THE ROLE OF MOISTURE AND COMMON INGREDIENTS IN QUALITY CHANGES IN STORED MODEL PEANUT CONFECTIONS

by

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(Under the Direction of William Kerr)

ABSTRACT

Model roasted peanut confections were formulated with addition of 3 levels (0, 2, and 5%) water, two levels (0 and 4%) sucrose and two levels (0 and 180 ppm) the antioxidant, tertiary butylhydroquinone (TBHQ) to a peanut paste. Color, texture, microstructure, sensory flavor and volatile aroma compounds were evaluated over 52 weeks of storage.

A modified Spectrum™ technique was used to evaluate six established roasted peanut flavor attributes: 'sweet', 'bitter', 'roasted peanutty', 'rancid', 'painty' and 'cardboard'. 'Sweet' and 'roasted peanutty' attributes were scored low in high moisture samples while 'rancid', 'painty' and 'cardboard' attributes were rated high. Roasted peanutty attribute decreased over storage time and oxidation related attributes, 'rancid', 'painty' and 'cardboard' scores intensified during storage time. Treatments with added antioxidants had higher 'roasted peanutty' scores and lower 'rancid' scores.

Headspace solid-phase microextraction (SPME) method was used to extract aroma components. Critical volatile compounds, hexanal, heptanal, 1-methylpyrrole, 2-methylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 2,3-dimethylpyrazine, and 2,3,5-trimethylpyrazine were tentatively identified by means of gas chromatography retention times employing authentic standards. Peanut pastes, treated with antioxidant had higher concentrations of pyrazine compounds and lower hexanal and heptanal. In general, samples with no added water had higher levels of specific pyrazines, hexanal and heptanal compounds. Pyrazines concentrations decreased during storage while hexanal and heptanal increased.

Color values, lightness (L*), hue angle (h°) and Chroma (C) of peanut paste decreased with added water. L*, h° and C increased during storage for all treatments. Texture profile analysis (TPA) of hardness, cohesiveness, adhesiveness, springiness, gumminess and chewiness revealed peanut pastes with added water had significantly higher hardness, gumminess, chewiness and adhesiveness and lower cohesiveness and springiness ($p<0.05$). Light and scanning electron micrographs of peanut paste with high moisture had aggregated protein bodies.

INDEX WORDS: Roasted Peanut paste, Sensory evaluation, Headspace solid-phase microextraction, pyrazines, Color evaluation, Texture profile analysis, Microstructure

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DEDICATION

To my wife, Shontaye Marie Abegaz, thank you for your continual love, unwavering support and prayers.

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CHAPTER 1

INTRODUCTION

Peanuts (*Arachis hypogaea* L.) have an economic value of approximately $1 billion in the United States (NASS, 2002). In the United States, peanuts are used for peanut butter (55.6%), roasted peanuts (21.7%), candy (20.5%) and others (2.1%). In confectionery products, peanuts contribute to flavor and texture. According to the United States Census Bureau (2001), approximately $200 million shelled peanuts were used by the confectionery industry, and peanuts account for 80% of the nuts used.

Peanuts are characterized by high oil content (~50% w:w) which makes them susceptible to lipid oxidation that leads to development of off-flavor as well as the loss of shelf life. 'Flavor-fade' accompanied by off-flavor development in peanut products is a concern to confectionery industry (Warner *et al*., 1996). Water is frequently ignored as an ingredient in confectionery, and the use of water is not as accurately controlled as it should be (Stansell, 1995). Moisture can be introduced to peanut confections intentionally or unintentionally during the processing, transport or storage. Addition of small amounts of water alter the quality of peanut butters (Felland and Koehler, 1997).

The overall objective of this research was to investigate the role of moisture in combination with common ingredients such as sugar and antioxidant on the quality of model roasted peanut confections during storage. Specific objectives were:

(a) To determine the effect of different concentrations of water, sucrose and TBHQ on sensory property of roasted peanut pastes.

(b) To evaluate the effect of water, sucrose and TBHQ levels on the concentrations of selected peanut aroma volatiles and the oxidation state of roasted peanut pastes.

(c) To determine the effect of water and sucrose levels on physical properties, color, texture, and microstructure of roasted peanut pastes.

(d) To investigate the partitioning, volatility and binding behavior of selected alkylpyrazines in simple model systems.

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CHAPTER 2

LITERATURE REVIEW

The embryo is the edible portion of the peanut, consisting of two cotyledons and a small radicle and plumule known as germ or "heart" (Woodroof and Leahy, 1940). Roasted peanut is highly nutritious, and contains thirteen essential vitamins and minerals including vitamin E, niacin, folate, vitamin B_6, thiamin, riboflavin, magnesium, phosphorus, copper, potassium, iron, zinc and calcium (Evans, 1982). Roasted peanuts are also a good source of protein and fiber. They consist of approximately less than 1% water, 30% protein, 46% fat, 18% carbohydrates and 3% ash (Tiemstra, 1973).

Roasted peanut products are popular because of their flavor, convenience and relative stability. The popularity of roasted peanuts in confections is only surpassed by chocolate. In confectionery, peanuts contribute to flavor (depending on the degree of roast) and texture (Murphy, 1995). In the United States, peanuts are used for peanut butter (55.6%), roasted peanuts (21.7%), candy (20.5%) and other items (2.1%) (Georgia Peanut Tour). Peanuts account for 60% of all nut sales (Evans, 1982). In 2001, peanut production in the United States was approximately 4.2 billion pounds (NASS, 2002). The marketing year average price per pound for 2001 was 0.234 dollars, and the value of production for the same year was approximately 1 billion dollars.

Flavor

Flavor is a very complex sensation composed of aroma and taste and may be complemented by tactile and temperature responses (Heath and Reineccius, 1986). Taste

is a gustatory perception such as sweet, salty, sour, and bitter and is caused by non-volatile chemicals in the mouth. Aroma is an olfactory perception caused by volatile substances emanating from products in the mouth. Tactile and temperature responses such as astringency, spice heat, cooling, bite and metallic are stimulated by nerve endings in the buccal and nasal cavities (Meilgaard *et al*., 1991).

Descriptive sensory evaluation

Descriptive sensory analysis is an important tool in which a sensory scientist employs highly trained subjects to identify, describe and quantify the sensory attributes of a food material or product (Lawless *et al*., 1991). Descriptive techniques can be used to obtain a complete sensory description of a product or to determine which sensory attributes are important to acceptance. It can also be used to maintain critical sensory characteristics for quality assurance or to compare differences amongst a variety of products that are currently available in the market place (Lawless, 1998, Chamber and Wolfe, 1996).

Several descriptive sensory 'systems' have been published, the main ones consisting of the Flavor Profile, Quantitative Descriptive Analysis (QDA®) and Spectrum™ Method. A total sensory description of an evaluated product takes into account all aspect of sensations perceived, which could be taste, olfactory, auditory, kinesthetic, etc. (Pal *et al*., 1995). It can also be used to evaluate limited aspects of a product such as taste, aroma, texture, and aftertaste (Hootman, 1992). In descriptive analysis, panel members under the direction of a panel leader, develop a lexicon, a list of terms with a limited number of attributes or characteristics of interest that are most likely to occur or expand to every characteristic that might conceivably apply to a product

(Chamber and Wolf, 1996). All attributes are grouped in a logical scheme, such as appearance, color, odor, and texture. After a list is developed, a score sheet is designed based on test objectives, which panelists use in determining the intensity of each attributes present in a product.

Sensory Peanut flavor lexicon

Johnsen et al., (1988) reported a comprehensive peanut flavor lexicon or sensory descriptors which is used by many investigators in the evaluation of peanut and peanut products. In 1988, a consortium of thirteen peanut industry professionals that convened at the Southern Regional Research Center in New Orleans developed the peanut flavor lexicon. They assembled a list of terms that described the flavors, basic tastes, and chemical feeling factors that are encountered in peanuts. The peanut industry professionals evaluated seventeen peanut samples that covered a variety of desirable and undesirable flavors. The team used 10 point scale with references for intensity. The peanut lexicon used at the Southern Regional Center has evolved to consist of the descriptors shown in Table 2.1.

Table 2.1 Lexicon of peanut flavor descriptors

Aromatics	
Roasted Peanutty	The flavor associated with medium roast peanuts and having fragrant character, such as methyl pyrazine notes.
Raw/beany	The flavor associated with light-roasted peanuts and having a legume-like character.
Dark roasted	The flavor associated with dark roasted peanuts having very browned or toasted character.
Sweet aromatic	The flavor associated with sweet materials such as caramel, vanilla, and molasses.
Woody/hulls/skins	The flavor associated with base notes (absence of fragrant top notes) and released to dry wood, peanut hulls, and skins.
Cardboard	The flavor associated with partially oxidized fats and oils, and somewhat reminiscent of cardboard.
Painty	The aromatic associated with linseed oil/oil-based paint.
Fermented/fruity	The flavor associated with immature improperly cured peanuts, freeze damaged peanuts, or a fermented peanut vegetation flavor associated with rotten plants, fruits, vegetables, or grain.
Tobacco	The aromatic associated with cured tobacco leaves.
Musty	The aromatic associated with wet dirt or mulch, or the odor associated with a dry closed cellar.
Eggy/sulfury	The aromatic associated with boiled old-egg proteins.
Burnt	The aromatic associated with very dark roast, burnt starches and carbohydrates (burnt toast or espresso coffee).
Green	The aromatic associated with uncooked vegetables, grass/twigs. stems, leaves and Cis-3-hexenal
Grainy	The aromatic associated with raw grain such as bran or sorghum.
Chemical/ plastic	The aromatic associated with plastic and burnt plastics.
Taste	
Sweet	The taste on the tongue associated with sugars.
Sour	The taste on the tongue associated with acids.
Salty	The taste on the tongue associated with sodium ions.
Bitter	The taste on the tongue associated with bitter agents such as caffeine or quinine.
Chemical Feeling Factors	
Astringent	The chemical feeling factor associated on the tongue, described as puckering/dry and associated with tannin or alum.
Metallic	The chemical feeling factor on the tongue described as flat, Metallic, and associated with iron and copper.

Factors that affect peanut flavor in peanut products

Cultivars, location and year of cultivation

Certain roasted peanut sensory attributes have been shown to be heritable traits (Pattee, et al., 1993, 1994, 1995, Isleib et al., 1995). Patee et al. (1998) evaluated the flavor of peanut paste from 122 cultivars and breeding lines as well as 42 year-by-location combinations from three major peanut producing regions. This study looked into the effect of genotypic variation, region and year of cultivation for differences in sweet, bitter, and roasted peanut attributes. They found out genotypic variation was significant for all three attributes, as was location-to-location variation within year and region. They also concluded that the sweetness attribute had the highest broad-sense heritability (H=0.28); that is, 28% of the total variability of sweet attribute is due to genetic factors.

Roasting Time

Buckholtz *et al*. (1980) investigated the influence of roasting time on sensory attributes of fresh Runner and Spanish varieties of roasted peanuts that were roasted at 63°C for 7, 8, 9 min to produce light, medium and dark roast samples. They conducted sensory evaluation with trained panel using a 9-point hedonic scale to rate strength and desirability of odor and flavor. Their results showed that medium and dark roast samples for both Runner and Spanish varieties were scored higher for strength of odor and flavor. Medium roast Runner variety had optimal flavor and odor score while dark roast was optimal for the Spanish variety.

Maturity and seed size

Maturity has a significant influence on peanut flavor. Sanders et al. (1989) performed descriptive flavor analysis of uniform size Florunner peanuts of five pod-color

based maturity classes from two crop years that were roasted to a Hunter L value of (50 ± 1). They found immature peanuts had lower roasted peanutty and sweet aromatic intensity. Bitter, sour, painty, and fruity/fermented intensities were higher in immature peanuts. The immature peanuts also roasted darker at a faster rate than mature peanuts and were therefore easier to over-roast. In a similar study, McNeill and Sanders (1998) studied the effect of five different classes of maturity from two crop years on storage quality of roasted Virginia-type peanuts stored at 37 °C for 12 weeks. Descriptive sensory evaluation revealed that most of the mature classes of peanuts had higher intensities of sweet and roasted peanutty attributes. Immature peanuts had higher intensity of painty attribute. Overall, immature peanuts had lower flavor impact and deteriorated faster. Pattee et al. (1982) observed significant differences in both flavor and color of peanut butters made from a 5.96 mm, 7.14 mm and larger size seeds of Virginia-type peanuts subjected to the same roasting conditions. They suggested that the 5.95 mm seeds had distinctly different roasting characteristics and that the flavor of the peanut butter produced from these seeds was less desirable than the other seed sizes. Bett and Boylston (1992) studied the storage effect on peanut quality of Florunner peanuts from two crop years and two commercial seed sizes that were stored for 12 weeks. They observed that storage time had a significant effect on the content of 9 of the 12 hetrocyclic compounds. They did not observe seed size and crop year interactions between these treatments with storage time. For the lipid oxidation products, storage time had a significant effect on the content of lipid oxidation products. However, there were significant interactions between seed size, crop year and storage time.

Moisture/water activity/relative humidity

Felland and Koehler (1997) studied sensory flavor changes in peanut butter samples with water activities (a_w) of 0.29, 0.39, and 0.56 respectively and stored at three different temperatures, 4°C, 25°C and 50°C stored for 29 days. They found out that peanut butters with 0.56 a_w had lowest roasted aroma and flavor, with more off-odor and off-flavor than the 0.39 a_w and 0.29 a_w samples. Woodroof (1945) observed addition of water at 39% (w/w) to peanut butter resulted in less desirable flavor and aroma. Reed et al. (2002) studied sensory changes in high oleic and normal oleic peanut types stored 0.19 a_w and 0.60 a_w for 7 weeks. They observed loss of peanutty flavor for samples stores at 0.60 a_w in both high and normal oleic peanuts. For both peanut types, 0.19 a_w samples had the highest painty, cardboardy, and bitter attributes during storage. Although not directly studying the effect of moisture, Brannan et al. (1999) observed defatted (22% oil) roasted peanuts, which had higher moisture content, had lower roasted peanutty score that also decreased during storage compared to full-fat (53%) roasted peanuts. They also observed defatted peanuts had intense rancid-related attributes that increased during storage compared to full-fat roasted peanuts.

Temperature

Pattee et al. (1999) investigated sensory attributes of roasted peanut paste stored at -10 °C and -23 °C for 13 months. They found out sweet taste was relatively stable, where as bitter and tongue burn attributes increased slightly. They also observed an increase in stale and fruity attributes and a decrease in roasted peanut attribute. Roasted peanut flavor was better stabilized at -23°C than at -10°C storage. Brannan et al. (1999) observed that full-fat (53%) and defatted (22%) roasted peanuts stored at 63 °C for 12

weeks had lower dark roast odor, roasted peanutty odor and flavor compared to those stored at 4 °C and 25 °C. Sanders et al. (1989b) studied the effect of Florunner windrow dried peanuts of five pod mesocarp colors maturity classes. They used three curing temperatures, ambient air (35°C), ambient + 8.4°C, and ambient + 16.8°C. Descriptive sensory evaluation of similar size and roast color peanuts revealed intensity ratings of roasted peanutty and sweet aromatic were lowest and fruity fermented, painty, sour, and bitter highest for immature peanuts cured at the higher temperatures.

Muego-Gnanasekharan and Resurreccion, (1992) evaluated the flavor changes of peanut pastes stored at 30°C, 40°C and 50°C for up to 1 year. Those peanut pastes that were held at 30°C had minimal flavor deterioration. Those samples stored at 50°C had increased browning, oxidized and cardboard flavors. Warner et al. (1996) investigated descriptive sensory changes of ground roast peanuts stored at 65°C for 68 days. They found roasted peanutty flavor decreased slightly the first 4-10 days of storage then leveled off. Rancid scores showed a marked increase from day 0 to 18 but leveled off during subsequent storage. Green attribute showed a slight decreasing trend during storage.

Fatty acid profile and flavor

Braddock et al. (1995) conducted sensory evaluation of high oleic (79% oleic acid, 2.9% linoleic acid) and normal oleic (55% oleic acid, 24.9% linoleic acid) that were stored at 25°C for 6 weeks. They found that peanutty flavor was more stable for high oleic than normal after 6 weeks of storage. Paint and cardboard flavors were higher in normal peanuts than in high oleic peanuts during storage.

Instrumental flavor analysis

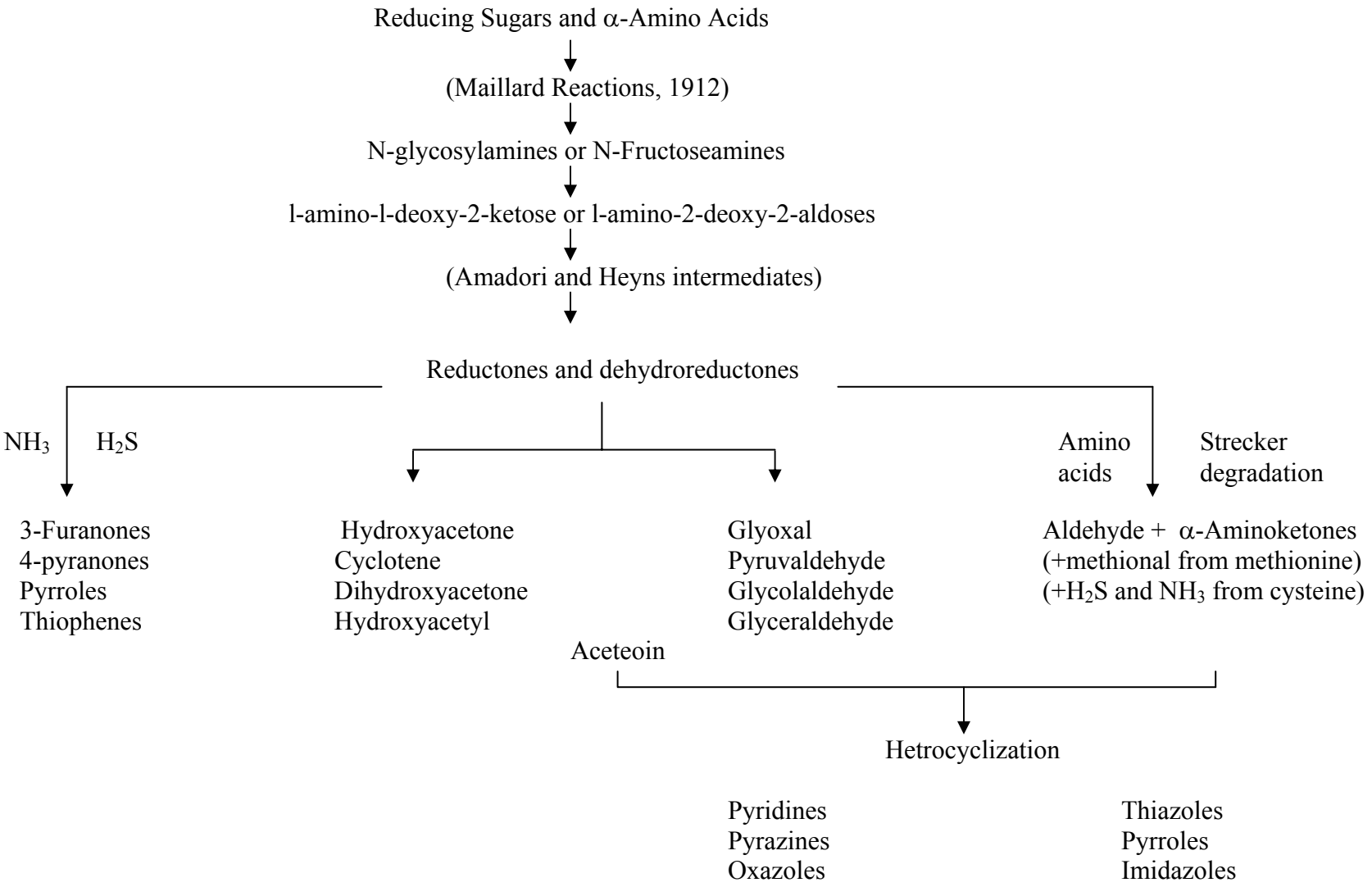
In the 1960s, the gas chromatograph-mass spectrometer (GS-MS), combined with computers and databases of mass spectra, was used to identify hundreds of chemical constituents in natural products. Biochemical characterization of flavor-active chemicals is accomplished by gas chromatography-olfactometry (GC-O) and other similar techniques such as gas chromatography-aroma extraction dilution analysis (GC-AEDA) or gas chromatography-CharmAnalysis (GC-CharmAnalysis). In each of these techniques, the essence is separated into their constituents using high-resolution GC, and the odor is assessed by sniffing the carrier gas as it flows with the carrier from the chromatograph (Acree, 1993).

Peanut volatile aromas

Roasted peanut flavor is a complex blend of hetrocyclic, lipid oxidation, and other volatile compounds formed during roasting through thermal degradation reactions, including Maillard reactions (Figure 2.1) between carbohydrate, free amino acids, and protein (Johnson et al., 1971, Bett and Boylston, 1992). Hetrocyclic compounds have browned, roasted, and nutty flavor notes (Bett and Boylston, 1992). Alkylpyrazines, in particular, have nutty, earthy flavor characteristics (Mason *et al*., 1966, Johnson *et al*., 1971, Buckholtz *et al*., 1980).

As early as 1952, Pickett and Holley noted that amino acids and carbohydrates are precursors of roasted peanut flavor. Newel et al. (1967) further verified that some specific amino acids and monosaccharides were the precursors of roasted peanut flavor.

Figure 2.1 Maillard Browning



The authors also indicated that specific amino acids, such as aspartic acid, glutamic acid, glutamine, aspargine, histidine, and phenylalanine were precursors of typical roasted flavor. Browning reactions in model systems comprised of monosacharides and amino acids resulted in the foramation of pyrazines, pyrroles, furans, and other low molecular weight products (Koehler et al., 1969; Koehler and Odell, 1970; Shaw and Berry, 1977; Shibamato and Bernard, 1977). Most peanut genotypes contain around 50% oil. Peanut oil is composed of approximately 80% unsaturated fatty acids, with oleic (18:1ω9) comprising an average of 50% and linoleic (18:2ω6) 30% of the total fatty acid composition (Mercer *et al*., 1990). The common peanut varieties and their compositions are presented in table 2.2.

Table 2.2 Fatty acid composition of common peanut varieties.

Fatty acid	Dixie Spanish (%)	S.E. Runner (%)	Virginia bunch (%)
Palmitic 16:0	12.9	10.0	9.1
Stearic 18:0	3.2	3.0	2.7
Oleic 18:1	43.1	50.6	56.9
Linoleic 18:2	3 4.5	31.2	24.9

Worthington and Hammons (1971)

Roasting of peanuts initiates lipid oxidation and the formation of carbonyl compounds. Lipid oxidation also continues during storage resulting in further increases in the content of aliphatic aldehydes, ketones, alcohols, and other lipid oxidation products. Products of linoleic acid oxidation include hexanal, heptanal, 2-heptanal, octanal, 2-octenal, 2-decenal, 2,4-decadienal, 1-octen-3-ol, and 2-pentylfuran. The most prevalent of such reactions is hexanal. Heptanal, octanal, 2-decenal, nonanal, and decanal are products of oleic acid oxidation. These compounds have rancid, painty, cardboardy and oxidized fat notes (Brown *et al*., 1971, Brown *et al.,* 1973, St. Angelo *et al*., 1984, Min *et al*., 1989).

Several investigators have identified the volatile components of roasted peanuts. Walradt et al. (1971) identified 187 compounds in medium brown roasted peanuts; 142 of

them including 17 pyrazines, were reported for the first time. Ho et al. (1982) studied the volatile flavor components of roasted runner peanuts (Neotec color of 25 ± 0.3). The investigators identified 187 compounds, 67 of which were reported as new roasted flavor. The authors identified twelve aliphatic hydrocarbons, seven aromatic hydrocarbons, seven alcohols, five acids, seven aldehydes and ketones. The aliphatic hydrocarbons did not play a significant role in the roasted peanut flavor and possessed relatively weak aroma. Only a small number of alchols, aldehydes and ketones were identified. They identified five lower acids, the main compound being isobutyric acid. It was described as being a major component in roasted peanut flavor and having butter like aroma. Three ester and six lactones were also identified. 2-crotolactone and 3-methyl-2-crotolactone had a nutty odor. 5-hydroxy-4-nonenoic acid was described as having a nutty fried aroma. They suggested that unsaturated lactones might play an important role in the roasted peanut flavor. A total of 21 alkylpyrazines were identified in the study. The pyrazine compounds had a pleasant roasted nut-like aroma. Maga (1992) has written an extensive review of pyrazines in foods. Seven pyrroles and seven pyridines were identified. N-methylpyrrole was described as having a sweet, woody odor. Eight thiazoles were identified. Among them, 2-isopropyl-4,5-dimethylthiazole and 2-propyl-4,5-diethylthiazole had a pleasant nutty aroma. In the study seven oxazoles were also identified. They were described as having a green nutty aroma. Other hetrocyclic compounds identified included eleven furanoid and three thiophenes and fifteen sulfides. Vercellotti et al. (1992) created an aromagram of a roasted peanut (Hunter L = 50) using direct GC-olfactory analysis (Table 2.3). They noted, as the peanut samples became rancid, positive attributes of the peanuts decreased. The rancid samples had increased hexanal and acetic acid.

Table 2.3 Analysis of roasted peanuts (Hunter L= 50) by direct GC-olfactory analysis

Peak identity	Aroma
Hydrogen sulfide	Sewer
Carbon sulfide	Yogurt
Sulfur dioxide	Chicken
Trimethylamine	Rotten eggs
Acrolein	Yogurt
Free methanol	Yogurt
Dimethyl sulfide	Paper mill/sulfur
Pentane/acetone	Nail polish
Diacetyl	Buttery
Methylpropanal	Fermented dairy
Diaminobutane	Sweaty socks/wet towels
N-methylprrole	Wood oil
Hexanal	Green beans/grassy
Dimethyl disulfide	Boiled milk/oniony
Methylpyrazine	Cooked beans
2,5-dimethylpyrazine	Toasted nuts/cereals
2-ethylpyrazine	Nutty/toasted pecans
2,6-dimethylpyrazine	Roasted peanuts
2,3-dimethylpyrazine	Sweet nutty(marzipan)
2-pentalfuran	Licorice/fruity
2-acetylthiazole	Roasted peanuts
2-methyl-5-ethylpyrazine	Sweet nutty
2,6-dimethyl-3-aminopyridine	Toasted cereal
2-acetylpyrazine	Roasted peanuts/popcorn
Benzaldehyde	Sweet almonds
Dimethylethylpyrazine	Chocolate
Tetramethylpyrazine	Barnyard/manure
Phenylacetaldehyde	Roses/jasmine/floral
Dimethyltetrasulfide	Bouillion/beef broth
2-methoxy-isobutylpyrazine	Earthy/peppers/raw peanuts
2,4-decadienal	Rancid oil
Benzothiophene	Licorice
Vinylphenol	Sweet chemical plastic
Pentadecane	Cheese casserole
Benzothiazole	Burned rubber
Hexadecane	Boiled beef

(Vercellotti *et al*., 1992)

Correlation of gas chromatogarph data with sensory data

Fore et al. (1976) demonstrated that ratios of either methylpropanal or 2(3)-methylbutanal to hexanal tended to decrease as flavor quality peanut butters decreased. Fore et al. (1979) conducted instrumental analysis of volatiles in air-and nitrogen-packed peanut butter samples from the same production lot, stored in the dark at 25°C for one year. During one year of storage, the authors observed ratios of methylpropanal and methylbutanal to hexanal were consistently higher for nitrogen- than for air packed samples. Brown et al. (1977) correlated volatile components of raw peanuts with flavor scores. They observed a decrease in ethanol peak area, ethanol to methanol ratio, and ethanol-to-total volatiles had increased Critical Laboratory Evaluation Roast (CLER) scores. CLER was developed to provide a qualitative and quantitative measurement of organoleptic quality (Holaday, 1971). Higher CLER score indicated better flavors. The correlation coefficients were -0.79 for ethanol peak area, -0.88 for ethanol-to-total volatiles, -0.87 for ethanol-to-methanol ratio, and -0.95 ln ethanol-to-methanol ratio. Buckholz et al. (1980) related volatile components of two varieties of peanuts, Runner # 1 and Spanish peanuts, of three different roasting times to sensory 9-point hedonic scale to rate strength and desirability of odor and flavor. Correlation of instrumental and sensory data observation showed that pyrazines correlated with sensory data. Volatile compounds such as 2-ethyl-3,6-dimethylpyrazine and 2-Vinyl-3,6(5)-dimethyl pyrazine correlated best with the aroma of roasted peanuts, while an unknown compound and 2-ethyl-6-methyl pyrazine correlated best with the flavor. The authors also developed equations to predict strength and desirability of odor and flavor. Lovegren et al. (1982) evaluated the gas chromatographic profile of raw Virginia peanuts. They observed that the combined peak areas of methanol, acetaldehyde, ethanol, and acetone groups (pentane, 2-

propanol, propanal, and acetone) usually comprised about 80% of the total volatile peak area. They concluded a "good" raw peanut is one that has not been damaged in any way and produces very low contents of volatile breakdown products of lipid oxidation and produces a very low volatile profile. St. Angelo et al. (1984) were able to "fingerprint" volatile profiles of raw peanuts from different countries as an indicator of quality. In addition, they were able to identify three major indicators of off-flavor. The first indicator was the presence of secondary lipid oxidation products such as hexanal, hexanol, and pentane. When these volatiles were at levels of approximately 5 ppm, the peanuts were judged rancid by a sensory panel. The second indicator of off-flavors was the presence of ethanol. The investigators observed, in some of the raw peanuts that were judged 'poor', that the ethanol content was approximately 8 ppm, compared to the normal range of 1-2 ppm. The third indicator of off-flavor was the presence of saturated hydrocarbons (10 to 16 carbons in length), substituted benzenes, and secondary products of lipid oxidation. Sanders and Greene (1989c) related the headspace volatile of 2-methylpropanal in peanuts of five consecutive peanut maturity classes. They observed quantitation as percent of total volatiles in ppm of the peanuts revealed a decrease in 2-methylpropanal as peanut matured regardless of seed size within maturity class. Crippen et al. (1992) related volatiles of two lots of Florunner peanuts of varying degree of roast to descriptive flavor data. They observed that pyrazines and some other compounds such as methylbutanal and methylpropanal correlated highly with dark roasted flavor. Woody/hulls/skins correlated highly with N-methylpyrrole. Several sulfur compounds related to dark roasted flavor, however, their characteristic aromas were not reminiscent of dark roasted peanuts. Desirable peanut flavors, such as roasted peanutty and sweet aromatic, did not correlate with gas chromatographic peaks. The authors concluded

that peanut flavor was very complicated and relationships between flavors and GC peaks was complicated by the lack of detection of compounds critical to flavor expression or by the combination of compounds that produce specific flavors. Brannan et al. (1999) correlated values of GC peaks, PV, and TBA with sensory attributes of stored full-fat and defatted peanuts.

Threshold levels of volatiles

Determination of flavor constituents of food is complicated by the large number of components present as well as the minute quantities in which many occur. Odor descriptions and olfactory threshold levels of volatiles present in foods are important as to the role of these volatiles in the flavor of foods. Koehler et al. (1971) reported odor threshold levels of selected alkylpyrazines in water and mineral oil. The investigators observed that, at low levels, alkylpyrazines had a peanut odor while at higher levels, the same compound produced burned odor. Shibamato (1986) listed the threshold levels of 46 pyrazines including alkyl-, phenyl-, alkoxy-, phenoxy-, phenylthio- and alkylthiopyrazines in water. He observed alkoxypyrazines possessed the lowest odortresholds while alkyl-pyrazines had the highest. Shibamato (1986) concluded that functional groups such as alkoxy and alkoxythio were closely related to the odor threshold of pyrazines; whereas the molecular shape of pyrazines probably does not strongly influence odor threshold. Masuda and Mihara (1988) reported the olfactory properties and threshold levels of alkylpyrazines and 3-substituted 2-alkylpyrazines. They observed that the odor threshold decreased with increasing number of carbon atoms in the side chain. In general, the odor treshold of 3-substituted 2-alkylpyrazines increase in the following order: $OCH_3 < OC_2H_5 \leq SCH_3 < SC_2H_5 < OC_2H_5 < OC_6H_5 \leq SC_6H_5$. Fors and Olofsson (1985) determined odor detection threshold and odor intensities

for a number of alkylpyrazines by dynamic olfactometry. The investigators stated that many of the threshold estimates reported in the literature are often related to concentrations of the compounds in different media, which usually consist of water or oil. They used air-dilution olfactometers that were used to estimate odor thresholds for a number of alkylpyrazines expressed as a concentration in the gas phase (air). They reported that the odor threshold values decreased with increasing number within a homologous series. Among the pyrazines they evaluated, substituents in the 2,5- and 2,6-substitutions had lower treshold values as compared to those in the 2,3-position. In a later study, Fors and Olofsson (1985) attempted to describe the odor qualities of the pyrazines they evaluated in their earlier study. They used ten panelists, and developed a list of 22 descriptors to describe the odor of 5 alkylpyrazines at four concentrations. The intensities of the descriptors increased with higher sample concentrations. Descriptors, such as pungent, solvent-like, and sweet, were common among all samples, whereas as most of the other terms were found to be only applicable for a few pyrazines. Fors and Olofsson (1985) also noted that common terms such as chocolate, nutty and roasted reported in the literature for alkylpyrazines were rarely used by their panel.

Volatility of organic flavor compounds

To a considerable extent the volatility of aroma compounds is controlled by the affinity of the compounds for a particular medium(s) in the food. Since most foods are complex, it is useful to relate them to model system. Buttery et al. (1973, 1971) studied the volatility of number of flavor compounds in pure water, vegetable oil, and water-vegetable oil mixtures. Buttery et al. (1973) observed that the air-vegetable oil partition coefficients at 25°C for aliphatic aldehydes (C4-C9) decreased with increase of the carbon length. The air-water partitioning coefficient increased for same aliphatic aldehydes. Buttery et al. (1971)

observed that air-water partitioning coefficients of the introduction of double bonds in aldehydes increased the water solubility of the aldehydes and thereby lowering their volatility in water solution. Buttery et al. (1971) also observed that increasing the alkyl side chain of pyrazines increased the volatility in water solution. The introduction of a methoxy group increased the volatility of the pyrazines about five to ten times, which may have to do with donation of electrons to the ring by the methoxy group.

Storage stability

Storage stability of peanut products is based on variety, harvest, processing and storage practices (Shewfelt and Young, 1977). The high degree of unsaturated fatty acids in peanuts makes them susceptible to lipid oxidation during storage, which is significant to the overall flavor of roasted peanuts. Lipid oxidation state of peanut products can be analyzed by peroxide value (PV), thiobarbituric acid (TBA), measurement of volatile carbonyl products and conjugated diene (St. Angelo *et al*., 1977). The limiting peroxide value (PV) critical for acceptability of roasted peanuts is 20-30 mEq/kg (Evranuz, 1993). Vercellotti et al. (1992) described good quality roasted peanuts with PV = 1.4 mEq/kg and oxidized PV= 111 mEq/kg.

Effects of moisture/water activity/relative humidity and other minor constituents on stability of peanut products

St. Angelo and Ory (1973) measured initial peroxide content of nine commercial peanut butters and observed no two samples had the same initial peroxide content. Their study suggested the quality of the peanuts before roasting and processing varied greatly and therefore had already had different stages of peroxidation. Peanuts contain proteins and metals such as tyrosinase (copper containing enzyme) and peroxidase (iron containing enzyme) (St. Angelo *et al*., 1971). Roasting can cause heat denaturation of enzymes forcing

them to lose their specific activities, however their ability to catalyze the peroxidation of fatty acids is not destroyed. St. Angelo and Ory (1973) investigated the causes and prevention of fatty acid peroxidation in peanut butter with several additives. They investigated peanut butter samples: control (no additive), cupric acetate, boiled peroxidase, boiled peroxidase plus EDTA, boiled tyrosinase, and water. Measurements of total conjugated diene hydroperoxide (CDHP) in μ mol per gram of peanut butter after 3 months storage for the additives were, 14.6, 6.8, 2.9, 1.4, 1.3, and 0.4 respectively. St. Angelo and Ory (1973) noticed water either promote or retard oxidation. They also investigated peanut oil as a carrier solvent for several metallo proteins and salts added to peanut butter. The additive included control, peanut oil, NaCl, cupric acetate, ferric chloride, tyrosinase, peroxidase, lipoxygenase. After three months of storage, sample containing added peanut oil increased to 4 μmoles of CDHP per g of peanut butter, sodium chloride did not have any effect when added in peanut oil. The metal salts cuppric acetate and feric chloride showed an increase of 9.5 and 7.2 respectively. Tyrosinase and peroxidase resulted in increased rates of oxidation but neither enzyme were as effective a catalyst as the free copper which had the highest peroxidation. Lipoxygenase, the primary catalyst of enzymatic oxidation of unsaturated fatty acids also gave increased peroxidation but it was less than that caused by metal containing proteins.

St. Angelo and Ory (1973) investigated the peroxidation of peanut butter samples stored for two months that had different concentrations of water added to them. With the addition of 4.8% water (w/w) peanut butter showed an apparent antioxidant effect. When 1.2% water (w/w) was added, rate of peroxidation did not differ from the control sample. However, when 0.6%(w/w) water was added, it behaved as a pro-oxidant. Felland and

Koehler (1997) studied the oxidation state of peanut butters with water activities (a_w) of 0.29, 0.39 and 0.56 respectively and stored at three different temperatures, 4 °C, 25 °C and 50 °C for 29 days. After 29 days of storage at the respective temperatures, the TBA values were low for all samples, however, samples with water activities (a_w) of 0.39 and 0.56 had relatively lower TBA values when compared to the control. Reed *et al*. (2002) investigated on the oxidation stability of normal and high oleic peanuts held at 19% or 60% RH for 7 weeks. In both types of peanuts, those held at 19 % RH had higher peroxide values compared to those held at 60 % RH. In a separate study, Mate *et al*., (1996) investigated lipid oxidation of roasted peanuts and oil roasted peanuts that were stored at high oxygen concentration (21%) and low oxygen concentration (< 2.5%) and each stored at 21% RH and 53% RH at 37 °C for 10 weeks. In the high oxygen concentration peanuts, at both RH both dry and oil roasted peanuts had higher PV and hexanal content than low oxygen concentration peanuts. Both dry-roasted and oil-roasted peanuts were much more susceptible to lipid oxidation at 21% RH than at 53% RH. Investigation by Evranuz (1993) of unblanched salted peanuts with moisture contents of 1.4%, 2.2% 2.9% and 3.9%, found out that samples with 1.4% and 3.9% moisture content had more rapid oxidation rate than intermediate moistures (2.2% and 2.9%).

Fatty acid profile and storage stability

Braddock et al. (1995) observed the hexanal content of normal-oleic (55% oleic acid, 24.9% linoleic acid) peanuts was higher compared to high-oleic (79% oleic acid, 2.9% linoleic acid) peanuts stored at 25°C for 6 weeks. They also observed the peroxide values were lower for high-oleic peanuts than normal oleic-peanuts during storage at 25°C and 40°C.

Temperature and stability

Peanut butter is stable to bacterial spoilage due to its low moisture content, but it has a limited shelf-life from the onset of off-flavors and odors caused by autoxidation (Woodroof, 1983). Especially, oil separation in peanut butter due to the difference in gravity of the solid particles and the oil facilitates in autoxidation where the oil is exposed to air. Evranuz (1993) observed from PV values of unblanched peanuts stored at 15°C, 25°C and 35°C for 70 days, oxidation took place even at 15°C and the rate of oxidation was especially accelerated at high temperatures.

Peanut Color

The color to which peanuts are roasted is important to the quality of peanut products. There is strong association between the color and the flavor, and the aroma which develops during roasting (Morris *et al*., 1966). Another important aspect of color and peanut quality is the effect of mold growth or aflatoxin on the color of the individual kernels. The peanut kernels darken when mold grows on them. Most shelling plants employ this darkening phenomenon to electronically sort individual kernels (Tiemstra, 1973). The characteristic color in peanuts results from the sugar-amino acid reactions that produce melanin (Hodge, 1953). Increasing roast temperature and roasting time intensifies the golden brown color of melanin. Caramelization of sugar is also a secondary source of color (Mason *et al*., 1966). Degree of roast, color intensity, and roasted peanut sensory attribute intensity are logically interrelated (Pattee *et al*., 1991). A time-temperature studies protocol or reference to degree of roast as light, medium or dark are usually used in peanut-roasting studies (Buckholtz, *et al*., 1980) and descriptive sensory flavor expression (Johnsen *et al*., 1988). Pattee et al. (1982 a, b) used Hunter L readings to indicate the degree of roast and to study the changes in

roasted peanut flavor as affected by seed size, storage time, and seed moisture content. They indicated that an L reading of 49 was equivalent to medium roast. Pattee et al. (1989, 1990) also used CIE L*a*b* color readings to describe the degree of roast in peanut paste samples use for sensory evaluation. Sanders et al. (1989 a,b) used Hunter L readings to measure the degree of roast and studied the effect of maturity and curing temperature effects on roast color and descriptive flavor. They also studied degrees of roast effect on alkylpyrazine production. Felland and Koehler (1997) studied the effects of moisture, temperature and storage time of increased water activity products on Hunter L readings. They observed the development of instantaneous color changes once water is thoroughly blended in peanut butter. The peanut butter products became darker, a decrease in Hunter L reading, as water was added. A study conducted by Brannan et al. (1999) on the effect of full-fat (53% oil) and defattted (22% oil) roasted peanuts stored at different temperatures found out defatted peanuts were lighter in color as indicated by a higher Hunter L and b readings and a lower a reading. They explained the lighter color in the defatted peanuts as being due to the decrease in melanin caused by the removal of oil, which is responsible for the color of oil. The Hunter a reading of defatted and full-fat samples also showed a decrease during storage. Pattee et al. (1982 b) studied raw peanuts with initial moisture content of approximately 6 and 9% that were eventually made into peanut butters. The results included Hunter L reading showing that 9% moisture level samples had a darker color than 6% moisture samples. The Hunter L a b readings of the raw peanuts with intact skins were significantly affected by storage time. This study also showed that the skins of the high moisture peanuts darkened more than the low moisture peanuts during storage. The Hunter b reading showed significant decreases, which indicated the dulling appearance of the raw high moisture peanuts during storage.

Sanders et al. (1989a) studied uniformed sized Florunner peanuts of five pod-color based maturity classes from two crop years. The immature peanuts roasted darker at a faster rate than mature peanuts and were, therefore, easier to over-roast. Chiou et al. (1991) observed two lots of mature kernels containing 3.40% and 10.50% moisture roasted at 150°C for 45 min had increased Hunter a readings of the roasted unskinned kernels with time while L and b readings decreased. They also observed that the change of visual color in peanuts containing 10.50% moisture was more pronounced than that of peanuts containing 3.40% moisture.

Texture

Processing and ingredient parameters can affect peanut butter texture (Woodroof *et al*. 1945). Young and Heinis (1989) noted that the addition of honey or corn syrup altered peanut butter flavors and viscosity. It has been suggested addition of moisture alters the quality of roasted peanut product (Felland, 1993). Nakayama (1992) observed that the addition of small amount of water to peanut butter gave a much stiffer butter. Added moisture also changed the viscosity of peanut butter.

A survey conducted by How and Young (1985) found that 71% of the people surveyed disliked sticky peanut butter. They also found selection of favorite brands is based on particle size variations, which produce smooth, creamy or crunchy peanut butter. Crippen et al. (1989) studied instrumental and sensory texture analysis and consumer preference of peanut butter with three different grinds, three salt concentrations, and three sucrose concentrations. They observed that sensory smoothness, hardness, spreadability, adhesiveness, ease of swallowing, and preference ratings of peanut butter were affected by different levels of grind size, sucrose concentrations, and salt concentrations. They found that

increased grind size decreased sensory smoothness, spreadability, adhesiveness and preference ratings, but increased instrumental hardness. Increased concentration of sucrose caused a decrease in instrumental hardness, sensory adhesivness and consumer texture ratings. Addition of salt increased the ease of swallowing and consumer preference of texture.

Muego et al. (1990) observed significant correlations of selected textural sensory attributes with instrumental hardness values of two commercial peanut butters and peanut paste samples. They observed significant Pearson correlations of grainy (0.80), spread (-0.76), and smoothness (-0.77) with instrumental hardness value.

The oil separation in peanut butter is due to the difference in specific gravity of the solid particles and the oil, which results in the gravitational separation of these components (Freeman and Singleton, 1952).

Peanut microstructure

Peanut microstructure characterization

Peanut cotyledon tissue is largely made up of isodiametric parenchyma cells. A cytoplasmic network surrounds parenchyma cells and other subcellular organelles. The major subcellular organelles of the parenchyma cells are lipid bodies, protein bodies, and starch grains (Young and Schadel, 1991). Yatsu and Jacks (1972) and Jacks et al. (1967) used transmission electron microscope (TEM) to characterize sub-cellular organelles. They characterized lipid bodies as particles about 1-2 micrometers in diameter bounded by a half unit-membrane, which measures 2-3.5 nanometer in width. Protein bodies in mature peanut seeds range 5-12 micrometers in diameter and starch grains range from 4-15 micrometers in diameter. Starch grains are characterized by central hilum.

Effect of environment on peanut seed microstructure

Poor environmental condition can affect the structural integrity of a peanut seed. Young and Schadel (1984, 1989) studied drought induced peanut seed cotyledon and tissue damage using light microscope (LM) and scanning electron microscopy (SEM). They observed the damage, (1) as appearing as a narrow band along the interface of the rounded outer surface and the flattened edge of the inner surface and (2) spotting on outer surface.

Effect of processing on peanut seed microstructure

Peanut processing involves the use and control of moisture, temperature, pressure, mechanical disintegration and solvents to increase the economic value of the peanuts. The application of process-specific conditions may require peanuts to be roasted, blanched, made into peanut butter, used in confections, pressed for oil, or treated for recovery of protein (Woodroof and Leahy, 1940). The result of process specific treatments is summarized in Table 2.5.

Young and Schadel (1990 a,b) used LM, SEM, and TEM to study the microstructure of raw and peanut cotyledons oven roasted for 16 min at 160 °C. They observed that roasting resulted in (a) pitting and pock-marking of the epidermis of the cotyledons due to the escape of steam and oil releasing during roasting; (b) loss of the cellular organization of cytoplasmic network surrounding the lipid bodies, protein bodies, starch grains; (c) alteration of the structure of cytoplsmic network, lipid bodies, protein bodies, and (d) decreased stain affinity of starch grains and heat destruction of some of the middle lamella of cell-to-cell junctions.

Young and Schadel (1993) observed the effect of oven roasting and oil cooking by LM, SEM and TEM at 160 °C at different time intervals. They observed that the thermal

modification exhibited by oil cooking was determined to be similar to oven-roasting. They also observed decreased electron affinity of starch grains in both oil-cooked as in oven-cooked peanuts.

Young and Schadel (1990b) used LM and SEM to evaluate the quality of homogenization on the microstructural features of stabilized peanut butter. They were able to determine the completeness of homogenization of broken cell and tissue fragments, protein bodies, and starch grains within the matrix of stabilized oil. Aryana et al. (2000) used LM to examine spatial distribution of various components found in peanut butters that were stabilized with 0, 1.5 and 2.5% palm oil, hydrogenated vegetable oil, and non-stabilized peanut butters. They concluded palm oil has a potential as a stabilizer in peanut butter but that shelf-life stability is likely to be less than those of hydrogenated vegetable oils stabilizers. They also observed palm oil stabilizers had less stable microstructure at high temperature that resulted in a low level of solid dispersion in the continuous oil phase.

Vix et al. (1972) used TEM to examine the ultrastucture of partially defatted peanuts due to hydraulic pressing. They observed that hydraulic pressing resulted in broken lipid body membranes, compressed cell walls, and coalesced protein bodies. Yatsu (1981) applied SEM to study the cell walls of peanut cotyledons that required an unusual amount of pressure to express peanut oil. He concluded that the extra pressure required by difficult-to-press peanuts was not due to cell material alone.

Table 2.5 Changes in cells due to processing (Woodroof and Leahy, 1940)

Processing	Cells and cell walls	Inter-cellular spaces	Nucleus	Aleurone Grains	Oil Droplets	Starch grains
Grinding or rolling almost to fineness of peanut butter	About 50% of cells ruptured & emptied of contents, many others were merely crushed, while from 10-25% were injured	No change when cells were un-injured.	No change when cells were uninjured, otherwise it was crushed	Relatively few were crushed. Most of them rolled about independently even when the cell wall was severely crushed	When the cells were crushed, the oil droplets ran together to form large drops of free oil. If cells were not crushed, no change occurred in oil droplets.	Some were crushed, while most of them were not.
Cooking at (121C) in the presence of high moisture	Turgidity destroyed; cell walls become slack, but only a few were broken	Almost eliminated.	Coagulated , granular, centrally located but tended to break up	Completely separated, scattered throughout cell and a few become lopsided. Total size and number unchanged.	Fusing of some droplets to form fewer and larger droplets within cells. A few drops of free oil appeared in each cell. Viscosity of oil greatly lowered.	Apparently destroyed or dissolved
Dry roasting at 149C	Cell walls remained unchanged	No change	Coagulated into hard mass center of cell	Drawn away from cell walls into hard mass around nucleus. The number size of grains was little changed. Proteins were precipitated and very granular	Fused into larger and fewer droplets within the cells. Small amount of oil escaped into the cell as free oil. Cell walls and skins became oil-saoked.	Remained same in number and slightly reduced in size

Processing	Cells and cell walls	Inter-cellular spaces	Nucleus	Aleurone Grains	Oil Droplets	Starch grains
Roasting in oil at 138C	No apparent change	No change	Coagulated but almost indistinct due to crowding in cell	Few grains were normal size, most of them were swollen 3 to 4 times original size due to absorption of oil. They were precipitated and very granular. Crowding in cells causes some grain to be distorted	Due to absorption of oil from cooking bath and consequent swelling, the original oil droplets lost their identity	No apparent change
Cold pressing at ordinary temperature and 5000-7000 psi	Most of cells completely crushed	None	Crushed	Mashed and distorted but many of them retained their identity	When the cells were crushed, the oil droplets ran together forming drops of free oil. If cells were not crushed, no change occurred in oil droplets.	Crushed
Hot pressing at 121 C or higher and 5000-7000 psi	Crushed	None	Crushed	Crushed	Viscosity of oil made very low. All droplets fused into drops of free oil.	Crushed

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CHAPTER 3

DESCRIPTIVE SENSORY ANALYSIS OF STORED MODEL PEANUT CONFECTIONS WITH DIFFERENT SUGAR, MOISTURE AND ANTIOXIDANT LEVELS[1]

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ABSTRACT: Model peanut confections with two antioxidant (TBHQ) levels (0 and 180 ppm), two sucrose levels (0 and 4%) and 3 moisture levels (0, 2 and 5%) were stored at 21 C for 52 weeks. Six sensory descriptors, 'sweet', 'bitter', 'roasted peanutty', 'rancid', 'painty' and 'cardboard' attributes were examined by a trained sensory panel. Samples with intermediate and high moisture had high 'rancid', 'painty' and 'cardboard' scores and low 'roasted peanutty' and 'sweet' scores. Samples with TBHQ had higher 'roasted peanutty' flavor and lower 'rancidity', 'painty' and 'cardboard' scores in low moisture treatments. Addition of sucrose increased sweetness while reducing bitterness and rancidity of peanut paste ($P \leq 0.05$). Significant two-way interactions were observed for all attributes.

KEYWORDS: Sensory evaluation, peanut paste flavor and moisture

INTRODUCTION

Moisture can be introduced to peanut products intentionally or unintentionally during processing, transport or storage. It has been suggested that moisture alters the quality of roasted peanut products (Felland, 1993). High moisture roasted peanut products have objectionable soggy nut flavor (Woodroof, 1983). Felland and Koehler (1997) observed that when moisture was added to peanut butter, the sensory properties of stored samples were markedly changed. Young and Heinis (1989) noted that the addition of honey or corn syrup altered peanut butter flavor and viscosity. Reed *et al*. (2002) found that high oleic and normal oleic peanuts with 0.19 a_w had the lowest peanutty

flavor loss, compared to those samples stored at 0.60 a_w. For both peanut types, 0.19 a_w samples had the highest painty, cardboardy, and bitter attributes during storage.

St. Angelo *et al*. (1972, 1973) observed that water could act as a pro-oxidant or antioxidant in peanut butter samples with different concentrations of added water. Brannan *et al.* (1999) observed that defatted roasted peanuts, which usually have higher moisture content, had lower roasted peanutty scores compared to full-fat roasted peanuts. They also found that defatted peanuts had intense rancid-related attributes that increased during storage.

Previous studies have shown that factors such as roasting time (Buckholtz et al. 1980), seed size (Pattee et al. 1982), maturity (McNeill and Sanders, 1998), relative humidity (Reed *et al*., 2002) and storage temperature (Pattee *et al*. 1999) affected peanut flavor during storage. However, there are no full sensory studies on the combinations of common ingredients, namely water, sugar and antioxidants, and their influence on peanut flavor during storage. The objective of this study was to determine the effect of added moisture, sugar and antioxidant on sensory flavor attributes of a peanut paste.

MATERIALS AND METHODS

Sample preparation and storage

Fresh, untreated, certified, aflatoxin negative roasted peanut paste was supplied by Seabrook Ingredients (Edelton, NC). Initial analysis of the peanut paste showed 53.94% oil, 0.86% water, fineness of grind (35 mils first scrape, 3 mils second scrape), free fatty acid 0.13%, and coliform MPN <3. Upon receipt it was placed in storage at -10

C and processed within one week. The peanut paste was first mixed using a model SPY-1824 paddle mixer (Marion Mixers, Inc., Marion, IA) to make sure there was no oil separation before sample preparations. A factorial arrangement was used to specify the levels of peanut paste and ingredients. Twelve treatments were prepared with three levels (0, 2 and 5%) added moisture, two levels (0 and 4%) of sucrose, and two levels (0 and 180 ppm) of the antioxidant, tertiary butylhydroquinone (TBHQ). Two separate batches were prepared for each treatment group. Enough material was prepared for each group to allow analysis at 6 storage times (0, 4, 8, 16, 32 and 52 weeks). Formulations for each treatment are shown in Table 3.1. Approximately 5.44 kg of peanut paste was heated inside a Sharp microwave oven, model R-510CK (Sharp Electronics Corp., Mahwah, NJ) to a temperature of 83 C and then placed in a model KSMC50S KitchenAid mixer equipped with a flat beat paddle (KitchenAid, St. Joseph, MI). A heating mantle maintained the temperature at 83 C. Refined 6X sucrose (Domino Sugar Co., New Orleans, LA), water, TBHQ (Eastman Chemical, Kingsport, TN) in refined peanut oil (CNT Refinery, Charlotte, NC), Dritex RC hydrogenated vegetable oil stabilizer (AC Humko, Memphis, TN) melted at 83 C and flour salt (Cargill, Minneapolis, MN) were added slowly while mixing for a total mixing time of 2 minutes. Peanut pastes were made and poured into a series of small plastic petri dishes (30mm diameter x 10mm depth), where the samples were allowed to cool and harden. The samples were covered with plastic lids that were pre-drilled with 1mm holes to allow air circulation.

Storage and sampling

The samples were placed in a controlled temperature (21C ± 0.1C) and humidity chambers (Model 435314, Hotpack SP Industries, Philadelphia) each set at a relative humidity (%RH ± 2.0%) close to 100 times the water activity (a_w) of the samples. As the a_w of the air is just %RH/100, this approach limited the amount of moisture lost or gained by the sample due to moisture transfer with the surroundings. Replicate samples were randomly pulled for sensory evaluation at 0, 4, 8, 16, 32, and 52 weeks of storage.

Water activity and moisture measurement

Water activity of the samples was determined on each sampling day. The water activity meter (Aqua lab series 3, Pullman, WA) was standardized at 21 C with the saturated salts 8.5 molal LiCl and 13.3 molal LiCl, with respective a_w of 0.25 and 0.50. Moisture was calculated as percent weight of moisture to the original weight of the sample (Ab 2-49 AOCS, 1993). The procedure was modified as follows: approximately 5.0g of peanut paste sample was thinly spread on an aluminum pan and dried in a convection oven (Precision mechanical oven, Chicago, IL) for 24hr at 100C.

Sensory evaluation

Sensory panel

Nine panelists, four males and five females from the Department of Food Science and Technology at University of Georgia were trained in descriptive analysis as described by Meilgaard *et al.* (1991). Criteria for the panelists were that they were: (1) between 18 and 50 years of age, (2) not allergic to peanut butter, (3) consume peanut butter at least

once a month, (4) able to pass a screening test that consisted of two sections, a taste test and aroma test and (5) available and willing to participate during training and testing sessions.

Training session

The panelists were trained for seven sessions, 90 min per session. Panelists were presented with fresh and older commercial peanut butter samples in order to acquaint them with different peanut flavor attributes. A lexicon of established peanut flavor descriptors (Johnsen *et al*., 1988) was used as a guide during terminology development. A final list of six peanut paste sensory attribute definitions was retained after a consensus by panel members (Table 3.2). Panelists were trained using reference standards corresponding to points on a 150-mm unstructured line scale (Table 3.3). Calibration of the panel was conducted by first obtaining an average panel rating; those not rating within 10 points of the average were asked to re-evaluate the sample and adjust their rating until a consensus was reached. The group, as a whole, was considered to be calibrated if the group's standard deviation was within 10 points from the mean attribute rating (Malundo *et al*., 1996).

Testing session

Peanut paste treatments were removed from storage an hour before sensory evaluation and were equilibrated to room temperature. Evaluations were carried out in partition booths illuminated by fluorescent lighting. The panelists rated attributes using a 150-mm unstructured line scale. In each booth, the panelists were presented

approximately 5.0g peanut paste samples in petri dishes that were labeled with three digit random numbers, along with reference standards, water, unsalted crackers and expectorant cups. The panelists were instructed to evaluate six peanut paste sensory attributes: 'sweet', 'bitter', 'roasted peanutty', 'rancid', 'painty', and 'cardboard'. The panelists were instructed first to familiarize themselves with the reference standard intensities (Table 3.3) and then place a half-teaspoon of peanut paste in their mouth to evaluate the flavor attributes. They were also instructed to evaluate the treatments in the order shown on the score sheets and eat unsalted crackers and drink distilled water between samples to clear the palate. Each panelist evaluated twelve peanut paste treatments the same day in two separate sessions with six randomly assigned in the morning and six randomly assigned for each panelist in the afternoon. Each panel session was replicated after 24 hr using the same procedure, but with different random orders of presentation for each panelist.

Statistical Analysis

Data were analyzed using the PROC MIXED routine in the SAS statistical software system, version 6.12 (SAS Institute, Cary, NC). The sources of variation and corresponding tests of significance for each of the fixed effects in the analysis are shown in Table 3.4. The LSMEANS statement with the PDIFF option was used for mean separation. The random effects consisted of replicate, session(replicate), panelists, panelist*replicate, and panelist*session(replicate).

RESULTS AND DISCUSSION

Sweetness: The perception of sweetness was not affected by the presence of antioxidant. Sucrose level, storage time and an interaction between TBHQ and moisture affected 'sweet' perception (Table 3.4). Obviously, treatments with higher sucrose levels had higher 'sweet' rating (Table 3.5). Treatments with higher moisture levels had lower perceived sweetness (Table 3.6). The decrease in sweetness with added moisture may be related to the dilution of sucrose by the moisture. In general, 'sweet' scores decreased with time, although the changes were not large (Table 3.7). Muego-Gnanasekharan and Resurreccion (1992) found no change in sweet taste during storage of peanut paste samples that were stored at 30, 40 and 50 C for up to 1 yr. As the treatments were maintained so as to limit moisture changes, the reason for the decrease in sweetness over time is uncertain. It may be that changes in other flavor component mask or decrease the perception of sweetness.

Bitterness: Sucrose level, storage time, and an interaction between TBHQ and moisture influenced the perception of 'bitter' flavor (Table 3.4). Those treatments with 4% sucrose added were perceived as less 'bitter' (Table 3.5). The interactions between 'sweet' and 'bitter' flavors are well known (Walters and Roy, 1994). Sweet materials can be used to mask bitter ones to some extent, and sweet and bitter tastes rely on similar sterochemical mechanisms. Previous studies (Pattee *et al*., 1998) suggested sweetness could be effective in simultaneously enhancing roasted peanut flavor and decreasing bitterness in peanuts. Generally, treatments with added moisture had slightly higher bitter

scores compared to treatments with no moisture addition. 'Bitter' score was significantly lower for treatments with no added moisture and 180 ppm TBHQ, compared to samples with no added moisture or TBHQ (Table 3.6). Generally, bitterness did increase with storage time (Table 3.7). This is probably from increased protein hydrolysis during storage which sometimes liberates bitter peptides (Damodaran, 1996). The increase in bitterness may be responsible for the decreased sensation of sweetness.

Lipid oxidation-related flavors: Lipids comprise 52% of the dry weight of peanuts. Over 75% of the fatty acids present in peanuts are unsaturated, with 48% oleic and 31% linoleic acids. Lipid oxidation continues during storage resulting in increases in the content of aliphatic aldehydes, ketones, alcohols, and other products of lipid oxidation (Bett and Boylston, 1992). In our study, lipid oxidation attributes were classified as either 'rancid', 'painty', and 'cardboard' flavors. Sucrose had a significant effect on 'rancid' flavor (Table 3.4). Treatments with 4% sucrose had significantly lower 'rancid' scores compared to those with 0% sucrose (Table 3.5). It is possibly that the sensation of sweetness masks or softens the sensation of 'rancid' flavor.

There was significant TBHQ and moisture interaction for 'rancid', 'painty' and 'cardboard' attributes. Generally, intermediate and high moisture treatments had higher 'rancid', 'painty', and 'cardboard' scores (Table 3.6). It was also observed that 'rancid', 'painty', and 'cardboard' scores were significantly higher for treatments with 0% moisture and 0 ppm TBHQ compared to 0% moisture and 180 ppm TBHQ treatments. St. Angelo and Ory (1973) observed that when water was added to peanut butter at 4.8% (w/w) it

had an apparent antioxidant effect, while at 1.2% (w/w), the rate of peroxidation did not differ from the control sample. However, when water was added at 0.6% (w/w), it behaved as a pro-oxidant. Possibly, TBHQ slowed down lipid oxidation in 0% moisture treatments. Although not strictly dealing with oxidation, Felland and Koehler (1997) found off-odors and flavors were higher in peanut butter samples containing 5% moisture. However, they also measured very low TBA values and concluded that 'off-flavor' was probably not due to oxidation alone. As 'roasted peanut' flavor was found to decrease with moisture, this may have left heightened sense of 'off-flavor' and aromas.

Storage time was significant for 'rancid', 'painty' and 'cardboard' attributes. Differences in 'rancid' scores developed after 8 weeks of storage and after 16 weeks for 'painty', and 'cardboard' attributes (Table 3.7). Samples with TBHQ still developed 'rancid', 'painty', and 'cardboard' flavors over time.

Roasted Peanutty flavor: The roasted, browned and nutty flavor notes of roasted peanuts have been attributed to alkylpyrazines. These compounds are formed through Maillard and other thermal degradation reactions between amino acids and sugars (Mason *et al*., 1966; Johnson *et al*., 1971 and Bett and Boylston, 1992). Moisture level affected the perception of 'roasted peanutty' flavor. Samples with intermediate and high moisture had the greatest change in 'roasted peanutty' flavor (Table 3.8). Samples with 5% moisture added had a 13.3% decrease in 'roasted peanutty' scores compared to 0% moisture samples. Felland and Koehler (1997) also found that 'roasted odor' and 'roasted flavor' scores decreased with addition of moisture in peanut butters. There was a

significant interaction between TBHQ and storage week. Treatments with TBHQ had significantly higher 'roasted peanutty' scores on week 4 and week 8 than those without TBHQ (Table 3.9). For both samples with and without TBHQ, 'roasted peanutty' scores decreased during storage. For treatments with TBHQ, after 52 weeks, 'roasted peanutty' scores dropped by 47.2% (62.5 to 33.0) (Table 3.9). Felland and Koehler (1997) found decreases in 'roasted odor' and 'roasted flavor' of peanut butters during 30 days of storage, while Pattee et al. (1999) observed decreased 'roasted peanut' attribute of peanut paste after it was stored at -10 C and -23 C for up to 13 months. Brannan et al. (1999) observed that for full-fat and reduced-fat peanuts stored at 25 C, 'roasted peanutty' flavor continued to decrease during 12 weeks of storage and Warner et al. (1996) also found 'roasted peanut' flavor decreased slightly during 68 days of storage at 65 C. Bett and Boylston (1992) suggested the decrease in 'roasted peanut' flavor during storage may be attributed to loss of peanut flavor volatile compounds by either degradation by lipid radicals and peroxides, or flavor entrainment by complexes between proteins and lipid hydroperoxides or its secondary products.

SUMMARY AND CONCLUSION

'Roasted peanutty' attribute decreased over storage time. Oxidation-related attributes such as 'rancid', 'painty', and 'cardboard' intensified over storage time. 'Sweet' and 'roasted peanutty' attributes in intermediate and high moisture samples were scored low over time. 'Bitter', 'rancid', 'painty', and 'cardboard' attributes were rated higher in intermediate and high moisture treatments, possibly due to 'roasted peanuty' flavor loss

resulting in 'off-flavor'. Treatments with added TBHQ had higher 'roasted peanutty' scores. In low moisture treatments, addition of TBHQ resulted in lower 'rancid', 'painty', and 'cardboard' scores. Addition of 4% sucrose resulted in higher 'sweet' scores, lower 'bitter', and 'rancid' scores. Significant two-way interactions were observed for all attributes. The level of moisture, sucrose and antioxidant that was considered in this study is relevant to confection industry that uses peanut products. These moisture levels could be picked up intentionally or unintentionally during processing and storage and could interact with sugar and antioxidant present, thus resulting in flavor changes in peanut confections during storage.

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Table 3.1 Factorial arrangement used for peanut paste, moisture content, and antioxidant components. Two replicate batches were prepared for each treatment.

Treatment	Ingredient (Weight Percentage)					
	Peanut paste	Sucrose	Water	Stabilizer	TBHQ (ppm)	Salt
1	96.58	0	0	2	0	0.42
2	96.58	0	0	2	180	0.42
3	94.58	0	2	2	0	0.42
4	94.58	0	2	2	180	0.42
5	91.58	0	5	2	0	0.42
6	91.58	0	5	2	180	0.42
7	92.58	4	0	2	0	0.42
8	92.58	4	0	2	180	0.42
9	90.58	4	2	2	0	0.42
10	90.58	4	2	2	180	0.42
11	87.58	4	5	2	0	0.42
12	87.58	4	5	2	180	0.42

Table 3.2 Definitions of attributes used to describe peanut paste.

Attribute	Definition[a]
Taste	
Sweet:	The taste on the tongue associated with sugars
Bitter:	The taste on the tongue associated with bitter solutions such as caffeine
Aromatics	
Rancid	The flavor associated with oxidized fats and oils
Roasted Peanutty	The flavor associated with medium roast peanuts
Painty	The aromatic associated with linseed oil/oil-based paint.
Cardboard	The aromatics associated with oxidized fats and reminiscent of cardboard.

[a]Johnsen et al. (1988) with some rewording

Table 3.3 Sensory attribute reference standards for descriptive sensory flavor analysis.

Attribute		Intensity[1]
Sweet[a]	2% sucrose solution (Fisher Chemical, Fair Lawn, NJ)	20
	5% sucrose solution	50
	10% sucrose solution	100
	16% sucrose solution	150
Bitter[a]	0.05% caffeine solution (Fisher Chemical, Fair Lawn, NJ)	20
	0.08% caffeine solution	50
Roasted peanutty[a]	dry roasted peanuts (Planter's, Nabisco Foods, East Hanover, NJ)	75
Rancid[b]	fresh peanut oil heated to 110ºC for 5hr	25
Painty[c]	0.04% paint solution (Colors, Martha Stewart living Omnimedia LLC, NY)	64
Cardboard[b]	wet cardboard	85

[a]Reference standards according to (Plemmons and Resurreccion, 1998)
[b]Reference standard according to Divino *et al*. (1996)
[c]Reference standard developed in our laboratory
[1]Intensity based on a 150-mm unstructured line scale

Table 3.4 Mixed procedure analysis of TBHQ, sucrose, moisture and storage time effects on descriptive sensory attributes of peanut paste.

Source of variation	Sweet	Bitter	Roasted peanutty	Rancid	Painty	Cardboard
TBHQ	NS	NS	**	*	NS	NS
Sucrose	**	**	NS	*	NS	NS
Moisture	**	NS	**	NS	NS	**
Storage time	**	**	**	**	**	**
TBHQ x sucrose	NS	NS	NS	NS	NS	NS
TBHQ x moisture	*	*	NS	**	**	**
TBHQ x week	NS	NS	**	NS	NS	NS
Sucrose x moisture	NS	NS	NS	NS	NS	NS
Sucrose x week	NS	NS	NS	NS	NS	NS
Moisture x week	NS	NS	NS	NS	NS	NS
TBHQ x sucrose x moisture	NS	NS	NS	NS	NS	NS
TBHQ x sucrose x week	NS	NS	NS	NS	NS	NS
TBHQ x moisture x week	NS	NS	NS	NS	NS	NS
Sucrose x moisture x week	NS	NS	NS	NS	NS	NS
TBHQ x sucrose x moisture x week	NS	NS	NS	NS	NS	NS

*, ** Tests of fixed effects are significantly different at ($P \leq 0.05$) or ($P \leq 0.01$) receptively.

Table 3.5 Least squares means ratings for sweet, bitter and rancid attributes of stored peanut paste as influenced by sucrose level.

Attribute	Sucrose Percentage	
	0	4
Sweet	24.7b	31.2a
Bitter	10.9a	9.4b
Rancid	12.9a	11.7b

[a]Means within a sensory attribute followed by the same letter are not significantly different ($P \leq 0.05$)

Table 3.6 Least squares means for sweet, bitter, rancid, painty and cardboard attributes of stored peanut paste as influenced by TBHQ and moisture interaction.

Attribute	TBHQ (PPM)	Moisture Percentage		
		0	2	5
Sweet	0	29.1a	28.2a	26.3b
	180	30.26a	26.4b	26.6b
Bitter	0	10.6a	10.1ab	9.2b
	180	9.2b	11.0a	10.8a
Rancid	0	14.2a	11.7b	12.6b
	180	9.7c	12.6b	12.6b
Painty	0	14.4a	13.6a	13.9a
	180	10.1b	15.1a	13.2a
Cardboard	0	18.6b	18.6b	21.6a
	180	15.2c	21.2a	21.4a

[a]Means within a sensory attribute followed by the same letter are not significantly different ($P \leq 0.05$)

Table 3.7 Least squares means for sweet, bitter, rancid, painty and cardboard attributes of stored peanut paste as influenced by storage time.

Attribute	Storage time (week)					
	0	4	8	16	32	52
Sweet	30.9a	28.5b	28.7b	27.6bc	26.7cd	25.4d
Bitter	11.0a	9.2b	7.9c	9.4b	11.8a	11.8a
Rancid	5.6 e	6.4e	9.6d	12.9c	17.6b	21.6a
Painty	9.2c	6.6d	9.0c	14.6b	20.0a	21.0a
Cardboard	15.7d	14.2d	15.6d	18.9c	23.7b	28.8a

[a]Means within a sensory attribute followed by the same letter are not significantly different ($P \leq 0.05$).

Table 3.8 Least squares means ratings for roasted peanutty attribute of stored peanut paste as influenced by moisture level.

Attribute	Moisture Percentage		
	0	2	5
Roasted peanutty	49.7a	43.7b	43.1b

[a]Means within a sensory attribute followed by the same letter are not significantly different (P≤ 0.05)

Table 3.9 Least squares means of roasted peanutty attribute of stored peanut paste as influenced by TBHQ and storage time interaction.

Attribute	TBHQ (PPM)	Storage time (week)					
		0	4	8	16	32	52
Roasted	0	59.1ab	47.2cd	44.6de	40.8e	37.0ef	33.9fg
Peanutty	180	62.5a	57.8b	49.9c	42.7de	37.4f	33.0g

[a]Means within a sensory attribute followed by the same letter are not significantly different (P≤ 0.05).

CHAPTER 4

THE ROLE OF MOISTURE IN FLAVOR CHANGES OF MODEL PEANUT CONFECTIONS DURING STORAGE[1]

[1]Abegaz, E.G., W.L. Kerr and P.E. Koehler. Submitted to *Lebensmittel-Wissenschaft und-Technolgie* 01/24/03

ABSTRACT: The effects of antioxidant, sugar, moisture, and storage time on oxidative stability were determined by peroxide value (PV), instrumental volatile, and descriptive sensory analysis. Peanut pastes with 2 g/100 g and 5 g/100 g added moisture had lower 'roasted peanutty' intensity and lower pyrazine concentrations than those samples without moisture added. Samples with 2 g/100 g and 5 g/100 g moisture added had lower PV as well as lower hexanal and heptanal concentrations. Significant positive correlations were observed between pyrazine compounds and 'roasted peanutty' attribute.
KEYWORDS: moisture; peanut paste; flavor; oxidation

INTRODUCTION

Some commercially available peanut butter products with high moisture include peanut butter and jelly in a jar, peanut butter in ice cream, low fat peanut spread (Rudolph *et al*., 1991), chocolate-peanut butter flavored milk (Meyer, 1993), and yogurt with peanut flavored clusters (Peterine, 1992). Fading of the characteristic peanut flavor, accompanied by off-flavor development in peanut products, is a concern of the confectionery industry (Warner *et al*., 1996).

Woodroof (1983) observed that roasted peanut products with high moisture content developed an objectionable soggy nut flavor. Felland and Koehler (1997) found that peanut butter products with added moisture developed less roasted aroma and roasted flavor, as well as more off-odor and off-flavors, during storage.

The reasons for 'flavor fade' are not clear, as are the role of moisture and the exact levels at which water enhances the process. Prevention or reduction of 'flavor-fade'

requires understanding the relationship between carbonyl-amine and lipid oxidation reactions (Warner *et al*., 1996). The volatile compounds in peanuts are produced as a result of non-enzymatic carbonyl-amine and lipid oxidation reactions. Newell et al. (1967) suggested that reactions between free amino groups and reducing sugars produce hetrocyclic nitrogen compounds and dark brown products. The hetrocyclic nitrogen compounds, such as pyrazines formed from carbonyl-amine reactions, are partially responsible for the characteristic roasted peanut flavor. Mason et al. (1966) identified 2-methylpyrazine, 2,5-dimethylpyrazine, trimethylpyrazine, and n-methylpyrrole in roasted peanuts, and suggested that these compounds produced characteristic nut flavors. Ho et al. (1981) were able to identify 131 volatile compounds in roasted peanuts, including aliphatic hydrocarbons, alcohols, aldehydes, ketones, acids, esters, lactones, pyrazines, pyrroles, pyridines, thiazoles, oxazoles, oxazolines, sulfides, and other heterocyclic compounds. As peanut butter has approximately 50 g/100 g of fat, the development of rancidity and other off-flavors is important to flavor. The oxidation of polyunsaturated fatty acids produce monohydroperoxides that become precursors for volatile aldehyde products such as nonanal, octanal, decanal, and hexenal (Min *et al*., 1989). Peanut butter products can develop off-flavors that are responsible for painty, cardboard, and oxidized flavors (Johnsen *et al*., 1988). However, little is understood regarding how moisture influences lipid oxidation in these products.

The objective of this study was to determine the effects of antioxidant, sugar, and moisture on chemical and flavor changes in model peanut butter confections during storage.

MATERIALS AND METHODS

Sample preparation

Untreated, certified, aflatoxin-negative roasted peanut paste was supplied by Seabrook Ingredients (Edelton, NC). Initial analysis of the peanut butter showed 53.94 g oil /100 g, 0.86 g H_2O/100 g, fineness of grind (35 mils first scrape, 3 mils second scrape), 0.13 g free fatty acid/100 g, and coliform MPN <3. Upon receipt, the peanut paste was placed in storage at -10°C until use. The peanut paste was first mixed using a model SPY-1824 paddle mixer (Marion Mixers, Inc., Marion, IA) to ensure a lack of oil separation before preparation of the samples.

A fractional arrangement was used to specify the levels of peanut paste and ingredients. Samples were prepared with addition of two levels of the antioxidant tertiary butylhydroquinone (TBHQ)(0 and 180 mg/kg), two levels of added sugar (0.0g sucrose /100g and 4.0g sucrose /100 g), and three levels of added moisture (0.0g H_2O /100 g, 2.0g H_2O /100 g and 5.0g H_2O/100g). Twelve treatment combinations were formulated. Approximately 5.4 kg of peanut paste was heated inside a Sharp microwave oven, model R-510CK (Sharp Electronics Corp., Mahwah, NJ), to a temperature of 83°C, then placed in a model KSMC50S KitchenAid mixer equipped with a flat beat paddle (KitchenAid, St. Joseph, MI). A heating mantle maintained the temperature at 83 °C.

Refined 6X sucrose (Domino Sugar Co., New Orleans, LA), water, TBHQ (Eastman Chemical, Kingsport, TN) in refined peanut oil (CNT Refinery, Charlotte, NC), melted Dritex RC hydrogenated vegetable oil stabilizer (AC Humko, Memphis, TN), and flour salt (Cargill, Minneapolis, MN) were added slowly while mixing for a total mixing

time of two minutes. Each batch of peanut paste was poured into a series of small plastic Petri dishes (30 mm diameter x 10 mm depth), and the samples were allowed to cool and harden. The samples were covered with plastic lids pre-drilled with 1 mm holes to allow air circulation.

Peanut paste storage

The peanut paste samples were placed in a controlled temperature (21°C ± 0.1°C) and humidity chambers (Model 435314, Hotpack SP Industries, Philadelphia) each set at a relative humidity (%RH ± 2.0%) close to 100 times the water activity (a_w) of the samples. As the a_w of the air is just %RH/100, this approach limited the amount of moisture lost or gained by the sample due to moisture transfer with the surroundings. Replicate samples were removed for sensory evaluation, peroxide value, and headspace gas chromatographic analysis at 0, 4, 8, 16, 32, and 52 weeks of storage.

Peroxide value

The oil from the peanut paste was extracted according to a method described by Woodroof (1983), and lipid oxidation was measured using a peroxide procedure (AOCS Cd 8-53). Peroxide value of the oil was determined in mEq peroxide per kg sample.

Volatile analysis

Peanut paste samples were removed from storage chambers for analysis at 0, 4, 8, 16, 32, and 52 weeks. A 5 g peanut paste sample, along with 10 ml of NaCl solution, was placed inside a stainless steel cylindrical container and fitted to a Sorval Omni-Mixer (Ivan Dorvall Inc., Newtown, CT). Once fitted, the samples were blended for 3 min. at 16,000 RPM, cooled on ice, transferred to a 40 ml vial with Teflon lined silicon septa,

and equilibrated for 24 hours. A Solid Phase Micro Extraction (SPME) fiber (50/30 μm divinylbenzene/Carboxen on polymethyl-Siloxane) (Supelco, Inc., Bellefonte, PA) was used to extract peanut volatiles. The fiber was first conditioned on the GC injection port for 5 min. at 270°C. The SPME syringe was cooled, then inserted through the septum of the vial, and the needle lowered into the headspace above the peanut pastes. Headspace volatiles were adsorbed for 20 min. at 21°C as the sample was stirred using a magnetic stirrer. The fiber was removed from the vial and inserted into the gas chromatograph injection port equipped with an SPME inlet liner 0.75ID. Sample volatiles were desorbed for 5 min. at 270°C, and the fiber was removed.

Analysis was conducted on a Hewlett-Packard 5890 Series II gas chromatograph coupled to a FID detector. Compounds were separated with a SUPELCOWAX™ 10 (30 m, 0.25 mm i.d., 0.25 μm film) column (Supelco, Inc., Bellefonte, PA). The GC oven was programmed to run at 40°C for 5 min., then ramped at 4°C/min. to 230°C using splitless injection mode. Nitrogen was used as carriers gas (140 kPA). The injector and detector temperatures were 270°C and 300°C, respectively. Data was acquired using the HP 3365 Series II ChemStation computer software interface.

Standard curves and retention time identification

Pure standards of 2,3-dimethylpyrazine(purity >99%), 2,5-dimethylpyrazine(purity >98%), 2,6-dimethylpyrazine(purity >98%), 2-methylpyrazine(purity >99%), 2,3,5-trimethtlpyrazine(purity >99%), 1-methylpyrole(purity >99%), hexanal, and heptanal were obtained from Aldrich (Milwaukee, WI). The standards were prepared at concentrations of 10 to 1000 ng/g in

hexane. Each standard was injected in triplicate, and quantified to provide a standard curve. Linear regression of ng quantity versus area response yielded an R^2 greater than 0.95 for all the standard curves. The adsorption and desorption processes were identical to that used for all peanut paste samples.

Sensory Analysis

A panel of nine judges from the Department of Food Science and Technology at the University of Georgia were trained in descriptive analysis as described by Meilgaard *et al.* (1991). Evaluations were carried out in partition booths illuminated by fluorescent lighting. The judges were presented with approximately 5.0 g peanut paste samples in petri dishes labeled with three digit random numbers, along with reference standards (Abegaz *et al*., 2002), water, unsalted crackers, and expectoration cups. Judges were instructed to first familiarize themselves with the intensity of each reference standard, then place a half-teaspoon of peanut paste in their mouth to evaluate the flavor attributes. They were also instructed to evaluate the samples in the order shown on the score sheets, and to eat unsalted crackers and drink distilled water between samples to clear the palate. The panelists evaluated six established flavor attributes: 'sweet', 'bitter', 'roasted peanutty', 'rancid', 'painty', and 'cardboard'(Johnsen *et al*., 1988). Judges rated the attributes using a 150 mm unstructured line scale. Low and high anchor points were included at 12.5 mm and 137.5 mm. Judges were calibrated. Each judge evaluated twelve peanut paste samples on the same day, with six samples in the morning and six in the afternoon sessions. Each panel session was replicated after 24 hrs using the same procedure, with different orders of presentation for each judge.

Statistical Analysis

Data was analyzed using SAS version 6.11 (SAS Institute, NC). Analysis of variance (ANOVA) of results at the statistical significance level of $p \leq 0.05$ was performed using the general linear model (GLM) procedure. A split-split-plot design was applied, where whole plot effect compared three added moisture levels (0.0, 2.0 and 5.0g H_2O /100g); the subplot effect compared two levels of added antioxidant (0, 180 mg/kg); and two levels of added sucrose (0.0 and 4.0 g/100 g) were compared for the sub-subplot effect. Sampling time of weeks 0, 4, 8, 16, 32, and 52 were employed for each moisture level. Correlation of sensory data with chemical components was determined using SAS correlation procedure.

RESULTS AND DISCUSSION

Peroxide value

The change in peroxide values (PV) during storage is illustrated in **Figs. 4.1**. Peroxide value measures the content of hydroperoxides, and is often used as an indicator of primary products of lipid oxidation (Gray, 1978). Antioxidant effect was significant to peroxide value measurements (**Table 4.1**). Samples with TBHQ had PV < 3 mEq/kg and were significantly lower than samples without TBHQ. For example, PV values at 4 weeks for samples with TBHQ and no sugar or moisture added were barely detectable, while those with the same sugar and moisture levels without TBHQ had a PV value as high as 33 mEq/kg sample (**Figs. 4.1**).

Addition of sugar was significant to peroxide value measurements (**Table 4.1**). Generally speaking, samples with 4g sucrose/100 g sample had lower peroxide values

than those without added sucrose. These differences in PV were especially pronounced with those samples containing no moisture addition.

The addition of moisture was also a significant factor in PV measurement (**Table 4.1**). For samples with no TBHQ, addition of 5 g H_2O /100 g sample revealed lower peroxide values when compared to 0 g H_2O /100 g samples. For example, samples with 5 g H_2O /100 g sample, 0 sucrose, 0 TBHQ had a PV of 20.8 mEq/kg after 52 weeks of storage, while comparative samples without added moisture had 35 mEq/kg (**Fig. 4.1**). That is, the presence of moisture limited the extent of lipid oxidation. Similar results have been observed for peanuts held at 21% and 53% relative humidity (Mate et al., 1996), where it was found that peroxide values were highest for those held at 21% RH as compared to 53% RH. Nelson and Labuza (1992) discussed two possible ways in which increased water activity can decrease the rate of lipid oxidation. Within a given range of increasing water activity, the ratio of water to lipid phase increases, and the polar ROOH groups move to the interface and hydrogen bond to water, effectively taking them out of the reaction. Moreover, water can also facilitate termination reactions involving the recombination of free radicals to form non-radical products.

Storage time was also a significant factor for peroxide values (**Table 4.1**). For samples without TBHQ, PV increased markedly within four weeks, with the exception of samples containing 5 g H_2O /100 g (**Fig. 4.1**). Those samples with 5g H_2O /100g had steadily increased PV through the 52 week period. Other samples had PV that increased more rapidly and decreased or remained constant over longer times. This type of behavior is an indication that later stages of lipid oxidation have been reached (Shahidi *et al*.,

1994). For TBHQ treated groups, PV values increased within 8 weeks and remained mostly constant thereafter. Two-way and three-way interactions is shown in **Table 4.1**.

Volatiles related to oxidation

In addition to peroxide values, several volatile components are produced which indicate lipid oxidation. Aldehydes are responsible for off-flavor notes, such as cardboardy and painty flavors, during storage (Frankel, 1998). These components are produced during the latter phases of lipid oxidation, through the reaction of oxygen with alkyl radicals.

The effects of antioxidants on hexanal and heptanal production were significant (**Table 4.2**). In general, levels of hexanal production were much higher than those of heptanal. Those samples with TBHQ displayed comparatively lower hexanal and heptanal production. For example, samples without TBHQ showed hexanal and heptanal production as high as 1551 ng/g and 49 ng/g, while the maximum value for samples with TBHQ were 736 ng/g and 28 ng/g, respectively. Plots of hexanal concentration vs time are shown in **Figure 4.2.**

Moisture was a significant factor for hexanal production (**Table 4.2**). In general, samples with higher moisture had less hexanal. For example, samples with 0 sucrose, 0 TBHQ and 5 g H_2O /100 g sample had hexanal levels that never exceeded 457 ng/g. In contrast, samples with 0 sucrose, 0 moisture or TBHQ contained up to 1155 ng/g (**Fig. 4.2**). This suggests added moisture had a protective effect against lipid oxidation as was also concluded from results of PV measurments.

Storage time was also significant to hexanal and heptanal production (**Table 4.2**). In most cases, maximum values of hexanal and heptanal were observed in weeks 4-16 (**Fig. 4.2**). These values were reminiscent of the results from peroxide values, which also peaked in week 4-16 (**Fig. 4.1**). Significant interaction terms for hexanal and heptanal are shown in **table 4.1**.

Volatiles related to roasted peanut flavor

Selected volatile compounds linked with 'roasted peanut' flavors were identified through comparison of retention times with those of authentic compounds. The roasted peanut odor is characterized by a variety of sugar-amine byproducts produced during roasting. Mason et al. (1966) suggested that a series of alkylpyrazines were responsible for roasted nut flavor. Brannan et al. (1999) and Reed et al. (2002) identified important volatiles, such as hexanal, octanal, nonanal, 1-methylpyrrole, pyridine, 2-methylpyrazine, 2,5 dimethylpyrazine, 2,6-dimethyl pyrazine, 2,3-dimethylpyrazine, and trimethylpyrazine in roasted peanuts.

For all the pyrazine compounds analyzed, excluding 2,3-dimethylpyrazine, the presence of TBHQ was a significant factor (**Table 4.3**). When analyzed as a group, samples with TBHQ contained higher levels of pyrazine compounds. However, differences between treatment groups with and without TBHQ were not always large or significant when a given combination of moisture/sugar/storage time component was considered.

There was a significant difference in all pyrazine compounds due to moisture levels. In general, samples without added moisture had higher levels of specific pyrazine

compounds. In some cases, the difference due to moisture level was fairly large. For example, in samples with 0 TBHQ, 0 sucrose and with 0, 2, and 5 g H_2O /100 g, concentrations of 2,5-dimethylpyrazine were 121, 94, and 87 ng/g, respectively (**Fig. 4.3**). For these same samples, the concentrations of 2-methylpyrazine were 104, 54, and 33 ng/g, respectively (**Fig. 4.4**). Similar trends were also observed for 2,6-dimethylpyrazine and 2,3-dimethylpyrazine. The decrease in pyrazines with added moisture may be due to increasing solubility of the pyrazines in the aqueous phase, which could have decreased the volatility of the compounds.

Storage time was also a significant factor for all pyrazine compounds (**Table 4.3**). In most cases, the pyrazine concentrations decreased with time. For example, the concentration of 2-methylpyrazine in samples with 0 moisture, 0 sucrose, or TBHQ added decreased from 101 to 42 ng/g from 0 to 52 weeks, and for 2,5-dimethylpyrazine they decreased from 124 to 80 ng/g (**Figs. 4.3 & 4.4**). From week 4-52, 2,3,5-trimethylpyrazine decreased by 7% (**Figs. 4.5**). The presence of 2,3-dimethylpyrazine could not be detected after eight weeks of storage (**Figs. 4.7**).

Bett and Boylston (1992), Braddock et al. (1995) and Reed et al. (2002) found a decrease in pyrazine concentrations in roasted peanuts during storage. The actual mechanism for the observed decrease of the pyrazines is not known; however, Bett and Boylston (1992) speculated that lipid radicals and peroxides might contribute to the degradation of these hetrocylic compounds.

Sensory evaluation

Mean sensory scores for stored peanut paste samples are shown in **Table 4a & b**. The perception of 'sweet' and 'bitter' attributes were not affected by the presence of TBHQ. Samples with higher moisture levels had lower perceived sweetness; however, these differences were not large (**Tables 4.4a & 4.4b**). In general, sweetness decreased, while bitterness increased, with time. These results are consistent with those of Reed *et al*. (2002) in roasted peanuts during storage. The presence of TBHQ did not affect the perception of bitterness, nor did the different levels of moisture. Bitterness increased with storage (**Tables 4.4a & 4.4b**). The interaction between sweet and bitter compounds are well known, and sweet and bitter tastes rely on similar stereochemical mechanisms (Lindsay, 1996).

Roasted peanutty scores for samples with TBHQ were slightly higher than those without TBHQ (**Tables 4.4a & 4.4b**). The difference between treatment groups with and without TBHQ were not large. Moisture levels affected the perception of roasted peanut flavor. Samples with 5 g H_2O /100 g sample had the lowest 'roasted peanutty' scores. This is consistent with the observation that the level of pyrazine compounds decreased with added moisture. Felland and Koehler (1997) also found that 'roasted odor' and 'roasted flavor' scores decreased with the addition of moisture at 2.5% and 5% at 25°C; however, they did not measure instrumental volatile concentration.

The perception of 'roasted peanutty' flavor decreased over storage time. Samples with the highest moisture addition had the greatest change in 'roasted peanut' flavor over time. After 52 weeks at 21°C, 'roasted peanutty' scores for samples without TBHQ,

sucrose, or moisture addition dropped from 65 to 38, while those with 5 g H_2O /100 g sample dropped from 62-28 (**Table 4.4b**). Warner et al. (1996) found that 'roasted peanut' flavor decreased slightly after 68 days of storage at 65°C, while Felland and Koehler (1997) found decreases in 'roasted odor' and 'roasted flavor' during 30 days of storage of peanut butter at 25°C. Therefore, the loss of 'roasted peanutty' flavor in the peanut butters during storage is most likely due to lower pyrazine concentrations and other volatiles.

For rancid and painty attributes, the presence of antioxidant was significant. Generally, samples with TBHQ developed less 'rancid' and 'painty' flavors during the first 8 and 16 weeks of storage, although the effect was not as large as might be expected. The added moisture was a significant factor to sensory oxidation parameters. The moisture levels did not have an immediate effect on 'rancid', 'painty', or 'cardboard' scores. However, with time, samples with 5 g H_2O /100 g sample had higher 'cardboard' and 'painty' scores, as storage time increased (**Tables 4.4a & 4.4b**). Although not strictly dealing with oxidation, Felland and Koehler (1997) found that off-odors and flavors were higher in peanut butter samples containing 5% added moisture. Contrary to our results for peroxide values and hexanal, sensory oxidation results for samples containing 5 g moisture added/100 g sample resulted in higher scores of sensory oxidation parameters. Felland and Koehler (1997) observed similar results, and concluded that 'off-flavor' was probably not due to oxidation alone. One possible explanation is that the reduction in 'roasted peanutty' flavors resulted in enhanced perception of off-flavors. The scores of oxidation and off-flavor attributes increased with storage time. For example, in samples without TBHQ, moisture, or sugar addition, 'rancid' scores increased steadily from 5.5 to

27 during 52 weeks of storage, while 'painty' scores increased from 9 to 28 (**Table 4.4b**). Although TBHQ was a significant factor, samples with TBHQ still developed 'rancid', 'painty', and 'cardboard' flavors over time.

Correlation of Sensory and chemical components

Correlation of sensory data with volatile components and PV is shown in **Table 4.5**. Hexanal and heptanal concentrations did not correlate with sensory oxidation and off-flavor attributes. However, other factors may contribute to 'rancid', 'painty' and 'cardboard' attributes. Brannan et al. (1999) also did not find a significant correlation of hexanal with oxidation attributes.

'Roasted peanutty' flavor correlated with 2-methylpyrazine (0.79), 2,3-dimethylpyrazine (0.65), 2,5-dimethylpyrazine (0.78), and trimethylpyrazine (0.73). 1-methylpyrrole correlated with 'sweet' (0.32), 'bitter' (0.20), and 'roasted peanutty' (0.49) attributes. Brannan et al. (1999) also observed that 1-methylpyrrole correlated with 'roasted peanutty' and 'bitter' attributes, and noted that this compound also had a sweet and woody aroma. PV correlated negatively with 'roasted peanutty' flavor and positively with 'rancid' and 'painty' attributes.

CONCLUSION

Peanut butter with added moisture resulted in a less intense 'roasted peanutty' character, also indicated by lower pyrazine concentrations. Oxidative related attributes such as 'rancid', 'painty', and 'cardboard' were higher in samples with 5 g H_2O /100 g sample. This was probably due to less intense ‘roasted peanut’ flavor in the samples with 5 g H_2O /100 g sample, leaving a heightened sense of 'off flavor' aromas. Samples with

no added moisture had higher PV values in agreement with hexanal and heptanal readings, indicating less oxidative stability than that of the samples with 5g H_2O /100 g sample. PV values also correlated with 'rancid' and 'painty' attributes. Pyrazine compounds, which exhibit characteristic peanut aromas, correlated with sensory 'roasted peanutty' flavor. For some of the sensory attributes, volatile compounds, and peroxide values, two-way and three-way interaction effects were significant for antioxidant, sugar, moisture, and storage time combinations, implying that these factors are important to the overall quality of peanut confections.

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Table 4.1 Significance of treatment effects on peroxide value (PV), as determined by analysis of variance

Treatments	PV (mEq/kg)
TBHQ	0.0001
Sucrose	0.0201
Moisture	0.0001
Time	0.0001
TBHQ*Sucrose	0.0219
Sug*Moisture	NS
TBHQ*moisture	0.0001
TBHQ*Time	0.0001
Sucrose*Time	0.0007
Moi*Time	0.0001
TBHQ*Sucrose*Moisture	NS
TBHQ*Sucrose*Time	0.0005
TBHQ*Moisture*Time	0.0001
Sucrose*Moisture*Time	NS
TBHQ*Sucrose*Moisture*Time	NS

NS = not significantly different ($p > 0.05$)

Table 4.2 Significance of treatment effects on volatile compounds, as determined by analysis of variance

Treatments	Hexanal	Heptanal
TBHQ	0.0001	0.0001
Sucrose	NS	NS
Moisture	0.0006	NS
Time	0.0001	.0001
TBHQ*Sucrose	NS	NS
Sug*Moisture	NS	0.0002
TBHQ*moisture	0.0006	0.0008
TBHQ*Time	0.0001	0.0001
Sucrose*Time	NS	NS
Moi*Time	NS	0.0001
TBHQ*Sucrose*Moisture	0.0003	0.0009
TBHQ*Sucrose*Time	NS	NS
TBHQ*Moisture*Time	NS	0.0005
Sucrose*Moisture*Time	NS	0.0001
TBHQ*Sucrose*Moisture*Time	0.0001	0.0001

NS = not significantly different ($p > 0.05$)

Table 4.3 Significance of treatment effects on volatile compounds, as determined by analysis of variance

Treatments	2-methyl pyrazine	2,5-dimethyl pyrazine	2,6-dimethyl pyrazine	2,3-dimethyl pyrazine	2,3,5-trimethyl pyrazine
TBHQ	0.0001	0.0001	0.0001	NS	0.0001
Sucrose	NS	NS	NS	NS	NS
Moisture	0.0001	0.0001	0.0001	0.0001	0.0001
Time	0.0001	0.0001	0.0001	0.0001	0.0001
TBHQ*Sucrose	NS	0.0084	NS	NS	0.0001
Sug*Moisture	0.0001	0.0001	0.0087	0.0004	0.0001
TBHQ*moisture	0.0001	0.0001	0.0001	NS	0.0043
TBHQ*Time	0.0155	0.0101	0.0001	NS	0.0005
Sucrose*Time	0.0033	0.0029	0.0001	NS	0.0079
Moi*Time	0.0001	0.0001	0.0001	0.0001	0.0001
TBHQ*Sucrose*Moisture	0.0001	0.0001	0.0003	0.0040	0.0001
TBHQ*Sucrose*Time	NS	0.0201	0.0001	NS	0.0066
TBHQ*Moisture*Time	0.0318	0.0176	0.0001	NS	0.0001
Sucrose*Moisture*Time	0.0001	0.0001	0.0001	0.0017	0.0001
TBHQ*Sucrose*Moisture*Time	NS	0.0059	0.0001	NS	0.0078

NS = not significantly different ($p > 0.05$)

Table 4.4a Mean sensory attributes of stored roasted peanut pastes with TBHQ

	TBHQ	Suc[1]	Moi[2]	Attributes					
Wk	mg/kg			SWT	BTR	RPT	RCD	PNT	CRB
0	180	0	0	28.6±2.3	10.9±2.2	68.6±2.7	4.6±1.6	6.6±1.1	18.6±2.1
	180	0	2	25.9±1.1	14.3±0.3	65.5±5.4	5.8±0.0	10.3±2.3	18.7±0.3
	180	0	5	28.9±0.6	13.0±3.9	59.3±6.9	6.0±0.2	7.9±0.4	16.5±5.4
	180	4	0	38.6±3.2	8.6±1.6	61.1±1.5	4.9±0.3	8.1±0.6	13.1±0.7
	180	4	2	33.7±4.2	8.7±0.8	59.6±2.9	4.6±0.6	9.1±1.5	14.5±5.0
	180	4	5	31.1±0.1	13.1±6.5	60.7±5.1	6.5±2.8	9.6±3.1	13.8±4.8
4	180	0	0	27.2±1.4	10.4±1.1	62.6±1.6	4.9±0.1	6.3±1.8	12.7±2.1
	180	0	2	25.8±0.5	13.3±3.5	58.7±2.8	5.9±0.4	6.8±0.9	14.5±0.8
	180	0	5	24.3±1.6	8.6±2.0	55.2±5.5	6.5±0.1	6.5±0.7	19.4±1.3
	180	4	0	31.3±0.9	6.6±2.5	61.1±2.4	5.1±0.3	7.1±2.6	9.4±4.4
	180	4	2	32.1±0.3	7.8±2.7	56.5±2.4	4.6±1.3	6.3±1.3	13.8±1.2
	180	4	5	32.4±2.1	8.0±2.3	56.2±4.2	7.2±0.5	6.1±1.4	16.0±0.1
8	180	0	0	28.6±1.0	9.8±0.4	55.6±3.2	8.0±0.5	7.8±0.2	12.7±6.2
	180	0	2	24.6±2.7	9.4±0.8	45.3±7.7	9.8±1.9	13.3±1.1	20.5±3.7
	180	0	5	25.8±1.8	7.6±1.2	48.7±4.6	9.8±0.2	9.9±0.7	15.3±1.4
	180	4	0	36.1±1.8	5.8±1.2	54.5±3.6	7.7±2.4	6.5±2.3	12.6±2.9
	180	4	2	31.2±0.6	4.9±1.7	51.1±0.5	9.8±2.1	8.7±2.1	16.3±2.4
	180	4	5	28.1±0.0	6.7±0.7	44.5±3.2	7.6±2.8	8.0±1.9	20.5±0.6
16	180	0	0	27.7±5.4	8.4±1.4	50.8±6.0	9.4±1.0	9.0±0.1	12.2±0.1
	180	0	2	22.8±0.5	10.6±1.4	39.6±5.3	14.7±1.9	19.9±2.5	19.3±1.8
	180	0	5	24.5±3.3	10.2±1.9	36.3±9.5	17.2±3.8	14.3±3.4	26.4±0.7
	180	4	0	35.4±0.6	6.2±1.5	46.5±1.3	10.4±0.4	11.9±4.7	15.5±3.8
	180	4	2	26.5±0.7	10.6±1.9	37.2±3.7	13.8±2.1	18.5±0.2	20.0±6.2
	180	4	5	30.9±1.6	8.5±2.3	37.4±2.4	13.4±1.0	16.8±4.2	18.1±5.4
32	180	0	0	21.8±0.4	12.2±1.2	41.6±2.9	13.8±0.2	26.8±1.0	23.0±0.5
	180	0	2	21.3±1.0	12.3±0.9	26.5±0.0	29.0±1.6	28.4±0.4	34.6±3.0
	180	0	5	17.2±1.6	9.4±0.5	20.1±0.2	28.4±1.9	27.3±0.9	32.3±1.3
	180	4	0	32.8±0.2	4.9±0.9	40.4±2.2	10.9±0.2	15.8±0.1	14.1±0.3
	180	4	2	26.7±1.3	11.2±2.2	31.6±0.1	20.0±1.0	31.7±0.3	29.8±2.4
	180	4	5	23.7±1.6	10.3±1.4	26.9±1.3	14.4±0.3	29.3±0.8	32.5±3.0
52	180	0	0	24.5±5.8	13.0±3.5	33.9±2.0	20.9±1.7	17.5±0.1	24.6±2.6
	180	0	2	22.3±0.1	12.4±2.0	22.5±3.8	23.8±1.1	22.5±0.6	35.3±8.0
	180	0	5	23.4±0.6	14.4±4.7	29.2±10.4	23.3±6.1	23.2±0.2	32.9±7.7
	180	4	0	32.8±0.2	10.4±0.8	38.3±5.9	20.7±3.0	17.9±4.3	26.1±0.5
	180	4	2	24.7±2.4	13.2±3.4	25.5±6.4	22.6±3.3	25.9±0.9	35.5±6.8
	180	4	5	26.2±6.1	10.5±1.1	26.6±3.9	19.3±0.9	20.4±1.7	27.5±0.4

Mean sensory scores (n =9) based on 150mm unstructured line scale
Suc[1] = g sugar added/100 g sample, Moi[2] =g moisture added/100 g sample
SWT = sweet, BTR= bitter, RPT= roasted peanutty, Wk=week
RCD = rancid, PNT= painty, CRD = cardboard

Table 4.4b Mean sensory attributes of stored roasted peanut pastes without TBHQ

	TBHQ	Suc[1]	Moi[2]						
Wk	mg/kg			SWT	BTR	RPT	RCD	PNT	CRB
0	0	0	0	32.5±8.0	10.1±4.3	65.2±0.3	5.5±1.5	9.3±3.3	15.3±7.4
	0	0	2	28.7±1.1	10.6±2.6	58.0±5.0	5.1±0.4	8.7±0.5	13.2±0.3
	0	0	5	22.2±0.1	12.8±4.7	61.5±0.2	6.3±1.2	10.5±6.1	17.3±1.2
	0	4	0	34.5±0.5	10.6±0.5	57.6±0.9	3.8±0.4	8.2±2.0	12.6±2.4
	0	4	2	35.7±5.7	9.6±0.1	50.1±1.5	5.4±0.9	9.0±1.2	16.0±0.0
	0	4	5	30.5±2.3	9.0±2.3	62.1±1.5	8.1±4.3	13.0±5.2	18.8±3.8
4	0	0	0	26.2±3.3	12.2±0.7	50.3±10.7	8.5±1.4	7.2±1.8	17.3±4.5
	0	0	2	24.9±0.2	7.7±3.6	43.9±0.2	5.8±1.8	6.7±1.6	11.0±0.7
	0	0	5	20.7±2.1	7.5±0.9	47.0±3.2	7.7±0.5	7.0±0.9	16.1±2.9
	0	4	0	35.3±2.5	9.5±2.1	43.4±4.0	6.7±0.5	6.6±2.2	12.5±9.2
	0	4	2	31.7±1.0	8.4±1.0	45.1±1.1	5.3±1.6	5.0±1.9	13.5±2.5
	0	4	5	30.8±3.3	6.5±1.8	53.7±3.3	7.7±1.0	7.5±1.7	14.3±2.6
8	0	0	0	22.1±0.2	9.2±0.0	50.3±1.4	14.3±2.1	12.6±5.5	11.6±6.0
	0	0	2	25.9±3.2	9.0±1.3	46.5±5.1	7.7±1.5	6.2±1.3	14.8±2.3
	0	0	5	23.2±3.0	7.3±0.9	35.±5.8	11.1±0.9	9.2±1.0	18.6±0.8
	0	4	0	33.7±1.8	10.6±0.7	46.5±1.0	11.3±0.2	8.5±4.0	13.3±5.1
	0	4	2	33.0±2.3	6.5±1.1	43.6±5.1	7.7±0.9	7.5±3.1	12.1±0.2
	0	4	5	31.1±0.2	7.5±1.2	45.6±2.2	9.5±0.0	9.2±0.9	18.7±1.8
16	0	0	0	21.4±2.5	10.0±1.7	47.1±5.6	17.7±1.3	19.0±0.0	18.8±2.1
	0	0	2	24.0±0.7	9.2±1.1	36.5±8.3	13.3±0.5	18.3±1.1	17.8±0.6
	0	0	5	23.8±0.7	8.5±1.5	35.4±3.8	15.3±0.7	18.6±2.1	28.3±0.1
	0	4	0	36.5±0.7	9.0±1.2	42.9±7.1	11.4±1.1	10.2±0.7	16.2±0.5
	0	4	2	32.0±1.1	6.0±0.1	37.5±0.6	11.7±1.5	15.4±1.3	17.7±2.1
	0	4	5	29.9±2.1	7.9±0.3	37.1±1.9	15.0±0.4	14.3±7.2	22.0±5.3
32	0	0	0	23.6±1.2	10.6±1.3	40.9±0.3	21.9±0.4	27.1±0.0	24.3±1.1
	0	0	2	16.5±1.6	10.8±1.6	32.8±0.9	24.2±1.5	34.2±1.4	31.7±0.2
	0	0	5	18.2±0.7	10.0±0.4	24.8±0.8	22.2±0.6	33.3±2.2	27.3±1.6
	0	4	0	25.9±0.8	10.7±0.3	37.0±1.8	21.7±0.1	33.8±1.6	27.6±0.3
	0	4	2	23.6±0.4	12.7±1.2	27.8±0.3	21.5±1.0	26.4±0.8	29.9±0.2
	0	4	5	21.6±0.5	11.6±2.1	34.6±0.9	15.7±0.1	28.1±0.3	30.1±0.6
52	0	0	0	23.1±2.6	23.1±0.0	37.7±3.6	27.3±0.2	27.9±0.2	34.4±4.3
	0	0	2	22.8±1.8	22.8±0.6	30.3±2.3	21.9±0.7	21.5±2.6	30.2±4.7
	0	0	5	24.7±5.3	24.7±0.1	27.3±4.3	20.6±2.0	21.8±0.8	28.4±3.3
	0	4	0	28.4±1.3	28.4±1.8	32.8±5.8	30.1±2.8	24.7±1.8	33.7±0.4
	0	4	2	29.1±3.0	29.1±0.1	28.9±1.3	23.3±2.4	27.1±3.2	31.5±1.7
	0	4	5	30.2±1.9	30.2±0.2	26.2±1.9	21.4±2.3	20.8±0.3	30.6±1.9

Mean sensory scores (n = 9) based on 150mm unstructured line scale
Suc[1] =g sugar added/100 g sample, Moi[2] =g moisture added/100 g sample
SWT = sweet, BTR= bitter, RPT= roasted peanutty, Wk=week
RCD = rancid, PNT= painty, CRD = cardboard

Table 4.5 Correlation values of GC peaks, PV with sensory attributes of stored roasted peanut pastes

	Sweet	Bitter	Roasted Peanutty	Rancid	Painty	Cardboard
Hexanal	NS	NS	NS	NS	NS	NS
Heptanal	NS	-0.31	NS	NS	-0.19	-0.18
1-methyl pyrole	0.32	0.20	0.49	-0.24	-0.22	-0.21
2-methylpyrazine	0.43	NS	0.79	-0.64	-0.59	-0.59
2,5-dimethyl pyrazine	0.40	NS	0.78	-0.68	-0.63	-0.59
2,6-dimethyl pyrazine	0.16	-0.17	NS	NS	-0.19	-0.30
2,3-dimethyl pyrazine	0.33	NS	0.65	-0.55	-0.53	-0.45
Trimethyl prazine	0.34	-0.20	0.73	-0.73	-0.68	-0.66
PV	NS	NS	-0.26	0.31	0.17*	NS

NS = not significant

Figure Legends

Fig. 4.1 Peroxide Value of roasted peanut pastes stored at 21°C (n = 2).
□ 0g sucrose/100g sample, 0g H_2O/ 100g sample
△0g sucrose/100g sample, 2g H_2O/ 100g sample
○ 0g sucrose/100g sample, 5g H_2O/ 100g sample
■ 4g sucrose/100 g sample, 0g H_2O/ 100g sample
▲4g sucrose/100 g sample, 2g H_2O/ 100g sample
● 4g sucrose/100 g sample, 5g H_2O/ 100g sample

Fig. 4.2 Hexanal concentration of roasted peanut pastes stored at 21°C (n =2).
□ 0g sucrose/100g sample, 0g H_2O/ 100g sample
△0g sucrose/100g sample, 2g H_2O/ 100g sample
○ 0g sucrose/100g sample, 5g H_2O/ 100g sample
■ 4g sucrose/100 g sample, 0g H_2O/ 100g sample
▲4g sucrose/100 g sample, 2g H_2O/ 100g sample
● 4g sucrose/100 g sample, 5g H_2O/ 100g sample

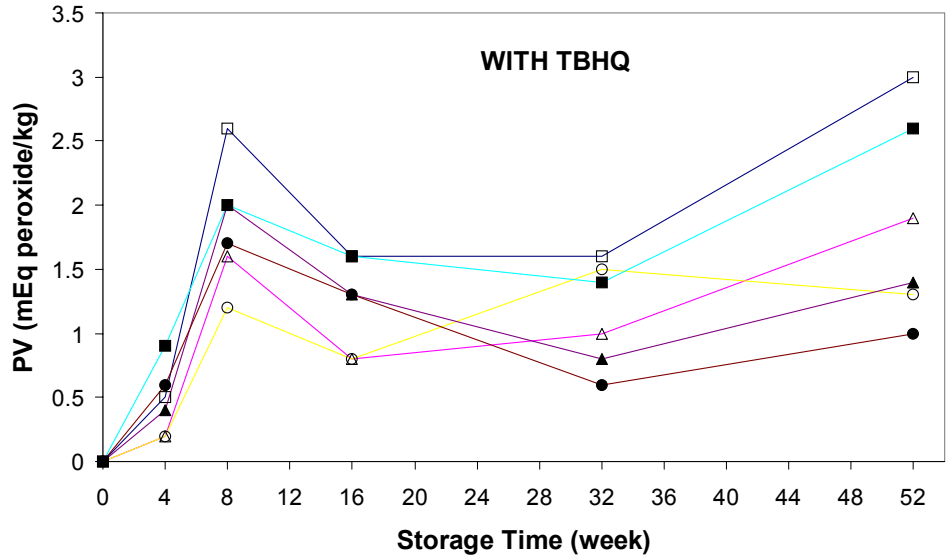
Fig. 4.3 2,5-dimethylpyrazine concentration of roasted peanut pastes stored at 21°C (n =2).
□ 0g sucrose/100g sample, 0g H_2O/ 100g sample
△0g sucrose/100g sample, 2g H_2O/ 100g sample
○ 0g sucrose/100g sample, 5g H_2O/ 100g sample
■ 4g sucrose/100 g sample, 0g H_2O/ 100g sample
▲4g sucrose/100 g sample, 2g H_2O/ 100g sample
● 4g sucrose/100 g sample, 5g H_2O/ 100g sample

Fig. 4.4 2-methylpyrazine concentration of roasted peanut pastes stored at 21°C (n =2).
□ 0g sucrose/100g sample, 0g H_2O/ 100g sample
△0g sucrose/100g sample, 2g H_2O/ 100g sample
○ 0g sucrose/100g sample, 5g H_2O/ 100g sample
■ 4g sucrose/100 g sample, 0g H_2O/ 100g sample
▲4g sucrose/100 g sample, 2g H_2O/ 100g sample
● 4g sucrose/100 g sample, 5g H_2O/ 100g sample

Fig. 4.5 2,3,5-trimethylpyrazine concentration of roasted peanut pastes stored at 21°C (n =2).
□ 0g sucrose/100g sample, 0g H_2O/ 100g sample
△0g sucrose/100g sample, 2g H_2O/ 100g sample
○ 0g sucrose/100g sample, 5g H_2O/ 100g sample
■ 4g sucrose/100 g sample, 0g H_2O/ 100g sample
▲4g sucrose/100 g sample, 2g H_2O/ 100g sample
● 4g sucrose/100 g sample, 5g H_2O/ 100g sample

Fig. 4.6 2,3-dimethylpyrazine concentration of peanut pastes stored at 21°C (n =2).
□ 0g sucrose/100g sample, 0g H_2O/ 100g sample
△0g sucrose/100g sample, 2g H_2O/ 100g sample
○ 0g sucrose/100g sample, 5g H_2O/ 100g sample
■ 4g sucrose/100 g sample, 0g H_2O/ 100g sample
▲4g sucrose/100 g sample, 2g H_2O/ 100g sample
● 4g sucrose/100 g sample, 5g H_2O/ 100g sample

Figure 4.1


WITH TBHQ
PV (mEq peroxide/kg)
Storage Time (week)
0
0.5
1
1.5
2
2.5
3
3.5
0
4
8
12
16
20
24
28
32
36
40
44
48
52

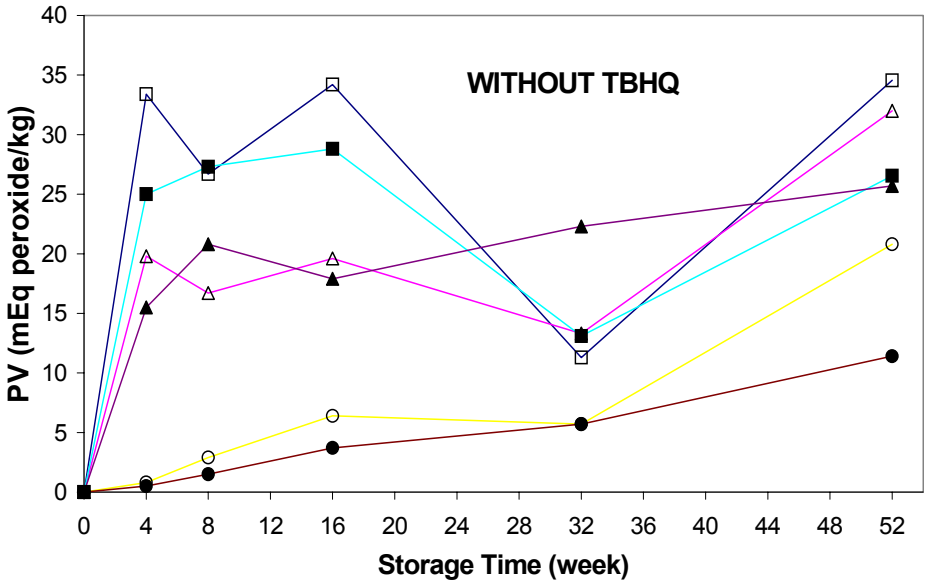
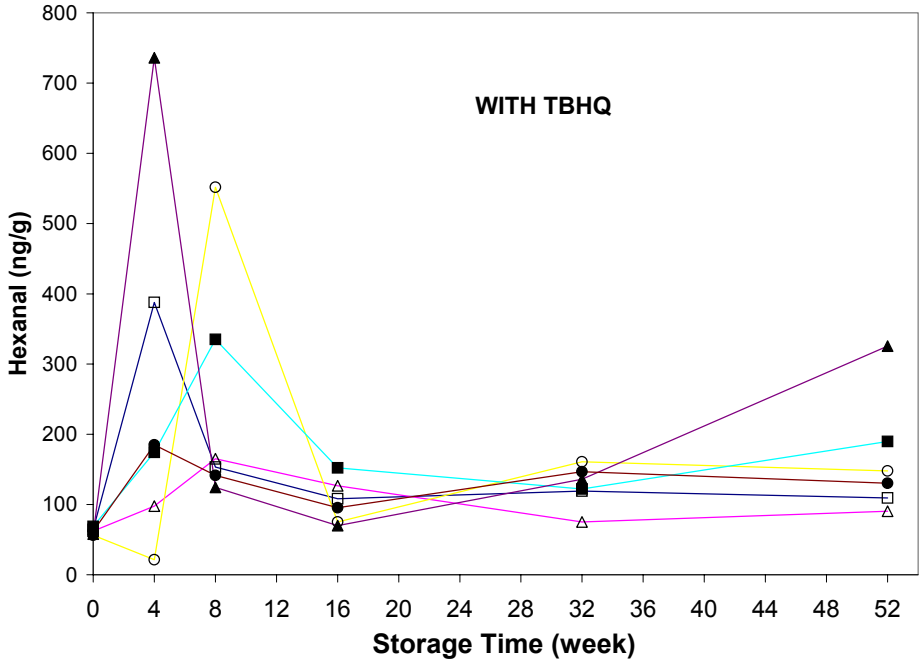

WITHOUT TBHQ
PV (mEq peroxide/kg)
Storage Time (week)
0
5
10
15
20
25
30
35
40
0
4
8
12
16
20
24
28
32
36
40
44
48
52

Figure 4.2


WITH TBHQ
Hexanal (ng/g)
Storage Time (week)
0
100
200
300
400
500
600
700
800
0
4
8
12
16
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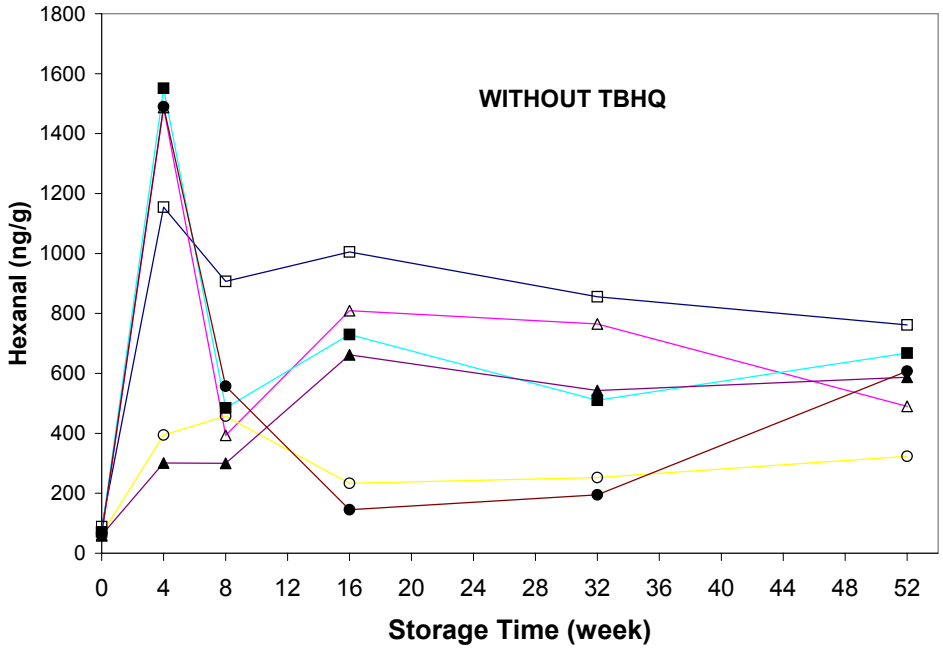
28
32
36
40
44
48
52


WITHOUT TBHQ
Hexanal (ng/g)
Storage Time (week)
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200
400
600
800
1000
1200
1400
1600
1800
0
4
8
12
16
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32
36
40
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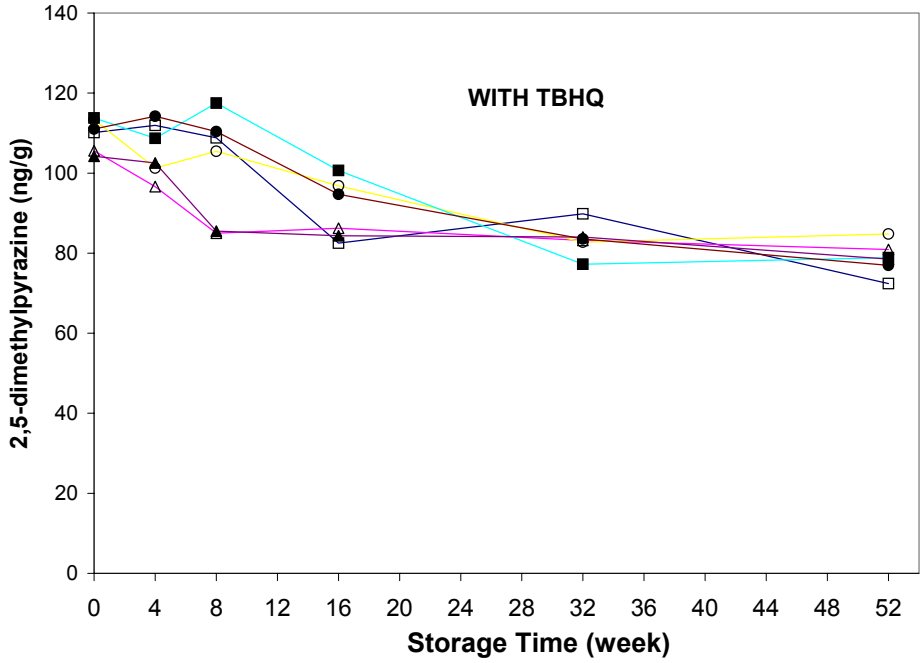
48
52

Figure 4.3


WITH TBHQ
2,5-dimethylpyrazine (ng/g)
Storage Time (week)
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20
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60
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16
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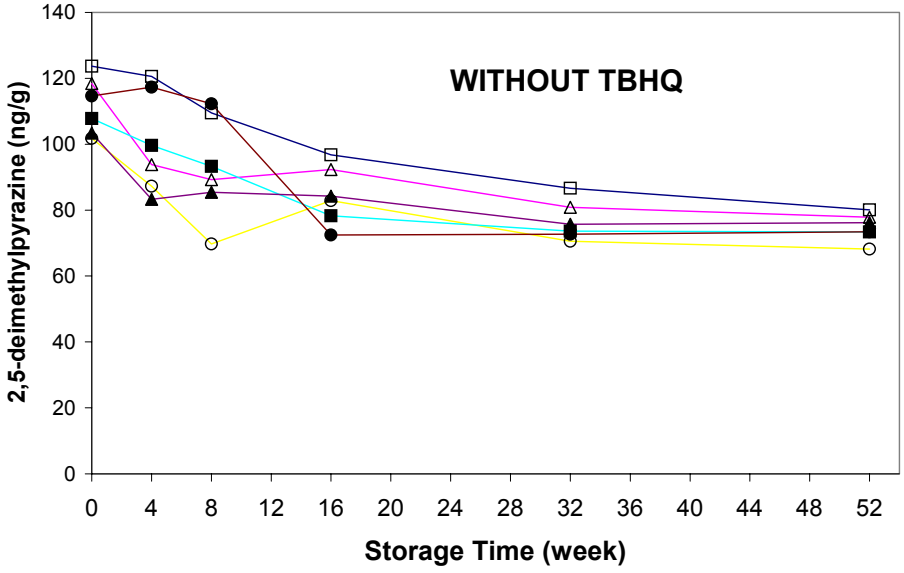
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2,5-deimethylpyrazine (ng/g)
Storage Time (week)
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20
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80
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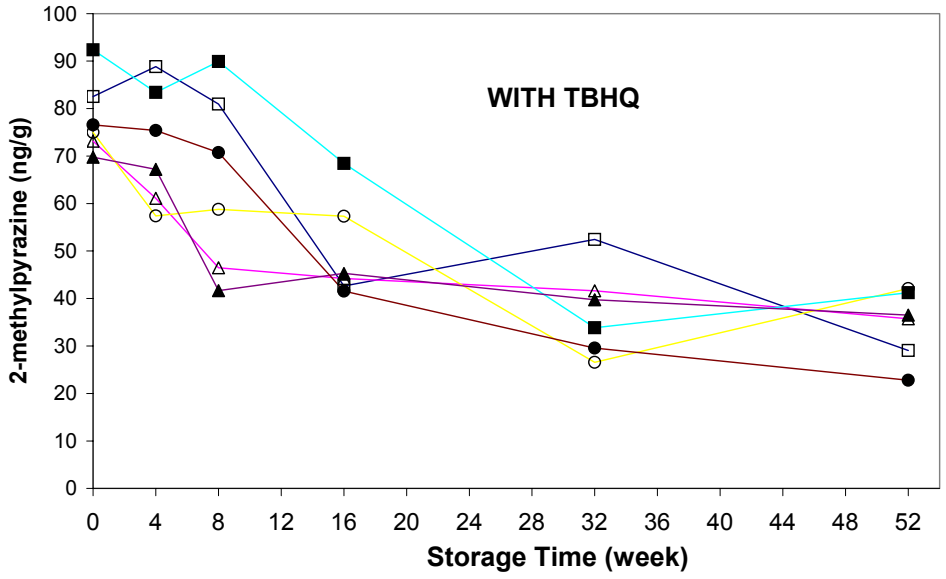
Figure 4.4


WITH TBHQ
2-methylpyrazine (ng/g)
Storage Time (week)
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10
20
30
40
50
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80
90
100
0
4
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12
16
20
24
28
32
36
40
44
48
52

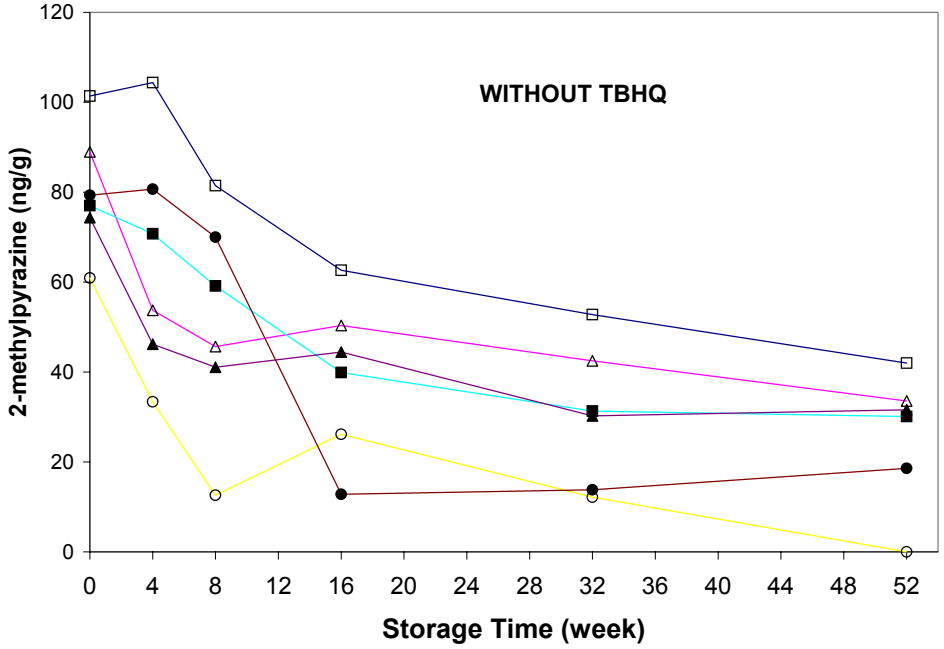
WITHOUT TBHQ
2-methylpyrazine (ng/g)
Storage Time (week)
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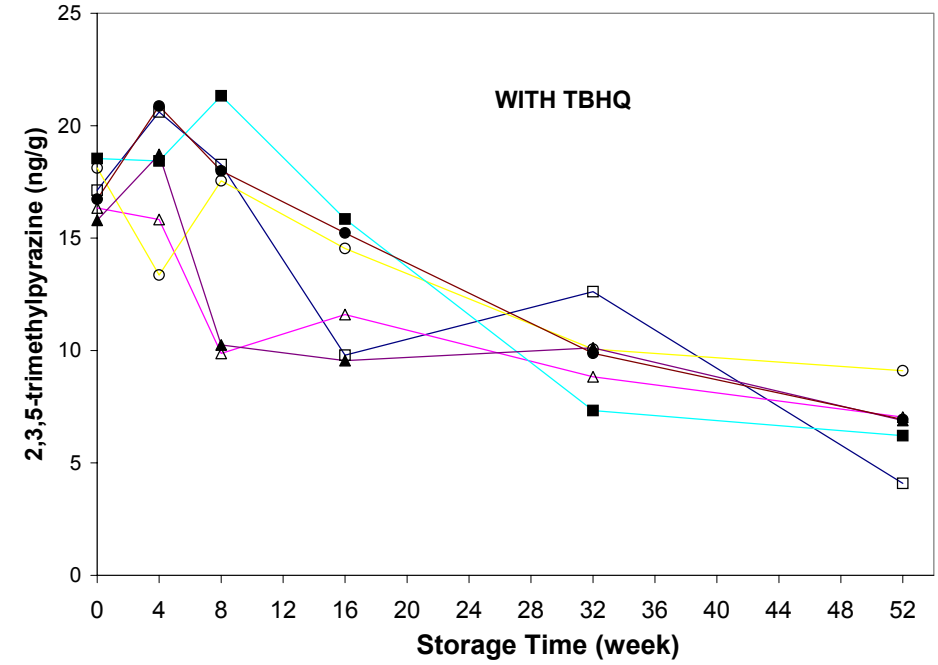
Figure 4.5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2,3,5-trimethylpyrazine (ng/g)
Storage Time (week)
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5
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15
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25
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4
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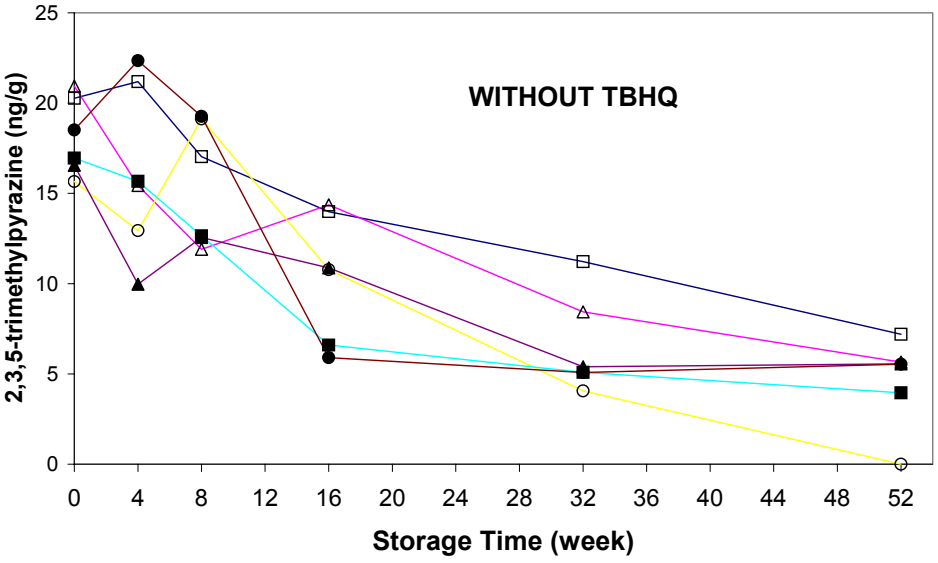
WITHOUT TBHQ
2,3,5-trimethylpyrazine (ng/g)
Storage Time (week)
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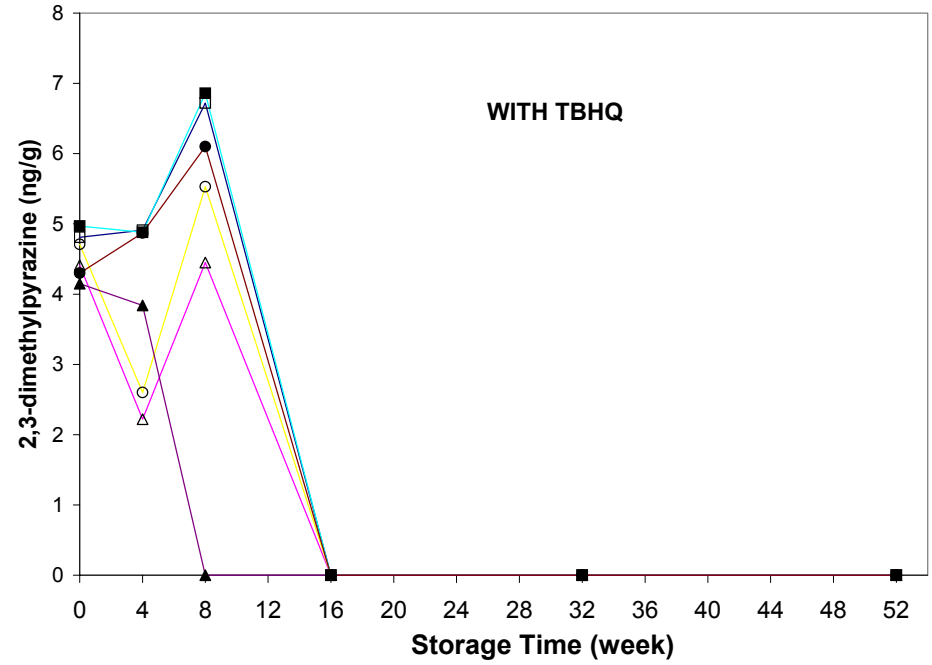
Figure 4.6


WITH TBHQ
2,3-dimethylpyrazine (ng/g)
Storage Time (week)
0
1
2
3
4
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7
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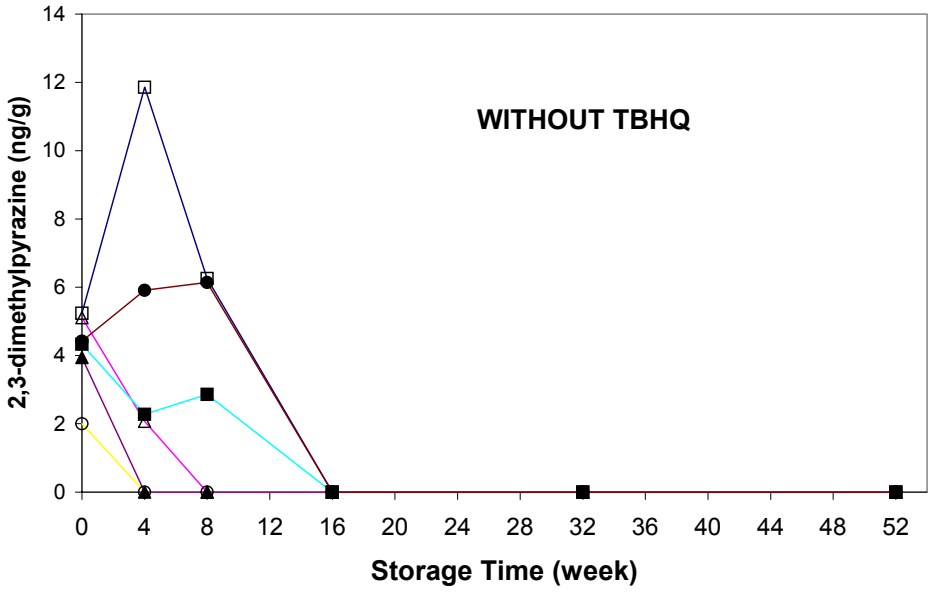
52


WITHOUT TBHQ
2,3-dimethylpyrazine (ng/g)
Storage Time (week)
0
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CHAPTER 5

THE EFFECT OF MOISTURE, SUGAR AND ANTIOXIDANT ON COLOR, TEXTURE AND MICROSTRUCTURE OF MODEL PEANUT CONFECTIONS[1]

[1]Abegaz, E.G., W.L. Kerr and P.E. Koehler. To be submitted to *Food Research International*

ABSTRACT: The effect of antioxidant, sugar, moisture, and storage time on color and texture and microstructure of model peanut confections were determined. The addition of moisture at 2 and 5% level resulted in lower lightness (L*), hue angle (h°) and chroma (C) values. Peanut paste treatments with added moisture had higher hardness, adhesiveness, gumminess and chewiness and lower cohesivness and springiness compared to no moisture-added treatments. Light and scanning electron microscopy showed peanut pastes treatments with 2 and 5% moisture had aggregates of protein bodies. Image analysis of LM micrographs confirmed the presence of aggregation of protein bodies in 2 and 5% moisture treatments.

KEYWORDS: peanut paste, moisture, color, texture, microstructure

INTRODUCTION

Texture plays an important role in consumer's acceptance of foods. Consumers may equate deviation from expected texture as poor quality. Processing and ingredient parameters do affect peanut butter texture (Woodroof *et al.* 1945). Young and Heinis (1989) noted that the addition of honey or corn syrup altered peanut butter flavors and viscosity. Cippen, Hamann and Young (1989) observed that sensory smoothness, hardness, spreadability, adhesiveness, hesion, ease of swallowing, and preference ratings of peanut butter were affected by different levels of grind size, sucrose, and salt concentrations.

Felland and Koehler (1997) observed that the addition of small amount of moisture in peanut butter resulted in darker color, lower peanutty roasted aroma, roasted flavor, and more off-odor and off-flavors. The addition of different concentrations of

water could also act as proxidant or antioxidant in peanut butter samples (St. Angelo, Ory & Brown, 1972, St. Angelo & Ory, 1973). Nakayama (1992) observed the addition of small amount of water to peanut butter gave a much stiffer butter.

Process specific conditions, whether peanuts are roasted, blanched, made into peanut butter, used in confection, pressed for oil, or treated for recovery of oil affect peanut seed cells (Woodroof and Leahy, 1940). Light microscopy (LM) and scanning electron microscopy (SEM) were used to study the effect of processing such as grinding procedures, degree of homogenization on peanut butter microstructure (Young and Schadel 1990b, 1991, Aryana, Resurreccion & Chinnan, 2000).

Since moisture is very important to the overall quality of peanut products, the objective of this study was to investigate how different levels of moisture in combination with different levels of antioxidant and sugar affect the color, texture and microstructure of model peanut confection during storage.

MATERIALS AND METHODS

Peanut paste

Fresh, untreated, certified, aflatoxin negative roasted peanut paste was supplied by Seabrook Ingredients (Edelton, NC). Initial analysis of the peanut paste showed 53.94% oil, 0.86% water, fineness of grind (35 mils first scrape, 3 mils second scrape), free fatty acid 0.13%, and coliform MPN <3. Upon receipt, the peanut paste was placed in storage at -10 °C until used.

Model peanut confection formulation

A factorial arrangement was used to specify the levels of peanut paste and ingredients. Twelve treatments were prepared with three levels (0, 2 and 5%) added

moisture, two levels (0 and 4%) of sucrose, and two levels (0 and 180 ppm) of the antioxidant, tertiary butylhydroquinone (TBHQ). Three separate batches were prepared for each treatment group. Enough material was prepared for each group to allow analysis at 6 storage times (0, 4, 8, 16, 32 and 52 weeks).

The peanut paste was first mixed using a model SPY-1824 paddle mixer (Marion Mixers, Inc., Marion, IA) to ensure there was no oil separation before sample preparations. Approximately 5.44 kg of peanut paste was heated inside a Sharp microwave oven (model R-510CK Sharp Electronics Corp., Mahwah, NJ) to a temperature of 83 °C and then placed in a KitchenAid mixer equipped with a flat beat paddle (model KSMC50S KitchenAid, St. Joseph, MI). A heating mantle maintained the temperature at 83°C. Refined 6X sucrose (Domino Sugar Co., New Orleans, LA), water, TBHQ (Eastman Chemical, Kingsport, TN) in refined peanut oil (CNT Refinery, Charlotte, NC), Dritex RC hydrogenated vegetable oil stabilizer (AC Humko, Memphis, TN) melted at 83 °C, and flour salt (Cargill, Minneapolis, MN) were added slowly while mixing, for a total mixing time of two minutes. Peanut pastes were made and poured into a series of small plastic petri dishes (30mm diameter x 10mm depth), where the samples were allowed to cool and harden. The samples were covered with plastic lids pre-drilled with a 1mm hole to allow air circulation.

Storage and sampling

The samples were placed in a controlled temperature (21°C ± 0.1°C) and humidity chambers (Model 435314, Hotpack SP Industries, Philadelphia) each set at a relative humidity (%RH ± 2.0%) close to 100 times the water activity (a_w) of the samples. As the aw of the air is just %RH/100, this approach limited the amount of moisture lost or

gained by the sample due to moisture transfer with the surroundings. Triplicate samples were randomly picked and evaluated for color and texture at 0, 4, 8, 16, 32 and 52 weeks of storage.

Color analysis

Color measurements of samles were made using Minolta Chromameter Cr-300 (Minolta Corporation, Ramsey, NJ). Readings were made from the bottom side of the petri dishes. Three sets of readings were obtained per treatment rotating between each measurement. CIE color values were measured for lightness (L*), hue angle (h°), and Chroma (C). A standard white reference tile was used for calibration.

Texture Profile Analysis

An Instron Universal Testing Machine (model 5500 Instron Corporation, Canton, MA) was used to measure the textural properties of peanut paste. Peanut paste treatments were removed from storage and were held undisturbed for at least one hour prior to any measurement. A 27 mm cylindrical probe was used to twice compress the sample area to 4% deformation (2mm). The crosshead speed was 0.83mm/sec during both the compression and return cycles. Texture profile analysis (TPA) curves were obtained and six textural parameters were obtained from analysis of the force-time plots. All measurements were repeated 3 times.

Microstructure analysis

Peanut paste microstructure was examined using light microscopy (LM) and scanning electron microscopy (SEM). The peanut paste treatments were prepared for examination as follows:

Fixation and dehydration

Peanut paste treatments (1 mm^3) were carefully sectioned with a razor blade. The treatments were subjected to a modified Karnovsky's fixative as described by Young and Schadel (1990b). The fixative was prepared by mixing 25 ml of 8% formaldehyde, 3.6 ml of 70% gluteraldehyde and 28.6 ml of 0.1M sodium phosphate buffer. The resulting mixture was adjusted to pH 7.0. The peanut paste treatments were fixed under vacuum for 30 minutes at room temperature and then held at atmospheric pressure for 48 hours at 4°C. This was followed by a 24 hour wash in six changes of 0.1M sodium phosphate buffer (pH 7.0, 4°C). The treatments were post-fixed for one hour in 1% osmium tetroxide in 0.1M sodium phosphate buffer (pH 7.0, 4C) then rinsed in 0.1 M sodium phosphate buffer (pH 7.0, 4C) for 30 minutes. Peanut paste treatments were dehydrated in a graded series of aqueous ethanol (10, 25, 50, 75 and 95%) solutions for 15 minutes at each concentration and then paced in three changes of absolute ethanol for 30 minutes each.

Infiltration/embedding

Peanut paste cubes were embedded in resin as described by Spurr (1969). Sections (3 mm) were cut using a RMC Microtome (RMC Products, Boeckeler Instruments, Tuscon, AZ) and glass knives.

Light Microscopy

The sections were deposited on a clean wet glass slide and allowed to dry. The sections were stained with acid fuchsin (Fisher Scientific Company, Fair lawn, NJ), and toluidine blue (J.T.Baker Chemical Co., Philipsburg, NJ) using methodology from Feder

and O'Brien (1968). Sections were examined with a Leica TCS SP2 microscope (Leica Microsystems Inc., Exton PA).

Scanning Electron Microscopy

After fixation and dehydration, peanut paste treatments were placed inside a Tousimis Samdri®-780 liquid CO_2 critical point drier (Tousimis Research Corporation, Rockville, MD). The dried treatments were mounted on aluminum stubs with double sided tape, and were coated with 30.6 nm gold at room temperature in a SPI-Module™ sputter coater fitted with a SPI-Module Digital Quartz Crystal Thickness Monitor (Structure Probe, Inc., West Chester, PA). Peanut paste treatments were viewed with a LEO 982 Field emission scanning electron microscope (FE-SEM, LEO Electron Microscopy, Inc., Thornwood, NY) at a working distance of 9 mm and an acceleration voltage of 5 kV.

Statistical Analysis

Data were analyzed using the PROC GLM routine in the SAS statistical software sytem, version 6.12 (SAS Institute Inc, Carry, NC). Mean seperations were performed using the LSD test at $p< 0.05$. Image analysis was conducted using Scion Imaging Software for the IBM PC (Scion Corporation, Frederic, Maryland).

RESULTS & DISCUSSION

Color evaluation

TBHQ and sugar levels did not have a significant effect on color values. There was significant moisture and storage time interaction ($P\leq 0.0001$) for lightness (L*), hue angle (H°) and chroma(C) (Table 5.1). At higher moisture levels, peanut paste treatments had significantly lower L*, h° and C values compared to low moisture treatments across

each storage time. As moisture was added at 2 and 5% to the peanut paste treatments, they became darker and dull in color. Felland and Koehler (1997) observed peanut butters with 2.5% and 5% added moisture had instantaneous color changes once water was thoroughly blended in peanut butter. The peanut butters became darker and had lower L readings. A study by Brannan, Koehler and Ware (1999) found defattted (22% oil) roasted peanuts had higher Hunter L and b values when compared to full-fat (53% oil) roasted peanuts. They believed the lighter color in the defatted peanuts was due to the decrease in the melanin once the oil was removed as melanin is responsible for the color of the oil. We suspect that the instantaneous change in color due to addition of moisture is due to change in the refractive index of the peanut paste.

Generally, L*, h° and C increased with storage duration reaching a maximum by week 16 (Table 5.1). Our results also agreed with observations made by Felland and Koehler (1997), where the authors also suggested darkening due to moisture could be detrimental to the quality of roasted peanut product unless accounted for in the initial prototype.

Texture evaluation

TBHQ was not significant for all texture properties. There was a significant interaction between sugar and moisture ($P \leq 0.015$) for hardness. Addition of moisture resulted in significant difference in hardness (Table 5.2). Moisture addition immediately produced harder texture in the peanut pastes. For example, for treatments with 0% sugar, mean hardness values for 0%, 2% and 5% moisture were 7.73, 22.69 and 27.37 kg respectively. Nakayama (1992) was able to produce stiffer peanut butter products with addition of a small increment of water. The reason for increased hardness is uncertain,

but is most probably related to a disruption of the continuous fat phase and aggregation of cellular components. Peanut pastes with 4% sugar and 0% added moisture resulted in harder texture compared to 0% sugar and moisture added treatments (Table 5.2). Increase in hardness due to sugar was not observed with 2 and 5% moisture added treatments. Crippen et al. (1989) found that instrumental measures of hardness were slightly less in peanut butter samples with added sugar, although sensory measures of hardness were unaffected in peanut butter samples. Muego, Resurreccion and Hung (1990), observed significant correlations of selected textural sensory attributes with instrumental hardness for two commercial peanut butters and peanut paste samples. They observed significant Pearson correlation of grainy (0.80), spread (-0.76) and smoothness (-0.77) attributes with hardness as measured by an Instron Universal Testing Machine. We observed 2% and 5 % moisture treatments had less spreadabilility and smoothness and appeared grainy as compared to 0% moisture treatments.

Cohesiveness, the strength of the internal bonds making up the body of a product (Szczesniak, 1963), had significant sugar and moisture interaction ($p \leq 0.013$). Generally, treatments with 0% added moisture had significantly higher cohesiveness compared to 2% and 5% moisture treatments. It was also observed that 4% sugar and 0% moisture treatments were less cohesive than 0% sugar and 0% moisture treatments (Table 5.2). Sugar was not a significant factor, however with intermediate and high moisture treatments (Table 5.2). It is possible interaction between sugar and in particular moisture have broken up the continuity of the peanut paste and thus reduced the internal bonds that held the peanut paste together.

Ahmed and Ali (1986) described the work necessary to remove the peanut butter from the plunger as an indicator of adhesiveness. Szczesniak (1963) defined adhesiveness as the work necessary to overcome the attractive forces between the surface of the food and the surface of other materials with which the food comes into contact (i.e. tongue, teeth, palate, etc). There was significant moisture effect ($p \leq 0.0001$) for adhesiveness. Peanut paste treatments with 2% and 5% moisture had significantly higher adhesiveness (Table 5.2). According to Syarief, Hamann, Geisbrecht, Young and Monroe (1985) and Crippen *et al*. (1989) the ease of swallowing is inversely related to adhesiveness. How and Young (1985) also reported that many consumers dislike sticky and adhesive peanut butter.

Springiness was calculated as the distance of the detected height of the product of second compression as divided by the original compression distance. Moisture was significant for springiness (Table 5.2). Mean values for treatments with 0% moisture had significantly higher springiness than 2% and 5% moisture treatments.

A similar trend was observed for gumminess and chewiness. 'Chewiness' is the energy required to masticate peanut paste to a state ready for swallowing, while 'gumminess,' is the energy required to disintegrate the peanut paste. There was significant interaction between sugar and moisture for gumminess ($p \leq 0.0002$) and chewiness ($p \leq 0.0028$). Treatments with 2 and 5% moisture had significantly higher gumminess and chewiness values than 0% moisture treatments (Table 5.2). In addition, treatments with 4% sugar and 0% moisture had significantly higher gumminess and chewiness values than 0% sugar and moisture treatments (Table 5.2).

Storage time was significant for cohesiveness ($p \leq 0.0003$), adhesivness ($p \leq 0.0001$), springiness ($p \leq 0.0001$) and chewiness ($p \leq 0.0001$). There was also significant interaction between moisture and storage time for hardness ($p \leq 0.0001$) and gumminess ($p \leq 0.0063$). Generally, hardness, adhesiveness, gumminess and chewiness increased slightly with storage (Table 5.3). Gills (1998) observed instrumental maximum force of penetration of hydrogenated vegetable oil stabilized peanut butters increased when stored for 160 days at 21°C. In the same study (Gills and Resurreccion, 2000) observed by sensory evaluation increased hardness values for the same peanut butters during storage. Cohesiveness and springiness appeared to be stable during storage except for an increase at week 16 (Table 5.3). The protein-protein interactions and the final state of the fat-phase of the peanut paste products may have affected the changes in textural property values during storage.

Microstructure evaluation

Light microscopy (LM)

Observation with LM revealed differences in the spatial relationships of microstructural features for the different moisture levels (Figure 5.1). Peanut pastes with 0% added water contained protein bodies and cell wall fragments well dispersed in a continuos oil matrix (Figure 5.1a). Peanut paste treatments with 2 and 5% added moisture exhibited aggregates of protein bodies (Figures 5.1b and 5.1c). In addition, 2% and 5% moisture treatments had denser spatial relationship of protein bodies, starch grains, and cell wall fragments as compared to 0% moisture treatments. Image analysis of the stained protein bodies showed that for perimeter lengths less than ~100μm, no difference was observed amongst treatments (Figure 5.2). However, the aggregates of mostly protein

bodies in 2 and 5% added moisture samples could be due to disruption of the fat matrix and enhanced interaction between the protein bodies due to moisture addition. These differences most likely contributed to different textural properties among the treatments. Aryana, Resurreccion and Chinnan (2000) stated aggregated protein bodies and cell wall fragments is undesirable in peanut butter because it is an indication of hardening. The authors also speculated that it could contribute to grittiness with time.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscope is a powerful tool that enables observation of peanut tissue, cells, and cellular content. SEM had been used to study the effect of processing on peanut seed microstructure such as epidermal cells, guard cells, stomata, vascular tissue, parenchyma cells, and cytoplamic network (Young & Schadel, 1990a). Young and Schadel (1990b) used SEM to reveal differences in the degree of homogenization among three commercially available brands of stabilized peanut butter. Grinding and or rolling to fineness of peanut butter results in about 50% of rupturing and emptying of cellular contents and 10-25 % uninjured cells (Woodroof & Leahy, 1940). Oil droplets ran together and form large drops of free oil during processing of peanuts for peanut butter. In our peanut paste treatments, we were able to observe epidermal cells, parenchyma cells, collapsed and intact cytoplasmic network, sub-cellular contents, and coalesced cellular content. We were also able to observe aggregation of cellular contents in 2 and 5% moisture treatments (Figures 5.3a, 5.3b and 5.3c). However, detecting differences in the spatial distribution of cellular contents between the different moisture levels was better achieved with LM. Young and Schadel (1990b) stated that SEM had limited capability for evaluating the differences amongst stabilized peanut butter with

different degrees of homogenization. They were able to detect incompletely homogenized cellular contents and tissue fragments, however, the use of LM provided them an excellent complement to SEM for a more through understanding of the spatial relationship of the microstructural features.

CONCLUSION

The levels of moisture considered in the study played a role in the color, texture, and microstrural changes in our model peanut confection. The addition of moisture at 2 and 5% level resulted in darker and dull peanut paste. Peanut pastes had lower lightness, hue angle and chroma values with the addition of moisture. The moisture level also had an effect on the textural properties. Peanut paste treatments with 2 and 5% moisture had higher hardness, adhesiveness, gumminess and chewiness compared with 0% moisture treatments. Treatments with 0% moisture had higher cohesiveness and springiness compared to 2 and 5% added moisture treatments. There were also interactions between sugar and moisture for some of the textural properties. LM micrographs showed 0% moisture treatments had protein bodies and cell wall fragments that were well dispersed in a continuous oil matrix. Peanut pastes treatments with 2 and 5% moisture had denser spatial distribution of cell wall fragments, protein bodies, and starch granules. These treatments also had aggregates of protein bodies. Image analysis of LM micrographs confirmed the visual observation. Aggregation of cellular contents in the 2 and 5% moisture treatments were also seen in SEM micrographs. The study implies that common ingredients such moisture and sugar, even at low concentration, play an important role in the overall quality of peanut confections. It is important for the confection industry to

consider these factors and their interactions when developing new products and improving existing products.

ACKNOWLEDGEMENT

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Table 5.1 Moisture versus storage time effect on color values of stored peanut pastes

Value	Moisture (%)	Storage time (week)					
		0	4	8	16	32	52
L*	0	51.6[a]	52.2[a]	52.0[a]	56.6[a]	53.1[a]	53.8[a]
	2	50.b[b]	50.8[b]	50.8[b]	55.1[b]	51.8[b]	52.6[b]
	5	46.1[c]	47.5[c]	48.0[c]	52.4[c]	49.4[c]	49.8[c]
H°	0	71.9[a]	72.6[a]	72.5[a]	72.9[a]	73.3[a]	74.6[a]
	2	71.5[a]	72.3[a]	72.3[a]	72.7[a]	73.0[a]	74.1[a]
	5	69.8[b]	70.8[b]	71.2[b]	71.6[b]	72.0[b]	72.7[b]
C	0	32.6[a]	32.9[a]	32.8[a]	35.0[a]	33.5[a]	32.9[a]
	2	31.6[b]	32.1[b]	31.9[b]	34.0[b]	32.9[b]	31.8[b]
	5	29.4[c]	30.3[c]	30.6[c]	32.8[c]	31.5[c]	29.8[c]

[a]Means for each color values within a column followed by the same letters are not significantly different ($p \leq 0.05$). Measurements on each treatment group were replicated three times.

Table 5.2 Sugar versus moisture effects on textural properties of stored peanut pastes

Property		Moisture (%)		
	Sugar (%)	0	2	5
Hardness (kg)	0	7.73[c]	22.6[b]	27.3[a]
	4	12.3[c]	23.6[b]	32.1[a]
Cohesiveness	0	0.540[a]	0.345[b]	0.273[c]
	4	0.463[a]	0.339[b]	0.316[b]
Adhesivness (kg.s)	0	4.63[b]	12.3[a]	13.5[a]
	4	7.77[b]	12.5[a]	11.4[a]
Springiness	0	0.871	0.780	0.695
	4	0.849	0.729	0.735
Gumminess (kg)	0	3.99[b]	7.26[a]	7.21[a]
	4	5.17[c]	7.59[b]	9.86[a]
Chewiness (kg)	0	3.45[b]	5.83[a]	5.21[a]
	4	4.40[c]	5.78[b]	7.45[a]

[a]Means within a row followed by the same letters are not significantly different ($p \leq 0.05$). Measurements on each treatment group were replicated three times.

Table 5.3 Storage time effect on textural properties of stored peanut pastes

Property	Storage time (week)					
	0	4	8	16	32	52
Hardness (kg)	19.1[b]	22.9[a]	21.9[a]	18.7[b]	20.8[a]	22.2[a]
Cohesivness	0.350[b]	0.345[b]	0.388[b]	0.465[a]	0.378[b]	0.350[b]
Adhesivess (kg.s)	7.32[b]	11.1[a]	12.4[a]	7.06[b]	12.7[a]	11.7[a]
Springiness	0.794[ab]	0.683[c]	0.741[bc]	0.840[a]	0.863[a]	0.737[bc]
Gumminess (kg)	5.63[b]	6.22[b]	7.24[a]	7.47[a]	7.08[a]	7.43[a]
Chewiness (kg)	4.47[b]	4.07[b]	5.45[a]	6.29[a]	6.24[a]	5.56[a]

[a] Means of a textural property across a row followed by the same letters are not significantly different ($p \leq 0.05$). Measurements on each treatment group were replicated three times.

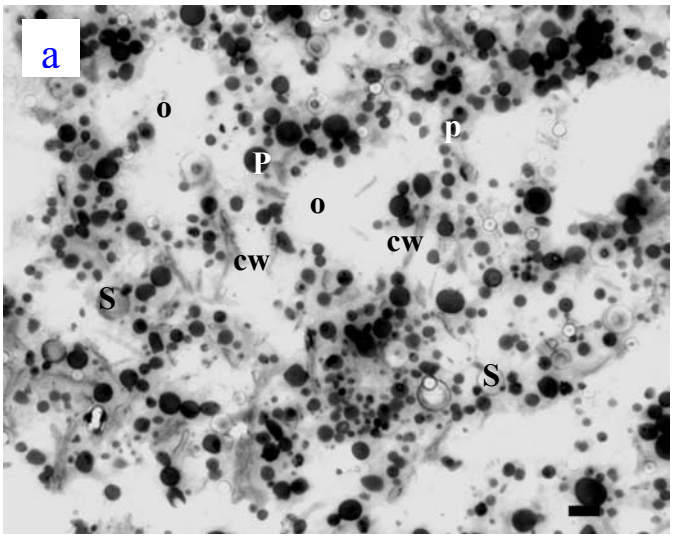
Figure Legends

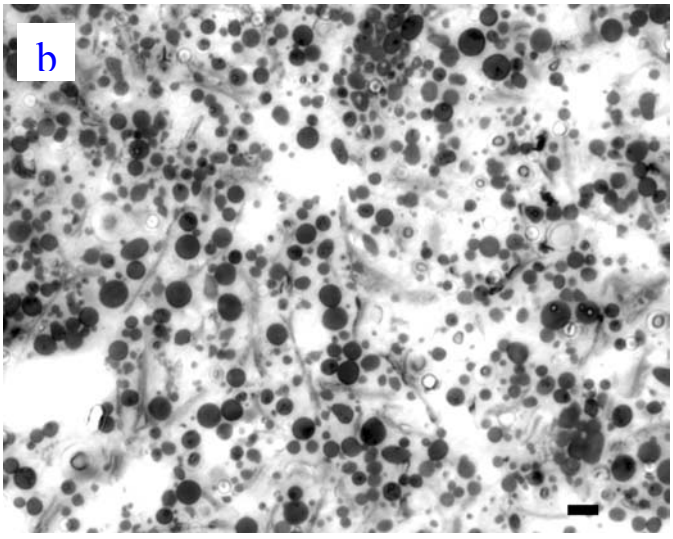
Figure 5.1 LM micrographs of peanut paste treatments with 180 ppm TBHQ, 4% sugar and added moisture of (a) 0%, (b) 2% and (c) 5%. CW- cell wall; O- oil matrix; P- protein bodies; S-starch granule. Scale bar = 10 μm; arrow = aggregation

Figure 5.2 Size distribution of protein bodies of peanut pastes with different levels of moisture. ▲ 0% moisture, ■ 2% moisture, ● 5% moisture

Figure 5.3 SEM micrographs of peanut paste treatments with 180 ppm TBHQ, 4% sugar and added moisture of (a) 0%, (b) 2% and (c) 5%. Scale bar = 20 μm; arrow = aggregation

Figure 5.1





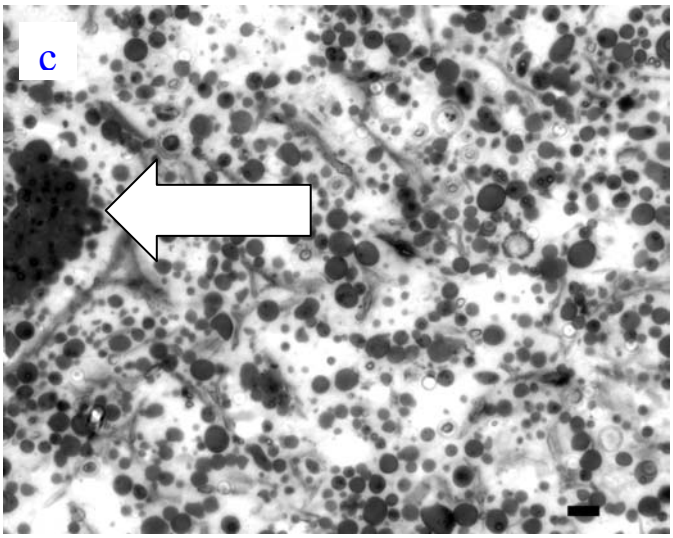


Figure 5.2

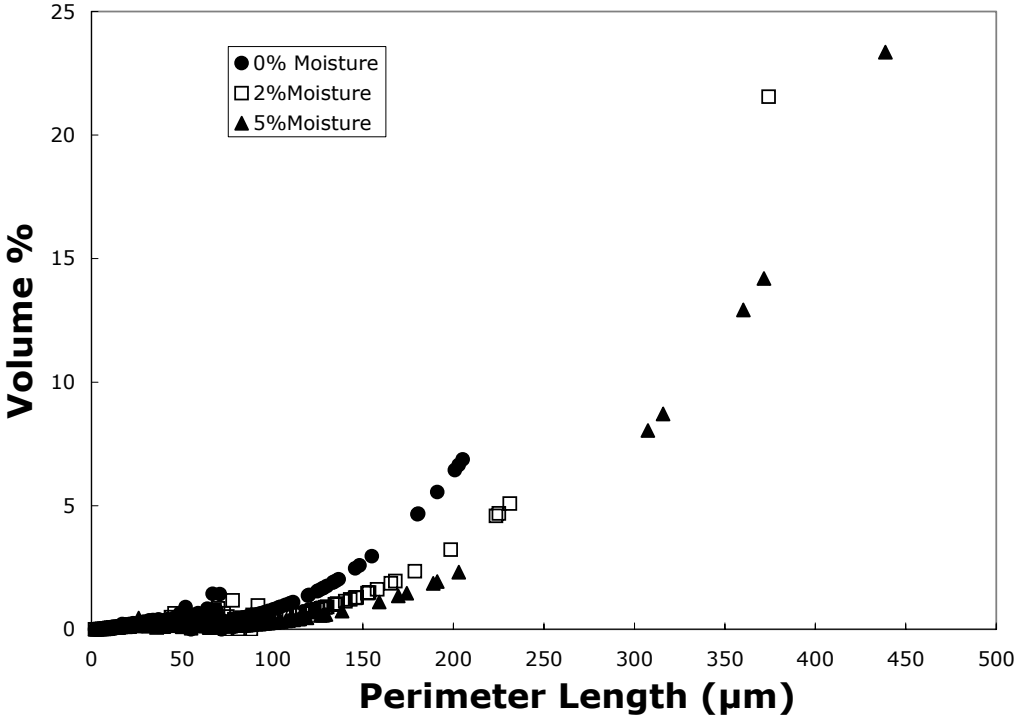
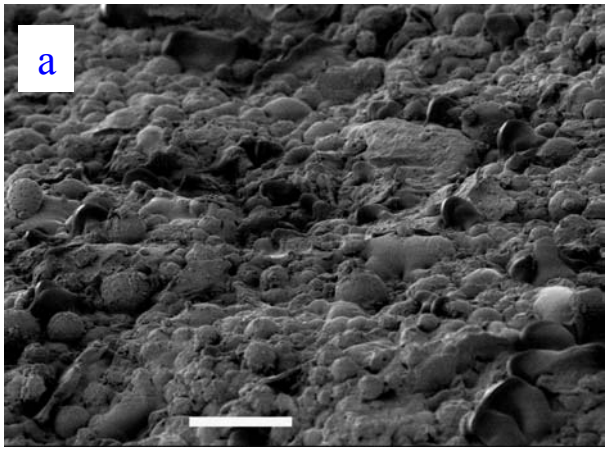
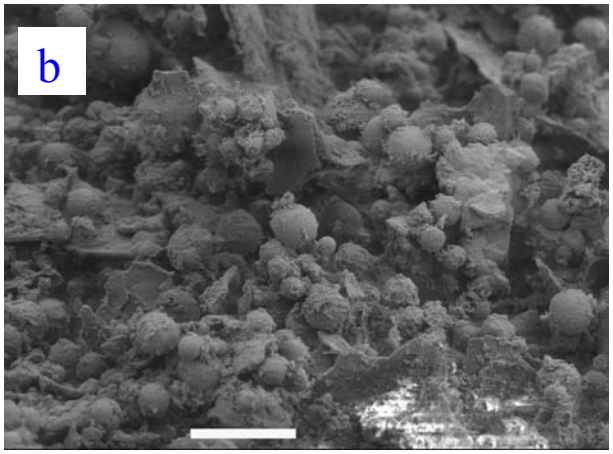
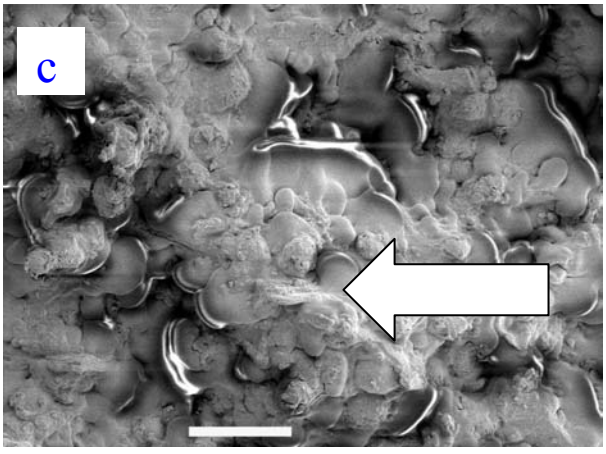

0% Moisture
2%Moisture
5%Moisture
Volume %
Perimeter Length (µm)
0
5
10
15
20
25
0
50
100
150
200
250
300
350
400
450
500

Figure 5.3







CHAPTER 6

PARTITIONING, VOLATILITY, AND BINDING PROPERTIES OF SELECTED ALKYLPYRAZINES IN MODEL SYSTEMS[1]

[1]Abegaz, E.G., W.L. Kerr and P.E. Koehler. To be submitted to *Journal of Agriculture and Food Chemistry*

ABSTRACT: Partitioning, volatility and binding properties in model systems were determined for selected pyrazines substituted with 1, 2, 3, 4 methyl groups. In oil-water (1:1) mixtures at 25°C, pyrazines substituted with one and two methyl groups partitioned mostly into the aqueous layer. Pyrazines, with tetra-methyl groups partitioned mostly into the oil layer and tri methyl substituted pyrazines partitioned equally in both the oil and aqueous layers. Mono- and di-substituted pyrazines had higher volatility in oil systems, and tri- and tetra-substituted pyrazines had higher volatility in aqueous model systems. Alkylpyrazines initially displayed faster irreversible binding to peanut paste treated with 5% percent water as compared to 0% water addition.

KEYWORDS: Partitioning, Volatility, Binding, Alkylpyrazines, Model systems

INTRODUCTION

Alkylpyrazines have been described as essential trace flavor components that are characteristic in many cooked, deep-fat fried, roasted and toasted foods (*1*). Some alkylpyrazine have been described as having a nutty character in roasted peanuts and important compounds produced after roasting of peanuts (*2*). Pyrazines are commonly used as determinant of flavor stability (*2*). Abegaz and co-workers (*3*) observed that peanut pastes treated with small, incremental amounts of water (0-5%) had decreased alkylpyrazine concentrations. Sensory evaluation by trained panel also confirmed that the intensity of roasted peanutty attribute intensity decreased with the addition of water (*4*). Two reasons are considered for the observed result. One possibility was that the alkylpyrazines became soluble in the aqueous phase and had low vapor pressure to come out of the food matrix. The second possibility involved since the addition of water to the

peanut pastes altered the texture and microstructure of the peanut pastes (*5*), it may have resulted in increased binding of peanuty aroma compounds. Since foods are complex, it is useful to use model systems that can provide an approximation of the behavior expected in the actual practical system. In the past, various authors have used a model system to study the volatilities of number of volatile compounds in pure water, pure oil, or water-oil mixtures (6-*8*). The objective of the current study is to investigate the oil-water partitioning, volatility and binding of selected alkylpyrazines in model systems in order to approximate what might have happened in the actual peanut paste treatments.

MATERIALS AND METHODS

Materials. Pure organic compounds: [2-methylpyrazine (2MP), 2,3-dimethylpyrazine (2,3-DMP), 2,5-dimethylpyrazine (2,5-DMP), 2,6-dimethylpyrazine(2,6-DMP) , 2-ethyl-3-methylpyrazine(2-E-3MP), trimethylpyrazine (TRMP), tetramethylpyrazine (TEMP)] and pure peanut oil were obtained (Aldrich, Milwaukee, WI). The peanut oil was stored under nitrogen, in the dark, at refrigeration temperature.

Partitioning experiments

Standard aroma solutions consisting of 2-MP, 2,5-DMP, 2-E-3MP, TRMP, and TEMP were prepared to a final concentrations of 2,4,6,8 and 10 ppm by adding them in odor-free distilled water in a graduated flask. The flask was shaken for one-half hour to ensure solubility of the aroma compounds. Solubility was checked by observing the surface of the water in the narrow neck of the flask.

An oil-water mixture was prepared by adding 20 ml of each of the standard solution and the same amount of pure oil was placed into a 50 mL Blue Max™

polypropylene conical tube. The mixture was vortexed for 30 minutes (Fisher Vortex Genie 2™, Scientific Industries, Inc., Bohemia, NY) and allowed to sit for five minutes. This solution was then transferred into a 40 mL vial with Teflon-lined septa, and equilibrated for 48 hours. A control, 40 mL of standard solution was also paced in a 40 mL vial and equilibrated for 48 hours. After equilibration of the mixture, the bottom aqueous layer was carefully removed using a pipette. The aqueous layer was passed through a 0.2 μm filter unit (Fisher Scientific, Pittsburgh, PA), and spectrophotometer (Spectronic® Genesys™ 2, Rochester, NY) readings were performed on the clear aqueous layer of four replication samples as well as the controls.

Partitioning calculation

Partitioning between oil-water (k) was calculated as:

$$k = \frac{\text{solute concentration in oil}}{\text{solute concentration in water}} \quad \text{at } 25\ ^{\circ}C$$

The solute concentration in the oil was determined by subtracting the concentration in the aqueous layer from the actual concentrations in the standards.

Quantification

A calibration curve of concentrations vs. absorbance at selected wavelength were developed for the standard solutions. Three replications were performed for each concentration levels. The coefficient of determination (R^2) for all the calibration curves was 0.99. The concentrations of each of the volatile compounds in the aqueous layer were determined from the calibration curves.

Volatility experiments

Dynamic headspace

A cocktail of aroma compounds, consisting of 2-MP, 2,3-DMP, 2,5-DMP, 2,6-DMP, TRMP and TEMP, were added in four model systems of (1) distilled water (2) homogenized oil and water mixture (90% fresh peanut oil, 9.5% water and 0.5% lecithin) (3) fresh peanut oil (PV = 1mEq/kg oil) and (4) rancid peanut oil (PV =60 mEq/kg oil) held in a graduated flask, and final concentrations was adjusted to 500 ppm for each systems. For each of the systems, 2 mL of the aroma solution was transferred to a 40 mL vial with Teflon-lined septa. The vials were equilibrated for 24 hours before headspace analysis.

Headspace solid phase micro extraction (SPME) technique was used to extract volatile compounds from the mediums, using a Divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber (Supelco, Inc., Bellefonte, PA). The fiber was first conditioned on the GC injection port for 5 min at 270°C and cooled for five minutes. It was then inserted through the septum of the vial into the headspace above the solution. Volatiles were adsorbed from the headspace for 20 minutes at 25°C while the medium was stirred using a magnetic stirrer. The fiber was removed from the vial and inserted into the injection port equipped with an SPME inlet liner. Sample volatiles were desorbed for 5 min at 270°C.

Three replicate aroma samples were made for each of the mediums. The headspace concentration of the volatiles above the mediums was measured at 0, 3, 5, and 10 days. The change in headspace concentration was measured over time.

Binding experiments

Static headspace

Peanut paste treatments, consisting of 5g each with two levels of added water, 0% (w/w) and 5% (w/w) were placed in a 40mL vial with Teflon-lined septa. The samples were left to equilibrate for 1 hour at 25°C. A cocktail of aroma compounds (3mL), consisting of 2-MP, TRMP and 2-E-3MP, in 1 mL hexane was placed in a sealed 40-mL vial. The aroma compounds were left to equilibrate at 25°C. A portion of the headspace (10mL), was withdrawn from the sealed vial over a period of one-minute using a gas-tight syringe. This same volume was injected into the vial containing the peanut paste treatments. The change in headspace concentration was measured over time by withdrawing 1mL samples of headspace for GC analysis over 10 minutes intervals for 60 minutes.

GC analysis for volatility and binding experiments

Analysis was conducted on a Hewlett-Packard 5890 Series II gas chromatograph coupled to a FID detector. The peak and peak areas were recorded by a HP 3365 Series II ChemStation computer software interface. Compounds were separated with a SUPELCOWAX™ 10 (30m, 0.25mm i.d., 0.25µm film) column obtained from (Supelco, Inc., Bellefonte, PA). Nitrogen was used as a carrier gas (140 kPA), and the oven was programmed to run at 40°C for 5 min, then ramped at 4°C/min to 120°C using splitless injection mode. The injector and detector temperatures were 270°C and 280°C respectively.

Each experiment was repeated three times; headspace concentrations were determined from FID peak areas and arithmetic means and standard deviations were calculated. Percentage coefficient of variation (SD x 100 ÷ mean) were also monitored

for the experiments. Changes in the headspace concentration were expressed as a change in the GC peak area, or as a relative percentage scale in which the first sample was considered as a 100%. For binding experiments, control experiments were performed in the absence of peanut pastes to determine the consumption of headspace volatiles by the sampling system, and these values were subtracted from the peanut paste sample results to obtain a corrected value for volatile binding.

RESULTS AND DISCUSSION

Partitioning experiment

The partitioning of selected alkylpyrazines is shown in **Figure 6.1**. The aroma compounds 2-MP and 2,5-DMP displayed lower oil-water partitioning coefficients. This was due to the high solubility these compounds had in water. Conversely, 2-E-3-MP and TEMP displayed higher oil-water partitioning coefficients, and thus remained mostly in the oil layer. TRMP partitioned equally in both the oil and aqueous layers. Our results agreed with water solubility and log octanol/water partitioning coefficient data reported for pyrazines (*9*). Information on oil-water and air-oil and water mixtures partitioning has important implications on flavor release of aroma compounds from food matrices, as well as the anticipated effect on sensory perception (*6,10*).

Volatility experiment

We also conducted experiments to measure the volatile headspace concentration of alkylpyrazines in four model systems: distilled water, fresh peanut oil (PV = 1mEq/kg oil), homogenized fresh peanut oil and water (9:1), and rancid peanut oil (PV =60 mEq/kg oil). The results of this experiment are shown in **Figure 6.2**. 2MP, 2,3-DMP, 2,5-DMP and 2,6-DMP had the lowest volatile headspace concentrations in water. Mono-

and di-substituted pyrazines displayed higher water solubility and thus resulted in lower air-water partitioning. These compounds also displayed lower solubility in both fresh and rancid oil, and, thus, higher air-oil partitioning. The headspace concentrations of these compounds were also lower in oil-water mixtures when compared to both 100% fresh and rancid peanut oil. Our results agreed with water solubility and air-water partitioning data for di-substituted pyrazines reported (*9*). Pyrazine compounds with 3 and 4 substituted methyl groups (TRMP and TETMP, and 2-E-3-MP) had higher volatile headspace concentrations in water due to the low solubility of these compounds in water, thus resulting in increased vapor pressure from the aqueous phase to the headspace. However, they had lower headspace concentration in both fresh and rancid oils due to their higher solubility and lower vapor pressure in these systems. This result also agrees with the oil-water partition experiment (**Figure 6.1**). Comparatively, the headspace concentrations of TRMP, and TETMP, and 2-E-3-MP were higher in oil-water mixtures than in 100% oil systems (**Figure 6.2**).

Results of the kinetics of headspace volatile concentrations of alkylpyrazines in the different systems over time are shown in **Figures 6.3** and **6.4.** Generally, 2-MP, 2,3-DMP and 2,5-DMP had similar rates of change in headspace concentration during storage (**Figure 6.3**). The rate of decrease in the headspace concentration for 2-MP, 2,3-DMP and 2,5-DMP in the first five days is the highest in rancid oil. We suspect that the rapid rate of decrease in rancid oil is possibly due to degradation by lipid radicals and hydroperoxides. In a study on the changes in alkylpyrazines compounds in peanuts stored for 12 weeks, Bett and Boylston (*11*) observed that greatest rate of decrease in the initial weeks of storage. They speculated that the decrease in the alkylpyrazines was due either

to degradation by lipid radicals and peroxides or to entertainment by complexes between proteins and lipid hydroperoxides or its secondary products. The lowest rate of decrease was observed in oil-water mixtures (**Figure 6.3**). The rates of change for 2,6-DMP, TRMP, and TEMP in the different mediums did not show a clear pattern **(Figure 6.4**). For some of these compounds, the headspace concentration even increased over time. The reason for this was not clear; however, this trend was possibly due to substitution and retrosynthesis of the pyrazines (*12*).

Binding experiment

The volatile compounds chosen in this experiment included 2-MP, 2-E-3-MP and TRMP (**Figure 6.5**). The binding of volatiles to peanut paste treatments (0% and 5% water addition) was investigated under static conditions, where the volatiles in the headspace were equilibrated with the peanut paste. In this experiment binding was used in its broadest term to include adsorption, absorption, and desorption as well as chemical and physical binding. It was interesting to note that binding was very rapid over the first 20 minutes and 70 to 80% of the volatiles were bound to the peanut pastes. The rate of binding leveled off after 20 minutes, of sampling. Hau et al. (*13*) demonstrated that alkanes, alcohols and ketones were strongly bound to starch. In addition, numerous studies have shown aromatic compounds and hetroaromatic compounds to bind irreversibly to biopolymers of low moisture content (*13*). Initial rate of binding was slightly higher for the 5% treated peanut paste samples. Therefore, it is possible that slightly higher irreversible binding in the 5% peanut paste treatments could result in flavor imbalance in the peanut paste treatments. Binding of flavors tends to suppress their perception, and frequently results in an imbalance in flavor profile (*14,15*).

CONCLUSION

The model study undertaken demonstrated that it was most probable that the reduced roasted peanutty perception in the peanut pastes with added water was from the combination of increased solubility of the peanutty aroma compounds in the aqueous layer, therby not being able to partition out of the peanut paste matrix. Furthermore, possible higher irreversible binding of aroma compounds to biopolymers in the peanut paste could have occured due to the addition of moisture to the peanut pastes.

ACKNOWLEDGEMENTS

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Figure 6.1 Oil-water partioning coefficeints at different concentrations of selected alkylpyrazines at 25°C. Data shown are averages of four replications. Error bars on the chart represent standard deviations.

Figure 6.1

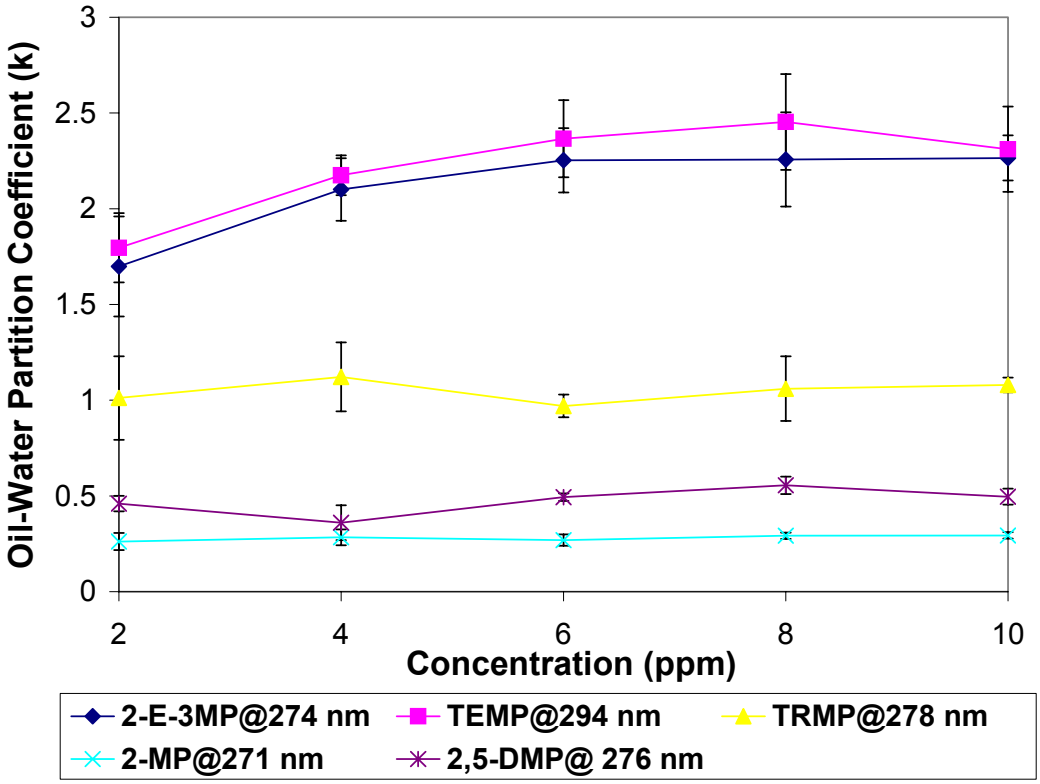

Oil-Water Partition Coefficient (k)
3
2.5
2
1.5
1
0.5
0
2
4
6
8
10
Concentration (ppm)
2-E-3MP@274 nm
TEMP@294 nm
TRMP@278 nm
2-MP@271 nm
2,5-DMP@ 276 nm

Figure 6.2 Headspace volatile concentrations of selected alkylpyrazines in model systems at 25 °C. Data shown are the average of three replications. Error bars on chart represent standard deviations.

Figure 6.2

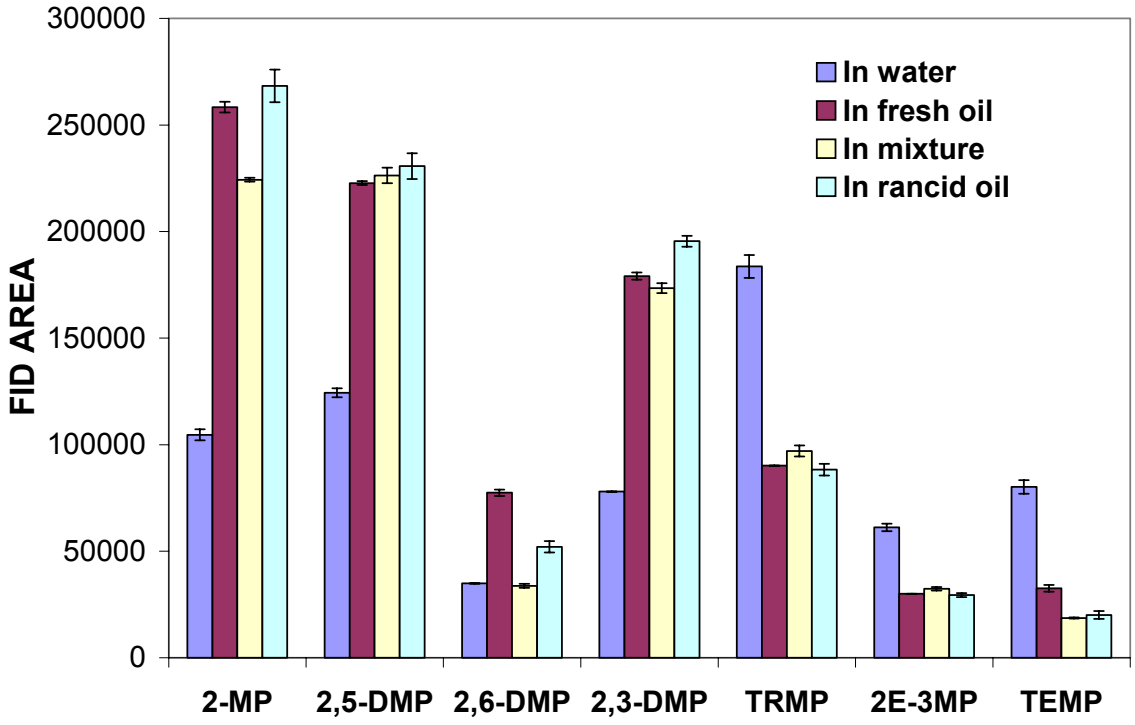

300000
250000
200000
150000
100000
50000
0
FID AREA
In water
In fresh oil
In mixture
In rancid oil
2-MP
2,5-DMP
2,6-DMP
2,3-DMP
TRMP
2E-3MP
TEMP

Figure 6.3 Percentage volatiles remaining in the headspace of selected alkylpyarzine in model systems during storage that were held at 25°C. Data shown are the average of three replications.

Figure 6.3

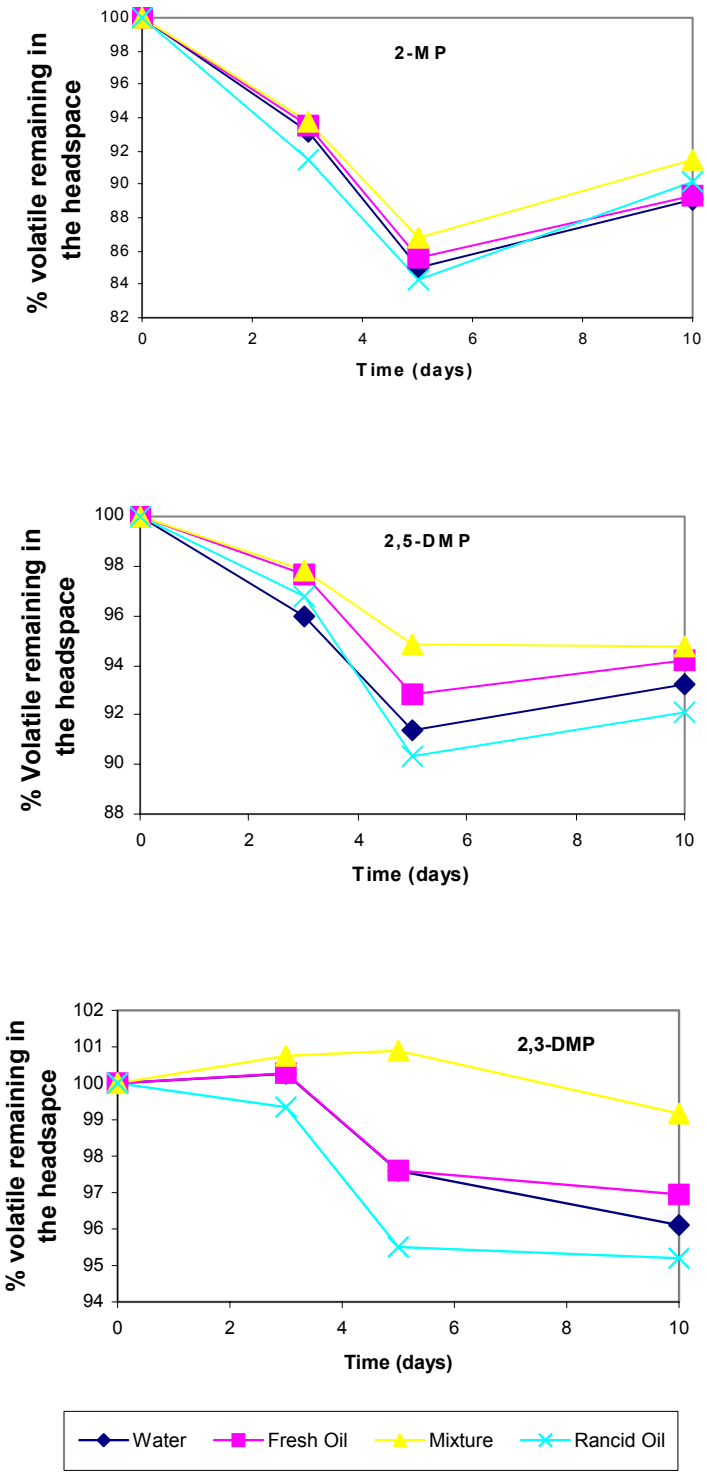

2-MP
% volatile remaining in the headspace
Time (days)
2,5-DMP
% Volatile remaining in the headspace
Time (days)
2,3-DMP
% volatile remaining in the headsapce
Time (days)
Water
Fresh Oil
Mixture
Rancid Oil

Figure 6.4 Percentage volatiles remaining in the headspace of selected alkylpyarzine in model systems during storage that were held at 25°C. Data shown are the average of three replications.

Figure 6.4

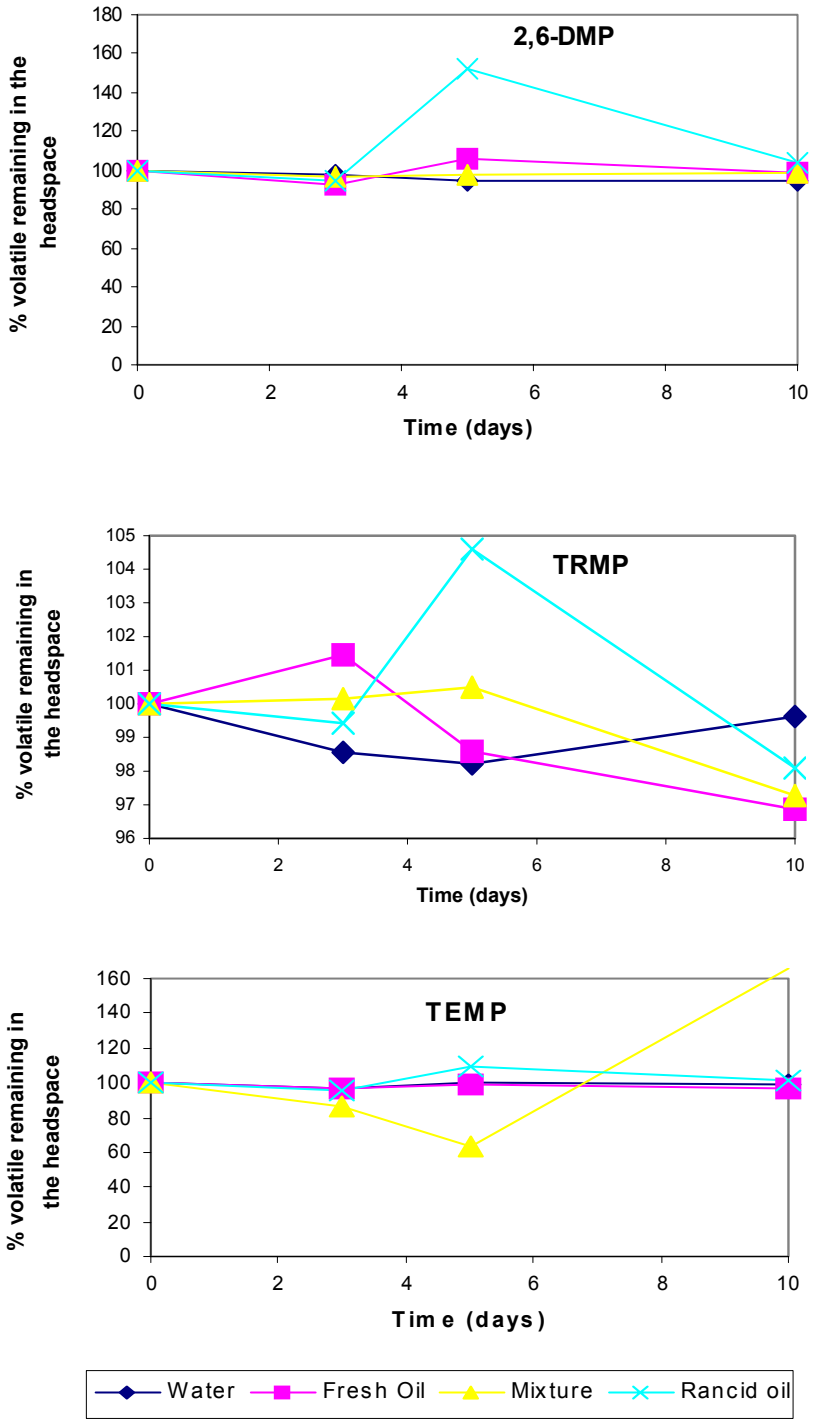
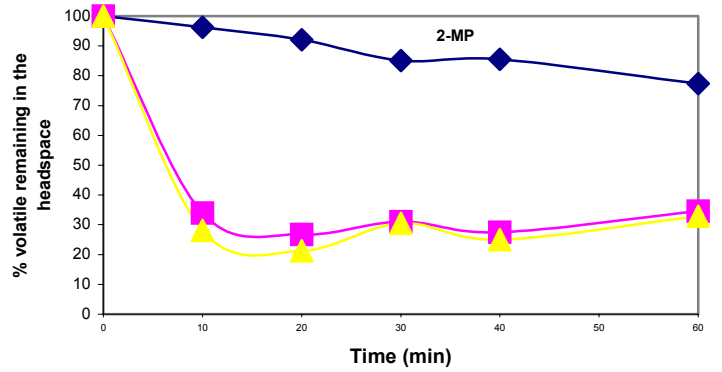
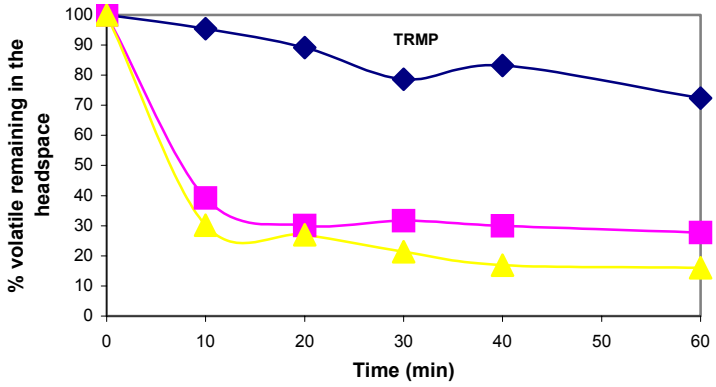
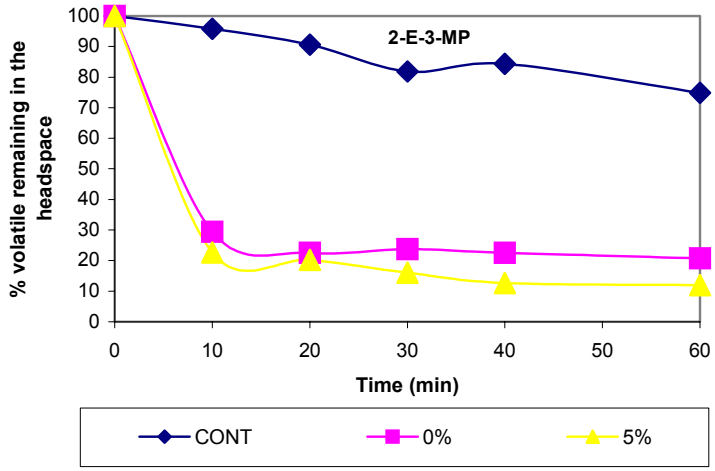

2,6-DMP
% volatile remaining in the headspace
Time (days)
TRMP
% volatile remaining in the headspace
Time (days)
TEMP
% volatile remaining in the headspace
Time (days)
Water
Fresh Oil
Mixture
Rancid oil

Figure 6.5 Binding kinetics of selected alkylpyrazines to peanut paste (5g) with blank (CONT), and added moisture (0 and 5%). Data shown are the average of three replications.

Figure 6.5


2-MP
% volatile remaining in the headspace
Time (min)


TRMP
% volatile remaining in the headspace
Time (min)


2-E-3-MP
% volatile remaining in the headspace
Time (min)
CONT
0%
5%

CHAPTER 7

SUMMARY AND CONCLUSIONS

Addition of 2 and 5% water resulted in significant change in color, texture, microstructure, flavor, and storage stability of peanut pastes. Intermediate and high moisture peanut pastes had high 'rancid', 'painty' and 'cardboard' scores. Control peanut pastes (0% water addition) had higher 'roasted peanutty', 'sweet' scores and higher concentration of pyrazines. The investigation of selected alkylpyrazines in model systems revealed some alkyl pyrazines were highly soluble in water and had low volatility in aqueous medium. Furthermore, significant binding of alkylpyrazines was observed by peanut pastes with added water.

TBHQ treated samples had higher 'roasted peanutty' flavor and lower 'rancidity', 'painty' and 'cardboardy' scores in control treatments. Oxidative related attributes such as 'rancid', 'painty' and 'cardboard' were high in 2 and 5% samples possibly due to lower 'roasted peanutty' flavor perception. Peroxide value, hexanal and heptanal concentrations were lower in these samples. Oxidative related attributes, PV, hexanal and heptanal increased during storage, while 'roasted peanutty', 'sweet' and pyrazine concentrations decreased.

The addition of 2 and 5% water resulted in darker and dull peanut pastes with low lightness, hue angle and chroma values. At this same level of water addition, hardness, adhesiveness, gumminess and chewiness increased and cohesiveness and springiness decreased. There were interactions between sugar and moisture for some of the textural

properties. LM and SEM micrographs showed control treatments had protein bodies and cell wall fragments that were well dispersed in a continuous oil matrix. Peanut pastes treatments with 2 and 5% added water had aggregates of protein bodies.

The study implied that common ingredients such water and sugar, even at low concentrations, play an important role in the overall quality of peanut confections. It is important for the confection industry to consider these factors and their interactions when developing new products or improving existing ones.