1996). Different α-amino carbonyls can participate in the Strecker degradation and produce a variety of pyrazines including 2,6-dimethylpyrazine, trimethylpyrazine, 2-ethyl-5-methylpyrazine, and methylpyrazine, which were all identified in the roasted peanuts in this study (Group 1). The alkyl group on the pyrazine is often obtained from α-amino carbonyl group of the reactant derived from sugar (Shibamoto & Bernhard, 1977). However, the distribution of reaction products in pyrazine formation can be influenced by reaction temperature, reactant ratio, presence of anitoxidants or prooxidants, and oxygen (Shibamoto & Bernhard, 1977). Each of these compounds had significant ($p < 0.05$)

increases in relative abundance after roasting, reported as follows: trimethylpyrazine (three-fold), methylpyrazine (two-fold), 2-ethyl-5-methylpyrazine (two-fold), and 2,6-dimethylpyrazine (was not detected in the raw samples). While many α-amino carbonyl fragments have been proposed, no intermediates or fragments in pyrazine formation have been isolated or identified to date (Shibamoto & Bernhard, 1977).

Another mechanism of pyrazine formation involves ammonia as the nitrogen source, which is released from pyrolysis of amino acids (Mottram, 1994). Glutamine has been shown to yield considerable amounts of ammonia with moderate heating (110 ℃). At high temperatures (180 ℃), asparagine, which was more abundant (two-fold) in the virginia-type peanut samples, and aspartic acid released high amounts of ammonia. Free ammonia can react with α-hydroxycarbonyl compounds and form α-aminoketones in an Amadori rearrangement (Adams et al., 2008). Methional was found more abundant in the roasted virginia and runner-type peanut samples (Group 1). This compound is likely to have formed as a product of methionine through the Strecker degradation (Balance, 1961). Methionine was two-fold more abundant in the virginia-type peanut samples than in the runners (Klevorn et al., 2019). Methional has been associated with a baked potato and brothy odor and has been reported in roasted peanuts previously (Greene et al., 2008; Chetschik et al., 2008) and roasted almonds (Erten & Cadwallader, 2017).

Dimethyl trisulfide was also found to be significantly more abundant in the roasted virgina and runner-type peanut samples (Group 1). This compound may have been produced by reactions with hydrogen sulfide, or by oxidation (Yu & Ho, 1995). The reported aroma of dimethyl trisulfide is onion-y/garlic-y and sulfur/cabbage-y and has been found in other studies to be a key component in roasted peanuts (Chetschik et al., 2008; Neta et al., 2010), cauliflower, broccoli, and cabbage (Buttery et al., 1976), wine (Guth, 1997), almonds (Erten & Cadwallader, 2016), and in boiled meat aroma (Golovnja & Rothe, 1980).

Twelve pyrazines were detected for the first time in peanuts by this research (**Figure 5**), including tetramethylpyrazine and isopropylpyrazine. Tetramethylpyrazine has been synthesized by a condensation reaction between 2,3-butanedione and 2,3-butanediamine, and from 2,5- dimethylpyrazine via ring alkylations with methyllithium (Burdock, 2010). This pyrazine has a slightly musty, nutty, cocoa-like aroma, and a nutty, musty cocoa, and chocolate-like taste (Ramli et al., 2006; Burdock, 2010). The flavor threshold for this chemical component is at 10 ppm whereas the aroma threshold detection value of 2-isopropylpyrazine is 100 ppb (Burdock, 2010). This pyrazine has been previously found in fish sauce and in cocoa (Shimoda et al., 1996; Flamen, 1989).

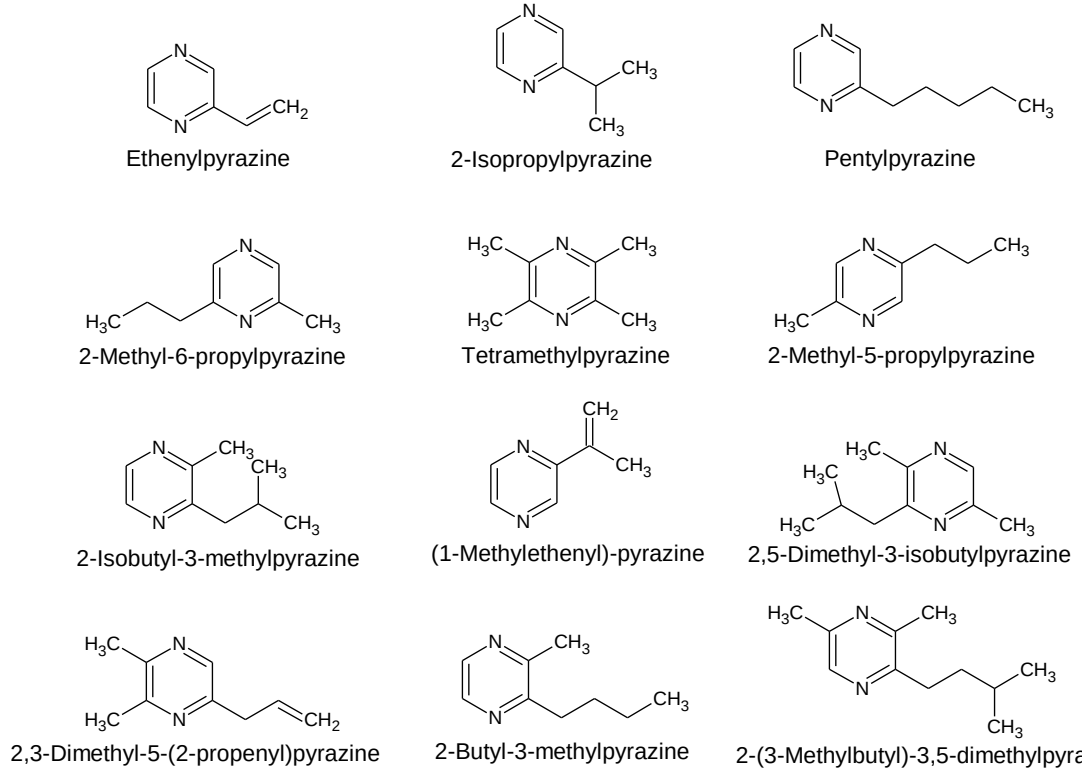


Figure 5. Pyrazine compounds reported in peanut samples in this study that have not been reported earlier

Five pyridine compounds were detected that previously have not been reported in peanuts (**Figure 6**) including pyridine and 2-ethylpyridine. These compounds have been found in coffee and tea (Flamen, 1989). Pyridine has also been found in cocoa beer, whiskey, roasted chicken, and oatmeal. This compound has been found to have grainy, beany, musty, earthy, nutty nuances of peanut and coffee, and raw potato flavors (Burdock, 2010).

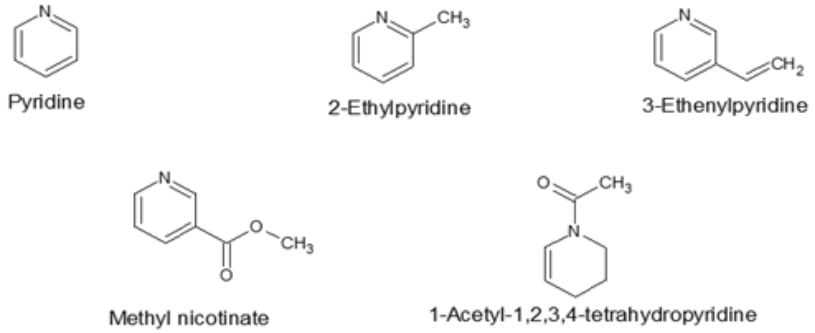


Figure 6. Pyridine compounds reported in peanut samples in this study that were not previously detected

Pyrrolines are another type of compound found to be significantly more abundant in the roasted virginia and runner-type peanut samples (Group 1), including 2-acetyl-1-pyrroline and pyrrole-2-carboxaldehyde, 1-ethyl-1H-pyrrole, 1-ethyl-1H-pyrrole-2-carboxaldehyde, 1-butyl-1H-pyrrole, and 2,5-dimethyl-1H-pyrrole. Pyrrolines are found in most heated foods and have been known to contribute both desirable and unfavorable aromas (Mottram, 1994). The aroma of pyrrole-2-carboxaldehyde has been reported as sweet and corn-like, (Mottram, 1994) and 2-acetyl-1-pyrroline has been associated with roasty/popcorn aromas reported in roasted peanuts (Chetschik et al., 2008; Neta et al., 2010; Matsui et al., 1998; Greene et al., 2008), and several other cooked products including roasted almonds (Erten & Cadwallader, 2017), bread crust (Schieberle and Grosch, 1985), cooked rice (Buttery et al., 1982), whey protein (Whetstine et al., 2005), and popcorn (Schieberle, 1991). The formation of pyrroles, along with pyrrolines and pyrrolidines come from the amino acid, proline (Mottram, 1994), which was significantly higher ($P < 0.05$) in virginia-type peanuts (two-fold) (Klevorn & Dean, 2018). 2-acetyl-1-pyrroline can form from proline reacting with pyruvaldehyde or dihydroxyacetone. Pyrroles are also a product of the Amadori reaction with carbohydrates such as fructose or 3-deoxyketose and proline as the reactant amino acid (Schieberle and Grosch, 1985; Mottram, 1994).

Five thiazole compounds and one oxazole were found to have significantly greater concentrations in roasted peanuts than in the raw: 4-methylthiazole, thiazole, 2-methylthiazole, 4,5-dimethylthiazole, 4-methyl-2-(1-methylethyl)-thiazole, and trimethyloxazole. Thiazole is closely related to the structures of oxazoles, but is more abundant in food volatiles, especially fried or roasted foods (Mottram, 1994). These compounds can arise from the degradation of thiamine, which reacts with 1,2-carbonyls and aliphatic aldehydes derived from amino acids in the Strecker degradation (Mottram, 1994). Both market-type samples contained 2-methoxy-4-vinylphenol in their roasted forms. This compound was previously found to be unique in peanut oil, compared to other common vegetable oils (Hu et al., 2014) and has been associated with sweet/licorice (Greene et al., 2008) and spicy/phenolic (Matsui et al., 2008) aromas in peanuts. It can be formed from ferulic acid, which is an intermediate in the degradation of lignin polymers in plants (Steinke et al., 1964; Fiddler et al., 1967; Walradt et al., 1971). Lignins are important to the peanut plant for structural support of the tissues and for protection from pathogens and herbivores (Bennett et al., 2017).

5. Conclusion

Investigation of the volatile compound profiles between runner and virginia market-types of raw and roasted peanuts revealed a number of differences, including 119 compounds previously unreported in peanuts. Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GCxGC-ToFMS) enabled detection of more components than previously possible, including the identification of 96 VOCs that differentiated the raw and roasted peanut samples. The roasted samples contained a greater abundance of volatile compounds than the raw samples, indicating the numerous changes in chemical composition formed during roasting. The roasted samples were abundant in nitrogen-containing compounds including pyrazines, furans, pyrroles, and pyridines. These compounds are products of the Maillard browning reaction, which are important for the development of the roasted peanut flavor, along with other characteristic attributes including aroma, color, and texture. The specific mechanism to achieve roasted peanut flavor is not yet known, however, the newly

detected compounds provide a broader knowledge of small molecular weight volatile compounds that may contribute to aroma activity. The raw peanut samples contained numerous alcohols and products of lipid oxidation. Although there were fewer differences between the market-types in the raw form, oxidation products were detected more abundantly in virginia-type peanut samples. This can be attributed to the higher levels of polyunsaturated fatty acids in virginia-type peanuts compared to runners. Further investigation into the aroma activity of these compounds could serve to find which compounds influence the flavor of the roasted peanuts. This could enhance the ability to understand the compounds most important to achieving characteristic peanut flavors.

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