STORAGE STUDY OF FLAVOR-FADE IN 16 CULTIVARS OF ROASTED PEANUTS

by

TAIJA STONER-HARRIS

(Under the Direction of Koushik Adhikari)

ABSTRACT

The main objective of this study was to compare the loss of roasted aroma or flavor-fade in peanut varieties and determine which cultivars are more resistant to flavor loss. Runner and virginia roasted peanut types of varying cultivars and oleic statuses were stored at room temperature (~23 °C) for 40 weeks with their volatiles identified and quantified using GC-MS analysis at 0, 8, 16, 24, 32, and 40 weeks. There were 22 volatile compounds identified throughout storage. Overall, high-oleic cultivars among the roasted peanut types were less oxidized after 40 weeks of storage while also maintaining stable pyrazine concentrations. Virginia cultivars exhibited lower concentrations of roasted flavor volatiles throughout storage as compared to runner cultivars. In comparison to GA06-RN, high-oleic cultivars of the runner-type are able to maintain or increase primary roasted flavor volatiles, while also resisting the development of oxidation products during storage.

INDEX WORDS: Gas-Chromatography-Mass Spectrometry (GC-MS), Aroma, Flavor, Oxidation, High-Oleic, Normal-Oleic, Pyrazines

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CHAPTER 1

INTRODUCTION

Peanuts are a significant commodity appreciated worldwide, with an average of approximately 47 million metric tons produced per year (American Peanut Council, 2022). The U.S. is currently the world's fourth-largest producer of peanuts, with the majority being produced in Georgia as of 2020 (National Peanut Board, 2022). It is the pleasant roasted flavor of peanuts that acts as the driving force for peanut consumption. The main peanut market types grown in the United States are runner, virginia, Valencia, and Spanish (Stalker & Wilson, 2016). Raw peanuts are composed of approximately 4.9-6.8% moisture, 20.7-25.3% proteins, 31-46% lipids, 21-37% carbohydrates, and a variety of minerals (Alhassan, Agbenorhevi, Asibuo, & Sampson, 2017). The composition and concentration of volatile compounds present determine the flavor of roasted peanuts.

Peanuts are susceptible to physicochemical changes as a result of chemical reactions that can occur during both roasting and storage (Wang, Adhikari, & Hung, 2017). The Maillard reaction and lipid oxidation are primarily responsible for these changes in peanuts. The Maillard browning reaction, which mainly occurs during roasting, generates the positive attributes of roasted peanuts or the "roasted" flavors and aromas (Wang & Adhikari, 2017; Williams et al., 2006). The reaction involves the production of volatile compounds including pyrazines, a class of heterocyclic nitrogen-containing compounds that are attributed to the pleasant flavor of roasted peanuts and are the most studied flavor volatiles (Stalker & Wilson, 2016). Peanuts are also susceptible to flavor deterioration and developing off-flavors during both roasting and

storage due to lipid oxidation. Lipids comprise approximately 46% of raw peanuts which generally increases as peanuts mature and approximately 80% of peanut's fatty acid content is unsaturated (Stalker & Wilson, 2016). The autoxidation of the unsaturated fatty acids in peanuts results in the formation of secondary oxidation products such as aldehydes and ketones, which manifest as off-flavors and aromas (Davis & Dean, 2016). During storage, the loss of the pleasant flavor attributes of roasted peanuts due to the development of off-flavors is known as "flavor-fade" and the mechanism for flavor-fade is still unclear (Wang & Adhikari, 2017).

Consumers' overall perception of peanut flavor is influenced greatly by whether the peanuts have predominantly roasted or oxidized flavors. High-oleic cultivars developed by the University of Florida in 1995 contain approximately 80% oleic and 3% linoleic acid content which extends the shelf-life and storage quality of roasted peanuts given their lower degree of fatty acid unsaturation (Braddock & Sims, 1995; Stalker & Wilson, 2016). These cultivars, now available within all major types of peanuts, have been shown to have higher stability against lipid oxidation and better resistance to flavor-fade as compared to normal-oleic cultivars (Braddock & Sims, 1995; Williams et al., 2006). Some studies have found opposing results in the difference between high- and normal-oleic cultivars. One study found that consumer acceptance of high-oleic and normal-oleic peanut flavors did not differ after storage while another found that high-oleic did receive higher consumer acceptance, but the acceptability was dependent on the type of cultivar (Nepote, Mestrallet, Ryan, Conci, & Grosso, 2006; Nepote, Olmedo, Mestrallet, & Grosso, 2009). Furthermore, few studies have investigated how multiple roasted peanut cultivars compare in regard to flavor-fade in storage. For a better understanding of the difference between peanut types, cultivars, and their susceptibility to flavor-fade during storage, more extensive research is necessary. It is hypothesized that high-oleic cultivars, irrespective of type, will be

more resistant to oxidation and less prone to flavor-fade or loss of roasted flavor during storage. The independent variables of this study are peanut type and storage time, and the dependent variables are indicators of oxidation and flavor-fade, namely, the aroma profiles. The overall objective of this study was to compare the loss of roasted aroma or flavor-fade in peanut varieties and determine which cultivars are more resistant to flavor loss

The specific purposes of this study were to:

1) analyze and compare the aroma profiles of eight commercially available roasted peanut cultivars during 40-weeks of storage to determine which cultivars and peanut types are more resistant to flavor-fade.

2) compare flavor-fade or loss of roasted flavors between the high-oleic and normal-oleic runner and virginia cultivars.

3) analyze the aroma profiles of 10 commercially available high-oleic runner peanut cultivars during 40-weeks of storage to compare flavor-fade or loss of roasted flavors with two normal-oleic cultivars.

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CHAPTER 2

LITERATURE REVIEW

Peanuts

Peanuts (*Arachis hypogaea*) are an oilseed that dates back over 10,000 years (National Peanut Board, 2022). Peanuts are natives of the Western Hemisphere, where they are thought to have originated in South America, growing in tropical and subtropical climates (American Peanut Council, 2022). With the discovery of peanuts' versatility, Spanish explorers are responsible for their spread throughout the new world, Asia, and Africa. Peanuts made their way to North America in the 1700s, where they were not yet grown extensively due to their perception as food for the poor as well as requiring slow and difficult growing and harvesting techniques. It was not until after the civil war that peanut production increased in North America and by the twentieth century a rapid demand for peanut products resulted from labor-saving equipment and practices (American Peanut Council, 2022). Today under the support of the farm legislation adopted by the U.S Congress in 2002, the United States peanut production is overseen by the U.S. Department of Agriculture USDA (American Peanut Council, 2022).

Peanuts are produced and consumed worldwide given their flavorful and affordable nature. Today, the bulk of peanut production comes from the warm climates of Africa, Asia, Australia, and North and South America, which totals approximately 47 million metric tons produced per year (American Peanut Council, 2022). The United States follows China, India, and Nigeria as the fourth largest peanut producer, as shown highlighted in Figure 2.1. Peanuts

are grown commercially in 13 states which include Alabama, Arkansas, Florida, Georgia, Louisiana, Missouri, Mississippi, North Carolina, New Mexico, Oklahoma, South Carolina, Texas, and Virginia (National Peanut Board, 2022). The largest peanut-producing state, Georgia, is responsible for growing almost 50% of peanuts, followed by Florida with over 11% and Alabama with over 10% (National Peanut Board, 2022). Within the United States, the major peanut-producing states are separated into regions. The Southeast region (Alabama, Florida, Georgia, Mississippi), is responsible for producing approximately 65% of US-grown peanuts (National Peanut Board, 2022).

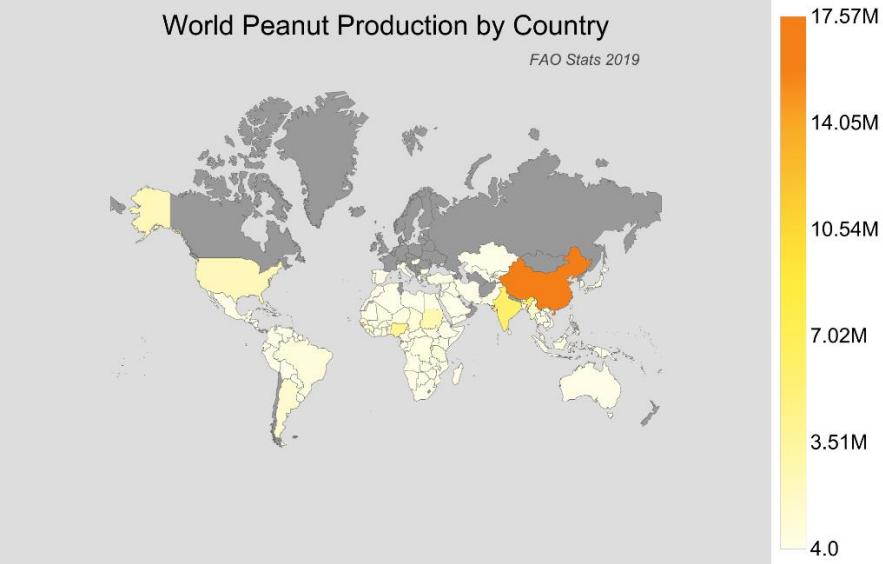

Figure 2.1 World's top peanut producing countries (Atlas Big, 2022)

Due to both wild and selective breeding a variety of peanuts exist today, all originating from the same plant, *Arachis hypogaea*. Peanuts are also known as groundnuts, given they flower above ground as an edible seed but mature underground (Agricultural Marketing Resource Center, 2021). Peanuts take approximately 120 to 160 frost-free days to harvest after planting (Whitley's Peanut Factory, 2022). Peanut flavor is greatly influenced by how their seeds are handled, processed, and stored as well as the influence of genetic, environmental, and

biochemical processes that can occur (Hui, 2010). Peanuts contain eight primary fatty acids; palmitic (C16:0), stearic (C18:0), arachidic (C20:0), behenic (C22:0), lignoceric (C24:0), oleic (C18:1n9c), eicosaenoic (C20:1n9c) and linoleic (C18:2n6c) acid, with oleic and linoleic being the dominant unsaturated fatty acids at a ratio of 1.5-2.0 in typical peanuts (Lykomitros, Fogliano, & Capuano, 2016a; Suri, Singh, Kaur, & Singh, 2019). Some studies have compared peanuts originating from countries such as Argentina, China, and the USA in their flavor and compositional qualities, demonstrating how the country of origin, growing, and postharvest can significantly affect peanut flavor (Bett, Vercellotti, Lovegren, & Sanders, 1994; Pattee & Singleton, 1972). Peanut flavors also differ among the different peanut types. The four basic market types are runner, Spanish, Valencia, and virginia. Within these four basic types exist many varieties, each with its distinctive nutritional compositions, sizes, and flavors (American Peanut Council, 2022). Depending on the type, certain climates are best for production and can result in different flavors in peanut products.

Runners, the dominant peanut type making up over 80% of peanuts produced in the U.S., are mainly grown in Georgia, Alabama, Florida, Texas, and Oklahoma. Approximately 54% of runners produced are used for peanut butter. The runner-type has a mostly uniform kernel size (National Peanut Board, 2022), while the virginia-type has the largest kernel size and is mostly grown in Virginia, North Carolina, South Carolina, and Texas. Virginia varieties are typically sold as salted or flavored peanuts and account for the majority of peanuts eaten in-shell (American Peanut Council, 2022). Spanish-type peanuts only account for 2% of U.S. production, primarily grown in Oklahoma and Texas, and are used for peanut candies due to their smaller kernel size (Whitley's Peanut Factory, 2022). The last type, Valencia is primarily grown in New Mexico and Texas. This type usually has three or more small kernels per shell and contains a

sweet flavor making it useful for all-natural peanut butter products. Some of the most popular food products in the U.S. today are roasted peanuts, peanut butter, and peanut candies. Currently, peanut butter alone accounts for $850 million of retail sales each year in the U.S (National Peanut Board, 2022).

Maillard reaction in peanuts

Pyrazine formation

The main reactions occurring in peanuts that result in volatiles that form roasted flavor are Maillard reaction, Strecker degradation, caramelization, and lipid oxidation (Hui, 2010). The Maillard reaction is one of two types of non-enzymatic browning that occur in food systems and is one of the key determinants of roasted peanut flavor and aroma (Davis & Dean, 2016). This reaction involves carbonyl-containing compounds, such as reducing sugars, interacting with the free amino group of amino compounds such as amino acids, proteins, and amines (Crnčević, 2018; Koehler, Mason, & Newell, 1969). Both thermal processing and prolonged storage can initiate Maillard browning in food (Vhangani & Van Wyk, 2021). Factors that influence Maillard reactions in food systems include pH, temperature, time, water activity, and the types of proteins and carbohydrates reacting (Crnčević, 2018). The reaction can take place in room temperature conditions but is accelerated when exposed to high temperatures. Under the right conditions, the Maillard reaction can result in high concentrations of volatiles responsible for desirable flavors and aromas, such as the unique roasted flavor of peanuts developed during roasting. Koehler and Odell (1970) found that pyrazines begin forming around 100°C and increase significantly when the temperature is continuously raised to 150°C. Suri et al. (2019) found that the optimal temperature to achieve desired quality characteristics of roasted peanuts flavors was 180°C for 10 minutes. Whereas Baker (2002) concluded that the highest sensory scores for roasted flavors

and aromas result from roasting at 175°C for 15 min. Most studies vary in optimal roasting temperatures for the desired aroma, but most temperatures range between 120°C and 180°C (Baker et al., 2003; Baker, Sims, Gorbet, Sanders, & O'Keefe, 2002; Koehler & Odell, 1970; Leunissen, Davidson, & Kakuda, 1996; Smith & Barringer, 2014; Suri et al., 2019). Enhanced color and aroma of food products are a result of the Maillard reaction, but undesirable quality changes can also result from this reaction amongst others under specific conditions such as extended storage periods of foods (Crnčević, 2018; Leunissen et al., 1996; Schirack, Drake, Sanders, & Sandeep, 2006).

The Maillard reaction mechanism occurs under a complex series of reaction pathways and intermediates. The complexity of the reaction can be simplified into three stages: early, advanced, and final according to Crnčević (2018). The early stage is initiated by the condensation between a carbonyl group of reducing sugar and the amino group of amino acids. This results in the formation of an unstable Schiff base that rearranges to produce the Amadori compound as shown in Figure 2.2. The compounds generated from Amadori degradation are responsible for the aroma in foods (Blank et al., 1988; Cerny, 2008). From there, the advanced stage involves the degradation of the Amadori compound into a complex variety of different products. The possible routes for degradation are dependent on the pH of the reaction, and the Amadori compounds can be degraded through numerous reactions including oxidation, dehydration, and enolization. The compounds generated are highly reactive and lead to the final stage of the Maillard mechanism. In this stage degraded Amadori compounds react together to form large molecular weight heterocyclic nitrogenous compounds which can react further to form melanoidins or high molecular weight brown pigments (Crnčević, 2018). The heterocyclic nitrogen compounds formed in foods include volatiles such as furans, pyrroles, pyridines,

imidazoles, and pyrazines (Hui, 2010). Of these products pyrazines are the primary class of heterocyclic compounds detected in peanuts, typically accounting for over 50% of this volatile class (Liu et al., 2011).

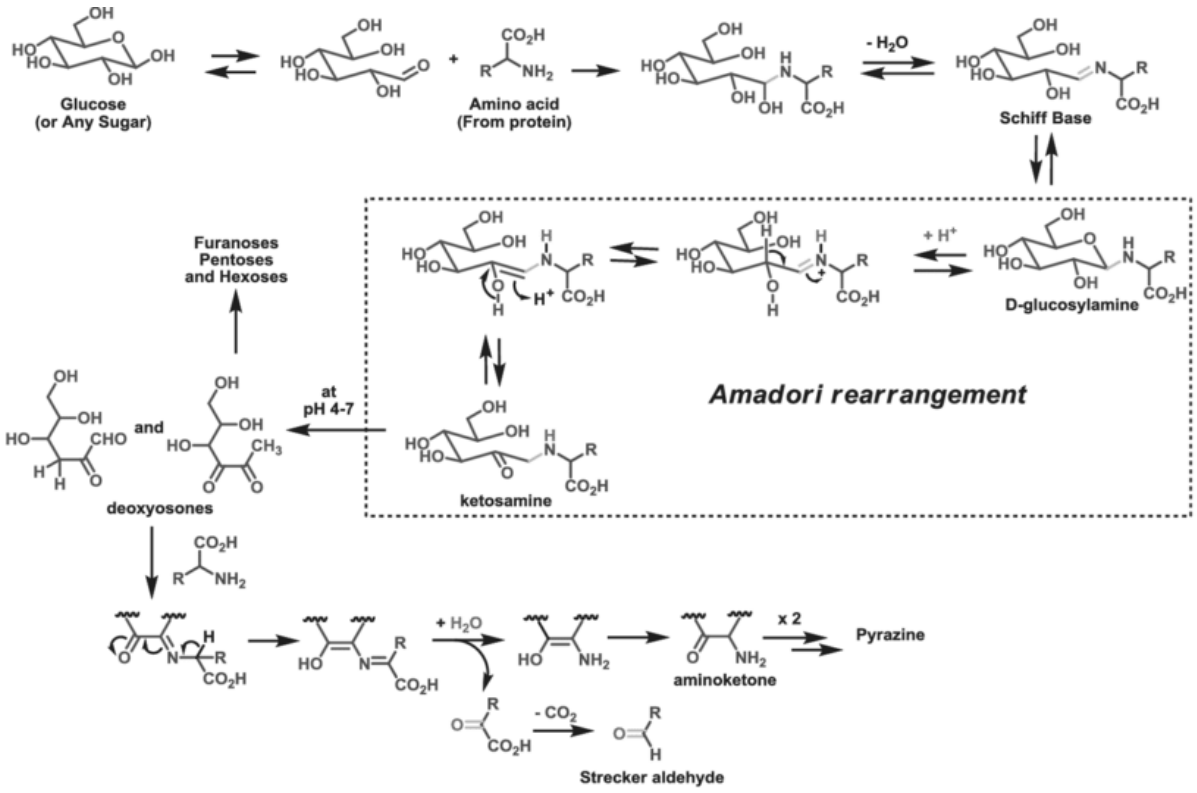

Figure 2.2 Example Maillard reaction mechanism (Traore, Arama, Medebielle, Doumbo, & Picot, 2016)

Flavor compounds

Flavor precursors are typically nonvolatile compounds that are converted to volatile compounds when exposed to certain conditions such as storage and thermal processing (Hui, 2010). Studies have found that the main flavor precursors of roasted peanut flavor are sugars, proteins, and amino acids (Klevorn, Dean, & Johanningsmeier, 2019; Mason, Newell, Johnson, Koehler, & Waller, 1969; Newell, Mason, & Matlock, 1967). Newell et al. (1967) determined amino acids and carbohydrates as the precursors of typical peanut flavor. Quantitative analysis of

peanuts during roasting showed a change in the concentration of both amino acids and monosaccharides, indicating chemicals reactions of those compounds considered flavor precursors. Further analysis determined that typical peanut flavor was associated with aspartic acid, glutamic acid, phenylalanine, asparagine, histidine, and glutamine and atypical or off-flavors were associated with threonine, tyrosine, and lysine (Newell et al., 1967). Similarly, Klevorn et al. (2019) identified 365 metabolites, finding virginia-type to generally be higher in free amino acids and differing from the runner in the contents of threonine, glutamic acid, leucine, lysine, and histidine. Some sugars identified in peanuts include myo-inositol, glucose, fructose, sucrose, raffinose, stachyose with sucrose being approximately 90% of the sugars present (Davis & Dean, 2016). Mason, Newell, Johnson, Koehler, and Waller (1969) reported data that confirmed that sucrose is the major sugar found in peanuts, which hydrolyzes during roasting into fructose and glucose that then take part in Maillard browning that leads to the formation of pyrazines.

Over 200 volatiles have been identified in roasted peanuts (Ho, Lee, & Chang, 1982; Lee, Chang, & Ho, 1982; Mason, Johnson, & Hamming, 1966). Pyrazines have been the most extensively studied volatile compound given their high yield of the pleasant flavor attributes of roasted peanuts. As previously stated, pyrazines and other heterocyclic nitrogen compounds are produced because of the Maillard reaction that occurs during peanut roasting (Baker et al., 2003; Wang et al., 2017a; Warner, Dimick, Ziegler, Mumma, & Hollender, 1996; Williams et al., 2006). Alkylpyrazines were some of the earliest reported aroma-active compounds in roasted peanuts, found to emit the typical “nutty” aroma (Johnson, Waller, & Burlingame, 1971; Mason et al., 1966). The earliest identification of pyrazines in roasted peanuts was from a study conducted by Mason et al. (1966). Five pyrazines; methylpyrazine, 2,5-dimethylpyrazine, 2-methyl-5-ethylpyrazine, trimethylpyrazine, and 2,5-dimethyl-3-ethylpyrazine were identified using nuclear

magnetic resonance, ultraviolet, and mass spectrometry from roasted Spanish peanuts. These five identified pyrazines were reported to produce the typical nutty flavors found in roasted peanuts. Other primary pyrazines found to contribute to peanut aroma are 2-ethyl-3,5-dimethylpyrazine and 2,3-diethyl-5-methylpyrazine (Gong et al., 2018; Matsui, Guth, & Grosch, 1998). Leunissen et al. (1996) found that the concentration of pyrazines increased as roasting conditions (temperature/time) increased in roasted peanuts. Sensory analysis of the roasted peanuts also revealed that low concentrations of pyrazines were desirable but higher concentrations lead to bitter flavors when temperatures surpass 177°C. Several studies (Baker et al., 2003; Braddock & Sims, 1995; Gama & Adhikari, 2019; Ng & Dunford, 2009; Wang, Adhikari, & Hung, 2017b) found that pyrazines produced after roasting were highly correlated with the roasted flavor and aroma of peanuts and 2,5-dimethylpyrazine is one of the most highly correlated to this pleasant flavor and aroma.

During peanut roasting, the once pea-like flavor is converted into a pleasant roasted and nutty aroma and flavor (Brown, Senn, Dollear, & Goldblatt, 1973). Although pyrazines are typically identified as the major volatile contributing to peanut aroma and flavor, many other flavor volatiles have been identified and reported. Lee et al. (1982) reported a total of 131 volatiles identified in roasted peanuts including, lactones, pyrroles, pyridines, sulfides, and thiazoles detected using infrared and mass spectrometry for identification. Benzaldehyde, benzeneacetaldehyde, methylpyrroles have all been reported to be major aroma contributors by various studies, emitting green, sweet, and nutty aromas (Braddock & Sims, 1995; Ho et al., 1982; Lykomitros, Fogliano, & Capuano, 2016b; Ng & Dunford, 2009; Wang et al., 2017b). Walradt, Pittet, Kinlin, Muralidhara, and Sanderson (1971) reported the initial finding of compounds 4-vinylphenol and 4-vinyl-2-methoxyphenol, volatile phenolic acids found in peanuts. Chetschik,

Granvogl, and Schieberle (2008) reported 20 new aroma active compounds identified in roasted peanuts including 2-acetyltetrahydropyridine, known for its popcorn-like aroma, in a study comparing raw West-African peanuts to pan-roasted peanut meal. Increased roasting temperature lead to high concentrations of volatiles such as furans like 5-methyl-2-furancarboxaldehyde, 5-methyl-2-furanmethanol, furfural and, 5-methylfurfural, known for their sweet, fruity, and roasted aromas (Gong et al., 2018; Lykomitros et al., 2016b). Both processing and storage lead to the formation of a variety of aroma volatiles found in peanuts, as well as a depletion of certain volatiles.

Oxidation and flavor-fade of peanuts

Lipid oxidation

Lipids makeup approximately 46% of peanut composition with approximately 80% being unsaturated (Davis & Dean, 2016). For a typical peanut, the fatty acid composition is approximately 50% oleic and 30% linoleic acid. The high level of unsaturated fatty acids makes peanuts susceptible to lipid oxidation, which leads to the formation off-flavors and flavor-fade in roasted peanuts. This reaction occurs in peanuts during both storage and exposure to higher temperatures and humidity. Oxidative changes accelerate at high temperatures, as shown by many studies that thermal treatment of peanuts and peanut oil increases oxidation products leading to undesirable flavors and affecting peanut shelf-life (Brown et al., 1973; Chetschik et al., 2008; Evranuz, 1993; Gong et al., 2018; K. Liu, Liu, & Chen, 2019). Lipid oxidation produces nonvolatile unstable hydroperoxides that act as precursors for volatile aldehydes, ketones, and alcohols. The decomposition of hydroperoxides involves a complex set of reaction pathways producing both volatile and nonvolatile products (Frankel, 1983). The reaction can be divided into three stages: initiation, propagation, termination (Figure 2.3).

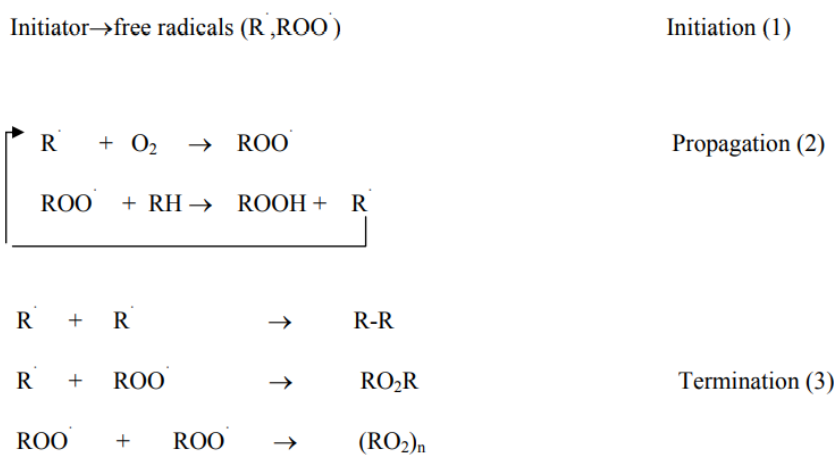

Figure 2.3 Autoxidation mechanism for lipids (Powell, 2004)

In the initiation step, free alkyl radicals are formed from the abstraction of hydrogen atoms from the methylene groups of lipids. The propagation step, a chain reaction, continuously regenerates reactive intermediates until the lipid radical reacts with triplet oxygen to form a lipid peroxyl radical. This is followed by the termination step, in which the peroxyl radicals react with themselves to yield stable non-reactive products. Hydroperoxides are a primary product of this reaction, formed in the propagation step.

For plant systems such as peanuts, both enzymatic and nonenzymatic mechanisms can oxidize lipids (Hui, 2010). For reactions involving enzymatic mechanisms, lipoxygenase can act as a catalyst, oxidizing polyunsaturated fatty acids to hydroperoxides. Although roasting peanuts inactivates enzymes, lipid oxidation can still occur due to the presence of transition metals such as iron and copper from lipoxygenase, that act as a catalyst in nonenzymatic reactions (Hui, 2010). Studies have identified aldehydes such as hexanal, octanal, nonanal, and decanal as the major by-products of oxidation, associated with off-flavors such as paint-like, cardboard-like, and oxidized in peanuts after various storage periods (Warner et al., 1996; Williams et al., 2006). Some of the harsh green aromas of roasted peanuts have been associated with low molecular

weight aldehydes such as hexanal, octanal, nonanal, 2-octenal, and 2-nonenal (Brown et al., 1973). Braddock and Sims (1995) observed a significant increase in the hexanal content of peanuts stored at room temperature (25°C) after 6 weeks, causing paint-like and carboard flavors. Hexanal is considered an indicator of oxidation levels in many food products, formed from the oxidation of linoleic acid (Bett & Boylston, 1992). The difference in fatty acid composition between peanut types affects the degree of autoxidation that will occur. Brown et al. (1973) reported that Spanish-types higher linoleate content caused higher concentrations of compounds such as octanal, 2-decenal, and 2,4-nonadienal, to form after roasting. The study also reported compounds such as 2-heptanal, 2,4-decadienal, and 2-nonenal to be associated with fatty and deep-fried aromas in roasted peanuts.

Throughout storage increased aldehyde content decreases the pleasant flavor and quality of roasted peanuts in addition to lowering the consumer acceptability (Grosso, Resurreccion, Walker, & Chinnan, 2008; Kai-Min, Louis Kuoping, Chin-Sheng, Zih-Sian, & Hsin-Chun, 2021; Wang et al., 2017a). Evranuz (1993) reported unblanched roasted peanuts stored at various temperatures and humidity led to the development of rancidity regardless of the temperature in a study storing roasted peanuts at 15 °C, 20 °C, and 35 °C. Similar results were reported by Pattee, Singleton, and Johns (1971), suggesting that peanuts oxidize at room temperatures when stored due to autoxidation. Wang et al. (2017a) reported increased aldehyde content along with decreased pyrazines in roasted peanuts during short storage, significantly affecting the consumer's overall liking of certain peanut types. Trends in increasing aldehyde content along with stable or decreasing pyrazine content have been shown to significantly affect consumer and sensory scores when peanuts are stored (Braddock & Sims, 1995; Warner et al., 1996; Williams

et al., 2006). With pleasant flavors of peanuts mostly attributed to pyrazines, the masking or depletion in their concentration due to increasing autoxidation products is an ongoing issue.

Flavor-fade

During storage, the once pleasant roasted flavors of peanuts begin to diminish with the onset of developing off-flavors, a phenomenon known as flavor-fade, and this occurs *via* a mechanism that is still unclear. Several studies identify similar volatile compounds involved in flavor-fade but differ in the mechanism by which the phenomenon happens (Bett & Boylston, 1992; Braddock & Sims, 1995; Warner et al., 1996; Williams et al., 2006). A study conducted by Warner et al., 1996 on ground roasted Florunner peanuts stored for 68 days analyzed the contribution of pyrazines and aldehydes to peanut flavor-fade. The volatiles resulting from the Maillard reaction and lipid oxidation were separated and identified using gas chromatography/mass spectrometry. The selected pyrazines (2,6-dimethylpyrazine, 2-methylpyrazine, 2-ethyl-5-methyl or 6-methylpyrazine, 2,3,5-trimethylpyrazine) had no significant change in concentration during the storage period whereas the aldehydes (hexanal, heptanal, octanal, and nonanal) increased in concentration during the storage period. Sensory analysis revealed that roasted peanut flavor did decrease slightly and oxidative or rancid flavors increased during storage. The results of this study suggested that the masking of pyrazines and other compounds that contribute to roasted flavor by low-molecular-weight aldehydes resulting from lipid oxidation might have been the cause of flavor-fade.

Williams et al. (2006) explored the flavor characteristics of roasted peanuts over short-term storage of 21 days using gas chromatography, chemosensory techniques, and a sensory panel. Their evaluations of the volatiles from the roasted peanuts found that pyrazine concentrations (2,3-diethylpyrazine, 2-methoxypyrazine, 2,3-dimethylpyrazine, 2-ethyl-3-

methylpyrazine, and 2,3,5-trimethylpyrazine) significantly decreased whereas hexanal concentration significantly increased over the 21 days. They found a correlation between the sensory analysis results and the volatile concentration changes throughout the study period. An increase in bitter, painty, and cardboard-like flavors was observed as storage time increased. The results of this study dismissed the masking of pyrazines as the cause of flavor-fade and instead suggested that the decrease in pyrazine concentration could be due to decomposition by lipid radicals. Similar results were reported by Wang et al. (2017a), finding short storage of 8 weeks resulting in increased aldehyde concentration with decreased pyrazine concentration, influencing consumer acceptability of roasted peanuts.

The rate at which flavor-fade occurs can be affected by many factors including storage conditions and time (Baker et al., 2002; Fernandes, Pereira, Fidalgo, Gomes, & Ramalhosa, 2020; Fu et al., 2018; Jensen, Danielsen, Bertelsen, Skibsted, & Andersen, 2005; Lee & Resurreccion, 2004; Martín, Asensio, Nepote, & Grosso, 2018). Lipid oxidation has been correlated to water activity (a_w) in peanuts in many studies. Some studies have suggested a pattern in which decreased roasted flavor in peanuts occurred over time with the highest decrease being observed in peanuts with higher a_w in storage (Baker, Sims, Gorbet, Sanders, & O'Keefe, 2002; Reed, Sims, Gorbet, & O'Keefe, 2002). Roasted peanuts being hygroscopic, readily pick up moisture even at low a_w. Baker et al. (2002) reported that the moisture content of the roasted peanuts was significantly affected by time and a_w of storage, leading to decreased roasted peanut sensory scores and increased rates of oxidation. Storage temperature strongly influences rates of oxidation, with the intensity of roasted flavors being reported to decrease with increased storage temperature. Grosso et al. (2008) reported roasted peanuts samples stored at 23, 30 and 40°C experienced increased carboard and oxidized flavors as hexanal content increased throughout

storage along with decreased roasted flavors. Lee and Resurreccion (2004) and Evranuz (1993) reported similar results, finding sensory properties and oxidation rates of roasted peanuts to be significantly influenced by storage a_w, temperature, and time. To combat flavor-fade in peanuts along with finding optimal storage conditions for roasted peanuts, scientists have found ways to genetically alter peanuts to increase their resistance to oxidation and flavor-fade.

High-oleic vs normal-oleic peanuts

Peanuts' susceptibility to oxidative rancidity is heavily dependent on their lipid content. It is the lipid content and high percentage of polyunsaturated fatty acids in peanuts that make them prone to lipid oxidation leading to the formation of volatile secondary oxidation compounds that can result in flavor loss or flavor-fade. The major oil components of peanuts are oleic and linoleic acid. Oleic acid is monounsaturated as compared to polyunsaturated linoleic acid, which makes it more suitable for long-term storage. High-oleic peanuts, which display similar flavors to conventional peanut cultivars, have been made using conventional breeding methods and genetic modifications (Shirasawa et al., 2016). Normal-oleic peanuts have a typical fatty acid composition of 50% oleic and 30% linoleic acid, whereas high-oleic peanuts contain closer to 80% oleic and less than 3% linoleic acid. The lower levels of fatty acid unsaturation make the high-oleic peanuts less susceptible to oxidizing than their counterpart. Several studies have shown that high-oleic peanuts have exhibited much higher oxidative stability than normal-oleic peanuts (Braddock & Sims, 1995; dos Santos et al., 2019; Martín, Grosso, Nepote, & Grosso, 2018; Mugendi, Sims, Gorbet, & O'Keefe, 1998; Nepote, Mestrallet, Accietto, Galizzi, & Grosso, 2006). Braddock and Sims, 1995 observed high-oleic peanuts retain the roasted peanut flavor and resisted the development of painty and cardboard-like flavors better than normal-oleic during 6 weeks of storage. The pyrazine content of the high-oleic varieties also

remained more stable and lower concentrations of aldehyde content were detected throughout the study duration. Another study conducted by Nepote, et al. (2006) reported similar results. Although the high and normal-oleic cultivars both exhibited a decrease in the roasted peanut flavor, the high-oleic cultivar exhibited less oxidized and cardboard-like flavors than the normal-oleic cultivar at the end of the 112-day storage period. Several other studies have found similar results in the oxidative resistance of high-oleic cultivars during different storage period lengths, all concluding the high-oleic varieties to be better maintain desirable qualities during storage (Martín, et al., 2018; Nepote et al., 2009; Reed et al., 2002; Wang et al., 2017a; Williams et al., 2006).

Peanut products are also susceptible to developing off-flavors and experiencing a flavor-fade. Kai-Min et al. (2021) reported peanut butter prepared with high-oleic peanuts has significantly longer shelf lives and more stable quality than other varieties. A study conducted by Riveros et al. (2010) compared the chemical and sensory stability of peanut pastes made from high-oleic and normal-oleic peanuts. The study found that the paste made from the high-oleic peanut cultivar had up to four times longer shelf life and exhibited lower concentrations of oxidation indicators throughout the 175-study period. The study also found that the normal-oleic cultivar had significantly higher peroxide values as well as cardboard/oxidized flavors. A study on the shelf life and physical properties of varying oleic/linoleic peanut oil blends found that the oil blends with higher-oleic content exhibited lower peroxide values as well as a lower intensity of off-flavors such as paint-like and cardboard (Davis et al., 2016). The study also used the oxidative stability index (OSI) to predict the relative shelf life of the oils and found that there was a significant improvement in OSI across the entire range of oil blends tested with increasing oleic/linoleic ratio. Research indicates high-oleic varieties have higher consumer acceptability

and storage abilities in regard to oxidation. A study by Chuantang et al. (2021) even found that this variety can have improved chemical and sensory qualities through the use of foliar fertilizer.

Analysis of volatiles by solid-phase microextraction

Food analysis is important for evaluating food products for a variety of reasons including chemical composition, nutritional value, safety, quality, and sensory perception. For example, the flavor has a central role in consumer acceptance and overall likability of foods (Wang et al., 2017b). There are a variety of certified methods, using highly efficient instruments to characterize the properties of foods. Volatiles from lipid oxidation have been monitored using many different extraction methods including solid-phase micro-extraction, electronic nose, ion mobility spectrometer, and automated dynamic headspace gas chromatography (Tzschoppe, Haase, Hoehnisch, Jaros, & Rohm, 2016). Headspace-solid phase microextraction (HS-SPME) technique has been one of the most widely used approaches for volatile compound profiling in various peanut oils, products, and samples (Kai-Min, Kuoping, Chin-Sheng, Zih-Sian, & Hsin-Chun, 2021; Tzschoppe, Haase, Hoehnisch, Jaros, & Rohm, 2016; Wang et al., 2017a; Wang, Adhikari, & Hung, 2017b). Solid-phase microextraction is a fast and easy solvent-free operation making it one of the most used techniques for the extraction of volatile compounds. Baker et al. (2003) reported SPME being a rapid and nondestructive method to determine pyrazine levels in peanuts, concluding that this method is valid for correlating roasted peanut volatiles to sensory perception of peanut flavor and aroma. However, this semi-quantitative method also has drawbacks such as its inability to measure precise quantities in sample headspaces and the limited number of commercially available stationary phases that are not uniformly sensitive to all compounds and limit the choice for selectivity.

The selectivity and sensitivity of SPME are increased when used with gas chromatography-mass spectrometry (GC-MS) to determine volatiles (Kataoka, Lord, & Pawliszyn, 2000). GC-MS analysis is commonly used to determine the identity and the quality of the compounds responsible for the flavor variations and off-flavor in peanuts (Braddock & Sims, 1995; Powell, 2004; Warner et al., 1996; Williams et al., 2006). Gas chromatography is a fast analysis method that provides high separation efficiency, and its properties are improved when used in combination with mass spectrometry. MS is the most applied spectrometric detection method for GC and typically it is utilized for the detection of target compounds (Lorenzo & Pico, 2012). GC-MS is an effective analysis technique of aroma and flavor volatiles for foods such as peanuts, roasted coconut, mango, guava, banana, and honey (da Silva et al., 2020; Jaleel et al., 2021; Jayalekshmy, Narayanan, & Mathew, 1991). When GC-MS is employed to examine the differences in peanut oil aroma based on variety, the optimal conditions for extracting peanut oil are achieved through the use of 50/30 µm DVB/CAR/PDMS fibers at 60 °C for 50 min according to Gong et al. (2018). Mixed coating fibers such as DVB/CAR/PDMS increase the retention capacity and extraction efficiency of volatiles. Gong et al. (2018) further reported that the 50/30 µm DVB/CAR/PDMS fiber, being bipolar, extracted greater amounts of volatile compounds and had a great extraction capacity for pyrazines as compared to four other adsorption fibers. The use of GC-MS allows the identification and quantification of a wide range of GC-amenable food additives, flavor and aroma components, and contaminants.

Objectives

The main objective of this study was to compare the loss of roasted aroma or flavor-fade in peanut varieties and determine which cultivars are more resistant to flavor loss. This was done by: 1) analyzing and comparing the aroma profiles of eight commercially available roasted

peanut cultivars during 40-weeks of storage to determine which cultivars and peanut types are more resistant to flavor-fade; 2) comparing flavor-fade or loss of roasted flavors between a high-oleic and normal-oleic runner and virginia cultivars; and 3) analyzing the aroma profiles of 10 commercially available high-oleic runner peanut cultivars during 40-weeks of storage to compare flavor-fade or loss of roasted flavors with two normal-oleic cultivars.

This research will serve as a means for peanut producers and manufacturers to gain further insight into how the different peanut types (runner, virginia) and cultivars behave during storage regarding oxidative changes and loss of desirable flavor qualities.

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CHAPTER 3

COMPARISON OF FLAVOR-FADE IN RUNNER AND VIRGINIA CULTIVARS WITH VARYING OLEIC STATUSES

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Abstract

The main objective of this study was to analyze and compare aroma profiles of eight commercially available roasted peanut cultivars during 40-weeks of storage to determine which cultivars and peanut types are more resistant to flavor-fade. Aroma volatiles from the roasted peanut samples were extracted using headspace solid-phase microextraction (HS-SPME) and identified and quantified using Gas Chromatography-Mass Spectrometry (GC-MS) analysis. There were two high-oleic and two normal-oleic cultivars within each peanut type (runner, virginia). A total of 22 volatile compounds were identified in the roasted peanut samples during storage. Pyrazines and benzene-derivatives were the major volatiles detected. Roasted flavor volatiles remained stable or increased in all cultivars, irrespective of type or oleic status, insinuating a lack of flavor-fade occurring during storage. The high-oleic cultivars, irrespective of type were observed to be more resistant to flavor changes and therefore less prone to flavor-fade or loss of roasted flavor during storage. Oxidation volatiles were primarily detected in the normal-oleic cultivars. In general, virginia cultivars remained the lowest in roasted flavor volatiles throughout 40 weeks of storage.

Keywords: GC-MS, pyrazine, oxidation, high-oleic, normal-oleic

Introduction

Peanuts (*Arachis hypogaea)* are classified as legumes, a plant family known for their edible seeds enclosed in pods. In the United States, the major market for peanuts is edible products, with an approximate average of 3.58 kg being consumed per capita in 2021 (National Peanut Board, 2022). In the United States, the four types of peanuts commercially grown are runner, virginia, Spanish, and Valencia. Of the four types, runner and virginia are the majority types grown in the United States. Runner-types have a uniform kernel size and are primarily used for processing peanut butter but are also used for candy and confections. Runners are the most common peanut type grown due to their attractive, uniform kernel size and roasting characteristics. Virginia-type have large kernels and are used for salted and packaged snack peanuts for places, being sold in the shell in places such as ballparks (American Peanut Council, 2022).

The unique and pleasant roasted flavors and aromas that develop during the roasting of peanuts act as the driving force for their consumption and consumer acceptability (Grosso & Resurreccion, 2006; Nepote, Olmedo, Mestrallet, & Grosso, 2009; Wang, Adhikari, & Hung, 2017a). The roasted peanut flavor is determined by the chemical composition and concentration of volatiles and influenced by how the peanuts are handled, processed, and stored. Peanuts are composed of various percentages of moisture, protein, lipid, carbohydrates, and minerals. This composition varies among the various peanut market types and cultivars. Lipids make up approximately 46% of peanut composition and are important factors in the flavor development and shelf stability of peanuts. After Lipids, Protein (~25.8%) and Carbohydrates (~16.1%) are the following abundant components in peanut composition, both acting as flavor precursors (Davis & Dean, 2016). During both roasting and storage, peanuts undergo physicochemical

changes, which include heat exchange, drying, and various chemical reactions (Wang, Adhikari, & Hung, 2017a). Of those chemical reactions, lipid oxidation and the Maillard reaction are primarily responsible for the flavors and aromas of peanuts. The Maillard reaction is primarily responsible for the pleasant attributes of peanuts whereas lipid oxidation is responsible for the off-flavors that develop in peanuts.

It is the high lipid content of peanuts that makes them susceptible to lipid oxidation during storage (Hui, 2010). The development of aldehydes, ketones, and alcohols from lipid oxidation in peanuts produce flavors that are considered undesirable. When peanuts lose their pleasant attributes to the development of oxidized flavors during storage, the phenomenon is known as "flavor-fade" (Reed, Sims, Gorbet, & O'Keefe, 2002; Warner, Dimick, Ziegler, Mumma, & Hollender, 1996; Williams et al., 2006). Flavor-fade is suggested to occur due to the degradation of pyrazines by lipid radicals or aldehyde masking, but the true mechanism is unclear. The rate or degree of flavor-fade in peanuts is influenced by the peanut genotype or their oleic status. Peanuts can be classified as normal-oleic or high-oleic, the latter containing higher oleic acid content (~80%) and lower linoleic acid content (~3%) and having a significant effect on oxidation rates and flavor-fade. Despite runner and virginia varieties having the same approximate fatty acid content, some storage studies have reported virginia varieties to experience decreased consumer liking as well as experiencing shorter shelf-lives, suggesting runner varieties have better storage stability (Klevorn, Hendrix, Sanders, & Dean, 2016; Lykomitros, Fogliano, & Capuano, 2016a; Mozingo, O'Keefe, Sanders, & Hendrix, 2004; Sheppard & Rudolf, 1991; Wang, Adhikari, & Hung, 2017b). Irrespective of type, the high-oleic cultivars of both the runner and virginia varieties have been shown to resist lipid oxidation and retain pleasant attributes better than normal-oleic cultivars during storage (dos Santos et al.,

2019; Isleib, Pattee, Sanders, Hendrix, & Dean, 2006; Nepote, Mestrallet, Accietto, Galizzi, & Grosso, 2006; Pattee et al., 2002; Riveros et al., 2010; Wang et al., 2017b).

Direct comparison of multiple cultivars within the virginia and runner types in the context of their volatile flavor profiles during storage has not been done, nor has a comparison of the differences between cultivars with varying oleic statuses. The objectives of this study are to 1) analyze and compare the aroma profiles of eight commercially available roasted peanut cultivars during 40-weeks of storage to determine which cultivars and peanut types are more resistant to flavor-fade; 2) compare flavor-fade or loss of roasted flavors between the high-oleic and normal-oleic runner and virginia cultivars.

Materials and Methods

Peanut Cultivars

There were eight cultivars of peanuts (Table 3.1) obtained from the National Peanut Research Laboratory (NPRL) in Dawson, GA, where they were grown in experimental fields in the same plot and time. All cultivars were planted in late April 2019 and harvested in early November 2019. The peanuts used for the present study were blanched and roasted for previous research before being placed in storage (Campbell, 2021).

Sample Preparation and Storage

The peanut cultivars were sealed and stored in separate 177 mL clear small plastic containers (Amazon, Satinoir Inc., Temara, Morocco), used to simulate transparent plastic containers and bags peanuts are sold in for retail, at room temperature (~23 °C) for a total of 40 weeks. Lights (2515 lumens, General Electric, Boston, MA., U.S.A) were kept on in the storage space throughout the 40 weeks starting March 29, 2021. Between 40-45 g of each peanut cultivar was added into five separate containers corresponding to one of the storage removal weeks. The

peanuts were removed after storage of 8, 16, 24, 32, and 40 weeks and placed in a freezer (-15°C) until the samples were analyzed. To prepare the peanuts for analysis, the peanut samples (equilibrated to 21 °C) were ground into small particles using a coffee grinder (Hamilton Beach Co., Southern Pines, NC), and exactly 1.5 g of the ground peanut samples were transferred in triplicates to a 20-mL screw-cap vial fitted with a screw cap containing a polytetrafluoroethylene/silicone septum. Exactly 1.970 mL of distilled water was added with 30 µL of an internal standard, 0.02 mg/mL 1,3-dichlorobezene (Sigma-Aldrich, St. Louis, Mo., U.S.A.) solution in methanol, to the vial.

Aroma volatile analysis

Extraction of volatiles

Headspace-solid phase microextraction (HS-SPME) technique was used for the extraction and analysis of peanut volatiles. The vials were equilibrated for 15 min at 55 °C in an autosampler (Model GC Sampler 80, Agilent Technologies, Santa Clara, Calif., U.S.A.). The autosampler agitated the vials at 250 rpm. After equilibration, a 50/30 µm divinylbenzene/carboxen/polydimethylsiloxane SPME fiber was exposed to the sample headspace for 20 min at 55 °C**.** Immediately following the fiber exposure, the analytes were desorbed to the injection port of the gas chromatography-mass spectrometry (GC-MS) at 250 °C for 5 min in splitless mode.

Separation, identification, and semi-quantitation of the volatiles

Gas Chromatography-Mass Spectrometry (GC-MS) analysis of the aroma volatiles in the various roasted peanut types at the five pull dates was done. The GC-MS system (Model 7890A/5977A, Agilent Technologies) equipped with an HP-5MS column (30 m × 250 µm × 0.25 µm) was used for separating the analytes. The carrier gas was helium with a linear flow velocity

of 1 mL/min. The column was maintained at an initial temperature of 35 °C for 2 min, programmed at 2 °C /min to 70 °C, and was increased at a rate of 6 °C /min to a final temperature of 230 °C. The MS detector scanned a mass range (m/z) from 30 to 400 m/z with a scan speed of 1.562 µ/s. All data were collected in triplicate. The data for the first time point (Week 0) was obtained from previous research done on the peanuts used in the present study (Campbell, 2021).

Identification of volatile compounds was based on both the mass spectra database (NIST/EPA/NIH mass spectral library, Version 2.2, 2014) and Linear Retention Indices or LRI (Wang et al., 2017a). The indices were calculated based on the retention time of a series of n-alkanes (C7-C30) using the same GC separation protocol (Sigma-Aldrich, St. Louis, MO). The experimental values were compared with literature values to validate the results. Semi-quantification and relative concentrations for the identified compounds were reported based on the internal standard, 1,3-dichlorobenzene, area.

Statistical Analysis

The volatiles data were analyzed by a two-way (cultivars and time being the main factors) analysis of variance (ANOVA) using the Generalized Linear Models procedure in SAS (version 9.4; SAS Inst., Cary, NC, U.S.A.). Differences among cultivars within a time point and also differences due to the time points within a cultivar were separated through post-hoc mean separation using Fisher's LSD (Least Significant Difference).

The cultivar by time point data for weeks 8, 24, and 40 were subjected to Multiple Factor Analysis (MFA) to discern patterns over time. Finally, factor scores for the cultivars from the MFA were subjected to Hierarchical Cluster Analysis (HCA) to cluster the cultivars in similar groups.

Results and Discussion

GC-MS analysis detected and identified 22 volatile compounds (Table 3.2) in the eight peanut cultivars throughout the 40 weeks of storage. Most volatiles detected were Maillard-derived and only a few were oxidation-derived.

Runner versus Virginia

When comparing the two types, the prevalent product of lipid oxidation, hexanal, was only detected in low concentrations in four of the cultivars throughout storage all of which were normal-oleic (Bail-VN, GA06-RN, Greg-VN, Tif-RN). Like hexanal, 1-octen-3-ol appeared in only the four normal-oleic cultivars among the two peanut types. Unlike the oxidation products, the major pyrazines (2,5-dimethylpyrazine, 2-ethyl-5-methylpyrazine, and 3-ethyl-2,5-dimethylpyrazine) were detected in all cultivars throughout storage in high concentrations irrespective of type or oleic status. Likewise, benzene derivates, benzaldehyde, and benzeneacetaldehyde, were detected in all cultivars in high concentrations. Table 3.3 shows that there are statistically significant differences in mean volatile compound concentrations by cultivar ($P \leq 0.001$) and by time ($P \leq 0.001$). Most volatile compounds also caused a significant interaction between cultivar and time ($P \leq 0.05$). Fisher's LSD posthoc test (Tables 3.4-3.10) revealed the significant differences in mean volatile concentrations for specific cultivars and time points throughout the storage period. For all other volatiles detected at low concentrations in the roasted peanut cultivars, their apparent absence and/or reappearance throughout storage is possibly due to their concentrations being below the limits of detectability of the GC-MS system rather than to the complete absence of these volatiles. Other factors influencing detectability include the semi-quantification method, roasting and storage conditions, and sample preparation.

Oxidized flavors and aromas formed during storage have a significant impact on the shelf-life of roasted peanuts and peanut-based products. Flavor-fade or the loss of roasted peanut flavor to the development cardboardy and painty flavors can result from chemical changes occurring due to lipid oxidation. Runner-type peanuts have been demonstrated in a previous study to resist the development of oxidation products and have higher consumer acceptability than virginia-type peanuts during storage (Wang et al., 2017b). In the present study, the major oxidation products were detected in both runner and virginia types throughout storage. Figures 3.1 and 3.2 show that known oxidation products, hexanal and 1-octen-3-ol, were detected in low concentrations in only the normal-oleic cultivars between the two peanut types. The low concentrations could be due to the peanut cultivars being dry roasted, which has been reported to cause less oxidation in peanuts throughout storage as compared to oil roasting (Campbell, 2021; Shi et al., 2017). Hexanal concentrations appeared erratic throughout storage, not following any particular pattern as shown in Figure 3.1. The reason for hexanal behavior throughout storage is unclear, as most storage studies done on peanuts consider hexanal a traditional marker for rancidity or oxidation and typically observe increased concentrations throughout storage (Braddock & Sims, 1995; Warner et al., 1996; Williams et al., 2006). Alternatively, 1-octen-3-ol, although present at low levels, did increase from week 0 to week 40 for all normal-oleic cultivars (Figure 3.2). Their presence indicates both peanut types are equally susceptible to the development of oxidation products during storage, although not likely to have any significant effects on the flavor of the peanuts due to their low levels. Both 1-octen-3-ol and hexanal are products of the oxidative breakdown of linoleic acid (Bett & Boylston, 1992; Lee et al., 1997). Linoleic acid makes up approximately 30% of the total fatty acid composition in normal-oleic peanuts and oxidizes up to 10 times faster than oleic acid, which could explain these compounds

not being present in the high-oleic cultivars. The results agree with previous studies**,** as normal-oleic cultivars are shown to be less resistant to the development of oxidative products during storage irrespective of peanut type (Braddock & Sims, 1995; Gong et al., 2018; Reed et al., 2002; Riveros et al., 2010; Wang et al., 2017b). In general, the normal-oleic runner cultivars exhibited higher concentrations of oxidation products than the normal-oleic virginia cultivars by the end of the storage period**.**

Flavor-fade in roasted peanuts is defined as the decrease of pleasant flavor and aromas accompanied by the onset of oxidized flavors, which is suspected to occur by either flavor degradation by oxidation products or flavor masking by aldehydes. Williams et al. (2006) reported a significant decrease in heterocyclic compounds, specifically pyrazines, and an increase in hexanal concentrations in a storage study done over 21 days with virginia peanuts. Similar results have been reported by multiple storage studies done on peanuts (Bett et al., 1994; Braddock & Sims, 1995; Reed et al., 2002; Wang et al., 2017b). However, Warner et al., 1996 found that most heterocyclic compounds remained constant throughout storage, with increasing aldehyde content. Despite the presence of oxidation products in some cultivars in the present study, the roasted flavor volatiles resulting from the Maillard reaction were significantly higher in concentration and remained stable in all cultivars irrespective of type or oleic status throughout storage. The results indicate neither of the suggested mechanisms of flavor-fade occurred in the peanuts throughout storage.

2,5-Dimethylpyrazine, known to be one of the best predictors of roasted flavors, was detected in high concentrations in all cultivars (Figure 3.3). The highest concentrations were found in the high-oleic cultivars of both peanut types (AU17-RH, Bail2-VH, GA13-RH, GA11-VH). Like previous studies done on roasted peanuts, 2,5-dimethylpyrazine was the major

pyrazine detected (Baker et al., 2003; Braddock & Sims, 1995; Lykomitros, Fogliano, & Capuano, 2016b; Wang et al., 2017a, 2017b). Roasted flavor volatiles, 2-Ethyl-5-methylpyrazine, 3-ethyl-2,5-dimethylpyrazine and the benzene derivatives behaved similarly throughout storage, being detected highest in the high-oleic cultivars of both peanut types (Figures 3.4-3.7). In general, pyrazines and other Maillard products exhibited increased concentrations in all cultivars, irrespective of type or oleic status. Such trends in pyrazine and Maillard product concentrations can be attributed to the low or absent oxidation products in the cultivars throughout storage, consequentially inhibiting flavor entrapment or degradation of the heterocyclic nitrogen compounds (Hui, 2010). During storage virginia-type roasted peanuts have been reported to have the most significant decreasing trend of pyrazines as compared to runner-type, along with shorter shelf-lives due to the onset of oxidation (Mozingo et al., 2004; Wang et al., 2017b). The present study found the major pyrazines to be detected highest in the high-oleic virginia cultivars (GA11-VH, Bail2-VH) as compared to high-oleic runners throughout storage. Between the two high-oleic virginia cultivars, GA11-VH had the highest concentrations of all major pyrazines as shown in Figures 3.3-3.5, which could attributed to its large kernel size. Virginia cultivars have a larger kernel size, which are typically classified as more mature (Rucker et al., 1994; Sanders et al., 1989). Determination of maturity of peanuts is often done by color measurements (L (lightness)-value), with lower L-values corresponding to a more mature peanut. Previous research done on the cultivars used in the present study found that GA11-VH had the lowest Hunter L-values for color measurements, suggesting it was more mature than other cultivars and may have more roasted flavor which explains this cultivar's high concentrations of pyrazines (Campbell, 2021). Overall, most roasted flavor volatiles or Maillard products were detected lowest in the normal-oleic virginia cultivars. The results further

demonstrate that oleic status may be a good indicator of how volatiles may behave during storage, irrespective of type. The ANOVA results (Table 3.3) revealed that most volatiles compounds caused a significant effect on the interaction of cultivar and time, suggesting that the relationship between volatile compound and cultivar differs depending on the time point or vice versa. Mean concentrations of volatiles were statistically different when comparing cultivars within each week, exhibiting no consistent trends (Tables 3.4-3.10). Comparing each week within individual cultivars revealed that mean concentrations were statistically significant as observable trends of increasing concentration occurred from week 0 to week 40 for Maillard products, even those cultivars with oxidation products present. The data does suggest that the presence of oxidation products in normal-oleic cultivars, irrespective of type, did not affect the concentrations of their roasted flavor volatiles.

The shelf-life of a typical normal-oleic peanut is two to three months at room temperature, whereas high-oleic peanuts have been reported to have twice that shelf-life (Braddock & Sims, 1995). The main mode of failure to determine peanut shelf-life is sensory analysis typically coupled with analytical methods such as GC-MS. Previous research has shown that off-flavors due to oxidation products in roasted peanuts are detected at concentrations as low as 6 ppb and that can increase to 7400 ppb in which levels are considered unacceptable by sensory panels (Brown et al., 1973; Grosso & Resurreccion., 2006; Schirack et al., 2006; Williams et al., 2006). Although the concentrations of the oxidation products (hexanal, 1-octen-3-ol) fall within the reported range, the off-flavors typically emitted from them would likely be overshadowed due to the high concentrations of Maillard products that are responsible for the typical roasted flavor of peanuts, further suggesting that flavor-fade did not occur in the peanut cultivars throughout storage.

High-Oleic vs Normal-Oleic

Runner Cultivars

Key roasted aroma volatiles detected in the roasted peanuts were present at similar concentrations in all runner cultivars irrespective of oleic status. As previously stated, oxidation products, hexanal and 1-octen-3-ol, were only detected in the normal-oleic cultivars throughout storage (GA06-RN, Tif-RN).

Throughout storage, most Maillard-derived volatiles were present in abundant amounts whereas most lipid-derived volatiles were absent, or only detected in trace amounts. Similar results were reported by Ha, Seo, Chen, Hwang, and Shim (2011), that found hexanal concentrations to be low in various vegetable oils kept at room temperature (25°C) as compared to oils kept at the higher temperatures of 80 and 105°C. In general, normal-oleic cultivars were the only oxidized samples amongst runners. Most major roasted flavor volatiles (2,5-dimethylpyrazine and 3-ethyl-2,5-dimethylpyrazine, benzaldehyde, benzacetaldehyde) were abundantly present in all runner cultivars but the highest levels were detected in the high-oleic cultivar AU17-RH and normal-oleic cultivar GA06-RN throughout storage (Figures 3.3, 3.5, 3.6, and 3.7). Irrespective of oleic status, all runner cultivars were able to resist flavor-fade during 40 weeks of storage. The volatile compound data for GA06-RN differed in the present study from what has been previously reported for this cultivar's behavior during storage. Wang et al. (2017b) found that GA06-RN experienced the lowest concentrations of pyrazines and was more oxidized than its high-oleic counterparts during 8 weeks of storage at room temperature (21°C). But the data in the present study further suggest why GA06-RN may be the current top choice for runner production (University of Georgia, 2022), given it was the only normal-oleic cultivar

to maintain such high levels of the major Maillard products compared to some of the high-oleic cultivars, despite the presence of oxidation products in the cultivar.

Virginia Cultivars

The aroma volatile results of the virginia cultivars reflected what was observed in the runner cultivars. Key pyrazines remained stable in all virginia cultivars, irrespective of oleic status. The lipid oxidation indicator, hexanal, was only detected in the normal-oleic cultivars throughout storage (Bail-VN, Greg-VN). Similarly, 1-octen-3-ol was also only detected in the normal-oleic virginia cultivars.

There was no significant decrease in pyrazines or other Maillard products in any of the virginia cultivars throughout storage, indicating a lack of flavor-fade by flavor entrapment or degradation by lipid radicals. 2,5-dimethyl pyrazine, 2-ethyl-5-methylpyrazine, and 3-ethyl-2,5-dimethylpyrazine, all associated with the positive attributes of roasted peanuts, were detected highest in the high-oleic cultivars (Bail2-VH, GA11-VH). The benzene derivatives, benzeneacetaldehyde and benzaldehyde, were also detected highest in the high-oleic virginia cultivars. The concentrations of Maillard products remained stable throughout storage for all virginia cultivars, even those cultivars with oxidation products present.

Multiple Factor Analysis

MFA was used to determine patterns or common structures in weeks 8, 24, and 40 pertaining to the peanut cultivars and volatile compounds. The volatile compounds were grouped into four major classes: oxidation products (Oxid-Products), aromatic Maillard products (Aromatic-MP), other Maillard products (MP-Other), and pyrazines for each respective week.

The ANOVA table (Table 3.3) shows that most volatile compounds caused a significant interaction between cultivar and time, suggesting the cultivars exhibited different behavior

during storage regarding volatile compound concentrations. Tables 3.4-3.10 further showed that significant differences were exhibited by the cultivars within each week, but the MFA biplot (Figure 3.8) shows that some cultivars behaved more similar to each other in regard to the presence of certain volatile compounds. The biplot shows that the normal-oleic cultivars of both peanut types were clustered closest to the oxidation products every week, agreeing with the ANOVA plots for the major oxidation products (Figures 3.1 and 3.2). The biplot also shows the high-oleic cultivars clustered closest to the Maillard products and pyrazines. Particularly, the high-oleic virginia cultivars (GA11-VH, Bail2-VH) in which the major pyrazines were detected at the highest levels. The results of the biplot agree with previous research done on flavor-fade in peanuts, as normal-oleic cultivars are typically associated more with the presence of significant levels of oxidation products and high-oleic cultivars are associated more with stable Maillard products during storage (Braddock & Sims, 1995; Martín, Grosso, Nepote, & Grosso, 2018; Mugendi, Sims, Gorbet, & O'Keefe, 1998; Riveros et al., 2010; Wang et al., 2017b). Figure 3.8 also shows factors one and two, new variables that explain 78.6% of the variation in the data and are based on the underlying relationship between the variables (volatile compounds). The first factor explains the majority of the variation in the data (47%) and is influenced by the oxidation products, pyrazines, and other Maillard products of weeks 8, 24, and 40 based on their coordinates. The second factor explains the second most variation in the data (31.6%) and is highly influenced by the aromatic Maillard products of weeks 8, 24, 40 based on their coordinates.

A cluster analysis dendrogram (Figure 3.9) resulting from the peanut cultivar scores in the MFA analysis, shows the hierarchical relationship among the runner and virginia cultivars. High-oleic cultivars were similar in their volatile compound behavior during weeks 8, 24, and

40, whereas most normal-oleic cultivars behaved similarly. The high concentrations of pyrazines and other Maillard products in GA06-RN resulted in it being clustered with the high-oleic cultivars, despite the presence of oxidation products in this cultivar. While the significantly higher concentrations of major pyrazines in GA11-VH as shown in Figures 3.3-3.5, resulted in this cultivar's separate cluster.

Limitations of the Study

The main limitation of this study was the inability to complete sensory or descriptive analysis for consumer perception of the peanut cultivars throughout storage because of the dearth of samples. Storage parameters of light and variation in packaging material and temperature were also not considered for their possible influence on roasted peanut volatiles during storage.

Conclusion

Flavor-fade is a major challenge in the peanut industry, the phenomenon refers to a gradual loss of roasted flavor and other pleasant attributes to increased oxidized and off-flavors. A total of eight cultivars between virginia and runner-types with varying oleic statuses were used to analyze the aroma profiles and compare flavor-fade or loss of roasted flavors during 40 weeks of storage. The composition of roasted runner and virginia peanuts were nearly identical. Pyrazines such as 2,5-dimethylpyrazine, 3-ethyl-2,5-dimethylpyrazine, and 2-ethyl-5-methylpyrazine and benzene derivatives were present in higher concentrations and more stable in the high-oleic cultivars after extended storage. Overall, virginia-type was found to have a lower concentration of roasted flavor volatiles than the runner-type. The high-oleic cultivars, particularly AU17-RH, GA13-RH, Bail2-VH, and GA11-VH exhibited similar flavor profiles and pose the best potential to extend the shelf-lives of peanuts and benefit the peanut industry.

Oxidation products were primarily detected in the normal-oleic cultivars irrespective of type. The lack of oxidation-derived volatile detection in high-oleic cultivars may be a result of their higher oleic acid (a monounsaturated fatty acid) content, therefore causing them to oxidize at a slower rate. The present study further proves that in general, high-oleic cultivars have better oxidative stability and shelf lives than their counterparts. Overall, after 40 weeks of storage all roasted peanuts irrespective of type or oleic status, exhibited a lack of flavor-fade given the increased concentrations of roasted flavor volatiles and low presence or absence of oxidation volatiles. The data suggest that 40 weeks may not have been enough time to observe significant changes in the volatile behavior of the peanuts during storage.

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Table 3.1. Roasted peanut cultivar profiles

Type	Cultivar	Oleic status	Abbreviation
Virginia	Gregory	Normal	Greg-VN
Virginia	Bailey	Normal	Bail-VN
Virginia	Bailey II	High	Bail2-VH
Virginia	Georgia 11J	High	GA11-VH
Runner	Tifguard	Normal	Tif-RN
Runner	Georgia 06G	Normal	GA06-RN
Runner	Georgia 13M	High	GA13-RH
Runner	AU NPL 17	High	AU17-RH

Table 3.2. Volatile Compounds identified in roasted peanut cultivars

Compound	Base Peak (m/z ± 0.5 amu)	Experimental LRI	Literature LRI
Oxidation products			
Hexanal	44	802	802 (Lozano et al., 2007)
2-Heptanone	43	891	900 (Lozano, Drake, et al., 2007)
Heptanal	70	903	899 (Pino et al., 2005)
1-Octen-3-ol	57	980	992 (Lozano, Drake, et al., 2007)
2-Phenyl-2-butenal	117	1239	1268 (Kim & Chung, 2009)
Pyrazines			
2,5-Dimethylpyrazine	42	910	911 (Pino et al., 2005)
2-Ethyl-5-methylpyrazine	43	999	1004 (Radulović et al., 2010)
Trimethyl pyrazine	42	1001	1005 (Radulović et al., 2010)
3-Ethyl-2,5-dimethylpyrazine	135	1082	1078 (Xie, Sun, Zheng, & Wang, 2008)
2-Ethyl-3,5-dimethylpyrazine	135	1088	1095 (Schirack et al., 2006)
3,5-Diethyl-2-methylpyrazine	149	1160	1166 (Parker et al., 2000)
2,5-Dimethyl-3-isobutylpyrazine	122	1200	1208 (Fadel et al., 2006)
Aromatic Maillard products			
Benzaldehyde	77	955	958 (Xie et al., 2008)
Benzeneacetaldehyde	91	1046	1047 (Radulović et al., 2010)
Acetophenone	105	1070	1076 (Methven et al., 2007)
4-Vinylguaiacol	135	1260	1320 (Fadel et al., 2008)
Other Maillard products			
1-Methyl-1H-Pyrrole	81	731	732 (Harrison & Priest, 2009)
Furfural	96	833	830 (Pino et al., 2005)
Dimethyl trisulfide	126	961	963 (Lozano, Drake, et al., 2007)
2-Pentylfuran	81	990	992 (Pino et al., 2005)
2-Pentylpyridine	93	1196	1203 (Cadwallader & Heo, 2001)
2,3-Dihydrobenzofuran	120	1212	1219 (Miyazawa et al., 2011)

Table 3.3. ANOVA results showing the main effects on the interaction of cultivar and time

	Effect		
Volatile Compounds	**Cultivar**	**Time**	**Cultivar × Time**
1-Methyl-1H-Pyrrole	***	***	NS
Hexanal	***	***	***
Furfural	***	***	NS
2-Heptanone	***	***	***
Heptanal	***	***	***
2,5-Dimethylpyrazine	***	***	NS
Benzaldehyde	***	***	***
Dimethyl trisulfide	***	***	***
1-Octen-3-ol	***	***	***
2-Pentylfuran	***	***	***
2-Ethyl-5-methylpyrazine	***	***	*
Trimethyl pyrazine	***	***	***
Benzeneacetaldehyde	***	***	***
Acetophenone	***	***	***
3-Ethyl-2,5-dimethylpyrazine	***	***	***
2-Ethyl-3,5-dimethylpyrazine	NS	NS	NS
3,5-Diethyl-2-methylpyrazine	***	***	***
2-Pentylpyridine	***	***	***
2,5-Dimethyl-3-isobutylpyrazine	***	***	***
2,3-Dihydrobenzofuran	***	***	***
2-Phenyl-2-butenal	***	***	***
4-Vinylguaiacol	***	***	***

*, **, *** Tests of the effects are significant at ($P \leq 0.05$), ($P \leq 0.01$), ($P \leq 0.001$) respectively, NS = Not significant.

Table 3.4. Changes in hexanal content (μg/kg[1]) in the peanut cultivars during storage

			Storage Time in Weeks					
Cultivar	**Type**	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Bailey	Virginia	Normal	$^{yz}27^{ab}$	$^{x}112^{ab}$	$^{xy}66^{cd}$	$^{yz}20^{ab}$	0^{b}	0^{b}
Gregory	Virginia	Normal	$^{z}24^{ab}$	$^{y}97^{bc}$	$^{z}19^{cd}$	$^{z}38^{ab}$	0^{b}	0^{b}
Bailey II	Virginia	High	0^{b}	0^{d}	0^{d}	0^{b}	0^{b}	0^{b}
Georgia 11J	Virginia	High	0^{b}	0^{d}	0^{d}	0^{b}	0^{b}	0^{b}
Georgia 06G	Runner	Normal	$^{yz}65^{a}$	$^{z}61^{c}$	$^{yz}79^{ab}$	$^{z}63^{a}$	$^{y}113^{a}$	0^{b}
Tifguard	Runner	Normal	$^{yz}53^{a}$	$^{w}155^{a}$	$^{wx}124^{a}$	$^{z}35^{ab}$	$^{xy}86^{a}$	$^{wx}122^{a}$
AU-NPL 17	Runner	High	0^{b}	0^{d}	0^{d}	0^{b}	0^{b}	0^{b}
Georgia 13M	Runner	High	0^{b}	0^{d}	0^{d}	0^{b}	0^{b}	0^{b}

[a-d] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)

[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)

[1] Calculated based on the internal standard (1,3-dichloro benzene)

Table 3.5. Changes in 1-octen-3-ol content (μg/kg[1]) in the peanut cultivars during storage

			Storage Time in Weeks					
Cultivar	**Type**	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Bailey	Virginia	Normal	$^{z}16^{a}$	$^{y}31^{a}$	$^{y}28^{ab}$	$^{yz}25^{bc}$	$^{x}46^{c}$	$^{x}50^{b}$
Gregory	Virginia	Normal	$^{z}18^{a}$	$^{xy}35^{a}$	$^{z}24^{b}$	$^{x-z}27^{bc}$	$^{x}37^{c}$	$^{w}53^{b}$
Bailey II	Virginia	High	0^{b}	0^{b}	0^{c}	0^{d}	0^{d}	0^{c}
Georgia 11J	Virginia	High	0^{b}	0^{b}	0^{c}	0^{d}	0^{d}	0^{c}
Georgia 06G	Runner	Normal	$^{z}0^{b}$	$^{y}31^{a}$	$^{y}34^{ab}$	$^{x}47^{a}$	$^{w}78^{b}$	$^{v}95^{a}$
Tifguard	Runner	Normal	$^{z}0^{b}$	$^{y}29^{a}$	$^{y}35^{a}$	$^{y}29^{d}$	$^{w}98^{a}$	$^{x}85^{a}$
AU-NPL 17	Runner	High	0^{b}	0^{b}	0^{c}	0^{d}	0^{d}	0^{c}
Georgia 13M	Runner	High	0^{b}	0^{b}	0^{c}	0^{d}	0^{d}	0^{c}

[a-d] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)

[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)

[1] Calculated based on the internal standard (1,3-dichloro benzene)

Table 3.6. Changes in 2,5-dimethyl pyrazine content (μg/kg[1]) in the peanut cultivars during storage

			Storage Time in Weeks					
Cultivar	**Type**	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Bailey	Virginia	Normal	$^{z}231^{c}$	$^{yz}417^{bc}$	$^{yz}540^{b}$	$^{yz}599^{b}$	$^{yz}474^{d}$	$^{y}692^{c}$
Gregory	Virginia	Normal	$^{z}177^{c}$	$^{yz}470^{bc}$	$^{yz}434^{b}$	$^{yz}539^{b}$	$^{yz}485^{d}$	$^{y}619^{c}$
Bailey II	Virginia	High	$^{z}504^{abc}$	$^{z}706^{b}$	$^{z}757^{ab}$	$^{z}767^{b}$	$^{y}1242^{ab}$	$^{y}1219^{b}$
Georgia 11J	Virginia	High	$^{z}685^{a}$	$^{y}1237^{a}$	$^{y}1117^{a}$	$^{y}1347^{a}$	$^{y}1466^{a}$	$^{x}1938^{a}$
Georgia 06G	Runner	Normal	$^{z}624^{ab}$	$^{z}489^{bc}$	$^{z}812^{ab}$	$^{z}628^{b}$	$^{y}1211^{ab}$	$^{y}1227^{b}$
Tifguard	Runner	Normal	$^{z}202^{c}$	$^{z}257^{c}$	$^{yz}487^{b}$	$^{yz}440^{b}$	$^{y}807^{cd}$	$^{y}803^{c}$
AU-NPL 17	Runner	High	$^{z}618^{ab}$	$^{z}538^{bc}$	$^{z}657^{b}$	$^{yz}699^{b}$	$^{xy}1039^{bc}$	$^{x}1245^{b}$
Georgia 13M	Runner	High	$^{z}460^{abc}$	$^{z}492^{bc}$	$^{z}442^{b}$	$^{yz}656^{b}$	$^{x}1171^{abc}$	$^{xy}975^{bc}$

[a-d] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)

[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)

[1] Calculated based on the internal standard (1,3-dichloro benzene)

Table 3.7. Changes in 2-ethyl-5-methyl pyrazine content (μg/kg[1]) in the peanut cultivars during storage

			Storage Time in Weeks					
Cultivar	**Type**	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Bailey	Virginia	Normal	101^{b}	206^{b}	278^{b}	238^{c}	367^{d}	265^{d}
Gregory	Virginia	Normal	$^{z}82^{b}$	$^{z}184^{b}$	$^{yz}293^{b}$	$^{yz}296^{bc}$	$^{yz}450^{d}$	$^{y}630^{cd}$
Bailey II	Virginia	High	$^{z}329^{ab}$	$^{z}418^{b}$	$^{z}515^{ab}$	$^{z}386^{bc}$	$^{y}1179^{b}$	$^{y}1090^{b}$
Georgia 11J	Virginia	High	$^{z}537^{a}$	$^{x}1082^{a}$	$^{xyz}780^{a}$	$^{xy}968^{a}$	$^{w}1589^{a}$	$^{w}1867^{a}$
Georgia 06G	Runner	Normal	$^{z}339^{ab}$	$^{z}304^{b}$	$^{z}398^{b}$	$^{z}459^{bc}$	$^{y}941^{bc}$	$^{y}832^{bc}$
Tifguard	Runner	Normal	$^{z}128^{b}$	$^{z}141^{b}$	$^{yz}377^{b}$	$^{z}273^{bc}$	$^{xy}716^{cd}$	$^{x}810^{bc}$
AU-NPL 17	Runner	High	347^{ab}	332^{b}	402^{b}	623^{ab}	566^{d}	622^{cd}
Georgia 13M	Runner	High	$^{z}237^{ab}$	$^{z}295^{b}$	$^{z}261^{b}$	$^{yz}479^{bc}$	$^{y}827^{bc}$	$^{y}683^{c}$

[a-d] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)

[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)

[1] Calculated based on the internal standard (1,3-dichloro benzene)

Table 3.8. Changes in 3-ethyl-2,5-dimethyl pyrazine content (μg/kg[1]) in the peanut cultivars during storage

			Storage Time in Weeks					
Cultivar	**Type**	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Bailey	Virginia	Normal	$^{z}91^{b}$	$^{z}181^{bc}$	$^{z}231^{c}$	$^{yz}281^{bc}$	$^{xy}443^{cd}$	$^{x}562^{cd}$
Gregory	Virginia	Normal	$^{z}59^{b}$	$^{yz}164^{bc}$	$^{yz}216^{c}$	$^{xyz}228^{bc}$	$^{xy}316^{d}$	$^{x}428^{d}$
Bailey II	Virginia	High	$^{z}213^{ab}$	$^{xy}337^{b}$	$^{y}457^{b}$	$^{xy}393^{bc}$	$^{x}909^{b}$	$^{x}1067^{b}$
Georgia 11J	Virginia	High	$^{z}352^{a}$	$^{y}749^{a}$	$^{y}697^{a}$	$^{y}829^{a}$	$^{x}1380^{a}$	$^{w}1627^{a}$
Georgia 06G	Runner	Normal	$^{z}175^{ab}$	$^{z}203^{bc}$	$^{z}271^{bc}$	$^{z}363^{bc}$	$^{y}636^{c}$	$^{y}714^{c}$
Tifguard	Runner	Normal	$^{z}76^{b}$	$^{z}123^{c}$	$^{z}212^{c}$	$^{z}190^{c}$	$^{y}465^{cd}$	$^{y}573^{cd}$
AU-NPL 17	Runner	High	$^{z}210^{ab}$	$^{yz}224^{bc}$	$^{yz}270^{bc}$	$^{y}429^{b}$	$^{x}647^{c}$	$^{x}705^{c}$
Georgia 13M	Runner	High	$^{z}119^{b}$	$^{yz}193^{bc}$	$^{yz}164^{c}$	$^{xy}350^{bc}$	$^{w}640^{c}$	$^{wx}558^{cd}$

[a-d] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)

[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)

[1] Calculated based on the internal standard (1,3-dichloro benzene)

Table 3.9. Changes in benzaldehyde content (μg/kg[1]) in the peanut cultivars during storage

			Storage Time in Weeks					
Cultivar	**Type**	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Bailey	Virginia	Normal	$^{z}103^{d}$	$^{yz}261^{cd}$	$^{xy}347^{cd}$	$^{xyz}306^{d}$	$^{xy}461^{cd}$	$^{x}479^{f}$
Gregory	Virginia	Normal	$^{z}98^{d}$	$^{xyz}293^{cd}$	$^{xyz}251^{d}$	$^{xyz}303^{d}$	$^{xy}340^{d}$	$^{x}447^{f}$
Bailey II	Virginia	High	$^{z}194^{cd}$	$^{z}360^{bcd}$	$^{z}383^{cd}$	$^{z}328^{d}$	$^{x}653^{bc}$	$^{xy}590^{ef}$
Georgia 11J	Virginia	High	$^{z}206^{cd}$	$^{xy}464^{abc}$	$^{xyz}415^{cd}$	$^{x}604^{c}$	$^{vw}823^{b}$	$^{v}904^{cd}$
Georgia 06G	Runner	Normal	$^{z}511^{ab}$	$^{z}550^{ab}$	$^{z}692^{a}$	$^{y}921^{ab}$	$^{wx}1238^{a}$	$^{w}1398^{a}$
Tifguard	Runner	Normal	$^{z}107^{d}$	$^{z}196^{d}$	$^{z}311^{cd}$	$^{z}236^{d}$	$^{xy}692^{b}$	$^{x}727^{de}$
AU-NPL 17	Runner	High	$^{z}573^{a}$	$^{z}555^{ab}$	$^{z}655^{ab}$	$^{xy}885^{ab}$	$^{wx}1096^{a}$	$^{w}1126^{b}$
Georgia 13M	Runner	High	$^{z}393^{abc}$	$^{y}641^{a}$	$^{yz}522^{abc}$	$^{wx}984^{a}$	$^{w}1168^{a}$	$^{x}943^{bc}$

[a-f] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)

[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)

[1] Calculated based on the internal standard (1,3-dichloro benzene)

Table 3.10. Changes in benzeneacetaldehyde content (μg/kg[1]) in the peanut cultivars during storage

			Storage Time in Weeks					
Cultivar	**Type**	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Bailey	Virginia	Normal	341^{ef}	526^{de}	661^{c}	437^{cd}	436^{e}	391^{e}
Gregory	Virginia	Normal	302^{f}	612^{de}	473^{c}	430^{cd}	397^{e}	439^{de}
Bailey II	Virginia	High	$^{z}764^{de}$	$^{yz}817^{d}$	$^{z}648^{c}$	$^{z}444^{cd}$	$^{y}1207^{d}$	$^{z}670^{cde}$
Georgia 11J	Virginia	High	$^{yz}900^{d}$	$^{z}642^{de}$	$^{z}591^{c}$	$^{z}749^{c}$	$^{y}1229^{d}$	$^{yz}861^{cd}$
Georgia 06G	Runner	Normal	$^{w}2970^{b}$	$^{z}1245^{abc}$	$^{z}1347^{a}$	$^{x}1943^{ab}$	$^{xy}1888^{abc}$	$^{yz}1504^{ab}$
Tifguard	Runner	Normal	301^{f}	291^{e}	408^{c}	243^{d}	540^{e}	439^{de}
AU-NPL 17	Runner	High	$^{w}3803^{a}$	$^{z}1464^{ab}$	$^{z}1417^{a}$	$^{x}1936^{ab}$	$^{zy}1918^{ab}$	$^{xyz}1758^{a}$
Georgia 13M	Runner	High	$^{w}2525^{c}$	$^{y}1646^{a}$	$^{z}1114^{ab}$	$^{wx}2213^{a}$	$^{xy}2047^{a}$	$^{z}1081^{bc}$

[a-f] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)
[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)
[1] Calculated based on the internal standard (1,3-dichloro benzene)

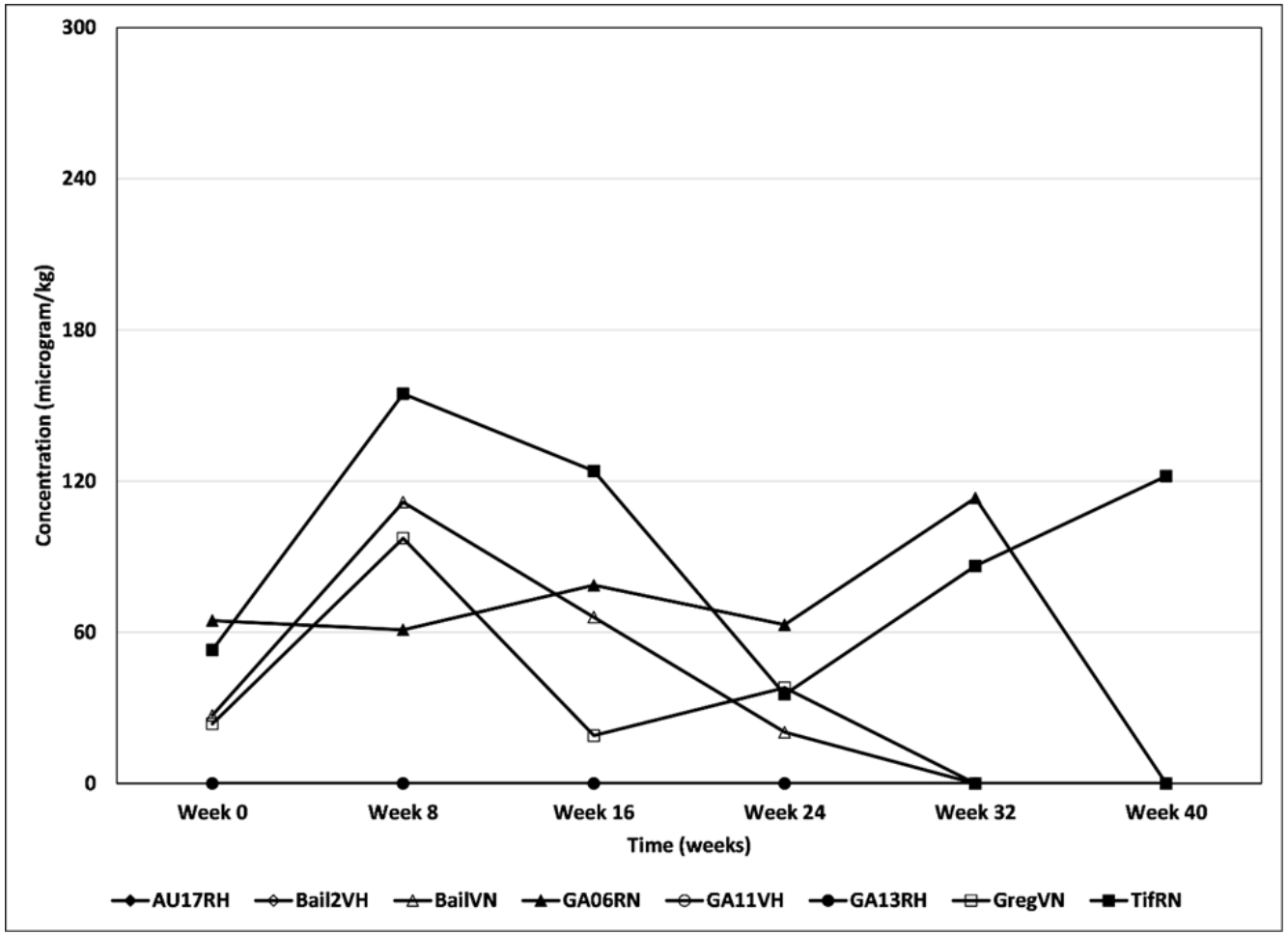

Figure 3.1. Hexanal of roasted peanut cultivars[1] at different storage times.

[1] AU17-RH = AU-NPL 17 runner [HO], Bail2-VH = Bailey II virginia [HO], Bail-VN = Bailey virginia [NO], GA06-RN = Georgia 06G runner [NO], GA11-VH = Georgia 11J virginia [HO], GA13-RH = Georgia 13M runner [HO], Greg-VN = Gregory virginia [NO], Tif-RN = Tifguard runner [NO]

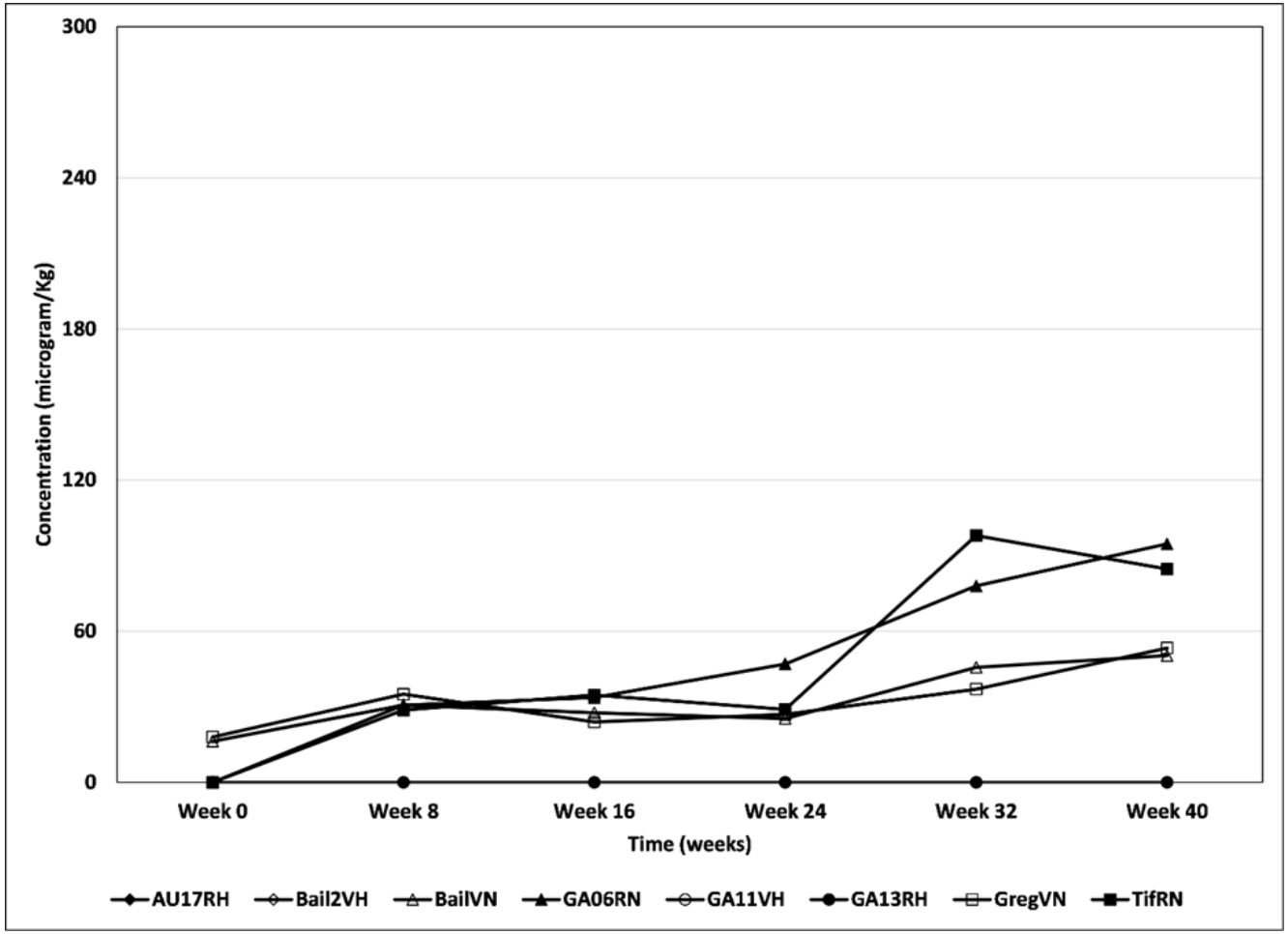

Figure 3.2. 1-Octen-3-ol of roasted peanut cultivars[1] at different storage times.

[1] AU17-RH = AU-NPL 17 runner [HO], Bail2-VH = Bailey II virginia [HO], Bail-VN = Bailey virginia [NO], GA06-RN = Georgia 06G runner [NO], GA11-VH = Georgia 11J virginia [HO], GA13-RH = Georgia 13M runner [HO], Greg-VN = Gregory virginia [NO], Tif-RN = Tifguard runner [NO]

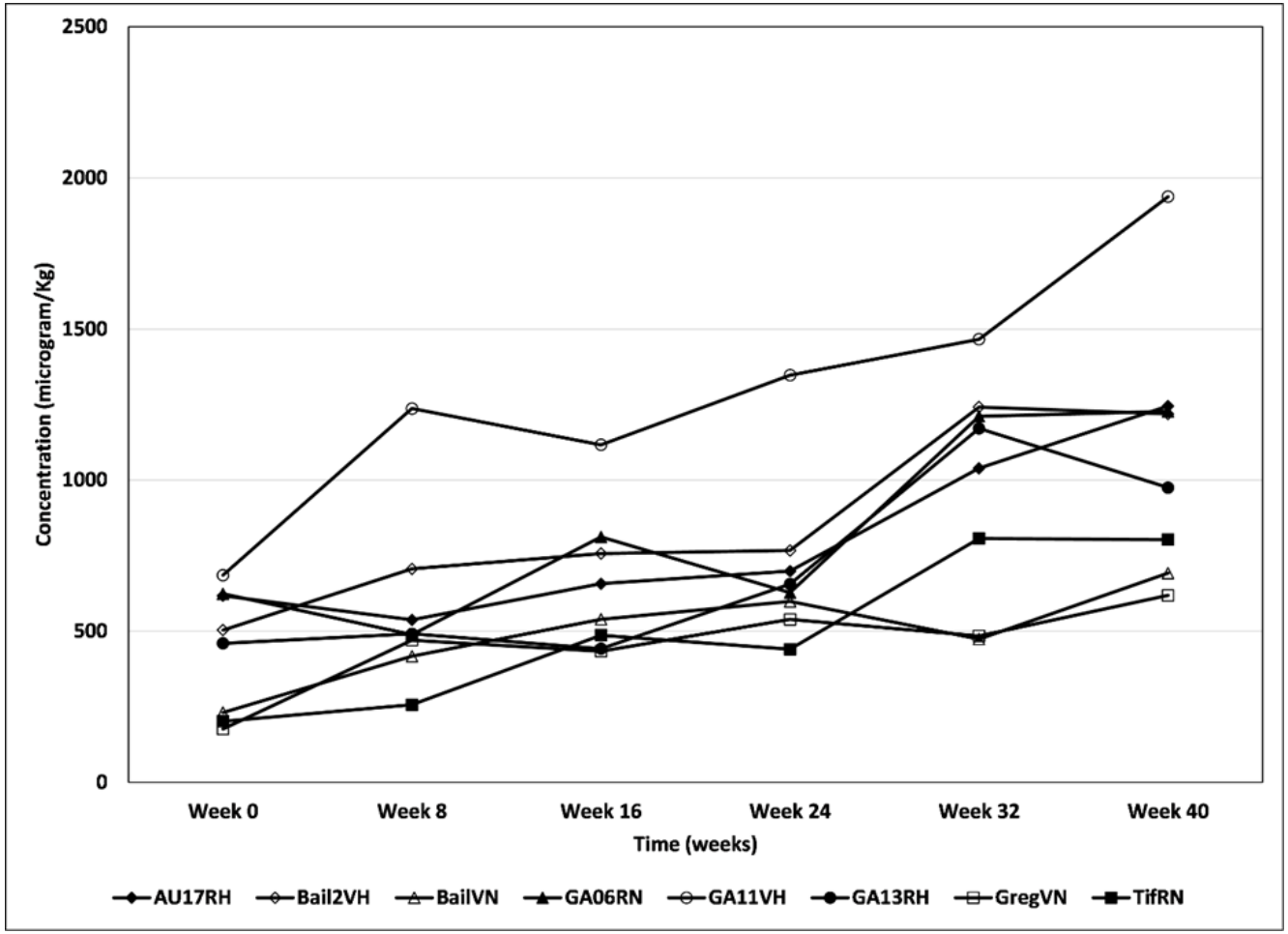

Figure 3.3. 2,5-Dimethylpyrazine of roasted peanut cultivars[1] at different storage times.

[1] AU17-RH = AU-NPL 17 runner [HO], Bail2-VH = Bailey II virginia [HO], Bail-VN = Bailey virginia [NO], GA06-RN = Georgia 06G runner [NO], GA11-VH = Georgia 11J virginia [HO], GA13-RH = Georgia 13M runner [HO], Greg-VN = Gregory virginia [NO], Tif-RN = Tifguard runner [NO]

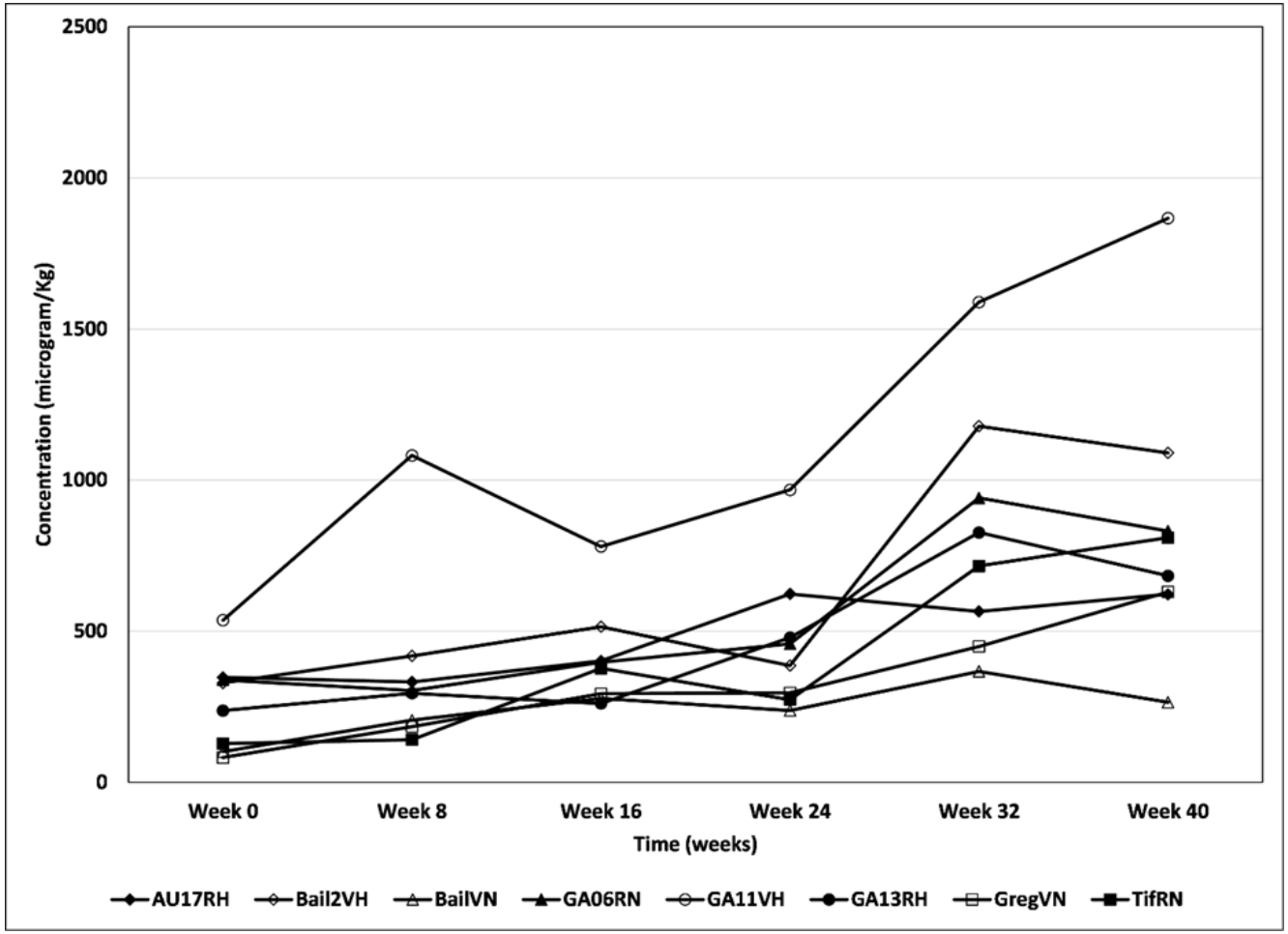

Figure 3.4. 2-Ethyl-5-methylpyrazine of roasted peanut cultivars[1] at different storage times.

[1] AU17-RH = AU-NPL 17 runner [HO], Bail2-VH = Bailey II virginia [HO], Bail-VN = Bailey virginia [NO], GA06-RN = Georgia 06G runner [NO], GA11-VH = Georgia 11J virginia [HO], GA13-RH = Georgia 13M runner [HO], Greg-VN = Gregory virginia [NO], Tif-RN = Tifguard runner [NO]

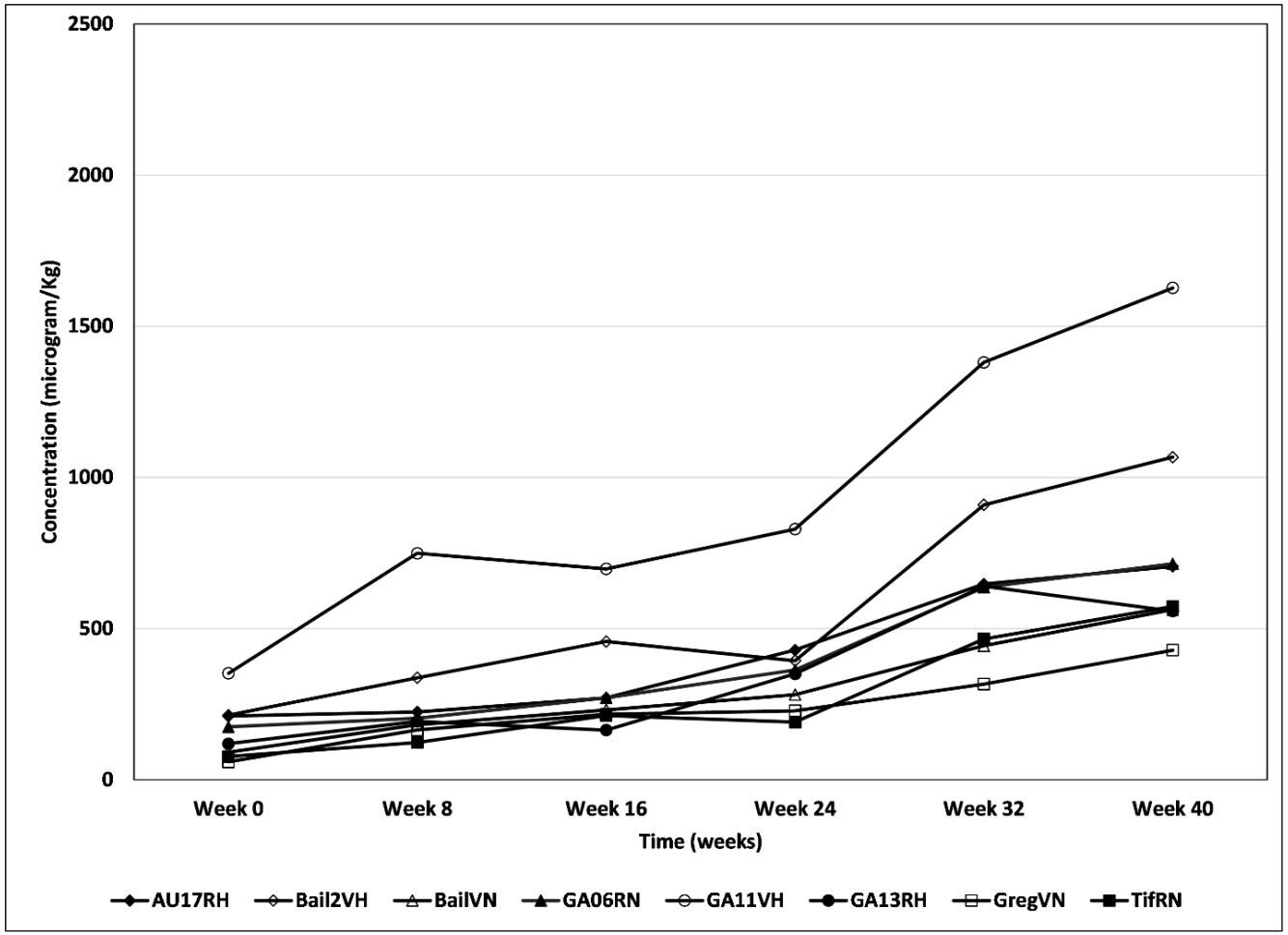

Figure 3.5. 3-Ethyl-2,5-dimethylpyrazine of roasted peanut cultivars[1] at different storage times.

[1] AU17-RH = AU-NPL 17 runner [HO], Bail2-VH = Bailey II virginia [HO], Bail-VN = Bailey virginia [NO], GA06-RN = Georgia 06G runner [NO], GA11-VH = Georgia 11J virginia [HO], GA13-RH = Georgia 13M runner [HO], Greg-VN = Gregory virginia [NO], Tif-RN = Tifguard runner [NO]

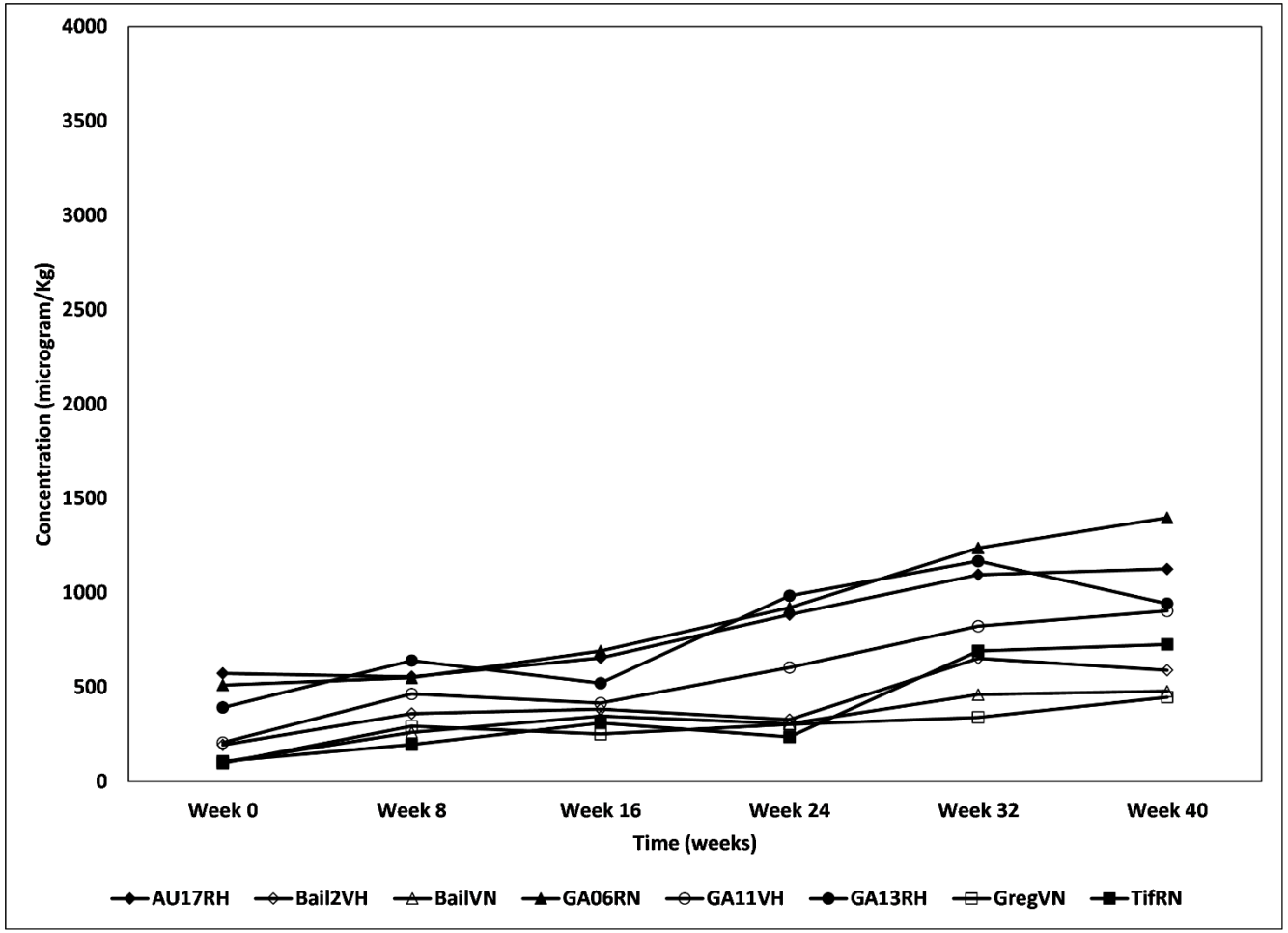

Figure 3.6. Benzaldehyde of roasted peanut cultivars[1] at different storage times.

[1] AU17-RH = AU-NPL 17 runner [HO], Bail2-VH = Bailey II virginia [HO], Bail-VN = Bailey virginia [NO], GA06-RN = Georgia 06G runner [NO], GA11-VH = Georgia 11J virginia [HO], GA13-RH = Georgia 13M runner [HO], Greg-VN = Gregory virginia [NO], Tif-RN = Tifguard runner [NO]

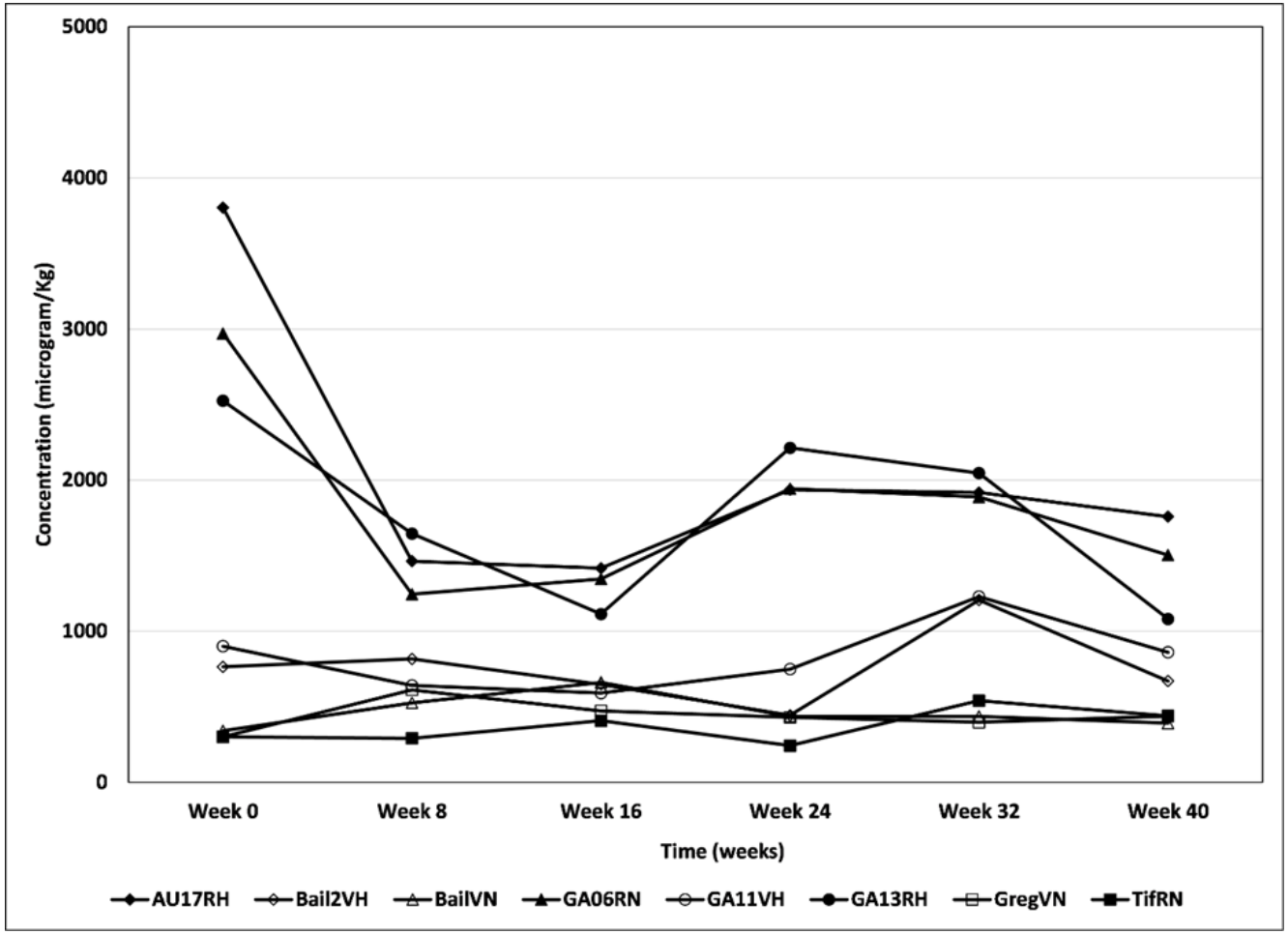

Figure 3.7. Benzeneacetaldehyde of roasted peanut cultivars[1] at different storage times.

[1] AU17-RH = AU-NPL 17 runner [HO], Bail2-VH = Bailey II virginia [HO], Bail-VN = Bailey virginia [NO], GA06-RN = Georgia 06G runner [NO], GA11-VH = Georgia 11J virginia [HO], GA13-RH = Georgia 13M runner [HO], Greg-VN = Gregory virginia [NO], Tif-RN = Tifguard runner [NO]

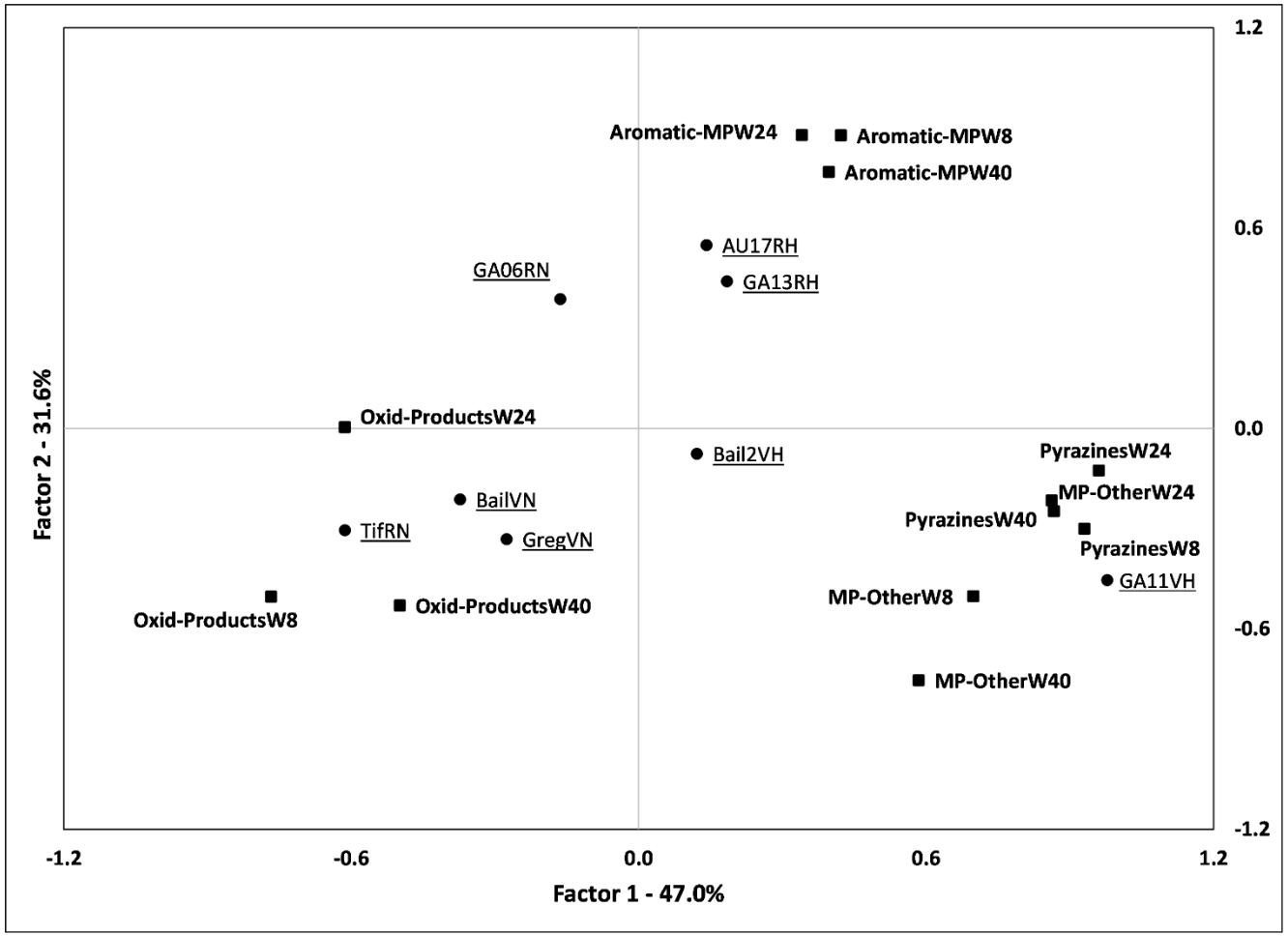

Figure 3.8. MFA biplot of peanut cultivars and roasted volatile compounds[1] for weeks 8, 24, and 40

[1]Oxid-Products = Oxidation products, Aromatic-MP = Aromatic Maillard Products, MP-Other = Other Maillard Products, GA06RN = Georgia 06G runner [NO], TifRN = Tifguard runner [NO], AU17RH = AU NPL 17 runner [HO], GA13RH = Georgia 13M runner [HO], BailVN = Bailey virginia [NO], GregVN = Gregory virginia [NO], Bail2VH = Bailey II virginia [HO], GA11VH = Georgia 11J virginia [HO]

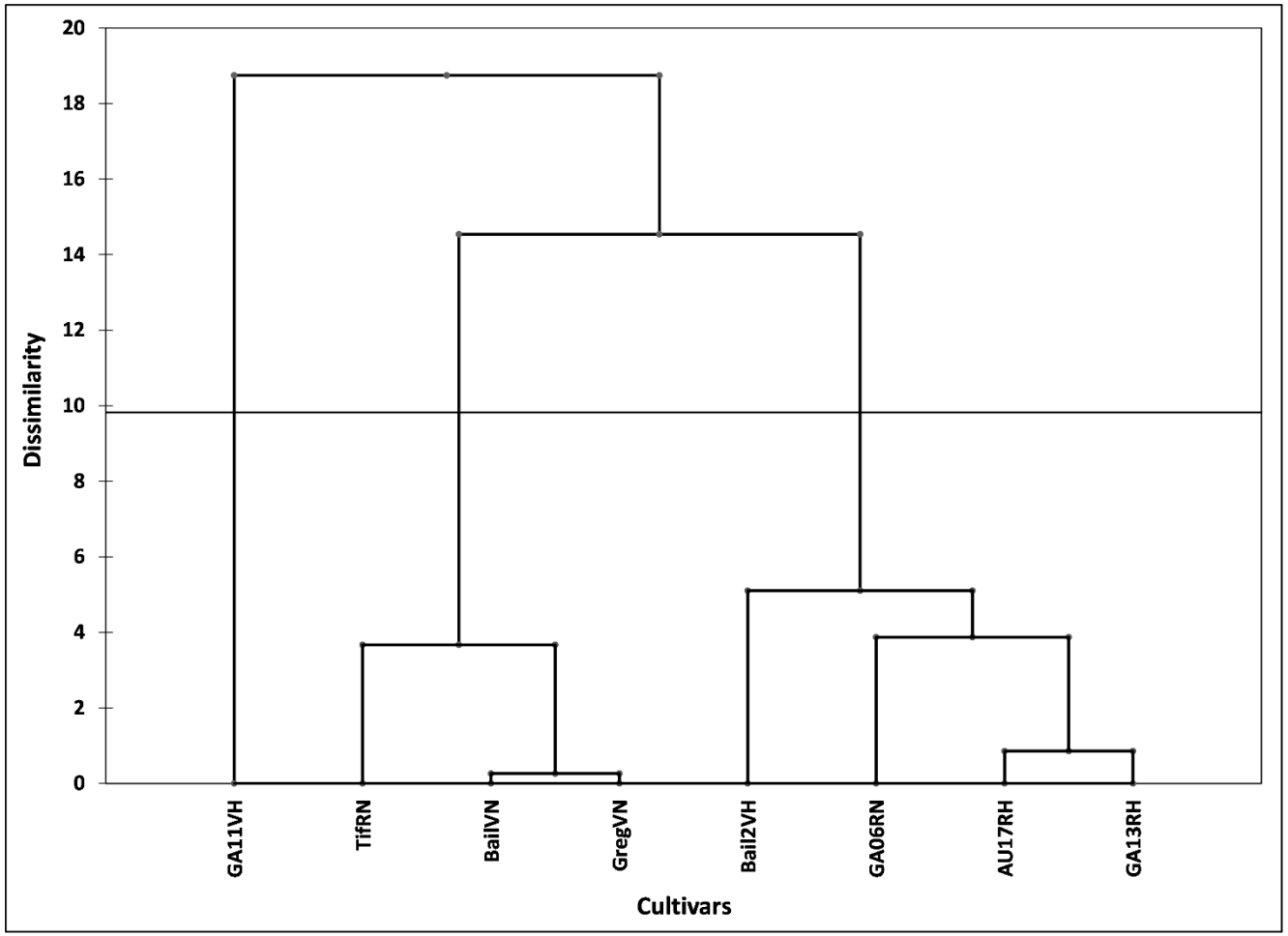

Figure 3.9. Dendrogram of roasted peanut cultivars[1]

[1] GA11VH = Georgia 11J virginia [HO], TifRN = Tifguard runner [NO], BailVN = Bailey virginia [NO], GregVN = Gregory virginia [NO], Bail2VH = Bailey II virginia [HO], GA06RN = Georgia 06G runner [NO], AU17RH = AU-NPL 17 runner [HO], GA13RH = Georgia 13M runner [HO]

CHAPTER 4

A COMPARATIVE STUDY OF FLAVOR-FADE IN HIGH AND NORMAL-OLEIC RUNNER PEANUTS

Stoner-Harris, T., Adhikari, K. To be submitted to *Journal of Food Science*.

Abstract

The main objective of this study was to compare the loss of roasted aroma or flavor-fade during storage of high-oleic runner peanut varieties compared to the normal-oleic runner cultivar, Georgia 06G. Twelve runner cultivars were stored at room temperature (~23 °C) for 40 weeks and analyzed at weeks 8, 16, 24, 32, and 40. Aroma volatiles from the roasted peanuts were identified and quantified using gas chromatography-mass spectrometry (GC-MS) analysis. Twenty-one aroma volatiles were detected in the roasted peanut cultivars. All runner cultivars maintained or exhibited increased concentrations of volatiles associated with roasted flavor, indicating an absence of flavor-fade throughout storage, in general. Oxidation products were primarily detected in the normal-oleic cultivars, Georgia 06G and Tifguard. Given the high-oleic cultivars' resistance to the development of oxidation products and retention of volatiles associated with roasted flavors, it can be concluded that the high-oleic cultivars fare better during storage.

Keywords: GC-MS, pyrazines, oxidation, volatiles

Introduction

Peanut (*Arachis hypogaea*), also known as the groundnut, earthnut, or goober, is a legume crop grown native to central Brazil, mainly known for its edible seeds. It is widely grown in the tropics and subtropics, mostly in the warm climates of Africa, Asia, Australia, and North and South America (National Peanut Board, 2022). World peanut production totals approximately 47 million metric tons per year as of 2020 (American Peanut Council, 2022). Worldwide peanut exports are approximately 3.6 million metric tons per year. After China, India, and Nigeria the United States is the world's fourth-largest producer, exporting 25-30% of its production (National Peanut Board, 2022). Approximately 56% of the peanuts grown in the United States were made into peanut butter in 2020. Today, peanuts have a farm value of 1 billion U.S. dollars and are the 12th most valuable cash crop grown in the United States (American Peanut Council, 2022).

The four peanut types grown in the U.S are runner, virginia, Spanish, and Valencia. Each of these peanut types has its distinctive size and unique flavor (American Peanut Council, 2022). Runners are the dominant peanut type in the U.S. making up more than 80% of the peanuts grown in the U.S. since the introduction of the variety Florunner in the early 1970s (American Peanut Council, 2022). Runners are grown mainly in Alabama, Florida, Georgia, Oklahoma, and Texas. Runners' popularity stems from their medium and uniformed kernel size, ability to produce consistently high yields, and their excellent roasting characteristics. This type is used primarily to make peanut butter. Around 1.3 million acres of runners were planted in 2020 across all 12 major peanut-producing states, and 54% of runners grown were used for the production of peanut butter (National Peanut Board, 2022).

Georgia-06G, a normal-oleic runner cultivar released in 2006, is the current top choice for runner production. Georgia-06G was found to have the highest pod yield, highest TSMK (totally sound mature kernels) grade, and highest dollar value return per acre compared to other runner-types in tests conducted from 2003 to 2005 (University of Georgia, 2022). This cultivar was also found to have the lowest disease incidence, exhibiting high resistance to spotted wilt disease caused by tomato spotted wilt virus (TSWV). Although Georgia-06G continues to be the top choice given its positive attributes, research has shown that other runner cultivars exhibit better oxidative stability and resistance to flavor-fade during storage.

High-oleic cultivars were developed to extend the shelf-life of roasted peanuts and have been shown to retain roasted peanut flavor and resist the development of off-flavors or flavor-fade better than normal-oleic peanuts during storage (Braddock & Sims, 1995; Martín, Grosso, Nepote, & Grosso, 2018; Nepote, Mestrallet, Accietto, Galizzi, & Grosso, 2006; Williams et al., 2006). Several high-oleic runner cultivars have demonstrated improvement in the storage quality of peanut and peanut products (Baker, Sims, Gorbet, Sanders, & O'Keefe, 2002; Braddock & Sims, 1995; Reed, Sims, Gorbet, & O'Keefe, 2002; The Peanut Grower, 2017). Wang, Adhikari, and Hung (2017a) found that the high-oleic runner cultivar, Georgia 13M, had more oxidative stability and better overall consumer acceptability when compared to Georgia 06G. Similar results were found in a study comparing the two cultivars over 8 weeks of storage (Wang, Adhikari, & Hung, 2017b). Therefore, further research is necessary to prove high-oleic cultivars are more capable of maintaining pyrazines for roasted flavor during storage and generating less oxidation products, so the best runner-type can be utilized for production. The objective of this study was to analyze the aroma profiles of 10 commercially available high-oleic runner peanut

cultivars during 40-weeks of storage to compare flavor-fade or loss of roasted flavors with two normal-oleic cultivars.

Materials and Methods

Peanut Cultivars

There were 12 cultivars of peanuts (Table 4.1) obtained from the National Peanut Research Laboratory (NPRL) in Dawson, GA, where they were grown in experimental fields in the same plot and time. All cultivars were planted in late April 2019 and harvested in early November 2019. The peanuts used for the present study were blanched and roasted for previous research before being placed in storage (Campbell, 2021).

Sample Preparation and Storage

The peanut cultivars were sealed and stored in separate 177 mL clear small plastic containers (Amazon, Satinoir Inc., Temara, Morocco), used to simulate transparent plastic containers and bags peanuts are sold in for retail, at room temperature (~23 °C) for a total of 40 weeks starting March 29, 2021. Lights (2515 lumens, General Electric, Boston, MA., U.S.A) were kept on in the storage space throughout the 40 weeks. Between 40-45 g of each peanut cultivar was added into five separate containers corresponding to one of the storage removal weeks. The peanuts were removed after storage of 8, 16, 24, 32, and 40 weeks and placed in a freezer (-15°C) until the samples were analyzed. To prepare the peanuts for analysis, the peanut samples (equilibrated to 21 °C) were ground into small particles using a coffee grinder (Hamilton Beach Co., Southern Pines, NC), and exactly 1.5 g of the ground peanut samples were transferred in triplicates to a 20-mL screw-cap vial fitted with a screw cap containing a polytetrafluoroethylene/silicone septum. Exactly 1.970 mL of distilled water was added with 30

µL of an internal standard, 0.02 mg/mL 1,3-dichlorobezene (Sigma-Aldrich, St. Louis, Mo., U.S.A.) solution in methanol, to the vial.

Aroma volatile analysis

Extraction of volatiles

Headspace-solid phase microextraction (HS-SPME) technique was used for the extraction and analysis of peanut volatiles. The peanut samples (equilibrated to 21 °C) were ground into small particles and exactly 1.5 g of the particles were transferred in triplicates to a 20-mL screw-cap vial fitted with a screw cap containing a polytetrafluoroethylene/silicone septum. Exactly 1.970 mL of distilled water was added with 30 µL of 0.02 mg/mL 1,3-dichlorobezene (Sigma-Aldrich, St. Louis, Mo., U.S.A.) solution (in methanol) to the vial. The vials were equilibrated for 15 min at 55 °C in an autosampler (Model GC Sampler 80, Agilent Technologies, Santa Clara, Calif., U.S.A.). The autosampler agitated the vials at 250 rpm. After equilibration, a 50/30 µm divinylbenzene/carboxen/polydimethylsiloxane SPME fiber was exposed to the sample headspace for 20 min at 55 °C**.** Immediately following the fiber exposure, the analytes were desorbed to the injection port of the gas chromatography-mass spectrometry (GC-MS) at 250 °C for 5 min in splitless mode.

Separation, identification, and semi-quantitation of the volatiles

Gas Chromatography-Mass Spectrometry (GC-MS) analysis of indicators of oxidation in the various roasted peanut types at the 5 pull dates was done. The GC-MS system (Model 7890A/5977A, Agilent Technologies) equipped with an HP-5MS column (30 m × 250 µm × 0.25 µm) was used for separating the analytes. The carrier gas was helium with a linear flow velocity of 1 mL/min. The column was maintained at an initial temperature of 35 °C for 2 min, programmed at 2 °C /min to 70 °C, and was increased at a rate of 6 °C /min to a final

temperature of 230 °C. The MS detector scanned a mass range (m/z) from 30 to 400 m/z with a scan speed of 1.562 µ/s. All data were collected in triplicate. The data for the first time point (Week 0) was obtained from previous research done on the peanuts used in the present study (Campbell, 2021).

Identification of volatile compounds was based on both the mass spectra database (NIST/EPA/NIH mass spectral library, Version 2.2, 2014) and Linear Retention Indices or LRI (Wang et al., 2017a). The indices were calculated based on the retention time of a series of n-alkanes (C7-C30) using the same GC separation protocol (Sigma-Aldrich, St. Louis, MO). The experimental values were compared with literature values to validate the results. Semi-quantification and relative concentrations for the identified compounds were reported based on the internal standard, 1,3-dichlorobenzene, area.

Statistical Analysis

The volatiles data were analyzed by a two-way (cultivars and time being the main factors) analysis of variance (ANOVA) using the Generalized Linear Models procedure in SAS (version 9.4; SAS Inst., Cary, NC, U.S.A.). Differences among cultivars within a time point and also differences due to the time points within a cultivar were separated through post-hoc mean separation using Fisher's LSD (Least Significant Difference).

The cultivar by time point data for weeks 8, 24, and 40 were subjected to Multiple Factor Analysis (MFA) to discern patterns over time. Finally, factor scores for the cultivars from the MFA were subjected to Hierarchical Cluster Analysis (HCA) to cluster the cultivars in similar groups.

Results and Discussion

A total of 21 volatile compounds were identified from roasted peanuts throughout the 40 weeks of storage. Table 4.2 lists the compounds identified, most of which were Maillard reaction derived and a small number of lipid oxidation derived volatiles.

High versus Normal-Oleic Runner Cultivars

Lipid oxidation has been shown to occur to a greater extent in normal-oleic peanuts than in high-oleic varieties when placed in storage (Nepote et al., 2006). Within the 12 runner cultivars, a relatively low concentration of alcohols, aldehydes, and ketones were detected throughout storage. Oxidation-derived volatiles, hexanal, and 1-octen-3-ol, were primarily detected in the normal-oleic cultivars (GA06-RN, Tif-RN). Both volatiles are associated with off-flavors/aromas in peanuts during storage. The volatiles that develop as a result of the Maillard reaction in peanuts are considered key compounds that contribute to roasted peanut flavor (Baker et al., 2003; Hui, 2010; Wang et al., 2017a, 2017b). An abundance of Maillard products, specifically pyrazines and benzene derivates, were detected in all runner cultivars irrespective of oleic status. Statistically significant differences in mean volatile concentrations by cultivar ($P \leq 0.001$) and time ($P \leq 0.05$) were observed in the 40 weeks of storage and all volatile compounds caused a significant interaction between cultivar and time ($P \leq 0.01$) (Table 4.3). The significant differences amongst time points and cultivars for the volatile compound mean concentrations can be found in Tables 4.4-4.10.

The headspace concentrations of the oxidation volatiles (hexanal, 1-octen-3-ol) were low, and Figures 4.1 and 4.2 show that these two oxidation products were primarily detected in the normal-oleic cultivars, GA06-RN and Tif-RN, from week 0 to 40. Previous studies done on the changes of peanut volatiles in storage have reported a significant increase of oxidation-derived

volatiles along with decreased pyrazines during storage, an indication of flavor-fade caused by possible degradation of heterocyclic compounds by lipid radicals. (Braddock & Sims, 1995; Reed et al., 2002; Wang et al., 2017b; Williams et al., 2006). However, Warner, Dimick, Ziegler, Mumma, and Hollender (1996) similarly found increasing trends in aldehyde concentration but found no significant change in pyrazine concentrations of roasted peanuts throughout storage, also an indication of flavor-fade but by a differing mechanism, aldehyde masking.

Unlike the previously mentioned studies, the pyrazines and other major Maillard products exhibited significantly increased concentrations throughout storage for all runner cultivars, while oxidation products exhibited little change indicating a lack of flavor-fade. Pyrazines are a key compound for the roasted nutty flavors and aromas of roasted peanuts. Mason, Johnson, and Hamming (1966) were the first to identify some of the pyrazines (2,5-dimethyl pyrazine, dimethyl-ethyl pyrazine, methyl-ethyl pyrazine, methyl pyrazine, and trimethyl pyrazine) to be highly correlated with roasted flavors in peanuts. 2,5-dimethyl pyrazine exhibited a significant increase for all runner cultivars throughout storage (Figure 4.1). Similarly, 2-ethyl-5-methylpyrzine and 3-ethyl-2,5-dimethylpyrazine exhibited stable or increased concentrations throughout storage across all runner cultivars, even those with low levels of oxidation products present (Figures 4.2 and 4.3). The stability of the pyrazine concentrations throughout storage suggests no degradation from lipid radicals or aldehyde masking took place.

Benzene derivatives, benzaldehyde, and benzacetaldehyde, behaved similarly to the pyrazines throughout storage (Figures 4.4 and 4.5). Stable or increased concentrations were detected at each time point across all runner cultivars for these two volatiles, both of which are known to contribute to the pleasant attributes of roasted peanuts (Braddock & Sims, 1995; Ho, Lee, & Chang, 1982; Lykomitros, Fogliano, & Capuano, 2016). Overall, pyrazines and Maillard

products were detected highest in the high-oleic cultivars from week 0 to week 40, indicating possible stability of these compounds in high-oleic cultivars if the onset of oxidation products occurred during extended storage.

A typical normal-oleic peanut has a shelf-life of two to three months at room temperature and high-oleic peanuts have been reported to last twice as long with less oxidation products and stable pyrazines (Braddock & Sims, 1995). Sensory analysis typically coupled with analytical methods such as GC-MS are the main modes of failure to determine peanut shelf-life. Off-flavors resulting from the lipid oxidation of peanuts have been reported to be detected at low concentrations such as 6 ppb up to 7400 ppb where studies report levels are considered unacceptable (Brown et al., 1973; Grosso & Resurreccion., 2006; Schirack et al., 2006; Williams et al., 2006). The high concentrations of Maillard products in the roasted peanuts throughout storage would likely overshadow any off-flavors that could be generated from the oxidation products (hexanal, 1-octen-3-ol) given their low levels in all runner cultivars irrespective of oleic-status.

Multiple Factor Analysis

MFA was performed on weeks 8, 24, and 40 data sets to analyze communalities and patterns within the 3 time periods in regard to the peanut cultivars and the detected volatile compounds. The volatile compounds were grouped into four major classes: oxidation products (Oxid-Products), aromatic Maillard products (Aromatic-MP), other Maillard products (MP-Other), and pyrazines for each respective week.

The MFA biplot (Figure 4.6) reflected the previous results of the volatile compounds in the runner cultivars. The two normal-oleic cultivars (GA06-RN, Tif-RN) were most closely clustered to the oxidation products of each week, reflecting the results shown in the ANOVA

plots (Figures 4.1 and 4.2) and mean separation tables (Tables 4.4 and 4.5) for the oxidation compounds. Between the two normal-oleic cultivars, Tif-RN was clustered closest to the oxidation products, suggesting it had the highest correlation to oxidation products throughout storage. All runner cultivars, irrespective of oleic status, were shown to be fairly high in the major Maillard products throughout storage in the ANOVA plots, but the high-oleic cultivars were most closely clustered around the Maillard products of each week opposite the oxidation products, as expected. Figure 4.6 shows factors one and two, new variables that explain the variation in the data and are based on the underlying relationship between the variables (volatile compounds). The first factor explains 37.8% of the variation in the data and is influenced by most of the Maillard products of weeks 8, 24, and 40 based on their coordinates. The second factor explains 23.4% of the variation in the data and is highly influenced by the oxidation products of weeks 8, 24, 40 based on their coordinates.

Limitations of the study

The main limitations of this study were storage parameters of light, variation in packaging material, and temperature were not considered for their possible influence on roasted peanut volatiles during storage and the lack of samples prevented the ability to complete sensory or descriptive analysis for consumer perception of the peanut cultivars throughout storage.

Conclusion

In this study, the effect of storage on runner-type volatile concentration has been investigated to compare high-oleic cultivars to normal-oleic cultivars, GA06-RN and Tif-RN. Overall, storage of 40 weeks resulted in a significant increase in Maillard-derived volatiles in all runner cultivars irrespective of oleic-status. GC-MS data identified benzene derivatives and pyrazines as the principal volatiles. In general, most runner cultivars were able to maintain stable

pyrazine and benzene derivative concentrations throughout storage. When comparing the high-oleic to normal-oleic runners, the high-oleic cultivars were able to resist the onset of oxidation-derived volatiles, whereas normal-oleic cultivars maintained stable concentrations of both hexanal and other oxidation-derived volatiles throughout storage. All volatile compounds detected throughout storage caused a significant interaction between the cultivars and time, indicating no trend in the cultivars throughout storage.

The data suggested that flavor-fade over extended storage does not always occur in roasted peanuts given the stability of the pyrazines in the present study and that 40 weeks may not be long enough for observable changes in volatile concentrations of the peanuts in the present study. Consumer or descriptive analysis would be beneficial to gain further information on the sensory qualities of the roasted peanuts. This study indicated that despite GA06-RN being the top choice for runner production, the variety of high-oleic runner cultivars in this study is possibly better options to extend roasted peanut shelf-life, given their better resistance to the development of oxidation products.

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Table 4.1. Peanut cultivar profiles

Cultivar	**Oleic status**	**Abbreviation**
Georgia 16HO	High	GA16-RH
Georgia 14N	High	GA14-RH
Tifguard	Normal	Tif-RN
Florida-07	High	FL07-RH
Flo-Run 331	High	Flo331-RH
TufRunner 511	High	Tuf511-RH
TufRunner 727	High	Tuf727-RH
Georgia 13M	High	GA13-RH
TufRunner 297	High	Tuf297-RH
Georgia 06G	Normal	GA06-RN
AU NPL 17	High	AU17-RH
TifNV	High	TifNV-RH

Table 4.2. Volatile Compounds identified in roasted peanut cultivars

Compound	Base Peak (m/z ± 0.5 amu)	Experimental LRI	Literature LRI
Oxidation products			
Hexanal	44	802	802 (Lozano et al., 2007)
Heptanal	70	903	899 (Pino et al., 2005)
1-Octen-3-ol	57	980	992 (Lozano, Drake, et al., 2007)
2-Phenyl-2-butenal	117	1239	1268 (Kim & Chung, 2009)
Pyrazines			
2,5-Dimethylpyrazine	42	910	911 (Pino et al., 2005)
2-Ethyl-5-methylpyrazine	43	999	1004 (Radulović et al., 2010)
Trimethyl pyrazine	42	1001	1005 (Radulović et al., 2010)
3-Ethyl-2,5-dimethylpyrazine	135	1082	1078 (Xie, Sun, Zheng, & Wang, 2008)
2-Ethyl-3,5-dimethylpyrazine	135	1088	1095 (Schirack et al., 2006)
3,5-Diethyl-2-methylpyrazine	149	1160	1166 (Parker et al., 2000)
2,5-Dimethyl-3-isobutylpyrazine	122	1200	1208 (Fadel et al., 2006)
Aromatic Maillard products			
Benzaldehyde	77	955	958 (Xie et al., 2008)
Benzeneacetaldehyde	91	1046	1047 (Radulović et al., 2010)
Acetophenone	105	1070	1076 (Methven et al., 2007)
4-Vinylguaiacol	135	1260	1320 (Fadel et al., 2008)
Other Maillard products			
1-Methyl-1H-Pyrrole	81	731	732 (Harrison & Priest, 2009)
Furfural	96	833	830 (Pino et al., 2005)
Dimethyl trisulfide	126	961	963 (Lozano, Drake, et al., 2007)
2-Pentylfuran	81	990	992 (Pino et al., 2005)
2-Pentylpyridine	93	1196	1203 (Cadwallader & Heo, 2001)
2,3-Dihydrobenzofuran	120	1212	1219 (Miyazawa et al., 2011)

Table 4.3. ANOVA results showing main effects on the interaction of cultivar and time

	Effect		
Volatile Compounds	**Cultivar**	**Time**	**Cultivar × Time**
1-Methyl-1H-Pyrrole	***	***	***
Hexanal	***	**	***
Furfural	***	***	***
Heptanal	***	***	***
2,5-Dimethylpyrazine	***	***	***
Benzaldehyde	***	***	***
Dimethyl trisulfide	***	***	***
1-Octen-3-ol	***	***	***
2-Pentylfuran	***	***	***
2-Ethyl-5-methylpyrazine	***	***	**
Trimethyl pyrazine	***	***	***
Benzeneacetaldehyde	***	***	***
Acetophenone	***	***	***
3-Ethyl-2,5-dimethylpyrazine	***	***	***
2-Ethyl-3,5-dimethylpyrazine	***	***	***
3,5-Diethyl-2-methylpyrazine	***	***	***
2-Pentylpyridine	***	***	***
2,5-Dimethyl-3-isobutylpyrazine	***	***	***
2,3-Dihydrobenzofuran	***	*	***
2-Phenyl-2-butenal	***	***	***
4-Vinylguaiacol	***	***	***

*, **, *** Tests of the effects are significant at ($P \leq 0.05$), ($P \leq 0.01$), ($P \leq 0.001$) respectively, NS = Not significant

Table 4.4. Changes in hexanal content (μg/kg[1]) in the peanut cultivars during storage

		Storage Time in Weeks					
Cultivar	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Georgia 06G	Normal	$^{y}43^{ab}$	$^{xy}61^{b}$	$^{x}79^{b}$	$^{xy}63^{a}$	$^{w}113^{a}$	$^{z}0^{b}$
Tifguard	Normal	$^{z}53^{a}$	$^{w}155^{a}$	$^{wx}124^{a}$	$^{z}35^{ab}$	$^{y}86^{a}$	$^{x}122^{a}$
Georgia 16HO	High	$^{z}0^{c}$	$^{y}47^{bc}$	$^{z}0^{c}$	$^{z}0^{c}$	$^{z}0^{b}$	$^{z}0^{b}$
Georgia 14N	High	0^{c}	0^{d}	0^{c}	0^{c}	0^{b}	0^{b}
Florida-07	High	11^{bc}	19^{cd}	9^{c}	10^{bc}	0^{b}	0^{b}
Flo-Run 331	High	0^{c}	0^{d}	0^{c}	0^{c}	0^{b}	0^{b}
TufRunner 511	High	0^{c}	0^{d}	0^{c}	0^{c}	0^{b}	0^{b}
TufRunner 727	High	0^{c}	0^{d}	0^{c}	0^{c}	0^{b}	0^{b}
Georgia 13M	High	0^{c}	0^{d}	0^{c}	0^{c}	0^{b}	0^{b}
TufRunner 297	High	0^{c}	0^{d}	0^{c}	0^{c}	0^{b}	0^{b}
AU NPL 17	High	0^{c}	0^{d}	0^{c}	0^{c}	0^{b}	0^{b}
TifNV	High	0^{c}	0^{d}	0^{c}	0^{c}	0^{b}	0^{b}

[a-d] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)
[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)
[1] Calculated based on the internal standard (1,3-dichloro benzene)

Table 4.5. Changes in 1-octen-3-ol content (μg/kg[1]) in the peanut cultivars during storage

		Storage Time in Weeks					
Cultivar	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Georgia 06G	Normal	[z]0	[y]31[a]	[y]34[a]	[x]47[a]	[w]78[b]	[v]95[a]
Tifguard	Normal	[z]0	[y]29[a]	[y]35[a]	[y]29[b]	[w]98[a]	[x]85[b]
Georgia 16HO	High	0	0[b]	0[b]	0[c]	0[c]	0[c]
Georgia 14N	High	0	0[b]	0[b]	0[c]	0[c]	0[c]
Florida-07	High	0	0[b]	0[b]	0[c]	0[c]	0[c]
Flo-Run 331	High	0	0[b]	0[b]	0[c]	0[c]	0[c]
TufRunner 511	High	0	0[b]	0[b]	0[c]	0[c]	0[c]
TufRunner 727	High	0	0[b]	0[b]	0[c]	0[c]	0[c]
Georgia 13M	High	0	0[b]	0[b]	0[c]	0[c]	0[c]
TufRunner 297	High	0	0[b]	0[b]	0[c]	0[c]	0[c]
AU NPL 17	High	0	0[b]	0[b]	0[c]	0[c]	0[c]
TifNV	High	0	0[b]	0[b]	0[c]	0[c]	0[c]

[a-d] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)
[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)
[1] Calculated based on the internal standard (1,3-dichloro benzene)

Table 4.6. Changes in 2,5-dimethyl pyrazine content (μg/kg[1]) in the peanut cultivars during storage

		Storage Time in Weeks					
Cultivar	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Georgia 06G	Normal	$^{yz}624^{ab}$	$^{z}489^{ab}$	$^{y}812^{ab}$	$^{xy}628^{ab}$	$^{x}1211^{a}$	$^{x}1227^{bc}$
Tifguard	Normal	$^{z}202^{d}$	$^{z}257^{b}$	$^{z}487^{cde}$	$^{z}440^{b}$	$^{y}807^{cde}$	$^{y}803^{d}$
Georgia 16HO	High	$^{z}283^{cd}$	$^{xyz}557^{a}$	$^{yz}402^{de}$	$^{xy}666^{ab}$	$^{yz}475^{f}$	$^{x}840^{d}$
Georgia 14N	High	$^{z}436^{bcd}$	$^{z}441^{ab}$	$^{z}533^{bcde}$	$^{z}655^{ab}$	$^{z}698^{ef}$	$^{y}1606^{a}$
Florida-07	High	$^{z}316^{cd}$	$^{z}434^{ab}$	$^{z}373^{e}$	$^{y}831^{a}$	$^{y}825^{cde}$	$^{y}898^{d}$
Flo-Run 331	High	$^{wxy}783^{a}$	$^{xyz}521^{ab}$	$^{wx}807^{ab}$	$^{z}421^{b}$	$^{w}868^{bcde}$	$^{v}1625^{a}$
TufRunner 511	High	$^{z}445^{bcd}$	$^{z}542^{ab}$	$^{xy}979^{a}$	$^{yz}690^{ab}$	$^{wx}1100^{abc}$	$^{w}1363^{ab}$
TufRunner 727	High	$^{yz}508^{abc}$	$^{z}447^{ab}$	$^{yz}679^{bcd}$	$^{yz}530^{b}$	$^{xy}794^{de}$	$^{x}1066^{cd}$
Georgia 13M	High	$^{z}460^{bcd}$	$^{z}492^{ab}$	$^{z}442^{de}$	$^{z}656^{ab}$	$^{x}1171^{a}$	$^{xy}975^{cd}$
TufRunner 297	High	$^{z}657^{ab}$	$^{z}370^{ab}$	$^{z}661^{bcde}$	$^{z}639^{ab}$	$^{y}1160^{ab}$	$^{y}1223^{bc}$
AU NPL 17	High	$^{z}618^{ab}$	$^{z}538^{ab}$	$^{z}657^{bcde}$	$^{z}699^{ab}$	$^{y}1039^{abcd}$	$^{y}1245^{bc}$
TifNV	High	$^{z}302^{cd}$	$^{z}453^{ab}$	$^{xy}763^{abc}$	$^{yz}521^{b}$	$^{x}1041^{abcd}$	$^{x}1034^{cd}$

[a-f] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)
[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)
[1] Calculated based on the internal standard (1,3-dichloro benzene)

Table 4.7. Changes in 2-ethyl-5-methyl pyrazine content (μg/kg[1]) in the peanut cultivars during storage

		Storage Time in Weeks					
Cultivar	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Georgia 06G	Normal	$^{z}339$	$^{z}304$	$^{z}398^{ab}$	$^{z}459^{abc}$	$^{y}941^{ab}$	$^{y}832^{cde}$
Tifguard	Normal	$^{z}128$	$^{z}141$	$^{z}377^{ab}$	$^{z}273^{c}$	$^{y}716^{bc}$	$^{y}810^{cdef}$
Georgia 16HO	High	$^{z}153$	$^{yz}371$	$^{z}258^{b}$	$^{yz}340^{bc}$	$^{yz}319^{d}$	$^{y}574^{ef}$
Georgia 14N	High	$^{z}295$	$^{z}241$	$^{yz}396^{ab}$	$^{yz}379^{bc}$	$^{y}602^{cd}$	$^{x}1343^{a}$
Florida-07	High	$^{z}182$	$^{yz}271$	$^{yz}251^{b}$	$^{xyz}428^{abc}$	$^{x}707^{bc}$	$^{xy}528^{f}$
Flo-Run 331	High	$^{yz}355$	$^{z}234$	$^{xyz}434^{ab}$	$^{x}690^{a}$	$^{xy}591^{cd}$	$^{w}1018^{bc}$
TufRunner 511	High	$^{z}236$	$^{yz}314$	$^{x}655^{a}$	$^{xy}547^{abc}$	$^{w}1083^{a}$	$^{w}1212^{ab}$
TufRunner 727	High	$^{z}252$	$^{z}291$	$^{z}332^{b}$	$^{z}398^{abc}$	$^{y}741^{bc}$	$^{y}934^{bcd}$
Georgia 13M	High	$^{z}237$	$^{z}295$	$^{z}261^{b}$	$^{yz}479^{abc}$	$^{x}827^{abc}$	$^{xy}683^{def}$
TufRunner 297	High	$^{yz}324$	$^{z}227$	$^{yz}373^{ab}$	$^{xyz}499^{abc}$	$^{xy}606^{cd}$	$^{x}708^{def}$
AU NPL 17	High	347	332	402^{ab}	623^{ab}	566^{cd}	622^{ef}
TifNV	High	$^{z}200$	$^{z}278$	$^{z}325^{b}$	$^{z}376^{bc}$	$^{y}807^{abc}$	$^{y}701^{def}$

[a-f] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)
[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)
[1] Calculated based on the internal standard (1,3-dichloro benzene)

Table 4.8. Changes in 3-ethyl-2,5-dimethyl pyrazine content (μg/kg[1]) in the peanut cultivars during storage

		Storage Time in Weeks					
Cultivar	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Georgia 06G	Normal	$^{z}175^{abc}$	$^{z}203$	$^{yz}271^{bc}$	$^{y}363^{abc}$	$^{x}636^{bc}$	$^{x}714^{bc}$
Tifguard	Normal	$^{z}76^{c}$	$^{z}123$	$^{z}212^{bc}$	$^{z}190^{d}$	$^{y}465^{d}$	$^{y}573^{def}$
Georgia 16HO	High	$^{z}101^{abc}$	$^{y}239$	$^{yz}180^{c}$	$^{y}261^{cd}$	$^{y}309^{e}$	$^{x}531^{f}$
Georgia 14N	High	$^{z}177^{abc}$	$^{z}182$	$^{z}267^{bc}$	$^{z}286^{bcd}$	$^{y}500^{cd}$	$^{x}907^{a}$
Florida-07	High	$^{z}90^{bc}$	$^{z}180$	$^{z}175^{c}$	$^{y}361^{abc}$	$^{x}532^{bcd}$	$^{x}561^{ef}$
Flo-Run 331	High	$^{z}229^{a}$	$^{z}207$	$^{z}332^{ab}$	$^{z}240^{cd}$	$^{y}571^{bcd}$	$^{x}820^{ab}$
TufRunner 511	High	$^{z}146^{abc}$	$^{z}247$	$^{y}457^{a}$	$^{y}415^{ab}$	$^{x}829^{a}$	$^{x}946^{a}$
TufRunner 727	High	$^{z}136^{abc}$	$^{z}168$	$^{yz}230^{bc}$	$^{xy}313^{abcd}$	$^{x}444^{de}$	$^{w}698^{bcde}$
Georgia 13M	High	$^{z}119^{abc}$	$^{z}193$	$^{z}164^{c}$	$^{y}350^{abc}$	$^{x}640^{b}$	$^{x}558^{f}$
TufRunner 297	High	$^{z}216^{ab}$	$^{z}156$	$^{yz}248^{bc}$	$^{y}376^{abc}$	$^{x}644^{b}$	$^{x}737^{bc}$
AU NPL 17	High	$^{z}210^{abc}$	$^{z}224$	$^{z}270^{bc}$	$^{y}429^{a}$	$^{x}647^{b}$	$^{x}705^{bcd}$
TifNV	High	$^{z}110^{abc}$	$^{yz}192$	$^{xy}286^{bc}$	$^{x}355^{abc}$	$^{w}626^{bc}$	$^{w}643^{cdef}$

[a-f] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)
[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)
[1] Calculated based on the internal standard (1,3-dichloro benzene)

Table 4.9. Changes in Benzaldehyde content (μg/kg[1]) in the peanut cultivars during storage

		Storage Time in Weeks					
Cultivar	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Georgia 06G	Normal	$^{z}511^{ab}$	$^{z}550^{ab}$	$^{z}692^{b}$	$^{y}921^{a}$	$^{x}1238^{b}$	$^{x}1398^{a}$
Tifguard	Normal	$^{z}107^{e}$	$^{z}196^{d}$	$^{z}311^{e}$	$^{z}236^{c}$	$^{y}692^{cd}$	$^{y}727^{f}$
Georgia 16HO	High	$^{z}153^{de}$	$^{x}390^{bcd}$	$^{xyz}271^{e}$	$^{xyz}329^{c}$	$^{xy}375^{e}$	$^{w}606^{f}$
Georgia 14N	High	$^{z}165^{de}$	$^{yz}223^{cd}$	$^{yz}274^{e}$	$^{yz}272^{c}$	$^{y}422^{e}$	$^{x}700^{f}$
Florida-07	High	$^{z}224^{cde}$	$^{z}424^{bc}$	$^{z}344^{de}$	$^{y}653^{b}$	$^{x}881^{c}$	$^{xy}786^{ef}$
Flo-Run 331	High	$^{z}226^{cde}$	$^{z}253^{cd}$	$^{yz}378^{cde}$	$^{z}275^{c}$	$^{xy}554^{de}$	$^{x}713^{f}$
TufRunner 511	High	$^{z}356^{bcd}$	$^{y}641^{a}$	$^{x}1058^{a}$	$^{x}942^{a}$	$^{w}1498^{a}$	$^{w}1373^{ab}$
TufRunner 727	High	$^{z}202^{cde}$	$^{yz}274^{cd}$	$^{xy}412^{cde}$	$^{xy}445^{bc}$	$^{x}484^{e}$	$^{w}753^{ef}$
Georgia 13M	High	$^{z}393^{abc}$	$^{y}641^{a}$	$^{y}522^{bcd}$	$^{wx}984^{a}$	$^{w}1168^{b}$	$^{x}943^{de}$
TufRunner 297	High	$^{z}480^{ab}$	$^{z}384^{bcd}$	$^{z}574^{bc}$	$^{y}870^{a}$	$^{x}1160^{b}$	$^{x}1174^{bc}$
AU NPL 17	High	$^{z}573^{a}$	$^{z}555^{ab}$	$^{z}655^{b}$	$^{y}885^{a}$	$^{x}1096^{b}$	$^{x}1126^{cd}$
TifNV	High	$^{z}135^{e}$	$^{yz}286^{cd}$	$^{y}383^{cde}$	$^{y}414^{c}$	$^{x}813^{c}$	$^{x}747^{ef}$

[a-f] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)
[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)
[1] Calculated based on the internal standard (1,3-dichloro benzene)

Table 4.10. Changes in Benzeneacetaldehyde content (μg/kg[1]) in the peanut cultivars during storage

		Storage Time in Weeks					
Cultivar	**Oleic Status**	**0**	**8**	**16**	**24**	**32**	**40**
Georgia 06G	Normal	$^{x}2970^{b}$	$^{z}1245^{bcd}$	$^{z}1347^{b}$	$^{y}1943^{b}$	$^{y}1888^{ab}$	$^{yz}1504^{ab}$
Tifguard	Normal	301^{g}	291^{g}	408^{e}	243^{d}	540^{d}	439^{d}
Georgia 16HO	High	613^{fg}	830^{def}	464^{e}	401^{cd}	718^{d}	828^{cd}
Georgia 14N	High	$^{yz}556^{fg}$	$^{yz}363^{fg}$	$^{yz}353^{e}$	$^{z}288^{d}$	$^{yz}436^{d}$	$^{y}828^{cd}$
Florida-07	High	$^{xy}1278^{d}$	$^{yz}994^{cde}$	$^{z}578^{de}$	$^{yz}843^{c}$	$^{x}1559^{bc}$	$^{yz}940^{c}$
Flo-Run 331	High	967^{def}	497^{fg}	550^{e}	472^{cd}	731^{d}	883^{cd}
TufRunner 511	High	$^{xy}2394^{c}$	$^{z}1757^{a}$	$^{x}2648^{a}$	$^{x}2471^{a}$	$^{xyz}2185^{a}$	$^{yz}1969^{a}$
TufRunner 727	High	1148^{de}	671^{efg}	839^{cde}	863^{c}	716^{d}	692^{cd}
Georgia 13M	High	$^{x}2525^{bc}$	$^{y}1646^{ab}$	$^{z}1114^{bc}$	$^{x}2213^{ab}$	$^{xy}2047^{ab}$	$^{z}1081^{bc}$
TufRunner 297	High	$^{x}2780^{bc}$	$^{z}810^{ef}$	$^{z}1055^{bcd}$	$^{y}1924^{b}$	$^{y}2076^{a}$	$^{y}1649^{a}$
AU NPL 17	High	$^{x}3803^{a}$	$^{yz}1464^{abc}$	$^{z}1417^{b}$	$^{y}1936^{b}$	$^{y}1918^{ab}$	$^{yz}1758^{a}$
TifNV	High	$^{z}753^{efg}$	$^{z}501^{efg}$	$^{z}571^{de}$	$^{z}655^{cd}$	$^{y}1319^{c}$	$^{z}758^{cd}$

[a-g] Column means (within a time point) with different superscripts (after the mean value) are statistically different ($P \leq 0.05$)
[v-z] Row means (within a cultivar) with different superscripts (before the mean value) are statistically different ($P \leq 0.05$)
[1] Calculated based on the internal standard (1,3-dichloro benzene)

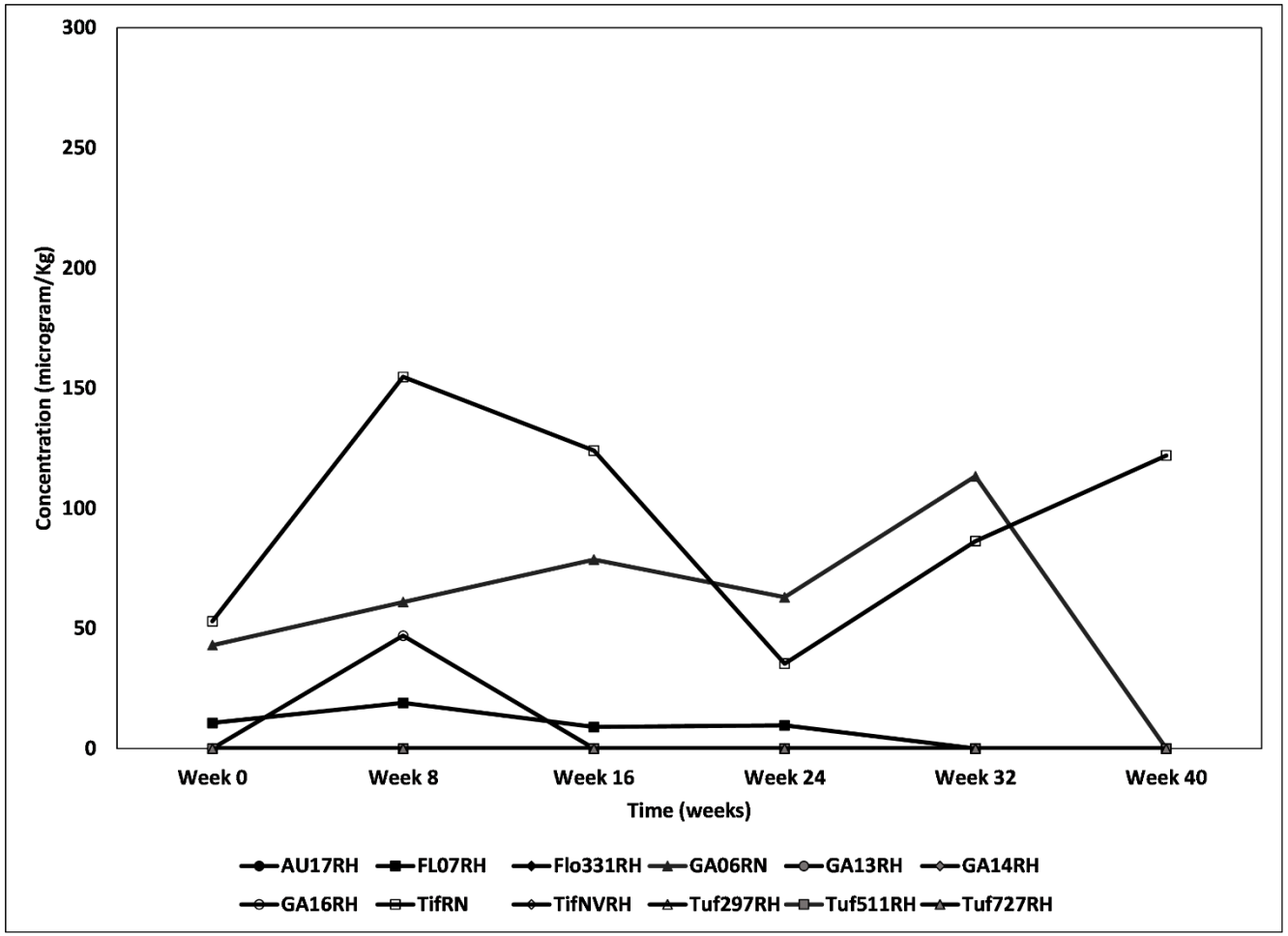

Figure 4.1. Hexanal of roasted peanut cultivars[1] at different storage times.

[1]AU17RH = AU NPL 17 runner [HO], FL07RH = Florida-07 runner [HO], Flo331RH = FloRun 331 runner [HO], GA06RN = Georgia 06G runner [NO], GA13RH = Georgia 13M runner [HO], GA14RH = Georgia 14N runner [HO], GA16RH = Georgia 16HO runner [HO], TifRN = Tifguard runner [NO], TifNVRH = TifNV runner [HO], Tuf297RH = TufRunner 297 runner [HO], Tuf511RH = TufRunner 511 runner [HO], Tuf727RH = TufRunner 727 runner [HO]

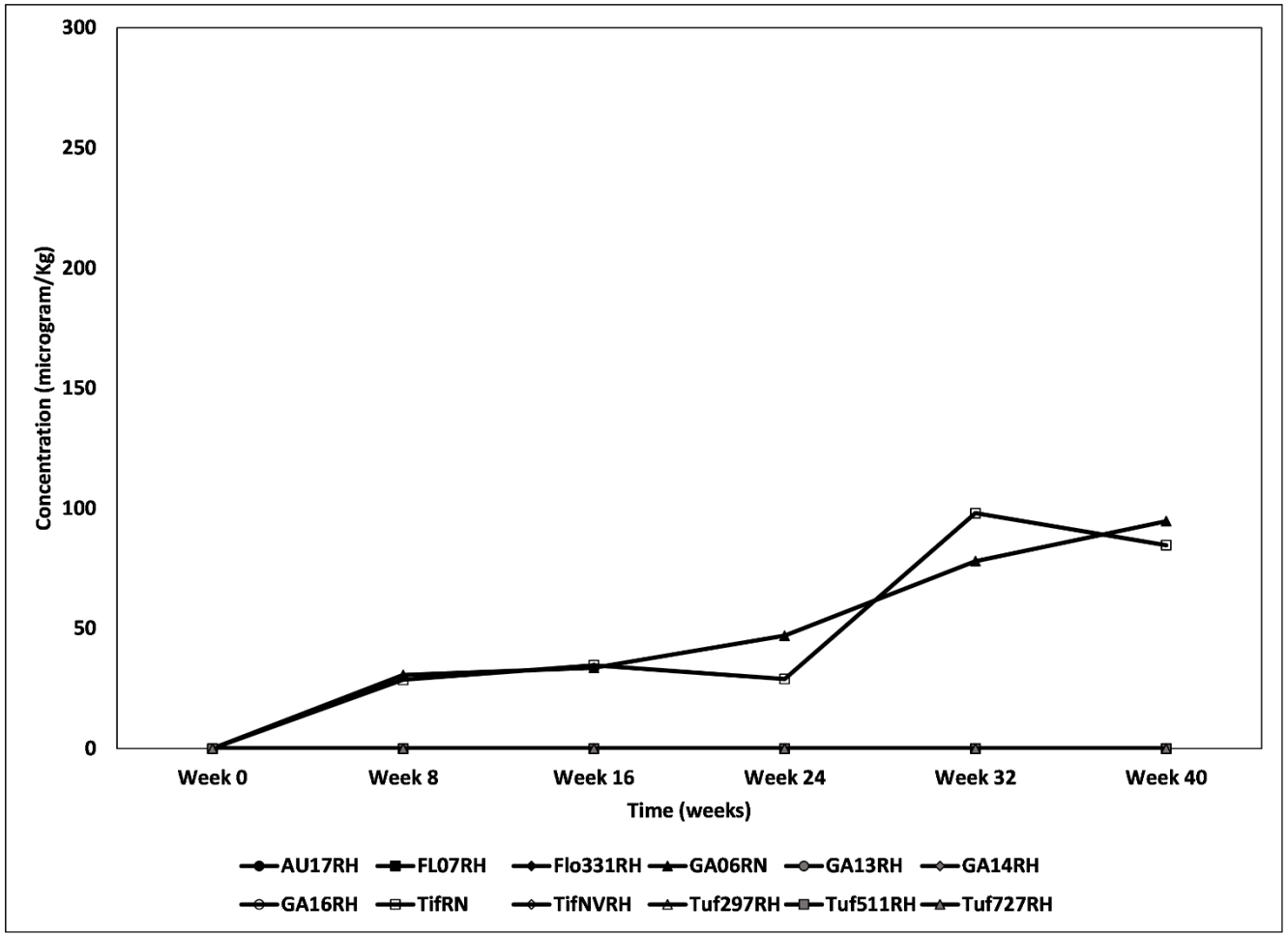

Figure 4.2. 1-Octen-3-ol of roasted peanut cultivars[1] at different storage times.
[1]AU17RH = AU NPL 17 runner [HO], FL07RH = Florida-07 runner [HO], Flo331RH = FloRun 331 runner [HO], GA06RN = Georgia 06G runner [NO], GA13RH = Georgia 13M runner [HO], GA14RH = Georgia 14N runner [HO], GA16RH = Georgia 16HO runner [HO], TifRN = Tifguard runner [NO], TifNVRH = TifNV runner [HO], Tuf297RH = TufRunner 297 runner [HO], Tuf511RH = TufRunner 511 runner [HO], Tuf727RH = TufRunner 727 runner [HO

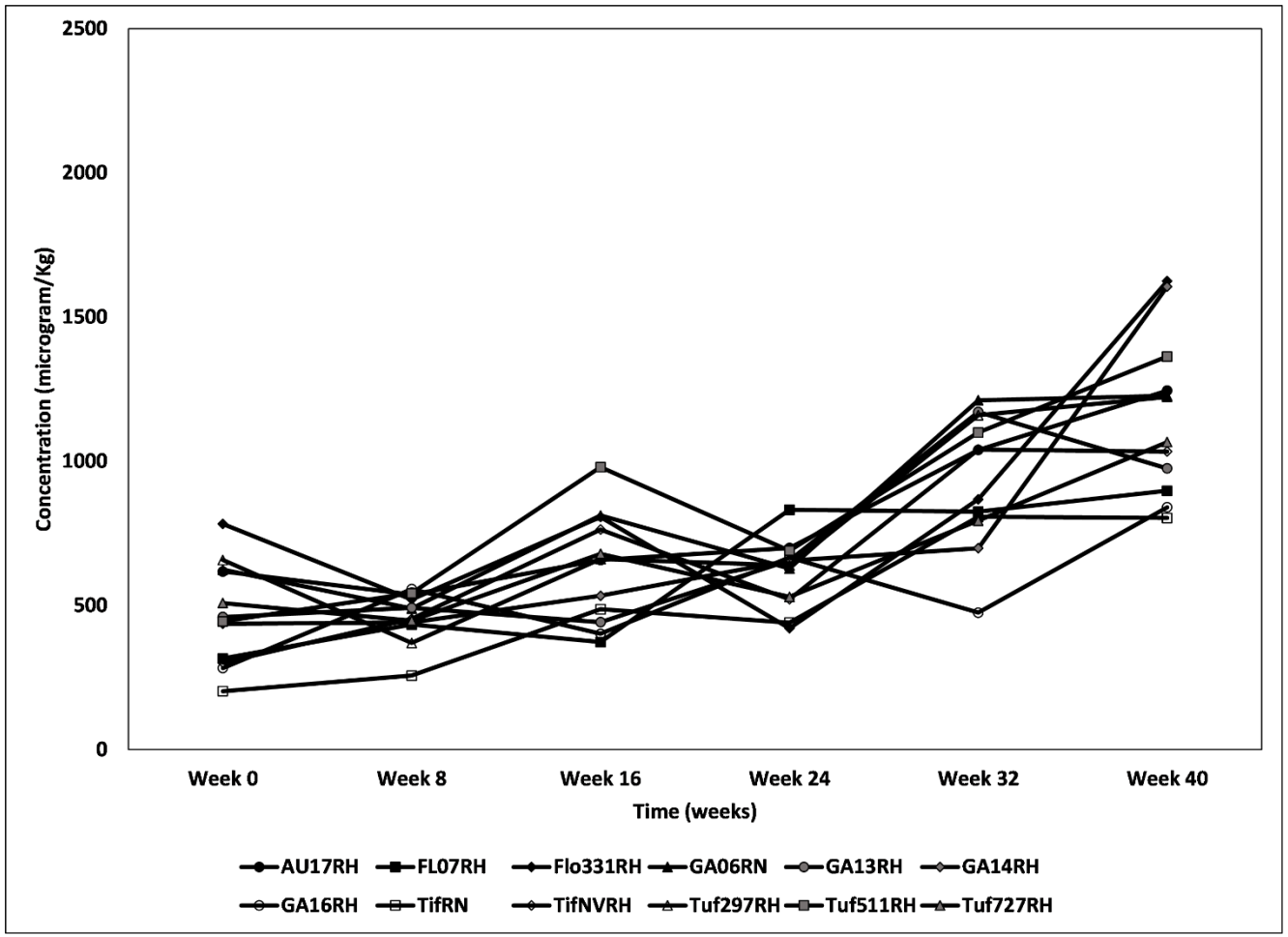

Figure 4.3. 2,5-Dimethylpyrazine of roasted peanut cultivars[1] at different storage times.
[1]AU17RH = AU NPL 17 runner [HO], FL07RH = Florida-07 runner [HO], Flo331RH = FloRun 331 runner [HO], GA06RN = Georgia 06G runner [NO], GA13RH = Georgia 13M runner [HO], GA14RH = Georgia 14N runner [HO], GA16RH = Georgia 16HO runner [HO], TifRN = Tifguard runner [NO], TifNVRH = TifNV runner [HO], Tuf297RH = TufRunner 297 runner [HO], Tuf511RH = TufRunner 511 runner [HO], Tuf727RH = TufRunner 727 runner [HO]

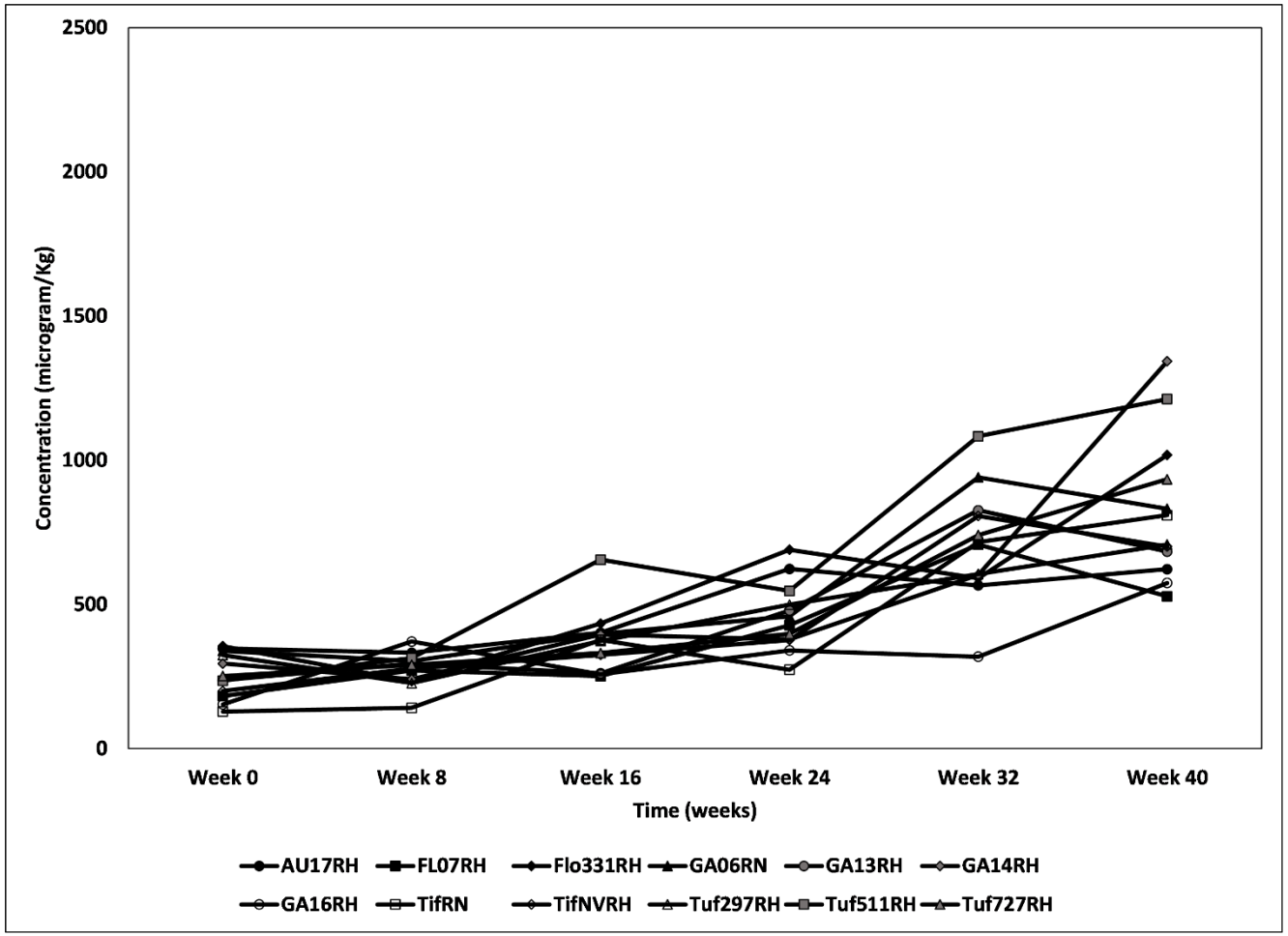

Figure 4.4. 2-Ethyl-5-methylpyrazine of roasted peanut cultivars[1] at different storage times.
[1]AU17RH = AU NPL 17 runner [HO], FL07RH = Florida-07 runner [HO], Flo331RH = FloRun 331 runner [HO], GA06RN = Georgia 06G runner [NO], GA13RH = Georgia 13M runner [HO], GA14RH = Georgia 14N runner [HO], GA16RH = Georgia 16HO runner [HO], TifRN = Tifguard runner [NO], TifNVRH = TifNV runner [HO], Tuf297RH = TufRunner 297 runner [HO], Tuf511RH = TufRunner 511 runner [HO], Tuf727RH = TufRunner 727 runner [HO]

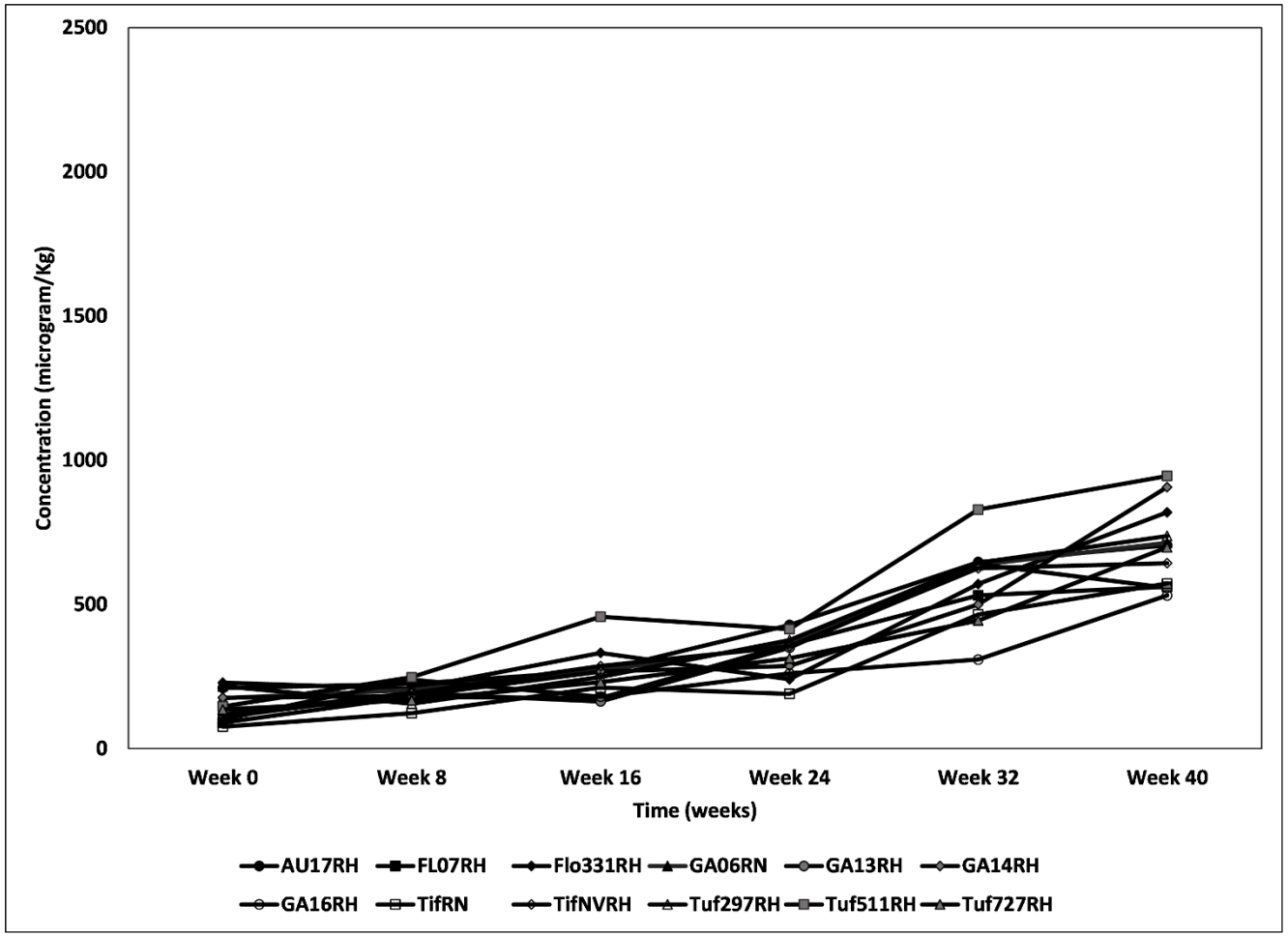

Figure 4.5. 3-Ethyl-2,5-dimethylpyrazine of roasted peanut cultivars[1] at different storage times.
[1]AU17RH = AU NPL 17 runner [HO], FL07RH = Florida-07 runner [HO], Flo331RH = FloRun 331 runner [HO], GA06RN = Georgia 06G runner [NO], GA13RH = Georgia 13M runner [HO], GA14RH = Georgia 14N runner [HO], GA16RH = Georgia 16HO runner [HO], TifRN = Tifguard runner [NO], TifNVRH = TifNV runner [HO], Tuf297RH = TufRunner 297 runner [HO], Tuf511RH = TufRunner 511 runner [HO], Tuf727RH = TufRunner 727 runner [HO]

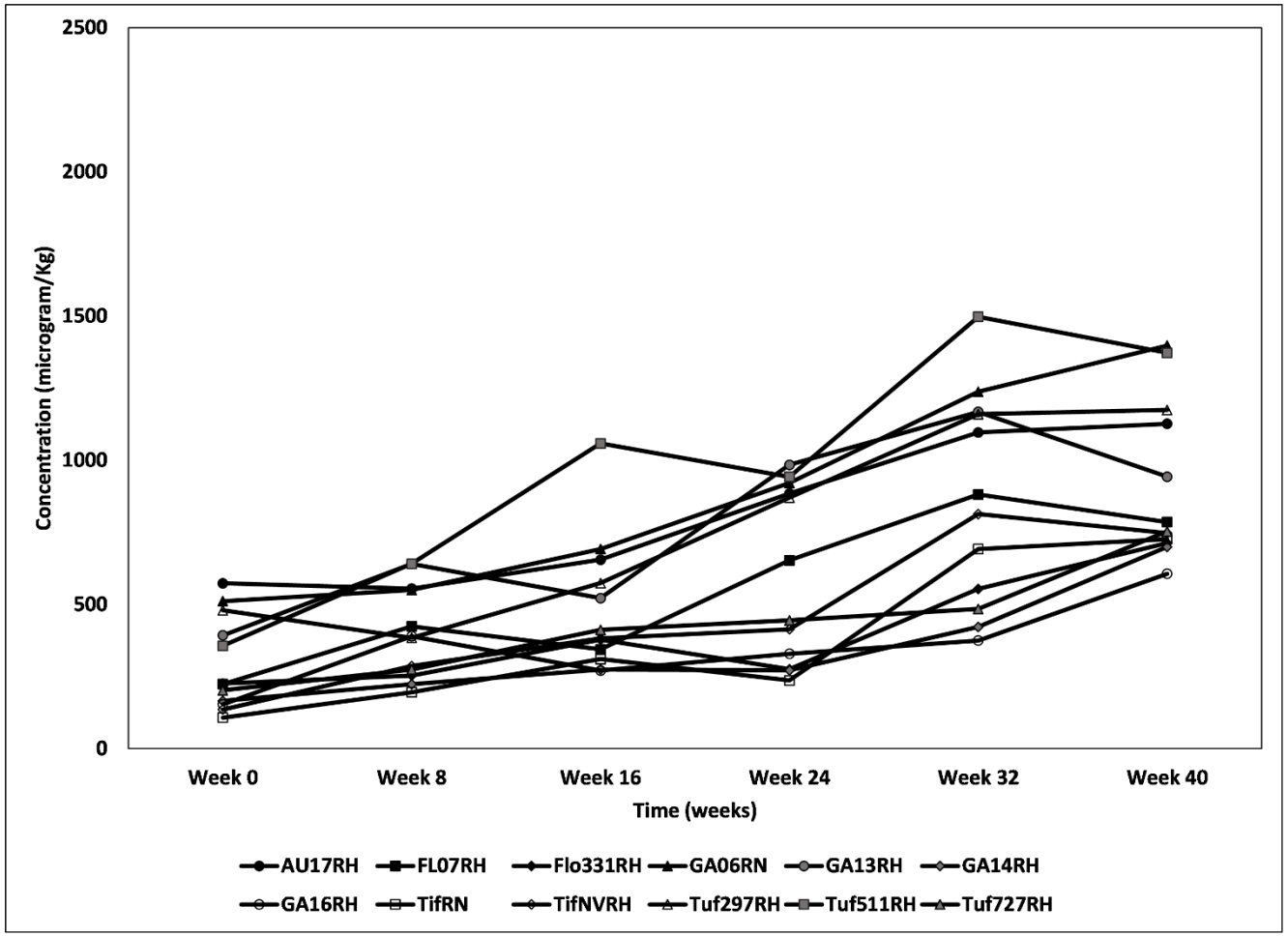

Figure 4.6. Benzaldehyde of roasted peanut cultivars[1] at different storage times.
[1]AU17RH = AU NPL 17 runner [HO], FL07RH = Florida-07 runner [HO], Flo331RH = FloRun 331 runner [HO], GA06RN = Georgia 06G runner [NO], GA13RH = Georgia 13M runner [HO], GA14RH = Georgia 14N runner [HO], GA16RH = Georgia 16HO runner [HO], TifRN = Tifguard runner [NO], TifNVRH = TifNV runner [HO], Tuf297RH = TufRunner 297 runner [HO], Tuf511RH = TufRunner 511 runner [HO], Tuf727RH = TufRunner 727 runner [HO]

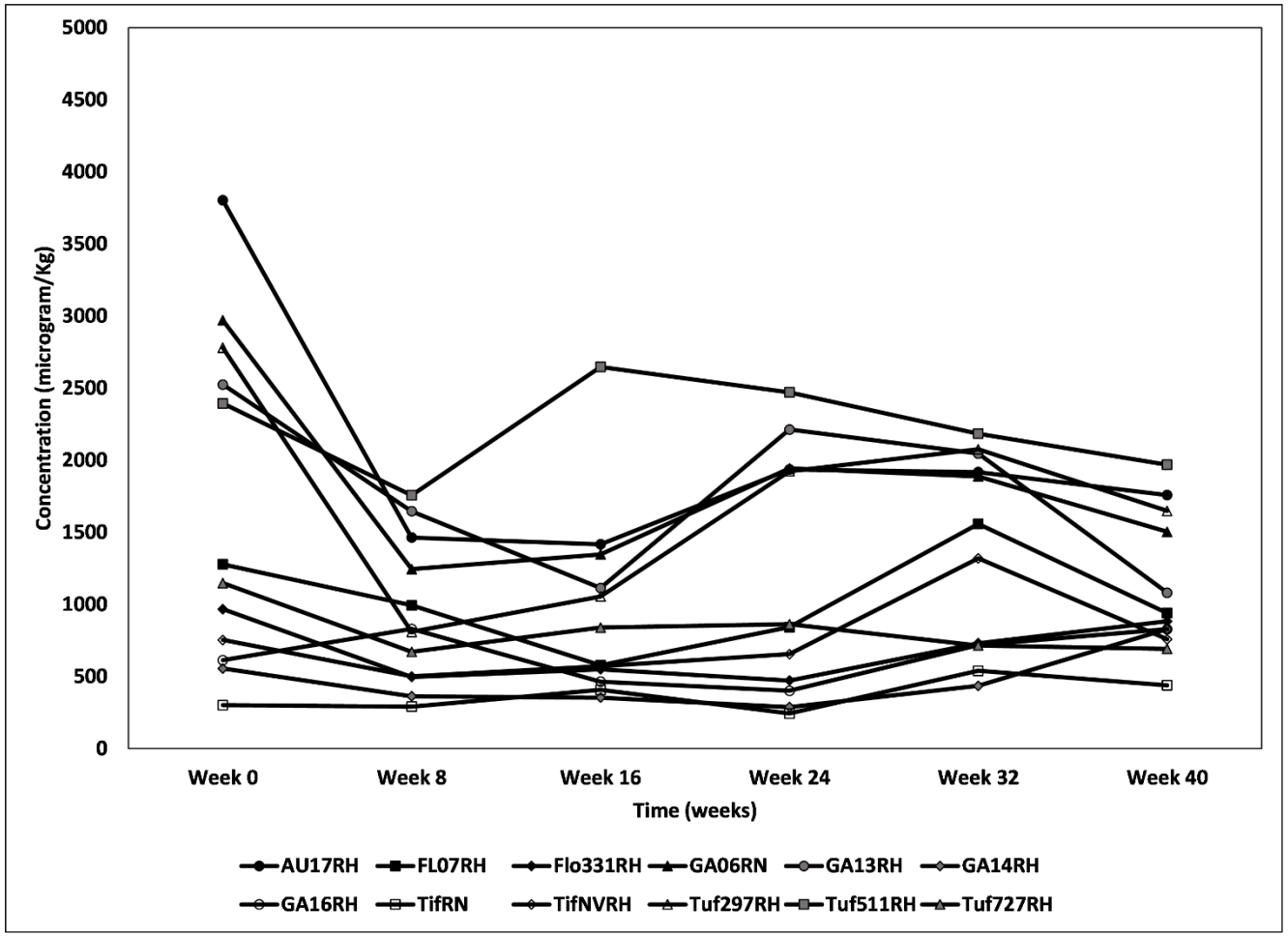

Figure 4.7. Benzeneacetaldehyde of roasted peanut cultivars[1] at different storage times.
[1]AU17RH = AU NPL 17 runner [HO], FL07RH = Florida-07 runner [HO], Flo331RH = FloRun 331 runner [HO], GA06RN = Georgia 06G runner [NO], GA13RH = Georgia 13M runner [HO], GA14RH = Georgia 14N runner [HO], GA16RH = Georgia 16HO runner [HO], TifRN = Tifguard runner [NO], TifNVRH = TifNV runner [HO], Tuf297RH = TufRunner 297 runner [HO], Tuf511RH = TufRunner 511 runner [HO], Tuf727RH = TufRunner 727 runner [HO]

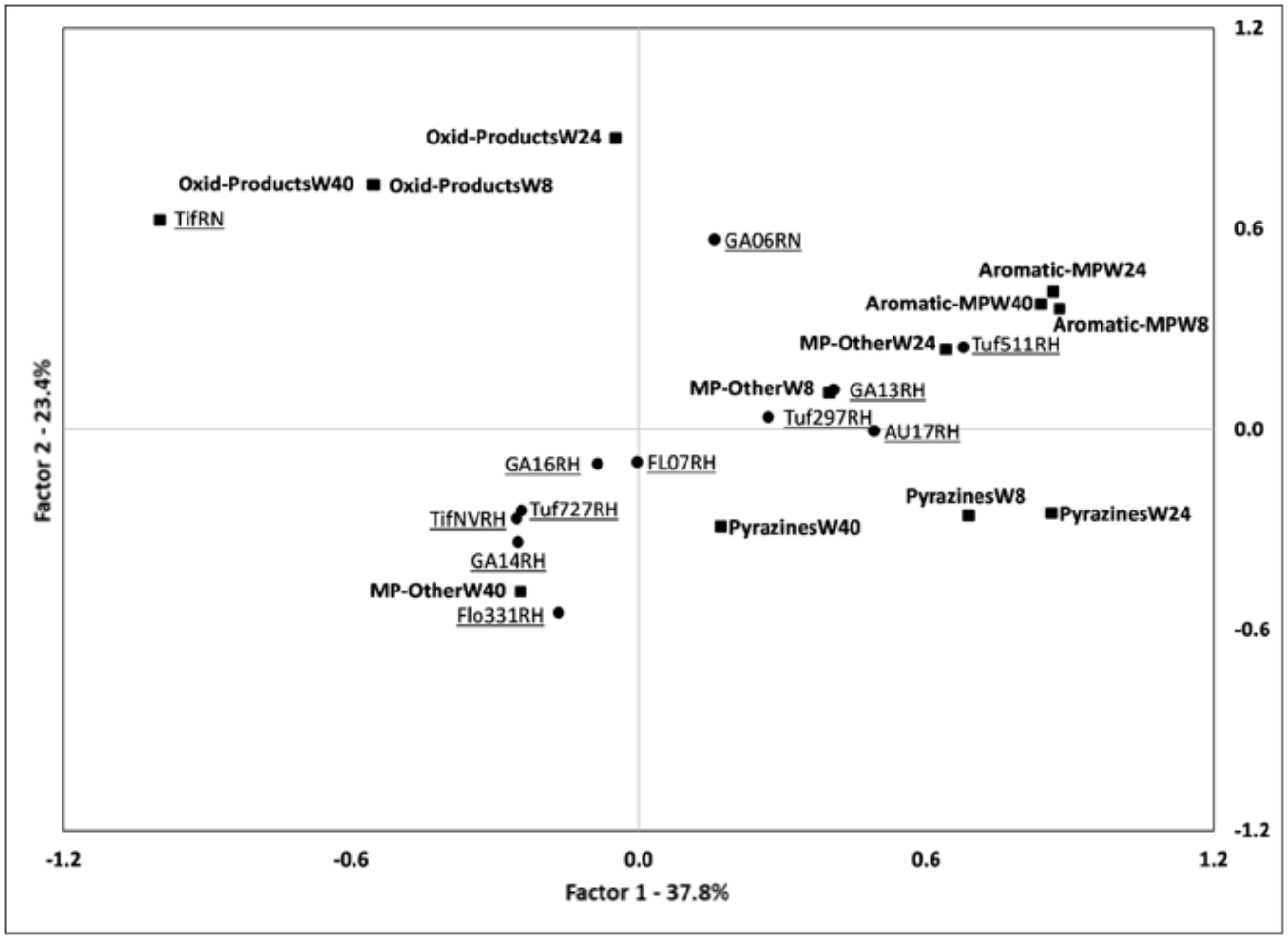

Figure 4.8. MFA biplot of roasted peanut cultivars and roasted volatile compounds[1] for weeks 8, 24, and 40

[1]Oxid-Products = Oxidation products, Aromatic-MP = Aromatic Maillard Products, MP-Other = Other Maillard Products, GA06RN = Georgia 06G runner [NO], TifRN = Tifguard runner [NO], AU17RH = AU NPL 17 runner [HO], GA13RH = Georgia 13M runner [HO], GA14RH = Georgia 14N runner [HO], GA16RH = Georgia 16HO runner [HO], FL07RH = Florida-07 runner [HO], Flo331RH = FloRun 331 runner [HO], Tuf297RH = TUFRunner 297 runner [HO], Tuf511RH = TUFRunner 511 runner [HO], Tuf727RH = TUFRunner 727 runner [HO], TifNVRH = TifNV runner [HO]

CHAPTER 5

CONCLUSIONS

Oil comprises approximately 50% of peanuts, making up the majority of their chemical composition and therefore being important to flavor development and shelf stability of peanuts. Peanuts are susceptible to chemical reactions during both roasting and storage that lead to changes in quality, including flavor-fade. There were 22 volatile compounds identified in this study that can be associated with flavor-fade in roasted peanuts. Overall, based on the data from the present study the high-oleic cultivars among the roasted peanut types were less oxidized after 40 weeks of storage while also having stable pyrazine concentrations.

All cultivars, irrespective of type or oleic status, were able to maintain stable pyrazine and other mallard-derived volatile concentrations throughout storage. Most, if not all cultivars also exhibited increased concentrations over 40 weeks in the storage of some of the primary roasted flavor volatiles (2,5-dimethylpyrazine, 2-ethyl-5-methylpyrazine, 3-ethyl-2,5-dimethylpyrazine, benzaldehyde, benzeneacetaldehyde). The peanuts cultivars with the highest concentrations of roasted flavor volatiles were the high-oleic cultivars of both peanut types and the normal-oleic cultivar, GA06-RN. In general, the virginia cultivars exhibited lower concentrations of roasted flavor volatiles throughout storage as compared to runner cultivars, irrespective of oleic status.

The oxidation-derived volatiles, known for contributing oxidized and off-flavors in roasted peanuts were primarily detected in the normal-oleic cultivars of both peanut types at low concentrations. Their presence indicates that the normal-oleic cultivars are less resistant to the

development of oxidation products and possibly more susceptible to flavor-fade, just as previous research has suggested. Of those cultivars, GA06-RN the top choice for runner production was included. This research showed that the high-oleic cultivars of the runner-type can compete with GA06-RN, in that they not only maintain or increase primary roasted flavor volatiles but also were more resistant to the development of oxidation products during storage. Over a more extended storage period, it may be more evident that the flavor-fade mechanism for this present study is aldehyde masking, due to the stable pyrazine concentrations of the roasted peanuts during the 40 weeks of storage.

This research can serve as a means for peanut producers and manufacturers to gain further insight into how the different peanut types (runner, virginia) and cultivars behave during storage regarding oxidative changes and loss of desirable flavor qualities. For future research, runner and virginia cultivars should be subjected to similar storage conditions to have their flavor volatiles analyzed along with consumer tests for sensory profiles and peanut preferences throughout extended storage. Future studies could also consider storage parameters such as light and packaging and various combinations of roasting times and temperatures to analyze how they affect the quality of roasted peanuts during storage.