THE EFFECT OF COCOA POWDER ON THE DEVELOPMENT OF OXIDATIVE RANCIDITY IN PEANUT PRODUCTS

by

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Abstract

The objective of this study was to observe the effect of natural cocoa powder versus 200 ppm of tocopherols on delaying the onset of oxidative rancidity in peanuts, peanut butter, and peanut oil. The samples were obtained from a single lot of blended Runner peanuts after roasting, grinding, and pressing. The samples were treated within a week of initial roasting with either 200 ppm of mixed tocopherols or 2.5% cocoa powder. The development of oxidation was monitored by peroxide value (PV) and gas chromatography monitoring of hexanal development. The peanut butter samples were assessed by a professional sensory panel using descriptive analysis for the development of rancidity. The data was analyzed using JMP SAS software. In peanuts, the cocoa powder sample developed significantly lower levels of oxidation identifiers than the tocopherol or control samples. In peanut oil, there was no significant difference in levels of oxidation identifiers between the treatments. In peanut butter, the PV was significantly higher in the tocopherol sample than the cocoa powder or control samples, but no significant difference was observed in hexanal. The results of the sensory analysis indicated that the cocoa powder depressed the perception of both positive and negative attributes compared to the tocopherol and control samples. This study showed that cocoa powder may be a more effective preservative than an untreated sample or a sample treated with 200 ppm of tocopherols in peanuts and peanut butter; however, cocoa powder at 2.5% w/w basis did not perform as a significant antioxidant in peanut oil.

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Chapter 1 Oxidation in peanuts and methods for preventing oxidation

Introduction

Lipid oxidation is a leading cause of quality deterioration in foods. Historically, synthetic antioxidant preservatives were added to food systems to delay the onset of oxidative rancidity. Consumer response to synthetic preservatives has become negative as a result of condemning reviews by scientific literature. This has opened an opportunity for non-synthetic antioxidants to be added to foods as preservatives. In recent years, a number of studies have shown that bioactive compounds in the non fat cocoa solids fraction of chocolate products have the ability to decrease oxidation of low density lipoprotein (LDL) cholesterol in humans and animals. The presence of antioxidant flavanols, specifically epicatechins, in cocoa inhibits free radical production. Current literature suggests that epicatechins may also play a role in decreasing oxidation in food products. Because peanuts contain a high level of unsaturated fats and are highly susceptible to oxidative rancidity, they may serve as good candidates for testing cocoa as an antioxidant. This review discusses the mechanisms of, and monitoring methods for lipid oxidation. Additionally, an overview of antioxidants and the potential for using cacao products as a natural antioxidant is examined.

Lipid oxidation

Lipid oxidation is a leading form of quality deterioration in foods. Lipolysis occurs as the fatty acids hydrolyze from the glyceride backbone of a triglyceride which is a precursor to lipid oxidation (Pike 2003). There are many factors, both intrinsic and extrinsic, that impact the susceptibility of lipids to oxidation (Shahidi and Zhong 2010). Extrinsic factors include oxygen

and a catalyst such as heat, light, radiation, or metals that interact with a lipid (Allen and Hamilton 1994). A high degree of unsaturation in a lipid, as indicated by the methylene bridge index, results in the lipid having an elevated intrinsic risk for oxidation (Shahidi and Zhong 2010). Unsaturated fats oxidize at a higher rate than saturated fats due to the unstable resonance structure of these molecules at the unsaturated bond. Oxidation in unsaturated lipids can be categorized as either the oxidation of highly unsaturated lipids that results in polymeric end products, or oxidation of moderately unsaturated fats that result in rancidity and reversion (Furia 1972).

Oxidative rancidity in foods is a series of reactions that lead to flavor and odor defects. The reactions of oxidation occur in three phases: initiation, propagation, and termination as seen in Figure 1.1.

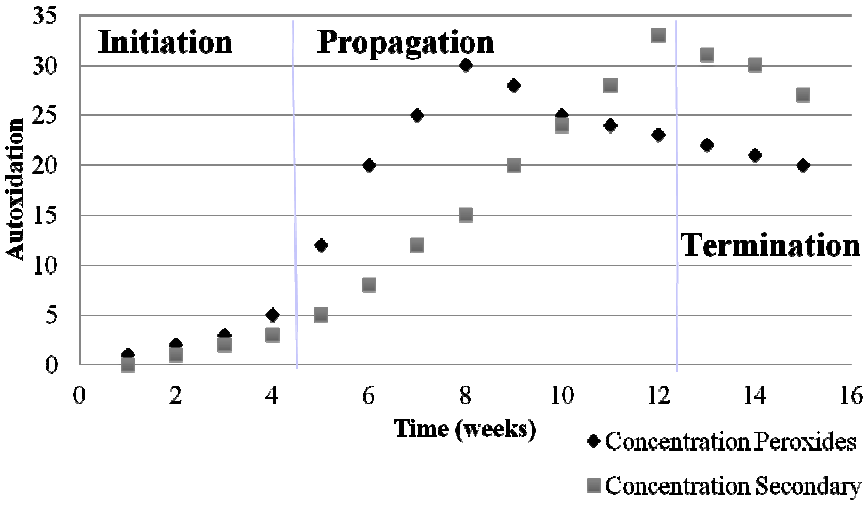

Figure 1.1 The phases of oxidation with concentrations of peroxides and secondary reaction products in a closed system over time (Pike 2003).

Oxidation begins as an imbalance between oxidant and antioxidant factors (Laitonjam). The imbalance occurs as the result of either an increase in oxygen species or decrease in antioxidants in a given system (Gulcin 2012). The increased presence of oxygen radicals leads to initiation.

Initiation is the least understood phase of oxidation and occurs as molecular oxygen and a catalyst such as heat, light, or enzymes begin to interact with the lipids (Frankel 2005). The initiator of oxidation defines the type of oxidation occurring in the lipid system. Oxidation initiated by an active radical in the system is categorized as autoxidation, oxidation initiated by light is photooxidation, and oxidation initiated by lipogenases is classified as enzymatic oxidation (Barriuso and others 2013). This review will focus on non-enzymatic oxidation. The non enzymatic catalysts cause an unsaturated bond to lose a hydrogen molecule, which then becomes a free radical. The production of free radicals occurs at a uniform, linear, rate during initiation. A critical mass of free radicals tips the system into the second phase of oxidation called propagation (Shahidi and Zhong 2010). Free radicals present in the system react with lipids to produce lipid peroxyl radicals, which then join to form hydroperoxides (Allen and Hamilton 1994). It is hypothesized that additional free radicals are produced during initiation, which leads to the continuation of the peroxide production at an exponential rate (Barriuso and others 2013). Peroxides, as seen in Figure 1.2, are colorless and odorless, and therefore do not contribute to the negative sensory characteristics associated with oxidative rancidity. Peroxides are transient, and often volatile, molecules.

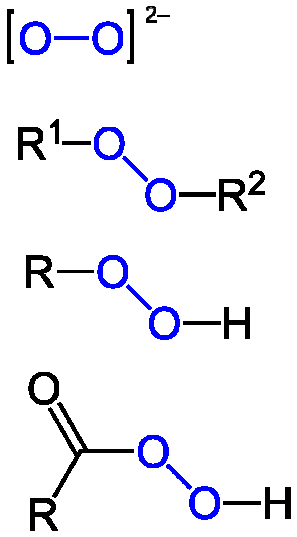

Figure 1.2 The peroxide group (in blue) seen as a peroxide ion, organic peroxide, organic hydroperoxide, and peracid (top to bottom) (Frankel 2005).

The onset of initiation can be prolonged, and the period of time the lipids spend in initiation can be extended, by adding an antioxidant to the system. The antioxidants interact with the free radicals to reduce continued reaction with the lipids. Chain-breaking antioxidants have the ability to disrupt initiation by donating hydrogen atoms to the radical to form a stable molecule before the radical would interact with an unstable structure. The amount of antioxidants in a system, however, is often finite and oxidative forces will eventually outpace the antioxidants (Frankel 2005). As the peroxides decompose and complex, the oxidation reaction moves into its second phase.

The second phase of lipid oxidation is called propagation (Frankel 2005). Typically, the second phase of oxidation occurs after an initiation lag period until a critical mass of peroxides has been produced, then the initiation and propagation reactions occur simultaneously until the substrate is exhausted. Propagation occurs at an exponential rate (Shahidi and Zhong 2010). During this phase, free radicals react with oxygen to form peroxyl radicals. These radicals then attack the next lipid molecule to continue the production of free radicals and peroxyl radicals.

The peroxyl radicals which are odorless and colorless, complex or decompose to form secondary products such as aldehydes and ketones (Figure 1.3). The aldehydes and ketones produced during propagation are highly aromatic and contribute to the off flavors and odors generally associated with oxidative rancidity (Shahidi and Zhong 2010).

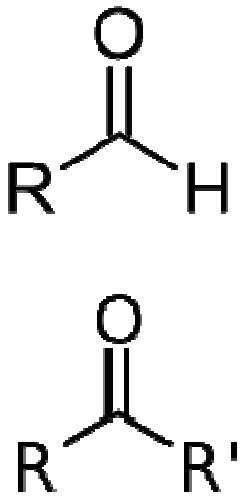

Figure 1.3 Aldehydes (top) and ketones (bottom) are common secondary products of oxidation (Frankel 2005).

Frankel (2005) was among the first to observe that a third, and final, phase called termination exists. During this phase, the substrates for the reaction: unsaturated lipids, oxygen, or active hydrogen atoms, are exhausted causing the reaction to come to an end (Shahidi 2010).

The total series of oxidation reactions can be seen in Figure 1.4 (Gordon 1990).

Initiation: $ROOH \leftrightarrow ROO^{\cdot} + H^{\cdot}$

$ROOH \leftrightarrow RO^{\cdot} + OH^{\cdot}$

$2ROOH \leftrightarrow RO^{\cdot} + H_2O + ROO^{\cdot}$

Propagation: $R^{\cdot} + O_2 \leftrightarrow ROO^{\cdot}$

$ROO^{\cdot} + RH \leftrightarrow ROOH + R$

Termination: $ROO^{\cdot} + ROO^{\cdot} \leftrightarrow ROOR + O_2$

$RO^{\cdot} + R \leftrightarrow ROR$

Figure 1.4 Oxidation reaction series (Gordon 1990).

Monitoring Lipid Oxidation

The progression of oxidation over multiple phases, leading to several different end products, requires a variety of test methods to monitor its development. Barriuso and others (2013) recommend using at least two methods of analysis to monitor this dynamic system. Most methods require lipid extraction prior to analysis. Chemical and physical extraction may impact the bioactive molecules present in lipids. It is recommended that a common extraction method for all analyses should be selected to reduce variability within a data set (Pike 2003).

The analyses can identify the primary products formed during initiation, such as peroxides, or the secondary products formed during propagation, such as aldehydes and ketones. Common tests used in industry to monitor the primary initiation products include peroxide value. Analysis available to monitor secondary products include p-Anistidine, hexanal, volatile organic compounds (VOCs), thiobarbituric acid test (TBA), dienes and trienes test, and gas chromatography (Pike 2003). While all of these tests are beneficial, this review will discuss two of the most commonly used oxidation analyses: peroxide value and gas chromatography.

The peroxide value (PV) test is one of the most commonly conducted tests in the food industry to determine the extent of lipid oxidation. It is relatively inexpensive to conduct, and is simple to conduct (Barriuso and others 2013). The results are expressed as milliequivalents (mEq) of peroxide per kg of lipid sample. The PV is a titration test that begins with dissolving at least 5 grams of oil in glacial acetic acid and isooctane (3:2 vol:vol). An excess of saturated potassium iodide is added to the acetic acid solution, and mixed for a controlled period of time. When this saturated solution reacts with peroxides, iodine is liberated. The mixed solution is then titrated with a standard sodium thiosulfate solution with a starch indicator. The titrated solution is monitored for a color change end point that determines the amount of peroxide present in the system (Pike 2003). The reaction observed by this test is as follows in Figure 1.5 (McClements and Decker 2005):

$$ROOH + 2KI \rightarrow ROH + I_2 + K_20$$

Figure 1.5 The Peroxide Value reaction series to determine the level of oxidation in lipids.

The result of the PV test are determined by the Figure 1.6 equation:

$$PV = \left(\frac{(S - B) * N}{W}\right) * 1000$$

Where: S = Volume or titrant (mL) for sample

B = Volume of titrant (ml) for blank

N = Normality of $Na_2S_2O_3$ (mEq/ml)

1000 = conversion of units (g/kg)

W = Sample mass (g)

Figure 1.6 The equation to determine the results of the Peroxide Value test (Pike 2003).

The results of a PV test indicate the amount of peroxides in a system. A result of 1-5 is considered low, 5-10 moderate, and greater than 10 high. The PV test must be performed with an understanding that product being measured is transient. Peroxides are unstable products of oxidation, and change quickly (Frankel 2005).

One area of concern in PV testing is a low reading can have multiple meanings. A low reading can be obtained if the product has oxidized very little during the initiation phase or if it has oxidized beyond the point of peroxide production and is in the termination phase (Pike 2003). This variability reinforces the need to use more than one method of analysis to determine the extent of oxidation in a system (Barriuso and others 2013). The results of the PV test can also vary based on the sample weight, temperature, and specificity of the test. Due to the variability among lipid sources, PV test is not recommended to compare lipids side by side; rather, it is primarily recommended to monitor the development of peroxides over time and compare trends within a single sample set (McClements and Decker 2008).

In addition to the previously mentioned sources of error, Allen and Hamilton (1994) identified several other potential sources of error that can arise when using the PV test. One error occurs when iodine is absorbed at the unsaturated bonds in fatty acids. The iodine is then unavailable for participation as an indicator in the titration. A second error occurs when additional iodine is released from potassium iodide by the pressure of oxygen in the solution. If the lipid sample is obtained using a method that requires heat, a third type of error occurs as a result of the synthesis or decomposition of peroxides that can continue during sample preparation, and can skew the results. Based on this source of error, it is recommended that lipid samples be extracted by mechanical methods without heat rather than chemical extractions and

all lipid storage and extraction should be done at low temperature. Despite these sources of error, the PV test is used across the food industry as a method to indicate potential oxidation-related sensory defects that will develop over time (Allen and Hamilton 1994).

In a study evaluating the impact of moisture and temperature on the shelf life of unblanched, salted, roasted peanuts, Evranuz (1993) used PV as the sole indicator of oxidation over time. The results of the test did not show a lag period prior to the onset of oxidation. The PV indicated that oxidation occurred in samples held at both high and low temperatures. The author made an assumption that 25 meq/ml PV was the end of shelf life for the sample peanuts. Based on that assumption, the study observed that the high moisture samples had shelf lives of 28 days, 10 days, and 11 days at 15 °C, 25 °C, and 35 °C respectively. PV provided a clear picture of the onset of oxidation, and the timing of the end of shelf life in the study. PV, however, due to the above mentioned sources of error, does not always provide conclusive results as was observed by Divino and others (1996).

Divino and others (1996) utilized the PV test as a benchmark test to evaluate a new analytical method, oxidative stability index (OSI) in raw and blanched peanuts with varying degrees of lipid content remaining after the defatting process. The PV test is the industry standard which requires new methods to be tested against PV for the industry to easily adopt the new method and compare past and present data sets (Barriuso and others 2013). The PV test indicated that there was a lower level of oxidation in the blanched peanut samples with lower fat levels. However, a correlation between fat content and oxidation was not observed in the roasted peanut samples. The study cited the measurement of the transient product, peroxides, as the cause of the discrepancy. The OSI test indicated that a correlation existed between the lipid

concentration in the sample and the susceptibility to oxidation in all of the samples. This study illustrated the importance of PV in monitoring oxidation commercially, but understanding the short-comings of the test to explain erratic results. Divino and others (1996) also used gas chromatography, the oxidative stability index, and sensory evaluation to understand the comprehensive effect of lipid oxidation in the defatted peanut systems. PV and sensory analysis confirmed the OSI observation of raw peanuts having more stable oil than roasted peanuts.

Foods containing peanuts often have other ingredients that can have an influence on the results of oxidation tests, such as PV. These ingredients can be an additional source of error in PV analysis. The impact of antioxidants, sugar, and moisture on the result of PV testing was investigated by Abegaz and others (2003). The study observed that peanut butter samples made with only added antioxidants maintained a very low PV level of 3 meq/ml after 4 weeks, while the sample with the same level of antioxidant and added sugar had a high PV of 33 meq/ml in the same period of time. The author hypothesized that the presence of sugar decreased the amount of available water in the system, and therefore created an environment more conducive to oxidation. The water in a lipid system can interface with polar peroxide molecules and making them unavailable for further oxidative reactions. Water in a lipid system also enables the termination reactions of free radicals. As a result these free radicals complex into stable molecules. The addition of only water to the peanut butter raised the PV to 20.8 meq/ml at 52 weeks. The addition of 5% water to the system was observed slowing the rate of oxidation over time. Overall, the addition of water at 2% and 5% resulted in a lower PV, hexanal, and heptanal concentrations.

A commonly used method for observing the accumulation of secondary oxidation products in lipid samples is static headspace gas chromatography (SHGC). This method can be used to monitor the quantity of targeted molecules based on the amount of time required for the compound to elute in a gas carrier through a solid column at a set temperature. The rate at which the volatile compound elutes through the column under a specific temperature can be used to determine the identity and concentration of that compound (Willard 1988).

In the case of peanuts, hexanal is easily isolated and identified as an indicator of oxidation (Mate and others 2002). Hexanal is formed as a secondary compound of the oxidation of linoleic acid (Warner and others 1996). While other molecules can be identified, hexanal remains the most prominent and commonly measured (Furia 1972). Because it is an odiferous secondary reaction product, hexanal has been observed to correlate strongly to sensory data indicating oxidative rancidity (Lee and others 2002).

In 1994, Dimick used gas chromatography/mass spectrometry (GCMS) to identify potential pyrazine and aldehyde formation over the shelf-life of peanuts. The peanuts in this study were blanched, roasted, and stored at 65 °C for one to sixty eight days. The storage temperature was selected as accelerated shelf life conditions. This study identified hexanal, heptanal, octanal and nonanal concentrations as valid molecules to monitor during the development of secondary reaction products of when peanuts oxidize. Each of these four compounds increased over time. Hexanal was identified as the primary indicator of oxidation. The concentration of hexanal increased in accelerated shelf-life during the propagation phase until day 55, and then began decreasing on day 68, which indicated the sample had entered into the termination phase of oxidation.

In 1996, Mate and others studied the impact of oxygen, relative humidity, and roasting on the onset of oxidation over time. Dry-roasted, oil-roasted, and blanched peanuts were stored at high and low levels of oxygen to determine the impact on shelf life. This study employed static headspace gas chromatography (SHGC) to monitor the development of hexanal as an indicator of oxidation across each of the peanut samples. The blanched peanut sample had a high level of hexanal from the initiation of the experiment. The authors suggest this was caused by a high level of lipogenase enzymes that were not denatured during the blanching process. In both roasted samples, however, the measurement of hexanal trended upward as oxidation progressed over time. Hexanal once again was shown to be a strong indicator of oxidation in peanuts.

Because hexanal is an aromatic compound, the quantification of hexanal may relate to observation of sensory attributes, as was observed by Lee and others (2002). The study observed the onset of oxidative rancidity in peanuts that were coated with a whey protein mixture. The mixture was used to create an oxygen barrier in an attempt to slow the onset of oxidative rancidity. The samples were stored at 40, 50, 60 °C and tested at 0, 5, 15, and 45 days. Hexanal correlated significantly to the roasted peanutty sensory attribute. The quantification of hexanal correlated strongly with the sensory data demonstrating that the addition of a coating did not significantly delay the onset of oxidative rancidity in roasted peanuts. Based on these results, Lee and others (2002) recommended the use of SHGC to monitor oxidation in peanut products.

Although analytical methods can provide exact measurements of specific molecules and show the progression of oxidation based on the presence of these molecules, sensory analysis remains the primary method to monitor the consumer perception of oxidation in foods. Taste is the most reliable way to determine the customer's acceptance of oxidation levels in foods. Some

compounds can impart an off flavor or odor at concentrations below the detectable limits of laboratory analysis, and perceptible limits vary from person to person. Shelf-life tests can be conducted by holding the product at a temperature similar to what it would experience in a store, or by storing the product at a higher temperature to simulate the shelf life of products at an accelerated rate. Over time, flavors such as grassy, beany, fishy, and painty develop in unsaturated oils as the result of lipid oxidation (Allen and Hamilton 1994).

Many studies have been conducted that utilize sensory analysis in conjunction with analytical methodology to obtain a complete picture of oxidation. In one study, Mugendi and others (1998) used 13 trained panelists to monitor the onset of rancidity in peanuts. The panelists evaluated roasted peanutty, raw/beany, cardboard, painty, sweetness, and dark roast flavors as well as crunchiness. The study was conducted for the purpose of observing the differences between high oleic- and normal oleic- peanuts over time stored at 40 °C/18% rh. The panelists observed a loss of roast peanutty flavor over time in both the high oleic- and normal oleic- peanuts. The authors define this change as flavor fade. They hypothesized that flavor fade is the result of the dissipation or chemical reactions degrading pyrazines which impart a roast/peanut flavor. The sensory observations also included a higher level of painty flavor perception in normal oleic peanuts. High oleic peanuts were observed to oxidize ten times slower than normal oleic peanuts, and were therefore recommended for use.

Due to the time and cost required to conduct sensory tests, studies have been conducted to correlate chemical to sensory analysis in an effort to reduce the reliance on descriptive analysis (Lee and Resurreccion 2006). The study conducted by Grosso and Resurreccion (2002) produced a correlation of hexanal quantification and a sensory rating to determine the endpoint

of acceptability of roasted peanuts coated with a whey protein, and uncoated. This was among the first correlations of sensory ratings with analytical values that can be found in literature.

In 2002, Grosso and Resurreccion also utilized GC to observe the development of hexanal as a result of oxidation. In their study, specific sensory descriptors were related to the level of hexanal in peanuts and peanuts treated with a cracker coating. The peanuts in this study were blanched to loosen the skins and then roasted at 138 °F with samples removed in five minute intervals. Regression analysis showed that roasted, peanutty, oxidized, and painty flavors were correlated to the level of hexanal in a system. Hexanal levels in conjunction with sensory results determined the end of shelf-life of the peanut products. Consumer ratings below a 5 on a 9-point hedonic scale were considered unacceptable and hexanal measurements between 5.39 and 5.54 µg/g resulted in this undesirable rating. These acceptability ratings may provide a tool to predict consumer acceptability of oxidation in products without requiring descriptive analysis throughout the life of the product. However, there have been a limited number of these analysis conducted to create a comprehensive tool.

Nepote and others (2006) built on the study conducted by Grosso and Resurreccion (2002) by observing correlations between PV, p-anistidine values (HV), conjugated dienes (CD), and conjugated trienes (CT) with oxidized, cardboard, and roasted peanutty flavor perception in Argentine peanut products stored at 23 °C and 40 °C. The peanuts observed were the high oleic, Granoleico, and normal oleic-, Tegua, peanut cultivars from Argentina. The changes observed in sensory attributes were greater in the samples stored at 40 °C. Correlations were calculated between each of the analytical methods and sensory descriptors for use in regression equations.

Based on this observation, Nepote and others (2009) applied the known correlations of peroxide value (PV), anistidine value (HV), and conjugated dienes and trienes (CD and CT) to consumer ratings of high- and normal- oleic peanuts from Argentina. The study observed acceptance of peanuts being positively associated with oleic/linoleic (O/L) ratio, crunchiness, sweetness, saltiness, roasted peanut notes, and hardness. Acceptance was negatively associated with cardboard, oxidized, and sour flavors. Peroxide value (PV), HV, and CD were positively related with the presence of cardboard, oxidized, sour, and bitter flavors. The chemical and negative flavor attribute indicators were also associated with a dislike rating of consumer acceptance. This study was conducted to observe characteristics of many normal- and high-oleic peanuts following roasting, and did not observe changes in these values over time. High oleic peanuts had higher levels of overall acceptance and roasted peanutty flavor than normal oleic peanuts. Values of acceptability were not related in this study.

Zajdenwerg and others (2011) studied the relationship between analytical methods and sensory oxidation values in Brazil nuts. In this study, dried Brazil nuts were stored at 80 °C to accelerate oxidation. The nuts were sampled every two days using PV, AV, tocopherol content quantification, solid-phase micro-extraction gas chromatography, and sensory analysis. The sensory judges were able to identify oxidized flavors after 4 days. The acceptability of the nuts based on panelist scores declined sharply after 12 days. At 12 days consumers also rejected purchase intent. The tocopherols present in the samples completely oxidized by day 16. A strong ($r > 0.95$) correlation was observed between the sensory data and all of the analytical data. The consumers rejected the samples when PV was 18.8 meq/mL, AV was 7.68, hexanal was 48.95 µm, α-tocopherol was 15.01 mg/kg, and γ and β tocopherols were 73.88 mg/kg. Based on

their findings, the authors recommended using analytical methods to monitor oxidation in Brazil nuts.

Lipid oxidation is a common and significant challenge throughout the food industry. Peanuts have particularly unique attributes that increase their susceptibility to oxidation. An opportunity exists to better understand the control of oxidation in peanut systems.

Lipid Oxidation in Peanuts

The case for Peanuts

Peanuts are the second largest harvested legume annually around the globe (Shin and others 2010). This legume serves as a popular snack, ingredient, and form of inexpensive protein worldwide (Win and others 2011). Peanuts were a demonized crop during the popular low fat diet craze of the early 1990s in the United States. As the low carbohydrate diets became in vogue, the popularity of peanuts boomed. Research conducted by the Peanut Research Board throughout these fluctuations in popularity focused on the health attributes of the peanut. One particularly important study was the observation of 31,000 Seventh Day Adventists that observed those whose eating patterns included daily consumption of nuts had a 25% lower risk of coronary vascular disease. This study was reinforced by two additional epidemiological studies: the reduction of blood pressure in participants of the DASH diet who regularly consumed nuts as well as participants in a Harvard weight loss study on a low fat diet who regularly consumed nuts. The research ultimately secured peanuts a role in a balanced, healthy diet (Stuart 2007).

Several studies have been conducted over the past decade to evaluate the role of peanuts in the diet (Kris-Etherton and others 2001). Jiang and others (2002) used the data from the Nurse's Study to observe the role of peanut butter in the diet, and found that participants who regularly consumed nuts, including peanuts, had a lower risk of Type 2 Diabetes. This reduction was more pronounced when nuts were used to replace refined grain snacks. A compilation of the data from five large epidemiological studies and eleven clinical studies indicated that nut consumption was inversely related to the incidence of coronary heart disease risk. The review attributed the inverse relationship primarily to the presence of healthy mono- and poly-unsaturated fats in peanuts as well as the high occurrence of fiber (Kris-Etherton and others

2001). High oleic peanuts may have an even higher level of health benefits compared to normal peanuts. The oleic fatty acid level in high oleic peanuts is 10% higher than olive oil and saturated fat levels are 30% lower than what is found in normal peanuts. The studies of lipids in peanuts resulted in a petition to the FDA to create a substantiated health claim relating nut consumption to a reduced risk of coronary heart disease, which was secured in 2003. The claim reads, "scientific evidence suggests but does not prove that eating 1.5 ounces per day of most nuts [such as name of specific nut] as part of a diet low in saturated fat and cholesterol may reduce the risk of heart disease" (Stuart 2007).

The presence of this claim in conjunction with a US trend in consuming mono-and poly-unsaturated fats in moderation as part of a healthy diet resulted in a boom in the peanut industry. In 2004 alone, peanut consumption rose 10% in the US, and peanuts were found in 107 new confectionary products and snack bars (Fuhrman 2005). Peanut consumption spans multiple age groups, ethnicities and economic brackets throughout the world (Rimal 2002). While health perception has helped increase the consumption of the humble peanut, it is the preferred taste that it contributes to foods that keeps consumers coming back for more (Stuart 2007). The unsaturated fats that make peanuts desirable nutritionally, however, also create an elevated risk of oxidation in peanuts.

Lipid oxidation in peanuts

Lipid oxidation is the leading cause of deterioration in peanuts (Lee and others 2002). Two key parameters that elevate the risk of lipid oxidation in peanuts are: the chemistry of the lipids in a kernel, and the common processing that occurs before peanuts are consumed. Lipid oxidation is a particularly serious problem in peanuts because they contain high levels of

unsaturated lipids (Mate and others 1996). Peanuts contain 45-50% lipids in the total weight of a kernel, of which approximately 80% are unsaturated (Divino and others 1996). Plant lipids are often composed of a mixture of triglycerides (Furia 1972). The fatty acid composition of normal oleic peanuts is typically 48% oleic and 31% linoleic acid (Williams and others 2006). Linoleic acid contains two unsaturated bonds, and oleic acid has one unsaturated bond. The unsaturated bonds are most susceptible to oxidation due to the less stable resonance structure. Oleic acid is more than 10 times less susceptible to oxidation than linoleic acid; however, both types of fatty acids will eventually oxidize (Figure 1.7) (Pickett and Holley 1951, Shahidi and Zhong 2010).

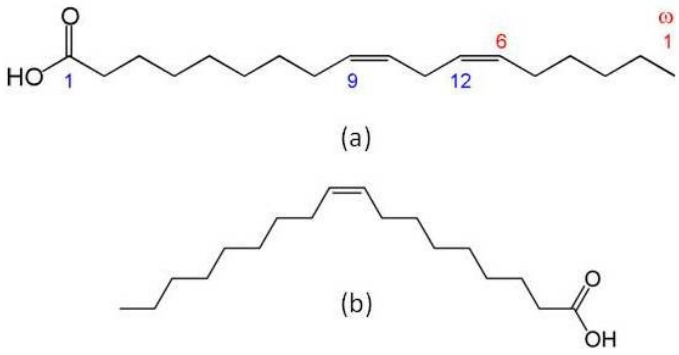

Figure 1.7 Linoleic (a) and oleic (b) acids that are present in high levels of peanut lipids.

Because peanuts are susceptible to oxidation, and the flavor quality is contingent on the amount of oxidation of the lipids, the shelf life of peanuts is typically defined as the number of days from roasting to the perception of oxidized off flavors. This shelf life is defined by companies for each product individually. Oxidized flavors are often described as painty and cardboard (Mugendi and others 1998, Grosso and Ressurrection 2002).

A second factor that contributes to oxidation in peanuts is the roasting process that peanuts typically undergo prior to consumption. It is very likely that roasting breaks down cellular structure. This breakdown allows the lipids to be exposed to other components of the

kernel and creates an increased exposure to oxygen in the environment. The other components of the kernel, such as trace amounts of heavy metals, can serve as catalysts to initiate oxidation at a faster rate (Frankel 2005). The heat of roasting also begins to break down the fatty acids, which increases the exposure of unsaturated lipids to oxygen and catalysts (Mate and others 1996). Additionally, roasting denatures enzymes that could promote enzymatic rancidity. The destruction of these enzymes may extend the amount of time to begin oxidation initiation (Lee and others 2002).

Lipid oxidation results in the key form of quality deterioration in peanuts: off odors and flavors (Lee and others 2002). The shelf life of peanuts is generally described as the number of days prior to the onset of oxidative rancidity (Grosso and Resurreccion 2002). The length of time required to reach the end of shelf life varies between products. Lipid oxidation is first observed in peanuts by the loss of the characteristic "roasted peanut" flavor, derived from pyrazines which complex during roasting, generally associated with freshly processed peanuts (Warner and others 1996). The lack of pyrazines in addition to a decrease in the content of nitrogen containing compounds increases the onset of flavor fade (Williams and others 2006). It is currently unclear in the literature if a reduction in the concentration of pyrazines in a system occurs, or if other more odiferous molecules increase in quantity and overpower the presence of pyrazines. After the "roasted peanut" flavor has been lost, the increase in secondary products such as aldehydes and ketones lead to off flavors and odors. The compounds typically formed in peanuts that decrease flavor acceptability include: hexanal, octanal, nonanal, and decanal. Hexanal (Figure 1.8) is the most prevalent odiferous compound in peanut oxidation, and is the primary result of the oxidation of the polyunsaturated linoleic acids (Warner and others 1996).

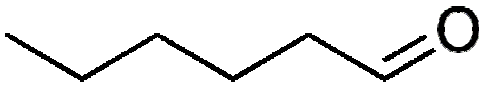

Figure 1.8 Hexanal, a common and frequently monitored secondary product of lipid oxidation in peanuts.

The largest peanut crops in the world are harvested in China and India. These locations generally require lengthy transportation to get the crop to processing facilities and export locations (McGee 2004). The unavoidable length of time built into the supply chain lends itself to requiring the implementation of methods that would protect the product from oxidation. Oxidative rancidity cannot be controlled by temperature, but can only truly be controlled by a reduction in molecular oxygen from the system (Allen and Hamilton 1994). This can be accomplished by reducing oxygen in the packaging environment, adding oxygen scavengers or antioxidants to the system, or altering the lipid make up of the peanuts.

Attempts to reduce oxidation in peanuts

The high susceptibility of nuts to oxidative rancidity has provoked a range of studies aiming to slow the reaction in finished products. The methods range from intrinsic changes of the ratios of fatty acids to extrinsic changes in packaging methods. Each application ultimately targets a longer shelf life by reducing oxidation in the system.

High Oleic Peanuts

In an attempt to slow oxidation in peanuts and extend shelf life, a line of peanuts called "high oleic peanuts" were developed. These University of Florida peanuts were created by selecting genetic strains of peanuts with high levels of oleic fatty acids (Norden and others 1987). By increasing the oleic fraction by 60% of the lipid fraction versus standard peanuts with only 48% oleic acids, the shelf life doubles (Figure 1.9). The hexanal (Figure 1.8), an aldehyde, content and peroxide content are delayed and remain lower than typical peanuts. The positive

flavor attributes, such as peanutty, are present for a longer period of time, while the negative flavor attributes, such as cardboard, are delayed (Braddock and others 1995). Normal-oleic peanuts typically have an oleic/linoleic (O/L) ratio of 1.5-2.0 in the United States. The high oleic variants have an O/L ratio of 9 or greater (Davis and others 2013). High oleic versions of both Spanish- and Runner- type peanuts are commercially available for production and consumption in the United States (Craft and others 2010). High oleic peanuts can be grown in both the South Eastern and South Central regions of the United States where normal oleic peanuts are typically grown. While environmental factors such as rain, drought, and harvest period play a role in the compositional and harvest index of peanuts, genetics have the highest level of significance in determining the O/L ratio (Singkam and others 2010). The ability to grow in multiple regions in the US, to consistently produce high oleic seeds, and to be easily accessed from suppliers have increased the harvest of high oleic peanuts in the US (Shin and others 2010).

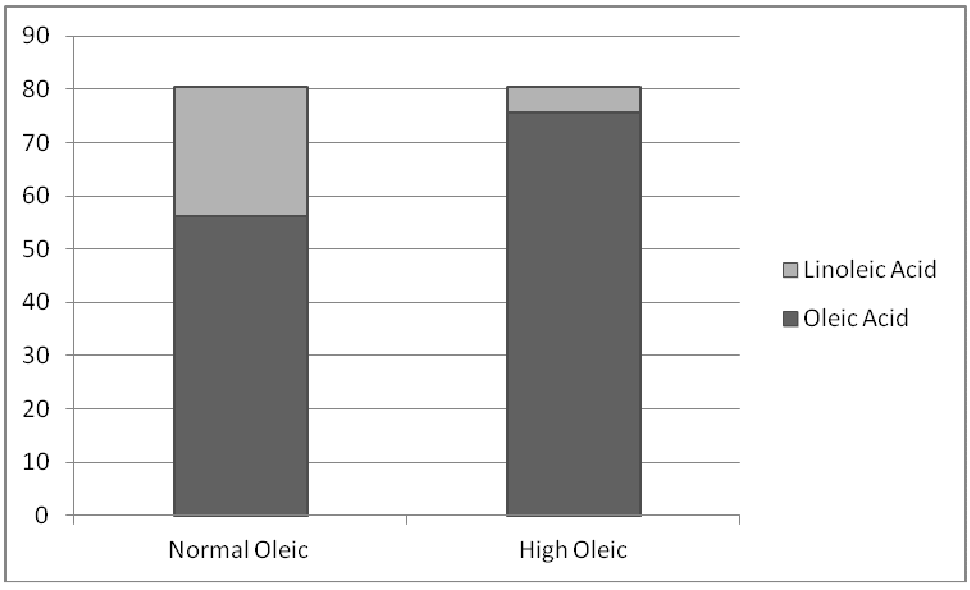

Figure 1.9 The percentages of linoleic and oleic acids in normal- and high- oleic peanuts (O'Keefe and others 1993).

High oleic peanuts have been tested against normal oleic peanuts in sensory studies. Fresh, high oleic peanuts are not significantly different in flavor from their normal counterparts; however, high oleic peanuts develop oxidized flavors slower than normal peanuts. A study by Riveros and others (2010) revealed that normal oleic peanuts had significantly higher PV, p-anistidine (AV), and conjugated diene (CD) values at the end of shelf life. At 4°C, high oleic peanuts had a four times longer shelf life, a two times longer shelf life at 23°C, and a three times longer shelf life at 40°C based on sensory acceptability. The end of shelf life in this study was determined by the Food Code in Argentina as a PV of no greater than 10 meq/ml. The increase in more stable oleic acid, and decrease in less stable linoleic acid resulted in a significant decrease in oxidation in peanuts.

In 2006, Isleib and others compiled data from sensory and compositional data of normal- and high- oleic peanuts. This study reviewed sensory descriptors including roasting peanut, astringent, over-roast, nutty, fruity, painty, stale, moldy, and petroleum. The compositional analysis included fatty acid profiles, oil concentrations, tocopherols, carbohydrates and paste color. Minor differences were observed between normal- and high- oleic peanuts in positive flavor attributes, such as roasting peanut and nutty, but no differences were observed in negative flavor attributes when the products were tasted fresh. The compositional analysis revealed that in addition to the anticipated differences in fatty acid profiles, minor differences occurred in the fat content, tocopherols, and carbohydrates. Overall, Isleib and others (2006) recommended the adoption of high oleic peanuts into the food system.

Shin and others (2009) also investigated the claim that high oleics may have higher levels of tocopherols than both normal oleic peanuts and what was then listed in the USDA National Nutrition Database. This database is used to create nutrition facts panel labels for foods for sale

in the United States. The purpose of the study was to update the level of tocopherols in peanuts based on the thought that the tocopherol levels were higher than listed in the database. No significant difference in tocopherol levels was observed between the normal (22.4 mg/100g), mid (23.9 mg/100g), and high (22.4 mg/100g) oleic peanuts. However, the peanuts tested were 10.5±1.5 mg/100g above what was listed in the USDA National Nutrient Database. Based on these results, the tocopherol levels in peanuts were adjusted to reflect the current crop.

The concept of antioxidants intrinsic to peanuts was explored again in 2010 by Craft and others. This study examined the level of antioxidants in Spanish high oleic, Runner high oleic, Runner, and Virginia peanuts by analyzing 80% v/v methanol extracts characterized by reverse-phase high performance lipid chromatography (RP-HPLC). Craft and others (2010) observed that genetic makeup plays the largest role in level of antioxidants present in peanuts. The high oleic peanuts had higher levels of antioxidants. The oxygen scavenging potential of all of the nut samples increased following oil roasting. This study again confirmed the benefits of using high oleic nuts.

Despite the many known benefits of extended shelf life and lower rates of oxidation, a growing problem exists when using high oleic peanuts in finished goods. Davis and others (2013) state that segregating the high oleic crop from the normal oleic crop throughout the growing, harvesting and post harvest processing has proven to be a challenge for the industry. This problem has become so prevalent that a method was created to rapidly quantify the level of high oleic fatty acids in a peanut sample using the density and refractive index of the nut oil (Davis and others 2013). Although this method is available for those purchasing peanuts to ensure they are receiving the correct crop, it does not eliminate the problem of an increasing

level of impure lots of high oleic peanuts. This challenge in the industry has given rise to more innovation around alternative methods to control oxidation in peanuts.

Mechanical methods for controlling oxidation in peanuts

One method known to reduce the rate of lipid oxidation is to reduce the exposure of oil to oxygen. Two basic options exist to reduce the exposure of peanuts to oxygen: the reduction of oxygen in packaging, and the coating of peanuts to form an oxygen barrier. The alteration of environmental oxygen in packaging has been recorded for many years. In 1979, Holaday and others observed a significant reduction in oxidation in peanuts and pecans packaged in a low-oxygen, high-CO_2 environment. While this time-tested method has been observed to extend the shelf life of packaged nuts up to twelve months, after the package is opened the protection against oxidation is lost.

The second mechanical method of controlling oxidation, coating the peanut with a thin barrier, has been explored by several studies. Edible coatings prevent both moisture loss and oxygen diffusion, which may assist in the reduction of oxidation in peanuts (Haq and Hasnain 2012). Fluidized bed systems were successfully tested as a method of adding a whey protein film coating to peanuts. This coating provided adequate coverage to reduce oxidation in less time than conventional panning methods (Lin and Krochta 2006). Edible coatings have also been explored when paired with other mechanical preservation methods such as ultra sonication. Ultra sonication currently has industrial applications to remove grease from equipment in areas that cannot be accessed for manual cleaning. When this technology is applied to nuts, the surface oil is removed which reduces the exposure to oxygen. This technique combined with edible film coatings has been shown to reduce oxidation by reducing the exposure of lipids to environmental oxygen and other initiators (Wambura and others 2010, 2011).

Antioxidant application as a method of controlling oxidation in peanuts

There are four major mechanisms by which an antioxidant can delay the onset of oxidation in lipids. The antioxidant can act by: donating a hydrogen molecule, donating an electron, adding the lipid to the aromatic ring of itself, or forming a complex between the lipid and the aromatic ring of itself (Furia 1972). Most commonly, oxidative rancidity can be delayed with the addition of an antioxidant that interferes with the initiation of oxidation. In this reaction, the free radical is stabilized by the resonance of the antioxidant which removes the free radical from participating in initiation and propagation of oxidation in a neighboring unsaturated lipid molecule (Allen and Hamilton 1994). Some scientists support the theory that the electron or hydrogen reaction is the primary interaction, and the formation of a complex is a secondary reaction (Furia 1972). To be successful, an antioxidant must have a reduction potential lower than the reduction potential of a free radical (McClements and Decker 2008).

There are many implications to consider before selecting an antioxidant preservative for a food system. A good antioxidant for a food product should not impact the flavor, odor, or color of a finished food when the antioxidant is used at an appropriate level. The antioxidant should be selected with the fat type, oxidation type, and mechanism of the antioxidant in mind. To be used in food, an antioxidant must have low order toxicity and the ability to be used in many fats. Recognition of safety must be declared by the government of the country in which the antioxidant is intended to be used. Preservative antioxidants acknowledged as generally regarded as safe (GRAS) by the FDA in the United States of America have been limited to 0.02% (200 ppm) weight of antioxidant based on the fat or oil content of the food (Furia 1972).

Antioxidants are typically divided into two categories: synthetic and natural. Synthetic antioxidants are compounds that are synthesized in a laboratory to inhibit the oxidation of lipids. Several synthetic preservatives are commonly used in the food industry and include butylated

hydroquinone hydroxyanisole (BHA), butylated hydroxytoluene (BHT), butylated hydroquinone (TBHQ), and propyl gallate (Carocho and Ferreira 2013). These preservatives act as chain-breaking antioxidants and are able to effectively slow the onset, or extend the initiation phase, of oxidative rancidity in lipids (Allen and Hamilton 1994).

In recent years, the toxicity of these compounds has been questioned by consumers and scientists alike (Joshi and others 2011, Shom and others 2011, Parke and Lewis 1992). Although, as Parke and Lewis (1992) argue, the synthetic preservative have achieved GRAS status from the FDA, consumer perception remains negative. Studies in rats concluded that high doses of these preservatives can be carcinogenic (Williams and others 1990), but studies in dogs have not drawn the same conclusions (Parke and Lewis 1992). The low doses required for antioxidant purposes do not appear to have carcinogenic effects, but as the concentration increases prooxidant activity can be promoted which may result in an increased level of cellular mutations. The conflicting reports have resulted in heightened consumer concerns about the toxicity of synthetic preservatives which has led to an increased interest in natural preservatives (Joshi and others 2011, Shom and others 2011).

Singh and others (2010) define a natural preservative as chemical constituents extracted from natural sources that offer an intrinsic ability to protect products. Natural preservatives can protect a product by acting as an antimicrobial, antioxidant, or pressure modifier. Currently, the most popular natural antioxidant used in the food industry is mixed tocopherols (Gulcin 2012) (Figure 1.10). Tocopherols have proven to be effective at appropriate doses, but become prooxidants if used at too high a level (Caracho and Ferreira 2013). The search for a preferred natural preservative antioxidant continues. There are hundreds of plant- and animal-derived products that can be used as natural preservatives. The bean of the cacao tree is one such plant

product that offers phenolic and alkaliod compounds which may act as a natural antioxidant (Singh and others 2010).

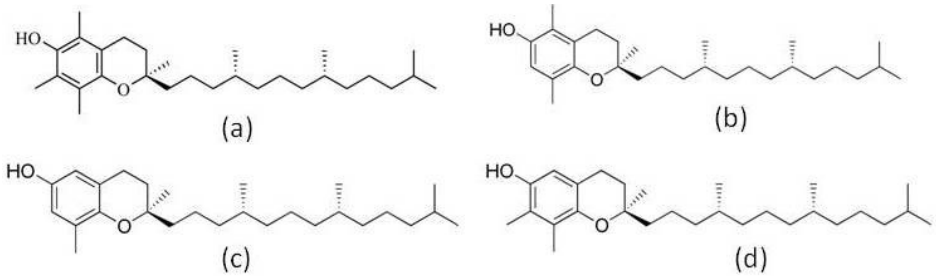

Figure 1.10 Mixed tocopherols are comprised of alpha (a), beta (b), delta (c), and gamma (d) configurations (based on Erickson 1973).

One major class of antioxidants is the flavanoid group. Seven categories of flavanoids exist: flavones, flavanones, flavanols, flavanonols, isoflavones, flavanols (catechins), and anthocyanins. This paper will focus on the flavanol (catechin) category. Catechins are phenolic compounds that act as free radical scavengers by rapidly donating a hydrogen from their hydroxyl group to a radical before it can interact with unsaturated lipids (Figure 1.11) (McClements and Decker 2008). Flavanols exist in four forms: two isomers in the trans configuration are –(-) and +(-) catechin, and two isomers in the cis configuration are –(-) and +(-) epicatechin (Figure 1.12).

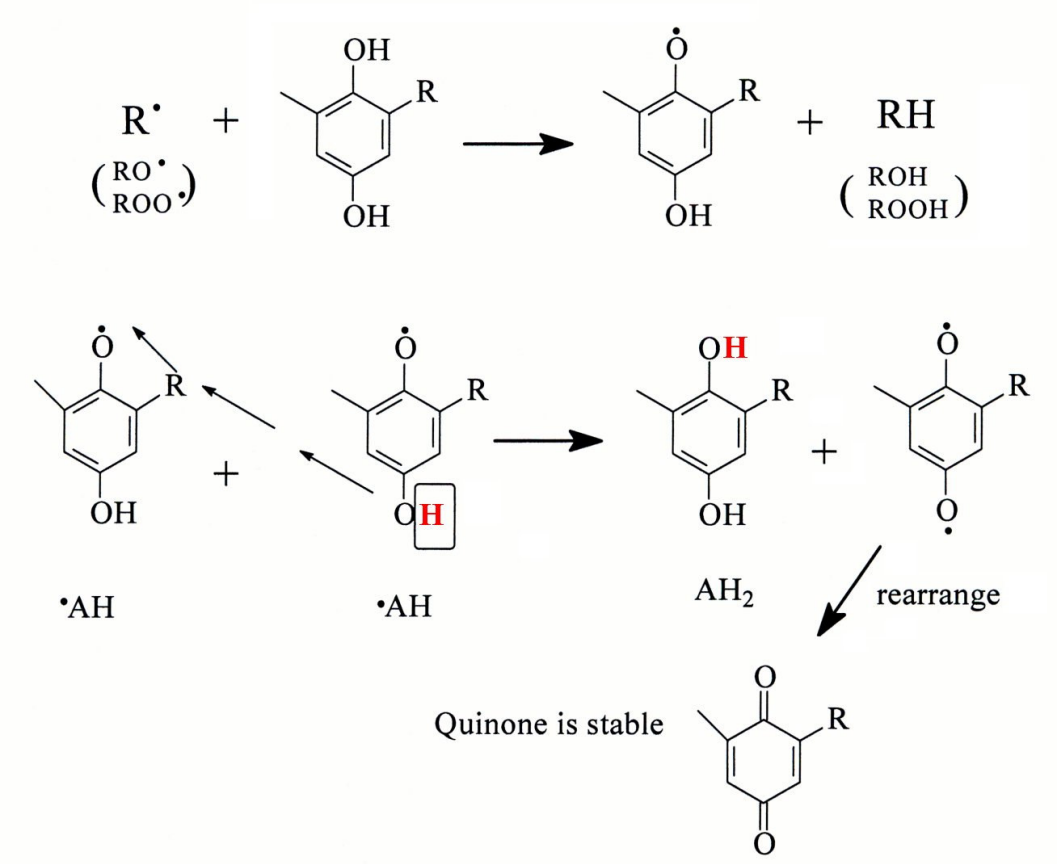

Figure 1.11 Reaction between a basic phenolic structure with a peroxide ion to form a stable structure.

The report, USDA Database for the Procyanidin Content of Select Foods (2004), describes procyanidins as polymers of flavan-3-ols, which can also be referred to as condensed tannins. As a result of the hypothesis that the consumption of foods that are high in procyanidins may reduce the risk of certain types of cancers, the USDA compiled data about the level of these compounds in common foods in the American diet. This report showed that cocoa powder has the highest level of procyanidin monomers, specifically +(-) catechins and –(-) epicatechins (Figure 1.12), available in the surveyed commonly consumed foods. Monomers have the highest level of bioactivity as they can interact easily at the cellular level without requiring the decomposition of polymers needed by larger procyanidin chains.

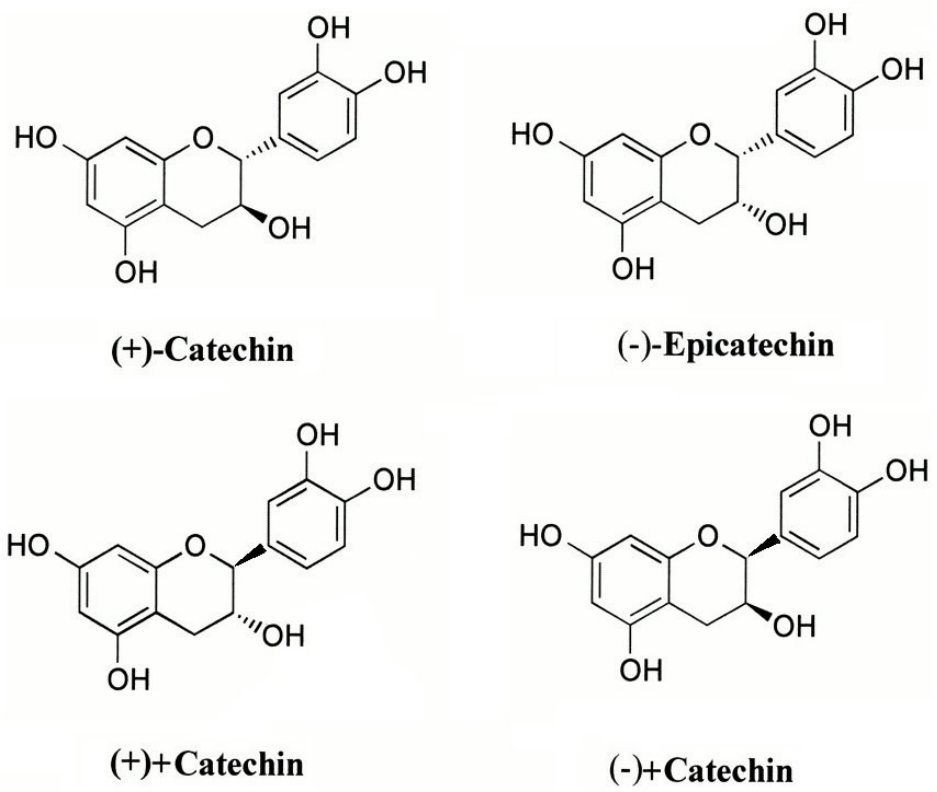

Figure 1.12 The structures of the catechin isomers (+)- catechin, (-)- epicatechin, (+)+ catechin, (-)+ catechin.

The addition of plant extracts from sources including pickled and dried mustard (Li and others 2012), jujube and pomegranate (Wambura and others 2010), oregano and olive oil (Olemdo and others 2009) and aguaribay and cedron essential oils (Olmedo and others 2012) in peanut products have shown the potential to reduce oxidation due to the high levels of antioxidant phenolics in these sources. Currently commercially available, mixed tocopherols are a popular option for a natural antioxidant (Shahidi and Zhong, 2010). The search for alternate natural preservatives is ongoing.

Cacao as an antioxidant

The cacao tree, *Theobroma cacao*, grows within 10 degrees north and south of the equator. It is a tropical plant that requires a delicate balance of heat, moisture, and shade. Cacao grows in the lower canopy of the forest, and thrives when shaded by taller tropical trees such as rubber and banana. The tree requires deep, fertile soil, and is grounded by a deep tap root. The tree produces pods that are harvested then opened, typically by hand, and the beans extracted from the pods are either naturally fermented, or they are spread to dry in the sun without undergoing the fermentation process (Knight 1999).

Most of the cocoa beans produced in the world are fermented, and the majority of this fermentation is conducted in small batches on the farm. Fermentation is conducted by piling the beans into a heap, and covering them with banana leaves or by storing the beans in a closed vessel such as a box. Fermentation typically lasts about 4 days. The beans are often turned after 2 days to promote the shift from anaerobic to aerobic fermentation (Knight 1999).

Fermentation of beans plays several key roles in the production of cocoa products. The beans are inoculated with wild, native microorganisms. These microbes are present on the tree, in the soil, and on the tools that are used to harvest and open the pods. The microbes digest the mucilage that surrounds the beans. As the sugars ferment, acid is produced which kills the beans after approximately 36 hours of fermentation. This acid also creates color and flavor change in the cocoa bean (Knight 1999). When the beans are first pulled from the pod, they are deep purple. Approximately 13% of the dry mass of an unfermented cocoa bean is pigment (Payne and others 2010). As fermentation progresses, the acid causes the pigment-containing cells to collapse which exposes them to other components of the bean. Exposure to air, light, and acid leads to degradation and complexing with other molecules that results in the beans changing in color from purple to brown. The bioactive compounds in cocoa, such as cyanidins, catechin and

epicatechin (Figure 1.12), also degrade and complex during the fermentation process. These reactions result in a decrease in the level of bioactive compounds in the bean post-fermentation (Knight 1999). Currently, 740 compounds have been identified in a raw cocoa bean. (Wilson and Hurst 2012)

The impact of processing, such as fermentation, on the level of available bioactives in cacao was investigated by Payne and others (2010). This study measured the quantity of catechin and epicatechin in a single lot of cocoa beans as they were fermented, dried, roasted, and treated with alkali (referred to in the industry as dutching). The study showed that beans immediately dried after harvest, either by sun-drying on the cacao farm or by freeze drying in a lab, exhibited levels of catechin and epicatechin monomers that remained 20% and 14% higher than fermented beans respectively. The processes of roasting and dutching also resulted in statistically significant losses of the bioactive monomers. As a result of roasting unfermented beans up to 120 °C resulted in an 82% decrease in the level of epicatechin. During roasting, the level of catechin rose steadily to a 696% increase over the initial levels. Fermentation also resulted in a significant loss of epicatechin, and increase in catechin. The authors attributed this change to the epimerization of (-)- epicatechin to (-)-catechin due to the heat during processing. The epimerization of (-)- epicatechin to (-)- catechin was suggested as the cause the reduction of epicatechin after dutching.

Based on the observation of Payne and others (2010), Hurst and others (2011) investigated the changes in stereochemistry of flavanols during fermentation, drying, roasting and dutching of cocoa. Payne and others (2010) observed a decrease in epicatechin during these processes. Hurst and others (2011) used high performance lipid chromatography (HPLC) to differentiate between each of the catechin isomers throughout processing. Unfermented,

unprocessed beans had the highest level of (-)- epicatechin followed by (+)-catechin and without any (-)- catechin observed. As processing continued, a shift from (-)- epicatechin to (+)-catechin and (-)- catechin was observed through fermentation and roasting. Ultimately, following alkalization (dutching), the level of (-)-catechin was the highest, followed by (-)-epicatechin and (+)- catechin. The authors hypothesize that heat and pH resulted in the epimerization of the flavanols, and that (-)- epicatechin was the most impacted isomer. Companies have exploited this information to create patents that outline how to use low impact processing to maintain the level of (-)- epicatechin in consumer goods (Mars Botanical 2013).

The bioactive compounds found in cocoa powder reside in both the lipid and non-fat cocoa solids of the cocoa bean. The lipid fraction, commonly referred to as cocoa butter, contains high levels of Vitamin E tocopherols. Tocopherols are a type of natural antioxidant found in plant and animal tissue cells that have alpha, beta, delta, and gamma forms. They are typically found in nature as a mixture of the four forms. The level of natural tocopherols is typically higher in plant lipids, which leads to a more stable form of fat that oxidizes slower than animal fats (Furia 1972). Erickson and others (1973) conducted a study using trimethylsilyl iodide (TMSi) to determine the forms of tocopherols that are present in cocoa butter. The peaks of gamma- and beta-tocopherols were difficult to differentiate, but the two make up 90% of the natural tocopherols in cocoa butter. The bean origin and processing, with or without alkali treatment of cocoa, impacted the level of tocopherols remaining in cocoa butter. Lipp and others (2001) confirmed the result of Erickson and others (1973), showing that cocoa butter primarily contains gamma tocopherols. The remaining tocopherols exist in lower amounts of alpha and beta forms. The levels of tocopherols typically vary from lot to lot of beans depending on

genetic variability. The presence of tocopherols can play a role in delaying lipid oxidation (Stahl and others 2009).

Unfermented cocoa beans contain on average 11-13% pigment cells which contribute to the bioactive enhancement of the cocoa bean (Knight 1999). As with tocopherols, polyphenol levels vary in cocoa based on origin and processing. Processing cocoa with alkali reduces the presence of bioactive compounds three-fold (Stahl and others 2009). The pigment cells are composed primarily of polyphenolic compounds (Singh and others 2010). The polyphenol anthocyanin contributes the color. The majority of the polyphenols in cacao are the flavanol catechin, and specifically –(-) epicatechin (Knight 1999). Epicatechin is a proven bioactive compound with high antioxidant capacity (Maleyki and Ismail 2010).

A 2006 study (Gu and others) revealed that the cacao-based commercially available product with the highest level of total antioxidants, procyanadins, catechins, and epicatechins was found in natural cocoa powder, which was the least processed and contained the fewest additional ingredients. Dutched cocoa powder, while not having many additional ingredients, was processed with alkali causing a reduction in the level of flavanols. Of the chocolate-type products assessed, unsweetened chocolate had the highest level of bioactive compounds because it had the fewest additional ingredients, while milk chocolate had the lowest level of bioactive ingredients because of the higher levels of additional ingredients and processing. The results of this study showed that while there are varying levels of health-promoting compounds, especially procyanadins, all cocoa containing products evaluated contained some level of antioxidant capacity (Gu and others 2006).

In addition to the study conducted by Gu and others (2006), Miller and others (2009) conducted a survey of commercially available cocoa containing products to investigate the

flavan-3-ol levels in cocoa powders, unsweetened baking chocolate, dark chocolate, semi-sweet chocolate chips, milk chocolate, and chocolate syrup. The study examined Oxygen Radical Absorbance Capacity (ORAC), total polyphenol content, epicatechin and catechin levels, total monomers, and flavan-3-ol monomers and polymers. Using these markers to create a comprehensive view of the bioactives in each of the products, the study found that cocoa powder had the highest level of flavan-3-ols, followed by baking chocolate, dark chocolate, baking chips, milk chocolate, and lastly chocolate syrup. This study also found that the addition of ingredients such as milk reduced the level of monomers. This study also agrees with the findings of Payne and others (2010) that additional processing results in a reduction of bioactives in cocoa products.

Payne and others (2010) observed that unfermented cocoa beans had more than 80% more epicatechin and catechin than fermented beans. Treating the cocoa beans with alkali was observed to decrease the epicatechin over 95% and the catechin 80%. When the beans were roasted to 120 °C, an increase of over 600% was observed in catechins. The authors hypothesize that the increase in catechins was due to polymerization of epicatechins.

Epicatechin in cocoa powder has been observed to be an effective antioxidant in several studies. Phenolics such as epicatechin have antioxidant ability due to the presence of an unsaturated aromatic ring with a hydroxyl group that can give up an electron for free radical quenching (Furia 1972). Experiments have shown that –(-) epicatechin suppressed lipid peroxidation in mammalian cell and cell model systems (Knight 1999). In 2010, Maleyki and Ismail presented the results of a study utilizing ferric reducing tests, antioxidant power assays, and stability tests of polyphenols which indicated that cocoa powder containing products may be more resistant to the onset of oxidation due to the presence of the antioxidant epicatechin. While

not formally tested, it is hypothesized that the development of the chocolate crumb process, a process that combines condensed milk with chocolate liquor to extend the shelf life of milk, was due to the preservative capacity of the polyphenols in chocolate liquor. Although many clinical studies have been performed to show the antioxidant capacity of cocoa, very few studies exist that have tested the potential of cocoa to serve as an antioxidant preservative in food systems (Knight 1999).

The monomers present in cacao have been observed to act as a preservative of the bean itself. While antioxidants in products such as olive oil have been observed to decrease over time, the preservative power of cocoa powder has been observed to remain for many years (Hurst and others 2009). Hurst and others (2009) studied the activity of flavan-3-ols in milk chocolate that was stored for one year, dark chocolate that was stored for two years, cocoa powders of varying ages up to 80 years, and 116 year old cocoa beans. The samples were tested using the oxygen radical absorbance capacity (ORAC), total polyphenol, and catechin/epicatechin tests. The chocolates tested contained levels of flavan-3-ols that remained statistically similar throughout the testing period. The cocoa powders and beans were tested against present day samples and were determined to have statistically similar levels of flavan-3-ols as well.

A fish preservation study was conducted in Nigeria to investigate the impact of fuel types on the increased preservative action in smoked fish. This study examined sawdust, charcoal, cocoa pod husks, and firewood as fuel for smoking mud fish. The results showed that the cocoa pod husks produced a significantly superior tasting product that the authors attribute to a reduced level of rancidity. The low level of rancidity was attributed to the addition of phenolic compounds from the cocoa pod husks that were not present in the wood based products. The

author also attributed the statistically significant lower level of bacterial and fungal counts on the skin of the fish to the phenolic compounds (Adebowale and others 2008).

Conclusions

Lipid oxidation is a significant problem in the food industry because it results in the overall deterioration and loss of shelf life in foods. In peanuts, oxidation is the shelf-life defining attribute. While synthetic preservatives that slow oxidation are available, consumers and scientists are becoming concerned over the potential toxicity of these ingredients. Natural preservatives may offer a solution to oxidative rancidity. Cocoa powder, with its high levels of polyphenols, may offer an opportunity for utilization as a natural preservative. Based on the understanding of the antioxidant capacity of cocoa powder in vivo, and the high risk of lipid oxidation in peanuts, future studies should be conducted to evaluate the preservative capability of cocoa powder in peanut-based products.

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Chapter 2 Cocoa powder as a natural preservative antioxidant in peanut systems[1]

Abstract

The objective of this study was to observe the effect of natural cocoa powder on oxidative rancidity in peanuts, peanut butter, and peanut oil versus 200 ppm of tocopherols. The samples, a blend of runner and high oleic peanuts from the southeastern United States, were treated within a week of initial roasting with either 200 ppm of mixed tocopherols or 2.5% (w/w) cocoa powder. The development of oxidation was monitored by Peroxide Value and GC/FID monitoring of hexanal development. The peanut butter samples were assessed by a professional sensory panel for rancidity. In peanuts, the cocoa powder sample developed significantly lower levels of oxidation identifiers than the tocopherol or control samples. In peanut oil, there was no significant difference in levels of oxidation identifiers between the samples. In peanut butter, the PV was significantly higher in the tocopherol sample than the cocoa powder or control samples, but there was no significant difference in hexanal. The results of the sensory analysis indicated that the cocoa powder masked both positive and negative attributes compared to the tocopherol and control samples. This study showed that cocoa powder may be a more effective preservative than an untreated sample or a sample treated with 200 ppm of tocopherols in peanuts however, cocoa powder at 2.5% (w/w) did not perform as a significant antioxidant in peanut butter, or peanut oil. Neither the addition of tocopherols or cocoa powder created a reduction in oxidative rancidity enough to justify the added costs of these ingredients.

[1] Abstract 255-141, presented as part of the 2013 IFT Annual Meeting.

Introduction

Peanuts are the second largest harvested legume globally (Shin and others 2010). As portions of the global population continue to become more focused on healthy proteins and oils, peanuts offer an inexpensive and readily available option (Shelke 2012). The unsaturated fats in peanuts may contribute to the inverse relationship between peanut consumption and the occurrence of Type 2 diabetes (Jiang and others 2002). The unsaturated fats that make peanuts desirable nutritionally, however, also create an elevated risk of oxidation in peanuts.

Lipid oxidation is the leading cause of quality deterioration in peanuts (Lee and others 2002). The shelf life of peanuts is defined as the number of days after production until rancid off flavors, such as cardboard and painty, are detected in the product in question (Mugendi and others 1998, Grosso and Resurrection 2002). This definition is typically created by a company for an individual product. Peanuts are composed of over 50% lipids (Craft and others 2010) of which approximately 80% are unsaturated. Typical peanuts contain 36-69% oleic, monounsaturated, fatty acids and 13-40% linoleic, polyunsaturated, fatty acids (Shin 2010, Williams and others 2006). The heat applied to peanuts during the roasting or frying process often serves as the initiator of oxidation (Mate 1996). Peroxides are initially formed during oxidation, followed by secondary compounds which are general aldehydes and ketones. Hexanal is the most commonly produced and measured secondary product formed in peanuts. Hexanal is formed as a result of the oxidation of linoleic acid (Warner and others 1996).

Historically, synthetic preservatives such as butylated hydoxyanisole (BHA), butylated hydroxytoluene (BHT), and tert-butylhydroquinone (TBHQ) have been employed to delay the onset of oxidation (Carocho and Ferreira 2013). Despite the GRAS status of these ingredients,

consumer concern over their potential carcinogenic nature exists. This concern has lead to a higher demand for natural preservatives (Joshi and others 2011, Shom and others 2011, Parke and Lewis 1992).

Several non-synthetic means of preventing or delaying oxidation in peanuts have been studied and employed. The first major attempt at naturally controlling oxidation in peanuts involved genetic selection of plants for levels of oleic acid at 80% in the 1980s (Norden and others 1987). Isolating the genetic form from planting through consumption presents a large challenge in the modern food system. High amounts of contamination with low- or normal- oleic peanuts are common (Davis and others 2013). As a result, the demand for natural preservative has increased.

Hundreds of plant- and animal- derived compounds that exhibit antioxidant capabilities exist (Singh and others 2010). The addition of plant extracts from sources including pickled and dried mustard (Li and others 2012), jujube and pomegranate (Wambura and others 2010), oregano and olive oil (Olemdo and others 2009) and aguaribay and cedron essential oils (Olmedo and others 2012) have show the potential to reduce oxidation in peanuts due to the high levels of antioxidant phenolics in these sources. Mixed tocopherols are currently a popular option for a natural antioxidant (Shahidi and Zhong 2010, Gulcin 2012). Mixed tocopherols are successful antioxidants in lipid systems when used at the correct concentration, but studies have observed tocopherols also behaving as prooxidants if used at elevated concentrations (Carocho and Ferreira 2013).

Cocoa containing products have been reviewed by the medical community for their antioxidant ability *in vivo* (Cooper and others 2008). Over 700 compounds have been identified

in cocoa (Wilson and Hurst 2012), of which flavan-3-ols function as powerful antioxidants in the non fat solids of the cocoa beans (Gu and others 2006). Of the flava-3-ols in the non fat cocoa solids, the monomer -(-) epicatechin is particularly concentrated in natural cocoa powder and has been identified as a powerful antioxidant (Stahl and others, 2009). The USDA Database for the Procyanadin Content of Selected Foods (2004) showed that cocoa powder has the highest level of procyanadin monomers, such as epicatechins and catechins, available in commonly consumed foods (2004). Cocoa powder with the lowest levels of processing; unfermented, and non-alkalized, has the highest levels of flavan-3-ols commercially available in the United States (Miller and others 2009, Payne and others 2010). Cocoa powder has been observed to be stable over long periods of time (Hurst and others 2009, Maleyki and Ismail 1996). Although many studies have been conducted analyzing the role of cocoa antioxidants in health, very few studies have assessed the potential for an antioxidant in food. The objective of this study was to examine the ability of cocoa powder to delay the onset and decrease the overall impact of oxidation compared to mixed tocopherols in peanuts, peanut butter, and peanut oil.

Practical Applications

Preservatives added to food products play a key role in the shelf life requirements of the modern food industry. Consumer perception towards synthetic preservatives has become negative based on reports of their potential carcinogenic nature. In response to these concerns, the industry has begun a search for naturally derived antioxidant preservatives. Currently, tocopherols are the most frequently used preservative antioxidant, but other sources such as rosemary extracts have also been introduced into the market. This study explored the opportunity for cocoa powder to be used as an option for industrial natural preservatives.

Materials and Methods

This study used three primary measures to observe the development of oxidation in the samples: peroxide value (PV), hexanal analysis (GC-FID), and sensory analysis. The PV analysis was selected due to its high usage in industry as a measure of oxidation. Hexanal analysis was chosen because it accurately monitors the development of secondary reaction products, such as hexanal in peanuts. Sensory studies were applied to the peanut butter samples because it is considered the gold standard in oxidation detection. Sensory analysis was not performed on peanuts or peanut oil in this study.

Cocoa Analysis

The cocoa powder was analyzed to determine the level of bioactivity specific to the lot of cocoa powder used in each treatment. The cocoa powder sample was analyzed for oxygen radical absorbance capacity (ORAC), total polyphenols as gallic acid equivalents, total procyanidins, catechin, and epicatechin levels as outlined by Hurst and others (2009).

Fatty Acid Distribution

The fatty acid distribution was determined from three individual lots of peanut oil by AOCS Official Method Ce 2-66: simplified method of determination of fatty acid distribution (Firestone 1992). This method was conducted to understand the oleic to linoleic (O/L) ratio of the samples tested.

Sample Preparation

One blended lot of runner-type normal oleic peanuts was obtained from the southeastern United States. Peanut samples were collected from this lot after roasting, peanut butter was

collected following grinding, and peanut oil was sampled after pressing under nitrogen flush. The samples were treated for the study within ten days of the roasting date.

The peanut samples were treated by panning in a ribbed, bench top pan (Troy Enterprises Co, Ltd, New Taipai City, Taiwan) (Kitts and others, 2007). Each sample was panned for two hours at the maximum pan speed. The cocoa powder sample was produced by creating a 1:3 suspension of cocoa powder in water using a high shear mixer (Charles Ross and Son Company, Hauppauge, NY, USA) on the high setting for one minute. This suspension was added to the peanuts tumbling in the pan to achieve the addition of 2.5% cocoa powder to the total pan load. The residual moisture was calculated to be 3% on a per-weight basis. Water was added to the tocopherol and control samples at 3% of the total pan weight in the panning process to accommodate this discrepancy. Abegaz and others (2004) observed that moisture in peanuts may lower hexanal values over time, and therefore needed to be eliminated as a variable. The tocopherol sample was treated by adding 200 ppm to the pan during the first 5 minutes of panning. The control sample was produced by adding 3% water to the pan and allowing the pan to spin for 2 hours.

The peanut butter and peanut oil samples were produced by adding 2.5% cocoa powder (w/w) or 200 ppm to the peanut butter or oil. The samples were mixed for 10 minutes (peanut butter) or 5 minutes (peanut oil) in a Hobart mixer (Hobart Corporation, Troy, OH, USA) on low speed. The control samples were mixed untreated.

After preparation, each sample was stored in a sealed glass jar (Ball, Broomfield, CO, USA). The samples were stored in an accelerated shelf life environmental chamber (Forma Scientific, Marietta, OH, USA) at 90 °F/50% relative humidity. The control peanut butter sensory test samples were stored in a 0 °F freezer.

Peroxide Value

The peanuts were ground with a Krups coffee mill (Millville, NJ, USA) for thirty seconds immediately prior to pressing. The peanut butter was pre-treated by the addition of 10% Celite on a w/w basis (TM 545 filtered, not acid washed, powder, Fischer Scientific, Pittsburgh, PA, USA)**.** The peanut and peanut butter samples were pressed in a Carver Laboratory Press Model C (Carver, Wabash, IN, USA) using up to 9 meteric tons over 3-5 minutes and tested immediately. The PV testing was based on the AOCS manual titration method Cd 8b-90 (Firestone 1992). The titration was conducted in an autotitrator on a Mettler Automatic Titrator (Mettler Toledo, Columbus, OH, USA). The limit of quantification for this analysis was 0.02 meq/kg.

Hexanal Analysis

The pressed oils were then tested for hexanal concentration. Using a disposable pipette (ThermoFisher Scientific, Waltham, MA, USA) 1 gram ±0.02 grams of pressed oil was weighed on an analytical balance (Mettler, Columbus, OH, USA) into a 22 mL headspace vial (Perkin-Elmer B010-4236 Waltham, MA, USA) and sealed with a vial seal (Perkin Elmer B010-4244 Waltham, MA, USA) using a bench top crimper (Chromacol, LDT, ThermoFisher Scientific, Waltham, MA, USA) until the cap could not be moved by hand. Each sample was prepared in triplicate for analysis. A 200 ppm hexanal standard (Sigma Aldrich, St. Louis, MO, USA) in mineral oil (Sigma Aldrich, St. Louis, MO, USA) was sampled for calibration after every ninth sample. The vials were loaded into a Perkin Elmer HS 40 automatic headspace sampler (Waltham, MA, USA) and the test was conducted using a gas chromatograph (HP5890A) equipped with a flame ionization detector (FID) (Agilent Technologies, Santa Clara, CA, USA). Separation of volatile compounds was achieved using a Porapak PS 80/100, 28.5 cm x 2 mm

column (Waters Corporation, Milford, MA, USA). The carrier gas was zero grade helium (MG Industries, Santa Rosa, USA) at 48 psi at a flow rate of 20 mL/min. The hydrogen generator used was a Packard 9400 Generator (Palo Alto, CA, USA), and the air generator used was a Whatman Zero Air Generator (GE Healthcare, Sugar Notch, PA, USA). The FID was maintained at 250°C, the needle was maintained at 110°C, the sample was transferred at 110°C, and the oven was maintained at 78°C. The column head pressure was maintained at 20 psi. The cycle time for each sample was set for 24 minutes, the thermostat time was 61 minutes, the pressurize time was 3 minutes, the injection time was 0.05 minutes, and the withdrawal time was 0.2 minutes. The level of quantification of this analysis was 2 meq/kg.

Sensory Analysis

The peanut butter samples were tested against a frozen control of the same treatment each week. The samples were randomized by a three digit code, and tasted twice in one day by two panels of 9 women trained in descriptive analysis of peanut products. The samples were analyzed for roast/toast, peanutty, painty, cardboard, and degree of difference on a 15 point scale.

Statistical Analysis

Data was analyzed with JMP SAS software Version 10 (2012). An analysis of variance (ANOVA) was used to determine the differences between samples at $p<0.05$. Cook's D was used to identify outliers (SAS 2012).

Results and Discussion

The cocoa powder used in experimentation was analyzed for oxygen radical absorbance capacity (ORAC), total polyphenols as gallic acid equivalents, total procyanidins, catechin, and epicatechin to understand the bioactivity of the sample (Table 2.1).

Table 2.1 The bioactive properties of the cocoa powder used to treat peanuts, peanut butter, and peanut oil.

	ORAC (µmol TE/g)	**Total Polyphenols (mg/g)**	**Total Procyanidins (mg/g)**	**Catechin (mg/g)**	**Epicatechin (mg/g)**	**Total Monomers (mg/g)**
Cocoa Powder	1120	100.8	52.2	1.95	12.16	99.8

The antioxidant levels observed in this cocoa powder were considered high when compared to common berries as well as commercially available cocoa powders (Zheng and Wang 2003, Hurst and others 2009, Miller and others 2009). Blueberries and cranberries have a consumer perception of being high antioxidant foods. Zheng and others (2003) conducted a study that showed these fresh berries have 28.9 and 18.5 µmol TE/g respectively. Hurst and others (2009) conducted an analysis of commonly available chocolate and cocoa products that showed Hershey's Natural Cocoa Powder contains 797±31 µmol TE/g, 58±1 total polyphenols, and 2.66 mg/g flavanol monomers. A study was conducted analyzing the top three commonly available cocoa powders. Each of the three had ORAC values less than 875, total polyphenols less than 60.5, epicatechin levels less than three and catechin levels less than one (Miller and others 2009). Based on these studies, the cocoa powder used in this study had higher-than-typical levels of bioactive compounds which may have the ability to increase the antioxidant preservative capacity.

The fatty acid distribution (Table 2.2) indicated that the average O/L was 2.03. This observation was consistent with the observation by Isleib and others (2006) that normal oleic peanuts from the United States typically have an O/L ratio of 2.13±0.53.

Table 2.2 Fatty acid distribution of three peanut oil samples.

Fatty Acid ↓	**% composition**	**% composition**	**% composition**
C16:0	9.0	9.0	9.0
C16:1	0.1	0.1	0.1
C17:0	0.1	0.1	0.1
C18:0	3.0	3.1	3.1
C18:1	54.2	53.7	53.8
C18:2	25.9	26.4	26.3
C18:3	0.1	0.1	0.1
C20:0	1.5	1.5	1.6
C20:1	1.3	1.2	1.2
C22:0	3.3	3.3	3.3
C22:1	0.1	0.1	0.1
C24:0	1.5	1.5	1.5
SUM	100.0	100.0	100.0
C18:1/C18:2	2.1	2.0	2.0

Samples of peanuts, peanut butter, and peanut oil were treated with cocoa powder or tocopherols to observe the ability of these ingredients to slow the onset of oxidative rancidity. The PV of the samples showed that the effect of time on peanuts, peanut butter, and peanut oil were treatment dependent ($P>0.0001$) (Figure 2.1). In peanuts, the treatments became significantly different from each other over time. The sample treated with cocoa powder had a significantly lower level of oxidation. This significant difference may be attributed to variability observed during processing. The presence of cocoa powder during the panning process created "slip", a smoother movement of the peanuts in the pan, that was not observed in the tocopherol or control sample due to the presence of powder (Kitt and others 2007). These samples did not have powder in the pan to induce the slipping motion that could have protected the outer cellular

structures from damage. The release of oil was observed in the tocopherol and control samples during processing due to the forceful movement in the pan with the absence of slip. This exposed oil would be at a higher risk of oxidation due to the more direct contact with oxygen and light compared to the cocoa panned pieces. Wambura and others (2010) observed by reducing the amount of oil on the surface of the peanut by using ultra sonication, and creating a barrier, the rate of oxidation slows. The reduction of oxidation in peanuts treated with cocoa powder contradicts the observation of Mugendi and others (1998). This study showed that a peanut coating in chocolate had a PV 10 times greater than an uncoated peanut. Despite the presence of additional antioxidants and the presence of a light barrier, the coated peanuts oxidized faster (Megundi and others 1998). Lee and others (2002) observed the presence of a whey coating around a whole peanut reduced oxidation by creating a barrier to oxygen and light. The peanut sample treated with cocoa powder may have had a reduced level of oxidation due to processing variability, the presence of a light barrier, or the presence of a moisture barrier.

In peanut butter, the tocopherol sample had significantly higher levels of oxidation (Figure 2.1). Tocopherols have been observed acting as a prooxidant in other studies using peanuts (Carocho and Ferreira 2013, Lee and others 2002). The cocoa powder sample also exhibited a significant level of oxidation. Cocoa powder is derived from the seed of the cacao tree, and has been observed to concentrate trace amounts of metals such as iron and copper from the soil. In addition to the potential prooxidant effect of the phenolics, the metals in the cocoa matrix may have acted as a catalyst to oxidation in the peanut butter sample and created a prooxidant effect (Mounicou and others 2003).

The primary difference between the peanut and peanut butter sample was the particle size of the peanuts. After the treatments were applied, the cocoa powder treated peanut samples had

the advantage of a light and oxygen barrier to reduce the onset of oxidation. The peanut butter samples did not have a protective layer. In addition to the absence of this protective layer, the peanut butter samples also had macerated cells that resulted in a higher level of oil exposure to oxygen. Air may have been trapped throughout the samples during mixing which could create pockets of oxidation. This incorporation of air did not occur in the pure peanut oil samples because there was not enough internal structure to retain the air. The peanut butter samples were at a disadvantage compared to the other samples due to the increased surface area of the nut pieces that were exposed to oxygen, light, and metal catalysts more aggressively than the peanut or peanut oil samples.

Unlike the peanut and peanut butter samples, peanut oil samples were not significantly different in PV over time (Figure 2.1). Peanut oil contains natural tocopherols that may have concentrated in the fat fraction of the peanut during pressing (Isleib and others 2006, Shin and others 2009). These tocopherols were not stripped from the samples prior to testing. Abuzaytoun and Shahidi (2006) observed that stripping the tocopherols from flax and hemp oils resulted in an accelerated onset of oxidation in the systems compared to samples with tocopherols.

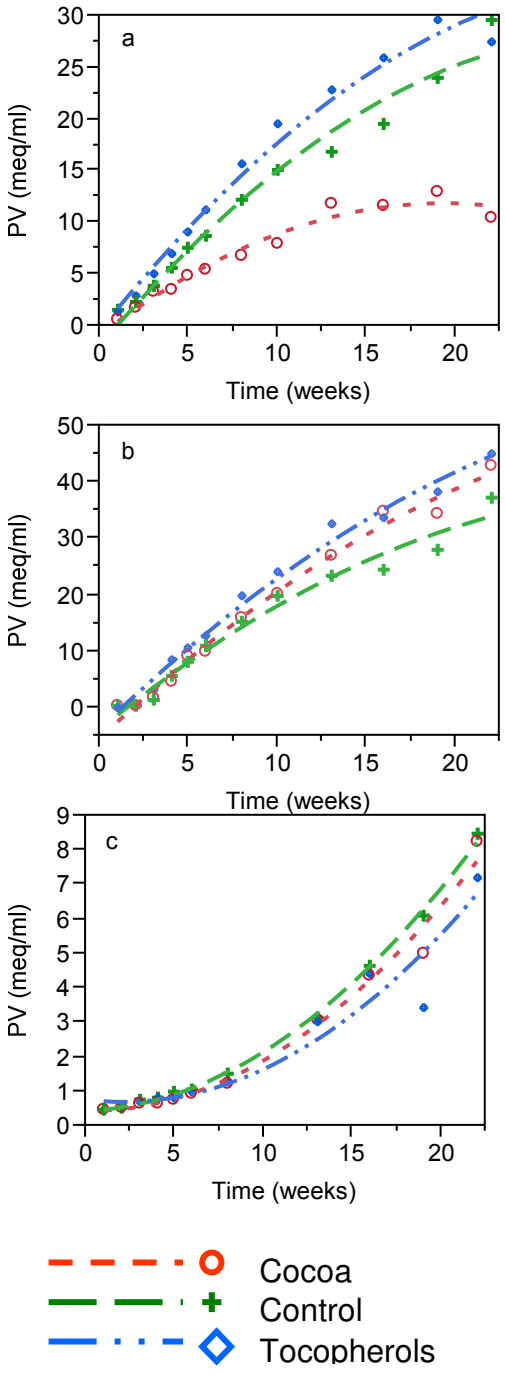

Figure 2.1 PV over time in peanuts (a) peanut butter (b), and peanut oil (c).

Wambura and others (2010, 2011) have studied the effect of addition of plant-derived extracts high in antioxidants when added to peanuts to delay the onset of oxidation. These studies have shown a significant reduction in oxidation in the treated samples compared to the

untreated samples. Cocoa powder has the highest level of proanthocyanidins per weight than any other commonly consumed product in the United States (USDA 2004).

The hexanal results showed that the effect of time on peanuts, peanut butter, and peanut oil was treatment dependant ($P>0.0001$). The hexanal results are expected to be delayed from the PV results because the PV analyzes a transient primary product in the oxidation reaction (Manning 2000). The presence of elevated PV observed in peanuts translated into hexanal levels as expected across all treatments. The peanut data showed that the cocoa powder treated sample had a significantly lower level of hexanal than the tocopherol and control samples that were statistically similar (Figure 2.2).

The peanut butter samples did not statistically differ in levels of hexanal (Figure 2.2). The variability observed in the samples in the last 12 weeks of the study made drawing overall statistical conclusions difficult. While the PV analysis showed a significant difference between treatments, the GC/FID did not confirm this with the presence of hexanal. The discrepancy between these two analyses may be attributed to PV being a measure of a transient product while GC/FID measures hexanal, which is far more stable. The PV may also have shown the primary product and the secondary product was slower to form, and the secondary products may have been more diverse. Hexanal was observed in the highest concentrations in oxidized peanuts by Dimick (1994), however there were eight other compounds that were also quantified in the study.

No significant difference was observed between treatments in peanut oil (Figure 2.2). The samples taken at week 10 were labeled as outliers using Cook's D test, and were removed from the data set for analysis. As observed in the PV analysis, the peanut oil samples underwent little oxidation which could have been the result of the aforementioned naturally occurring antioxidants or processing aides. Tocopherols have been identified across most breeds of

commercially available peanuts in the United States (Shin and others 2009 and Isleib and others 2006). The presence of this fat soluble antioxidant may have slowed the onset of oxidation in peanut oil.

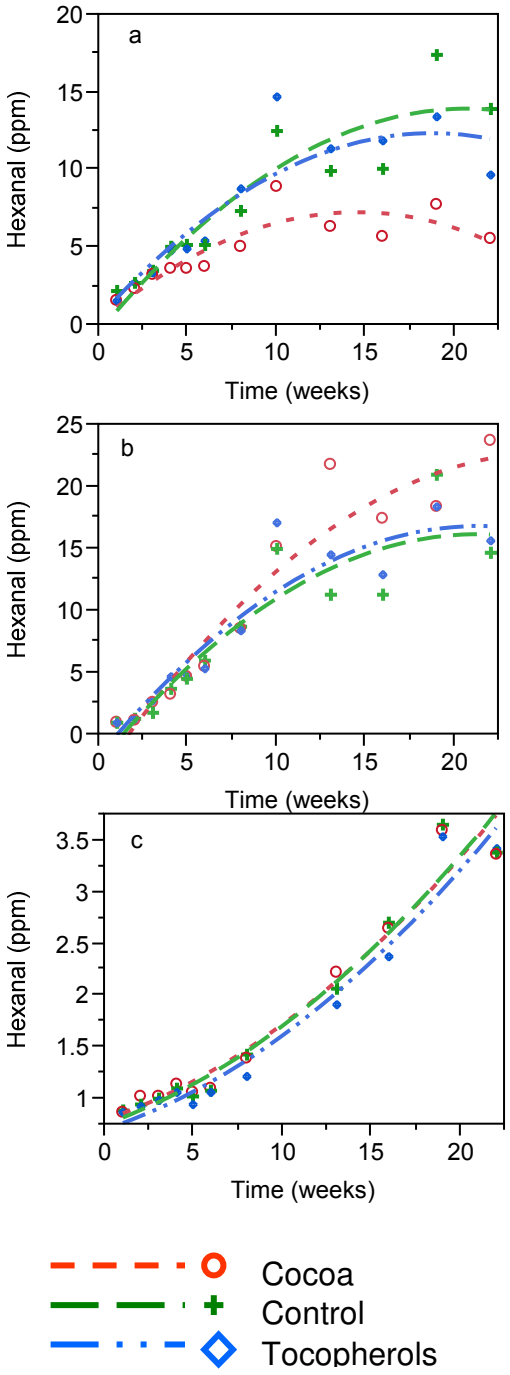

Figure 2.2 Hexanal concentration over time in peanuts (a) peanut butter (b), and peanut oil (c).

Five sensory attributes: two positive, two negative, and one neutral, were examined in peanuts butter samples. The two positive attributes examined were peanutty, and roast/toast (Figure 2.3). The results for the peanutty sample indicated that there is not a significant interaction between time and treatment in the perception of peanutty (P=0.537). The samples were not significantly different from each other. The peanutty perception in shelf life samples decreased compared to the frozen control at a rate of 0.17 units per 10 weeks. The results for the roast/toast samples showed that the effect of time on roast/toast perception is treatment dependent (P=0.0141). The samples were not significantly different from each other. The roast/toast perception in shelf life samples decreased compared to the frozen control at a rate of 0.08 units per 10 weeks. An interaction was observed in the first 10 weeks of testing, after which tocopherols appear to have a larger decrease in the perception of roast/toast in the second half of testing.

The decrease in positive flavor attributes such as peanutty and roast and increase in negative flavor attributes have been previously observed. Williams and others (2006) confirmed what Warner and others (1996) had studied a decade earlier in that the presence of positive flavor attributes in roasted peanuts can be attributed to pyrazines. These pyrazines remain constant throughout the shelf life of peanut products, but the positive flavors become masked by the lower molecular weight aldehydes developed during oxidation (Williams and others 2006 and Warner and others 1996).

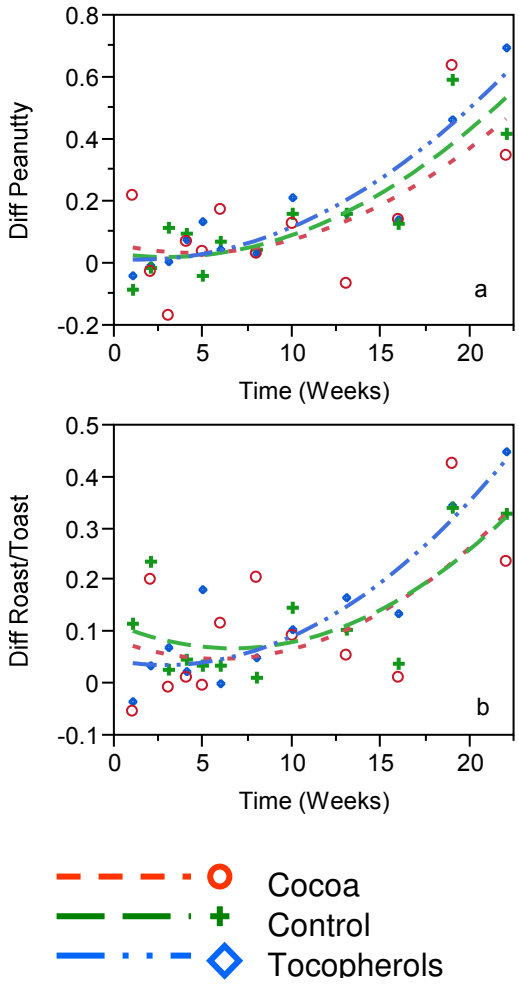

Figure 2.3 The changes in the differences between frozen control and aged peanut butter samples over time of positive flavor attributes; peanutty (a) and roast/toast (b).

The negative attributes assessed were cardboard and painty (Figure 2.4). The results of the cardboard analysis showed that the effect of time on cardboard perception was treatment dependent (P=0.0376). The samples were not significantly different from each other over time. The cardboard perception in shelf life samples increased compared to the frozen control at a rate of 0.17 units per 10 weeks. The samples trended closely in the first ten weeks, after which the tocopherols appear to have a larger increase in the perception of cardboard. The painty results indicated that the effect of time on perception was treatment dependant (P=0.0002). The samples

were not significantly different from each other. The samples in the last 7 weeks of testing were very erratic which makes it difficult to draw firm conclusions from this data set. The increased perception of oxidized flavors such as painty and cardboard was observed over time by Grosso and Resurrection (2002) in peanuts. As the level of low molecular weight aldehydes formed from oxidation, the level of undesirable oxidized flavors also increased. The increase in oxidized flavors led to the determination of shelf life based on the presence of off flavors.

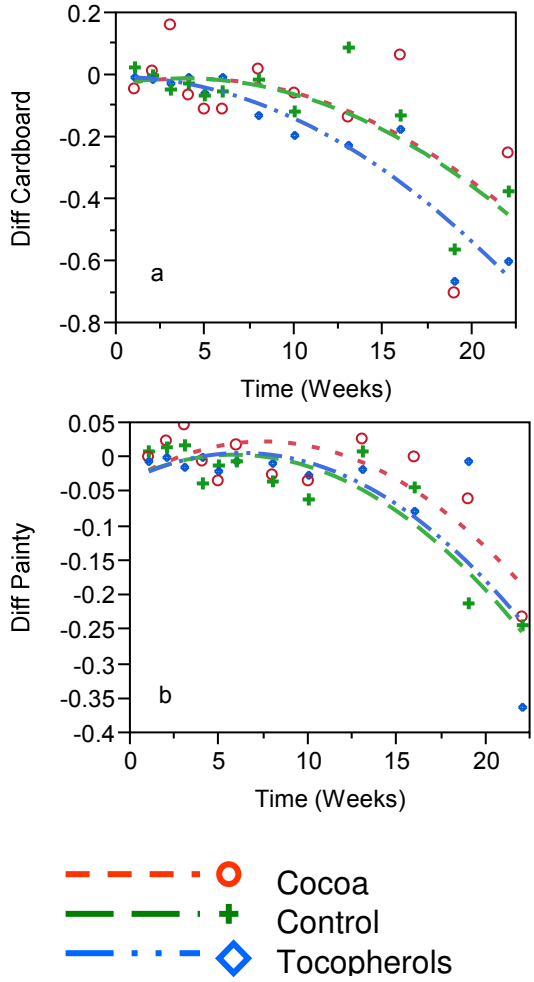

Figure 2.4 The changes in the differences between frozen control and aged sample over time of negative flavor attributes cardboard (a) and painty (b).

The final attribute analyzed was the overall degree of difference between the samples. This attribute was selected as a neutral point of observation. The effect of time on the overall degree of difference was treatment dependent (P=0.0133). The samples were not significantly different from each other. The total degree of difference between the shelf life and frozen control samples increased by 0.6 units per 10 weeks (Figure 2.5).

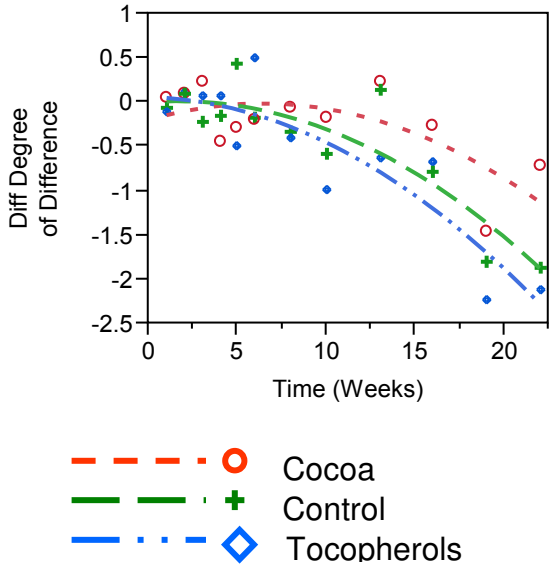

Figure 2.5 The changes in the differences between frozen control and aged sample over time of the overall degree of difference.

Conclusion

This study yielded mixed results for cocoa powder as a natural antioxidant. Peanuts panned with cocoa powder presented a significantly lower incidence of oxidation indicators than samples treated with tocopherols or the control. Peanut butter treated with cocoa powder exhibited a reduction in oxidation compared to tocopherols, but a statistically significant difference was not observed in the hexanal analysis. Peanut oil treated with cocoa powder or tocopherols did not exhibit a significant difference in oxidation indicators over time. Overall, cocoa powder at 2.5% w/w basis did not perform as a significant antioxidant in peanut butter, or peanut oil. Cocoa powder at 2.5% w/w basis did show potential to serve as a natural antioxidant in peanuts.

Future Studies

While this study did not provide conclusive evidence that cocoa powder or tocopherols act as an antioxidant across these three peanut systems, it did present areas for further study, primarily the lipids tested and the form of the cocoa. This study was based on the understanding that chocolate crumb theory, the product created by preserving sweetened condensed milk with chocolate liquor, was true. Published research does not exist to prove that the addition of chocolate liquor impedes the development of oxidation over time. This study indicated that rather than extend the initiation period of oxidation, the addition of chocolate liquor may have masked off flavors. Future studies could be conducted to determine if chocolate liquor is a stronger inhibitor of oxidation than cocoa powder due to miscible formats and tocopherols in the lipid fraction of the liquor in addition to the bioactive compounds in the cocoa solids. Another study could be conducted on saturated fats such as dairy fats to observe if cocoa powder could act as an antioxidant in that system. The level of cocoa powder added to the system may also impact its ability to serve as an antioxidant. Additionally, creating extracts of bioactive compounds from both the lipid and non-fat portions of the cocoa bean may provide an even greater opportunity to explore cocoa as a natural antioxidant. Extracts may offer an opportunity to make a cocktail of the desirable bioactives in cocoa without the negative addition of prooxidant trace heavy metals.

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Chapter 3 The correlation of Peroxide Value and GC/FID hexanal quantification with descriptive analysis to monitor oxidative rancidity in peanut butter

Abstract

This study observed the ability of Peroxide Value (PV) and hexanal quantification using Gas Chromatography with Flame Ionization Detection (GC/FID) to predict the observation of oxidation by sensory analysis in peanut butter treated with natural antioxidants. Samples were treated with antioxidants, stored at accelerated shelf life conditions, and tested analytically and with sensory for 21 weeks to monitor the progression of oxidation. This study found that both PV and hexanal quantification were able to predict the increase in negative flavor attributes and decrease in positive flavor attributes in at least one of the treated samples (R^2= 0.7). This study demonstrated that PV and GC/FID may provide a less expensive and less time consuming method of monitoring oxidation in peanut butter samples treated with natural antioxidants and untreated.

Introduction

Peanuts are a healthy and popular snack in the United States (Fuhrman 2005). The unsaturated fats that make peanuts nutritionally desirable create a negative impact on shelf life due to their increased susceptibility to oxidation compared to saturated fats (Braddock and others 1995). Sensory analysis is considered the gold standard in observing the development of oxidation over time and the impact of oxidation on consumer acceptability (Grosso and Resurreccion 2002). Although sensory testing is able to accurately monitor the development of oxidation, the analysis can be costly and time consuming (Lee and Resurreccion 2006).

Studies have been conducted to relate analytical methods of physical attributes such as water activity, color measurements, and mechanical tests as well as chemical attributes such as static headspace gas chromatography (SHGC), peroxide value (PV), p-anistidine (AV), and conjugated dienes (CD) to descriptive analysis of peanut products with varying degrees of success (Lee and Resurreccion 2006, Lee and others 2002, Nepote and others 2009). Lee and Resurreccion (2006) were unable to show a correlation between sensory descriptors and physical attributes such as water activity and color measurements, however Lee and others (2002) and Nepote and others (2009) observed correlations between descriptive analysis attributes and chemical observations such as peroxide value, p-anistidine, SHGC, and conjugated diene testing. These studies have indicated that analytical methods may provide useful tools for screening peanut products for oxidation.

Antioxidants are frequently added to peanut products to delay the onset of oxidative rancidity. Wambura and others (2010, 2011) observed extracts from rosemary, tea, jujube and pomegranate delayed oxidation in peanuts. Other studies have observed extracts of foods such as mustard seeds and oregano also exhibiting the potential to serve as antioxidants in peanut

products (Li and others 2012 and Olemedo and others 2009). As discussed in Chapter 2, cocoa powder may also delay oxidation in peanuts. Despite the variety of antioxidants analyzed, mixed tocopherols extracted from soy are the most common antioxidant used in the food industry (Shahidi and Zhong 2010). As consumer demand for nature-derived antioxidants increases, the industry would benefit from being able to provide safe, effective alternatives to synthetic antioxidants.

The process of determining the antioxidant potential of nature-derived compounds currently relies heavily on sensory testing. While sensory analysis is the preferred industry method of observing oxidation in foods, it is a costly and time consuming (Grosso and Resurreccion 2002). The ability to screen peanut products treated with antioxidants analytically to determine an end point which can then be validated by sensory analysis could enable a more rapid understanding of antioxidant potential.

This study was conducted to observe the ability of PV and SHGC to monitor the onset of oxidation in peanut butter treated with tocopherols and cocoa powder.

Practical Application

Sensory analysis is currently used throughout the food industry to monitor oxidation in products. This study indicated that PV and hexanal quantification by GC/FID may serve as analytical methods to monitor oxidation in peanut butter with and without antioxidants. The application of these methods may allow food manufacturers to monitor oxidation in peanut butter in a shorter amount of time and at a lower total expense than what formal descriptive analysis currently requires.

Materials and Methods

A single lot of normal oleic Runner peanuts was obtained from the southeastern United States. The peanuts were dry roasted and ground in a commercial peanut butter processing operation. The peanut butter samples were treated with antioxidants within ten days of the initial roasting. Cocoa powder was added to the peanut butter at 2.5% (w/w) and mixed tocopherols were added at 200 ppm by blending the antioxidants into the peanut butter using a Hobart mixer (Hobart Corporation, Troy, OH, USA) on low speed for 10 minutes. The control sample was mixed under the same conditions without an antioxidant addition.

Following treatment, the samples were added to sealed glass jars (Ball, Broomfield, CO, USA), and stored in an environmental chamber (Forma Scientific, Marietta, OH, USA) at accelerated conditions of 90 °F/50% relative humidity. The control samples were stored at 0 °F in a freezer. The samples were removed from the environmental chamber on the day of analysis for PV and GC/FID treatment. The samples were removed from the environmental chamber and freezer for sensory testing the 24 hours prior to analysis to allow the samples to equilibrate to room temperature prior to testing.

Peroxide Value

To extract the oil, the peanut butter samples were pre-treated with 10% (w/w) Celite (TM 545 filtered, not acid washer, powder, Fischer Scientific, Pittsburgh, PA, USA). The samples were loaded into a test cylinder so that it was not more that 75% full, and the oil was expressed using a Carver Laboratory Press Model C (Carver, Wabach, IN, USA) using up to 9 meteric tons over 3-5 minutes, and analyzed immediately following pressing. PV testing was conducted based on the AOCS manual titration method CD 8b-90 (Firestone 1992). The titration was

carried out in an autotitrator with readout on a Mettler Automatic Titrator (Mettler Toledo, Columbus, OH, USA). The limit of quantification for this analysis was 0.02 meq/kg.

Hexanal Analysis

The remaining oil samples produced by the above mentioned Carver Press were used to conduct the GC/FID analysis for hexanal. Using a disposable pipette (ThermoFisher Scientific, Waltham, MA, USA) 1 gram ±0.02 grams of pressed oil was weighed on an analytical balance (Mettler, Columbus, OH, USA) into a 22 mL headspace vial (Perkin-Elmer B010-4236 Waltham, MA, USA) and sealed with a vial seal (Perkin Elmer B010-4244 Waltham, MA, USA) using a bench top crimper (Chromacol, LDT, ThermoFisher Scientific, Waltham, MA, USA) until the cap could not be moved by hand. Each sample was prepared in triplicate for analysis. A 200 ppm hexanal standard (Sigma Aldrich, St. Louis, MO, USA) in mineral oil (Sigma Aldrich, St. Louis, MO, USA) was sampled for calibration after every ninth sample. The vials were loaded into a Perkin Elmer HS 40 automatic headspace sampler (Waltham, MA, USA) and the test was conducted using a gas chromatograph (HP5890A) equipped with a flame ionization detector (FID) (Agilent Technologies, Santa Clara, CA, USA). Separation was achieved using Porapak PS 80/100, 28.5 cm x 2 mm column (Waters Corporation, Milford, MA, USA). The carrier gas was zero grade helium (MG Industries, Santa Rosa, USA) at 48 psi at a rate of 20 ml/min. The hydrogen generator used was a Packard 9400 Generator (Palo Alto, CA, USA), and the air generator used was a Whatman Zero Air Generator (GE Healthcare, Sugar Notch, PA, USA). The FID was maintained at 250 °C, the needle was maintained at 110 °C, the sample was transferred at 110 °C, and the oven was maintained at 78 °C. The column head pressure was maintained at 20 psi. The cycle time for each sample was set for 24 minutes, the thermostat time

was 61 minutes, the pressurize time was 3 minutes, the injection time was 0.05 minutes, and the withdrawal time was 0.2 minutes. The level of quantification of this analysis was 2 meq/kg.

Sensory Analysis

The peanut butter samples were tested aged against a frozen control by a panel of 9 women previously trained on the attributes for descriptive analysis of oxidation in peanut products. The samples were presented to the panelists coded by randomized three digit numbers. The samples were assessed for peanutty, roast/toast, painty, cardboard, and degree of difference on a 15 point scale.

Statistical Analysis

Data was analyzed using JMP SAS software Version 10 (SAS 2012). A correlation analysis was conducted to observe the ability of analytical methods to predict the absence or presence of oxidation attributes.

Results and Discussion

Sensory analysis is considered the best method to observe oxidation in nut products; however, the cost of maintaining a trained panel, and the time required to conduct the analysis is extensive. Several attempts have been made to correlate various analytical data to sensory observations in peanut products (Abegaz and others 2004, Grosso and Resurreccion 2002, and Lee and Resurrection 2006).

Many studies have observed trends of sensory attributes changing in a similar progression to the changes observed using analytical methods. Olmedo and others observed aguaribay and cedron essential oils (2012) and oregano and olive oil (2009) to have increased levels of oxidation in analytical methods such as PV, AV, and CD and an increased level of oxidized flavors such as peanut (oxidized) and cardboard. Riveros and others (2010) observed a similar occurrence of PV, AV, and CD increasing over the shelf life with a rate that corresponded with an increase in peanutty (oxidized) and cardboard. These changes were more prevalent in normal oleic peanuts, but also occurred in high oleic peanuts over time at varying storage temperatures. While these studies observed similar trends in the increase of oxidized flavors and analytical oxidation indicators, statistics were not conducted to understand the significance of the correlation.

Lee and Resurreccion (2002) were among the first to observe a correlation between analytical oxidation markers and sensory analysis in peanut products. In that study, consumer acceptance scores were used in conjunction with mechanical tests, color measurements, water activity and moisture measurements to observe the impact of water activity on consumer acceptability. Nepote and others (2006) observed both an increase in negative sensory attributes and a decrease in positive flavor attributes correlating with PV, AD, CD, and CT analysis. These

two studies laid foundation levels of correlation between sensory and chemical analysis of oxidation in peanuts.

In this study, correlation analysis was conducted to predict the changes in positive and negative flavor attributes in peanut butter treated with antioxidants using the analytical methods PV and SHGC quantification of hexanal (Table 3.1). Strong correlations between sensory and analytical data were defined by Lee and Resurrection as having an R^2 of 0.7 or greater. Good correlations between sensory and analytical data were defined by Nepote and others (2006) as having an R^2 of 0.6 or greater. These R^2 values are lower than what would be anticipated in an analytical correlation due to the inherent variability of sensory analysis. Based on this value of significance, PV was able to predict oxidation in at least one treatment for each of the five attributes (Table 3.1). PV was not able to strongly predict oxidation in samples treated with cocoa powder. This may be attributed to the ability of cocoa powder to mask both positive and negative flavor attributes in peanut butter. The control and tocopherol samples did not contain cocoa powder, and were able to correlate strongly. PV has been observed to positively correlate with rancidity and peanutty and negatively correlate with roasted peanutty (Abegaz and others 2004) (Figure 3.1).

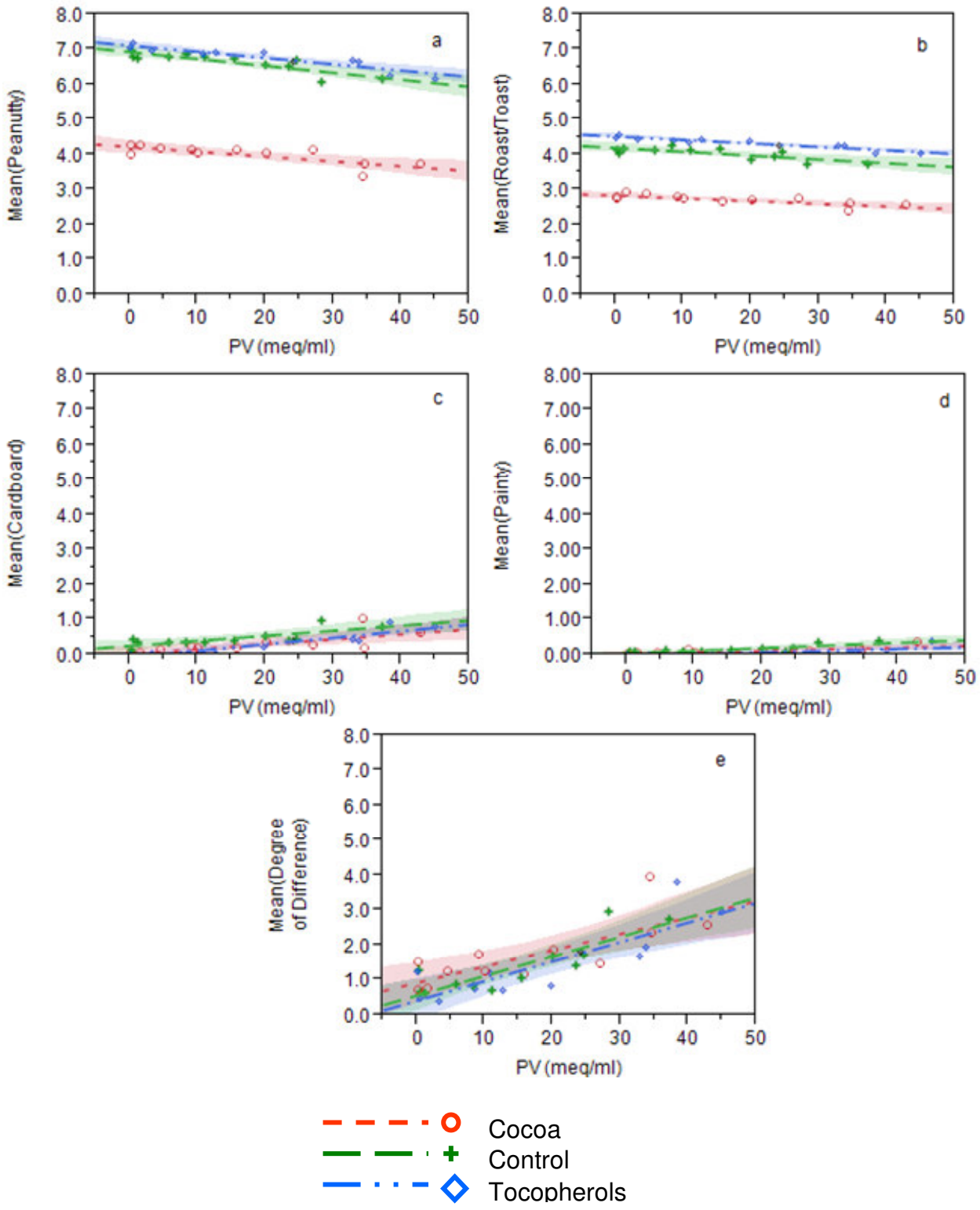

Figure 3.1 The ability of PV to predict peanutty (a), roast/toast (b), cardboard (c), painty (d), and degree of difference (e) in peanut butter.

Because PV measures colorless, odorless, and transient peroxides, it is not anticipated that PV would correlate with sensory analysis (Frankel 2005). The rate of oxidation observed by PV and sensory analysis observed in Chapter 2 appear to be capturing the log phase of oxidation. During this phase, both peroxides and secondary reaction products are being produced at an exponential rate. It can then be hypothesized that while PV and sensory correlated strongly in this study, it may be attributed to the aromatic secondary products being formed at that stage of oxidation rather than the peroxides themselves.

Hexanal was also utilized to predict the sensory perception of oxidation in peanuts butter (Figure 3.2). Because hexanal is an odiferous compound, it is anticipated that the presence of hexanal would correlate strongly to the perception of oxidized off flavors (Frankel 2005). The ability of hexanal to predict oxidation in peanut pastes in this study contradicts the findings of Abegaz and others (2004). In that study, hexanal did not significantly predict the development of oxidized flavors such as cardboard. This discrepancy was attributed to the diversity of secondary products formed as a result of the oxidation of linoleic acid. Although there are many secondary products formed during oxidation, hexanal has been observed in the highest concentrations which may have resulted in the correlation between hexanal and oxidation attributes in the control and tocopherol samples (Warner and others 1996). Grosso and Resurreccion (2002) have observed a correlation between overall consumer acceptability of peanut butter with hexanal concentrations. Hexanal was unable to predict oxidation flavors in the peanut butter treated with cocoa powder. The cocoa powder may have increased the level of other secondary oxidation compounds other than hexanal, or may have created a lower initial perception of pyrazines which created a lower overall perception of peanutty attributes.

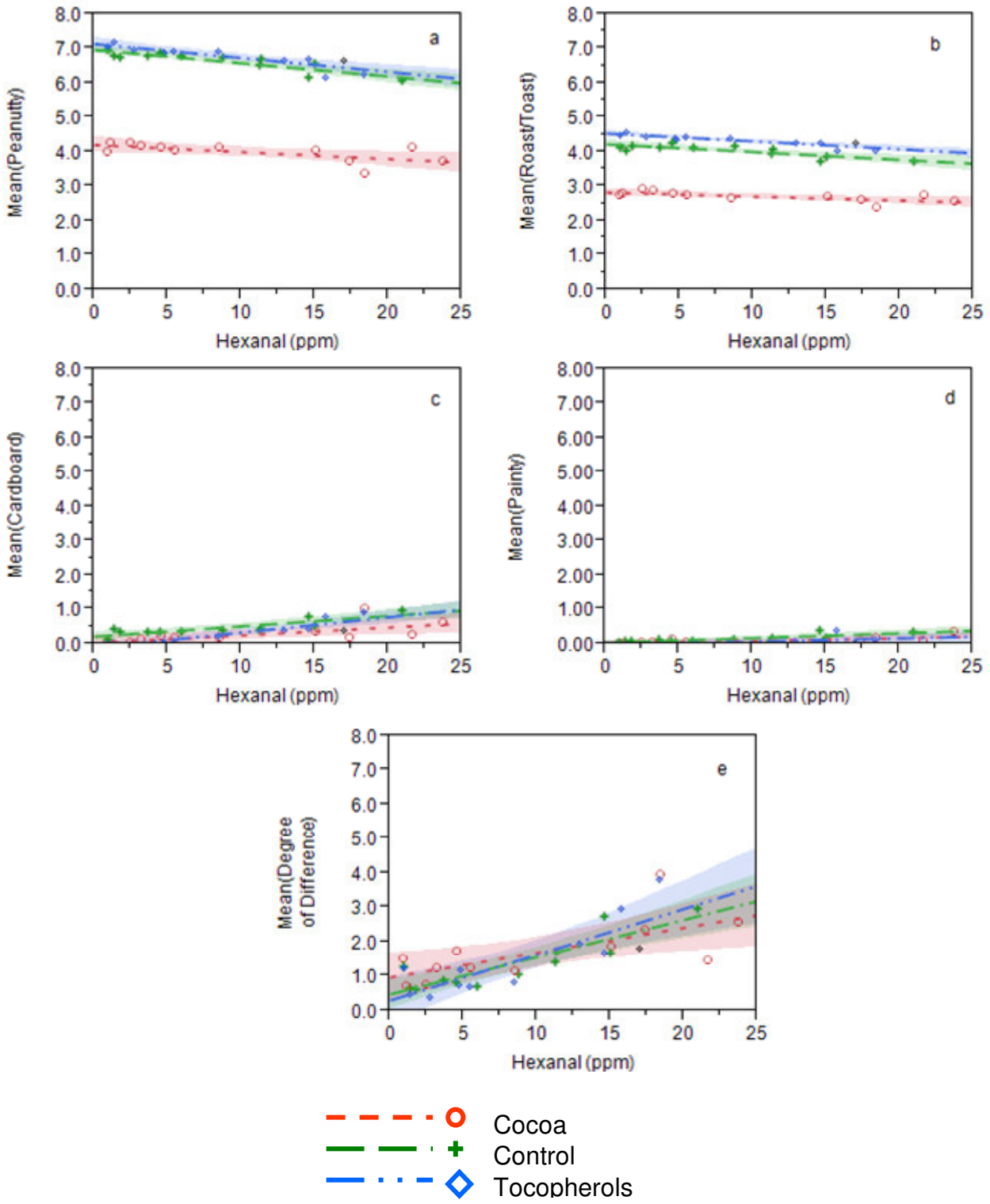

Figure 3.2 The ability of hexanal to predict peanutty (a), roast/toast (b), cardboard (c), painty (d), and degree of difference (e) in peanut butter.

Table 3.1 The R^2 values in the prediction of sensory attributes based on PV and hexanal.

		Peanutty	Roast/Toast	Cardboard	Painty	DOD
PV						
	Control	0.74*	0.55	0.59	0.72*	0.73*
	CP	0.58	0.62**	0.54	0.62**	0.61**
	Toco	0.85*	0.89*	0.83*	0.52	0.71*
Hexanal						
	Control	0.79*	0.66**	0.71*	0.68**	0.76*
	CP	0.41	0.47	0.47	0.55	0.46
	Toco	0.76*	0.82*	0.81*	0.33	0.69**

*denotes significant (very strong correlation) R^2 value based on Lee and Resurrection (2002).
** denotes significant (good correlation) R^2 value based on Nepote and others (2006).

The samples that were determined to have a significant correlation (Table 3.1) were used to determine how the change in 10 units of the analytical measure would change the sensory values (Table 3.2). It was observed that the peanutty and cardboard attributes were able to be well determined by PV and GC/FID of hexanal. These findings agree with those of Grosso and Resurreccion (2002) as well as Nepote and others (2009) that observed peanutty and cardboard to be the strongest correlated to analytical measure. The overall Degree of Difference (DOD) was also strongly predicted. Because this is a confounding sensory term, it is not often used. It can, however, give an idea of how much the sample has changed from its initial starting point which may impact consumer perception of oxidation.

Table 3.2 The change in sensory values for every 10-unit increase in PV and hexanal.

		Peanutty	Roast/Toast	Cardboard	Painty	DOD
PV						
	Control	-0.2	-	-	0.07	0.6
	CP	-	-0.07	-	0.04	0.5
	Toco	-0.2	-0.09	0.2	-	0.7
Hexanal						
	Control	-0.4	-0.2	0.3	0.1	1.1
	CP	-	-	0.2	-	-
	Toco	-0.2	-0.2	0.4	-	1.3

The ability to predict the change in sensory quantification of oxidized flavors based on analytical methods used in tandem with a consumer test may provide a powerful tool. This information may indicate the end point of consumer acceptance of a level of oxidation may be a very powerful tool to screen antioxidants in peanut systems. Future work is required to understand the ability of analytical methods to monitor oxidation in peanut products beyond peanut butter. Additionally, this tool could help to understand how various antioxidants may impact both the sensory and analytical observations of oxidation.

Conclusion

PV and SHGC quantification of hexanal were able to significantly predict the oxidation flavors, particularly peanutty and cardboard, observed by descriptive analysis in the control and tocopherol peanut butter samples. The analytical methods were not able to predict oxidation as strongly in the peanut butter treated with cocoa powder. As was observed in Chapter 2, the inclusion of cocoa powder adds a variety of flavors that may have impacted the ability of the descriptive panelists to observe the oxidation flavors. This study indicated that PV and GC/FID quantification of hexanal may be helpful tools in monitoring oxidation of peanut butter treated with tocopherols.

Future Studies

The ability of PV and GC/FID quantification of hexanal to predict sensory observation may serve as a tool to predict consumer acceptability. A large group analysis is required to understand the PV and hexanal levels at which the consumer no longer believes the product is acceptable for consumption. That information, in conjunction with the data observed in this study, may be able to predict consumer acceptability using PV and GC/FID quantification of hexanal.

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Appendix A Raw Data

Table A.1 The raw data of PV in peanuts.

	Peanuts								
	Control			Tocopherols			Cocoa Powder		
	1	2	3	1	2	3	1	2	3
1	1.516	1.467	1.421	1.322	1.235	1.404	0.66	0.69	0.663
2	2.305	2.21	2.251	2.958	2.898	3.086	1.666	1.714	1.685
3	3.718	3.994	4.028	4.803	5.229	4.956	3.496	3.181	3.159
4	5.917	5.553	5.482	6.847	6.847	7.071	3.306	3.418	3.522
5	7.324	7.517	7.764	9.091	9.086	9.367	5.013	4.891	4.77
6	9.033	8.589	8.246	11.65	10.93	11.345	5.619	5.374	5.341
8	12.05	12.34	12.324	15.644	15.754	15.864	7.289	6.461	6.791
10	15	15.085	15.114	19.724	19.418	19.225	7.856	7.862	7.843
13	16.824					22.755			
16	19.536					25.973			
19	24.035					29.659			
22	29.575					27.486			

Table A.2 The raw data of PV in peanut butter.

	Peanut Butter								
	Control			Tocopherols			Cocoa Powder		
	1	2	3	1	2	3	1	2	3
1	0.167	0.167	0.19	0.166	0.137	0.13	0.195	0.175	0.179
2	0.377	0.401	0.43	0.418	0.414	0.408	0.309	0.29	0.318
3	1.388	1.223	1.285	3.084	3.248	3.081	1.64	1.629	1.717
4	5.498	5.732	5.982	8.689	8.416	8.518	4.826	4.7	4.623
5	8.67	8.371	7.888	10.873	10.879	10.543	9.552	9.332	9.054
6	11.36	11.323	10.629	12.51	12.443	13.153	10.228	10.131	9.758
8	15.182	15.424	15.318	19.932	20.112	19.491	16.012	15.655	15.906
10	20.088	19.815	19.845	24.471	23.571	24.093	20.115	20.098	20.415
13	23.367					32.743			
16	24.468					33.678			
19	28.172					38.226			
22	37.087					44.859			

Table A.3 The raw data of PV in peanut oil.

	Peanut Oil								
	Control			Tocopherols			Cocoa Powder		
	1	2	3	1	2	3	1	2	3
1	0.44	0.451	0.435	0.444	0.429	0.478	0.485	0.476	0.474
2	0.532	0.488	0.571	0.541	0.576	0.591	0.522	0.529	0.536
3	0.753	0.74	0.759	0.702	0.697	0.698	0.664	0.667	0.628
4	0.78	0.841	0.834	0.79	0.801	0.804	0.691	0.602	0.639
5	0.937	0.984	0.958	0.865	0.768	0.857	0.825	0.697	0.782
6	1.074	1.041	1.037	1.009	0.993	0.995	0.904	0.911	0.899
8	1.481	1.477	1.516	1.294	1.31	1.314	1.242	1.222	1.228
10	2.134	2.115	2.152	2.033	2.047	2.048	1.642	1.641	1.612
13	3.133					3.042			
16	4.643					4.406			
19	6.081					6.081			
22	8.465					7.213			

Table A.4 The average PV of each vehicle per week.

	Overall Averages								
	Peanuts			Peanut Butter			Peanut Oil		
	Cont	Toco	CP	Cont	Toco	CP	Cont	Toco	CP
1	1.468	1.320	0.671	0.175	0.144	0.183	0.442	0.450	0.478
2	2.255	2.981	1.688	0.403	0.413	0.306	0.530	0.569	0.529
3	3.913	4.996	3.279	1.299	3.138	1.662	0.751	0.699	0.653
4	5.651	6.922	3.415	5.737	8.541	4.716	0.818	0.798	0.644
5	7.535	9.181	4.891	8.310	10.765	9.313	0.960	0.830	0.768
6	8.623	11.308	5.445	11.104	12.702	10.039	1.051	0.999	0.905
8	12.238	15.754	6.847	15.308	19.845	15.858	1.491	1.306	1.231
10	15.066	19.456	7.854	19.916	24.045	20.209	2.134	2.043	1.632
13	16.824	22.755	11.807	23.367	32.743	27.01	3.133	3.042	3.059
16	19.536	25.973	11.648	24.468	33.678	34.583	4.643	4.406	4.375
19	24.035	29.659	13.007	28.172	38.226	34.406	6.081	6.081	4.98
22	29.575	27.486	10.513	37.087	44.859	42.988	8.465	7.213	8.256

Table A.5 The raw hexanal data in peanuts.

	Peanuts								
	Control			Tocopherols			Cocoa Powder		
Weeks	1	2	3	1	2	3	1	2	3
1	2.27	2.268	2.034	1.658	1.164	1.655	1.669	1.56	1.56
2	2.51	2.685	2.778	2.595	2.93	2.639	2.301	2.467	2.37
3	3.304	3.633	3.493	3.224	3.472	3.459	2.97	3.17	3.428
4	4.635	5.76	4.647	4.26	5.107	4.86	3.764	3.451	3.44
5	4.295	6.724	4.518	4.695	4.992	5.04	3.354	3.586	3.895
6	4.991	5.092	5.571	5.136	5.43	5.845	3.621	3.751	4.024
8	7.491	7.458	7.167	8.002	9.242	9.186	4.598	5.812	4.633
10	8.994	9.506	8.7	9.306	10.76	9.064	5.141	5.402	5.317
13	8.702	8.787	12.29	10.777	10.61	12.649	6.159	6.505	6.484
16	9.282	10.383	10.386	11.36	12.85	11.24	5.512	5.818	
19	20.639	18.16	13.645	12.652	12.96	14.532	7.875	7.537	7.653
22	13.679	14.303	13.824	9.6	9.414	10.121	5.614	5.505	5.637

Table A.6 The raw hexanal data in peanut butter.

	Peanut Butter								
	Control			Tocopherols			Cocoa Powder		
Weeks	1	2	3	1	2	3	1	2	3
1	0.937	0.975	0.895	0.953	0.865	0.919	1.057	0.916	0.942
2	1.322	1.533	1.148	1.151	1.47	1.307	1.072	1.222	1.214
3	1.601	1.912	1.838	2.569	2.821	2.604	2.514		
4	3.618	3.767	3.606	4.473	4.889	4.777	3.096	3.184	3.354
5	4.691	4.253	4.455	4.956	4.994	4.474	4.557	4.576	4.683
6	5.493	5.98	6.197	4.402	5.899	5.842	5.34	5.551	5.722
8	8.245	9.161	8.735	8.747	8.493	7.926	8.833	8.194	
10	11.143	10.905	11.937	9.304	9.377	9.877	9.628	13.26	9.184
13	11.809	10.172	11.859	16.078	14.72	12.946	25.27	25.682	14.191
16	10.178	13.952	9.921	12.753	13.46	12.668	18.78	16.733	16.664
19	15.362	28.717	18.888	16.185	17.76	21.047	16.92	18.298	19.951
22	14.106	15.028	14.721	15.351	16.41	15.412	25.98	22.982	22.321

Table A.7 The raw hexanal data in peanut oil.

	Peanut Oil								
	Control			Tocopherols			Cocoa Powder		
Weeks	1	2	3	1	2	3	1	2	3
1	0.879	0.87	0.892	0.911	0.79	0.876	0.929	0.836	0.819
2	0.868	0.942	1.03	0.883	0.919	0.967		0.973	1.079
3		0.987	1.032	0.936	0.99	0.993	0.98		1.074
4	1.004	1.085	1.198		1.011	1.102	0.995	1.075	1.322
5	0.955	1.022	1.08	0.899	0.933	1.01	0.947	1.021	1.234
6	0.976	1.075	1.176	0.954	1.023	1.194	1.039	1.102	1.179
8	1.327	1.407	1.52	1.094	1.276	1.289	1.378	1.411	1.393
10	1.561	1.566	1.762	1.492	1.482	1.48	1.483	1.644	1.792
13	1.793	2.25	2.156	1.872	1.969	1.89	2.102	2.312	2.239
16	2.702	2.539	2.89	2.24	2.419	2.459	2.551	2.722	2.695
19	3.453	3.721	3.761	3.201	3.527	3.874	3.076	3.868	3.817
22	3.215	3.239	3.7	3.518	3.46	3.278	3.29	3.302	3.496

Table A.8 The average hexanal level of each vehicle per week.

	Overall Averages (Hexanal)								
	Peanuts			Peanut Butter			Peanut Oil		
	Cont	Toco	CP	Cont	Toco	CP	Cont	Toco	CP
1	2.191	1.492	1.596	0.936	0.912	0.972	0.880	0.859	0.861
2	2.658	2.721	2.379	1.334	1.309	1.169	0.947	0.923	1.026
3	3.477	3.385	3.189	1.784	2.665	2.514	1.0095	0.973	1.027
4	5.014	4.742	3.552	3.664	4.713	3.211	1.096	1.057	1.131
5	5.179	4.909	3.612	4.466	4.808	4.605	1.019	0.947	1.067
6	5.218	5.470	3.799	5.890	5.381	5.538	1.076	1.057	1.107
8	7.372	8.810	5.014	8.714	8.389	8.514	1.418	1.220	1.394
10	9.067	9.709	5.287	11.328	9.519	10.691	1.630	1.485	1.640
13	9.926	11.344	6.383	11.280	14.580	21.714	2.066	1.910	2.218
16	10.017	11.817	5.665	11.350	12.959	17.392	2.710	2.373	2.656
19	17.481	13.383	7.688	20.989	18.330	18.390	3.645	3.534	3.587
22	13.935	9.712	5.585	14.618	15.723	23.762	3.385	3.419	3.363

Table A.9 The average sensory responses of each vehicle per week.

Vehicle	Treatment	Temp	Weeks	Peanutty	Roast/Toast	Cardboard	Painty	DoD
PB	CP	0	1	4.2	2.69	0	0	1.54
PB	CP	0	2	4.23	3	0.01	0.04	0.83
PB	CP	0	3	4.08	2.91	0.21	0.1	1
PB	CP	0	4	4.26	2.9	0.05	0.04	0.81
PB	CP	0	5	4.19	2.81	0.1	0.09	1.43
PB	CP	0	6	4.24	2.88	0.07	0.08	1.05
PB	CP	0	8	4.19	2.86	0.2	0.02	1.11
PB	CP	0	10	4.17	2.79	0.28	0.07	1.69
PB	CP	0	13	4.07	2.83	0.11	0.13	1.69

PB	CP	0	16	3.86	2.62	0.22	0.07	2.1
PB	CP	0	19	4	2.83	0.3	0.12	2.47
PB	CP	0	22	4.08	2.81	0.37	0.11	1.89
PB	CP	90	1	3.98	2.74	0.05	0	1.49
PB	CP	90	2	4.26	2.79	0	0.02	0.73
PB	CP	90	3	4.25	2.91	0.05	0.05	0.76
PB	CP	90	4	4.19	2.89	0.11	0.05	1.25
PB	CP	90	5	4.15	2.82	0.21	0.12	1.73
PB	CP	90	6	4.06	2.76	0.18	0.07	1.25
PB	CP	90	8	4.15	2.66	0.17	0.05	1.16
PB	CP	90	10	4.04	2.7	0.34	0.11	1.87
PB	CP	90	13	4.13	2.78	0.25	0.1	1.45
PB	CP	90	16	3.72	2.61	0.16	0.07	2.37
PB	CP	90	19	3.36	2.41	1	0.18	3.94
PB	CP	90	22	3.73	2.57	0.62	0.34	2.59
PB	Control	0	1	6.91	4.23	0.17	0.06	1.24
PB	Control	0	2	6.81	4.3	0.47	0.1	0.76
PB	Control	0	3	6.89	4.2	0.3	0.1	0.39
PB	Control	0	4	6.9	4.19	0.31	0.08	0.73
PB	Control	0	5	6.83	4.3	0.3	0.08	1.28
PB	Control	0	6	6.87	4.17	0.32	0.08	0.51
PB	Control	0	8	6.79	4.21	0.37	0.1	0.75
PB	Control	0	10	6.74	4.03	0.41	0.11	1.1
PB	Control	0	13	6.71	4.08	0.51	0.1	1.57
PB	Control	0	16	6.83	4.15	0.34	0.15	0.98
PB	Control	0	19	6.67	4.06	0.44	0.14	1.18
PB	Control	0	22	6.58	4.08	0.44	0.14	0.91
PB	Control	90	1	6.99	4.12	0.14	0.05	1.29
PB	Control	90	2	6.82	4.06	0.47	0.09	0.67
PB	Control	90	3	6.78	4.18	0.35	0.08	0.61
PB	Control	90	4	6.8	4.14	0.34	0.11	0.88
PB	Control	90	5	6.87	4.27	0.37	0.09	0.85
PB	Control	90	6	6.8	4.13	0.37	0.08	0.69
PB	Control	90	8	6.74	4.19	0.38	0.13	1.09
PB	Control	90	10	6.58	3.88	0.52	0.17	1.67
PB	Control	90	13	6.55	3.97	0.42	0.09	1.43
PB	Control	90	16	6.7	4.11	0.47	0.2	1.75

PB	Control	90	19	6.08	3.72	1	0.35	2.98
PB	Control	90	22	6.16	3.75	0.81	0.39	2.78
PB	Toco	0	1	7	4.47	0	0	1.16
PB	Toco	0	2	7.17	4.6	0.05	0.02	0.6
PB	Toco	0	3	7	4.53	0.02	0	0.49
PB	Toco	0	4	6.98	4.44	0.02	0	0.83
PB	Toco	0	5	7.04	4.56	0.01	0	0.72
PB	Toco	0	6	6.99	4.44	0.06	0	1.21
PB	Toco	0	8	6.99	4.43	0.08	0	0.47
PB	Toco	0	10	6.89	4.39	0.21	0.04	0.84
PB	Toco	0	13	6.88	4.44	0.21	0.01	1.04
PB	Toco	0	16	6.82	4.39	0.24	0.02	1.27
PB	Toco	0	19	6.75	4.4	0.29	0.11	1.58
PB	Toco	0	22	6.89	4.51	0.19	0.03	0.85
PB	Toco	90	1	7.05	4.5	0.01	0	1.27
PB	Toco	90	2	7.18	4.57	0.06	0.02	0.48
PB	Toco	90	3	6.99	4.46	0.05	0.01	0.42
PB	Toco	90	4	6.91	4.42	0.03	0	0.75
PB	Toco	90	5	6.9	4.37	0.07	0.02	1.22
PB	Toco	90	6	6.95	4.44	0.07	0	0.71
PB	Toco	90	8	6.95	4.38	0.21	0.01	0.87
PB	Toco	90	10	6.68	4.29	0.41	0.06	1.82
PB	Toco	90	13	6.71	4.27	0.43	0.03	1.68
PB	Toco	90	16	6.67	4.26	0.41	0.1	1.95
PB	Toco	90	19	6.28	4.05	0.95	0.12	3.81
PB	Toco	90	22	6.19	4.06	0.79	0.39	2.96

Table A.10 The raw sensory data of peanut butter control samples

			Peanutty		Roast/Toast		Cardboard		Painty		DoD	
Wks	**Pnlt**	**Reps**	**0**	**90**	**0**	**90**	**0**	**90**	**0**	**90**	**0**	**90**
1	1	1	7.1	6.8	4.4	4.0	0.0	0.0	0.0	0.0	1.1	1.6
1	1	2	6.5	7.1	4.9	4.9	0.0	0.0	0.0	0.0	2.5	2.3
1	2	1	6.7	6.9	3.8	3.8	0.0	0.0	0.0	0.0	0.6	0.6
1	2	2	6.6	6.8	4.1	3.7	0.2	0.4	0.0	0.0	0.8	1.6
1	3	1	7.3	6.7	4.5	3.4	0.0	0.0	0.0	0.0	1.9	2.0
1	3	2	7.0	7.1	4.5	4.5	0.6	0.0	0.0	0.0	2.8	2.3
1	4	1	6.9	7.1	4.1	3.8	0.4	0.5	0.2	0.1	0.2	1.4
1	4	2	7.6	7.1	3.7	4.1	0.2	0.2	0.1	0.1	1.2	1.5
1	5	1	5.8	6.9	3.3	3.7	0.7	0.2	0.2	0.1	3.0	1.1
1	5	2	6.9	6.7	3.5	3.6	0.2	0.2	0.2	0.2	1.2	0.8
1	6	1	7.2	6.8	4.3	4.5	0.4	0.4	0.2	0.2	0.5	1.0

1	6	2	7.1	7.1	4.1	4.5	0.2	0.2	0.1	0.1	2.5	2.1
1	7	1	7.0	6.9	4.3	4.3	0.2	0.2	0.1	0.1	0.2	0.0
1	7	2	6.6	6.7	4.1	3.8	0.2	0.2	0.1	0.2	0.4	0.4
1	8	1	6.2	7.1	5.1	3.3	0.0	0.0	0.0	0.0	2.7	1.0
1	8	2	7.0	7.9	4.0	5.3	0.0	0.0	0.0	0.0	0.0	3.2
1	9	1	7.7	7.5	4.8	4.9	0.0	0.0	0.1	0.1	0.4	0.4
1	9	2	7.4	6.9	4.9	4.1	0.0	0.2	0.2	0.1	0.4	0.0
2	1	1	5.8	7.1	4.9	4.2	0.2	0.2	0.0	0.0	0.0	0.0
2	1	2	6.3	7.1	4.7	4.3	0.2	0.4	0.0	0.0	0.0	0.0
2	2	1	7.2	6.9	4.4	3.9	0.3	0.3	0.2	0.1	0.0	0.0
2	2	2	6.8	6.7	4.1	3.9	0.3	0.5	0.1	0.1	0.0	0.0
2	3	1	7.1	7.2	4.2	4.3	0.3	0.3	0.1	0.1	1.2	1.3
2	3	2	7.1	7.2	4.3	4.2	0.3	0.3	0.1	0.1	1.8	2.0
2	4	1	7.1	6.2	4.5	3.5	0.4	0.4	0.2	0.3	3.7	2.7
2	4	2	7.3	7.1	4.4	4.3	0.2	0.4	0.3	0.2	2.3	1.3
2	5	1	6.2	6.2	3.7	3.6	0.8	0.8	0.1	0.1	1.8	1.0
2	5	2	6.9	6.9	4.2	3.8	0.3	0.6	0.1	0.1	0.0	1.0
2	7	1	7.1	7.1	4.3	4.3	0.3	0.3	0.1	0.1	0.9	0.9
2	7	2	6.9	6.7	4.2	3.9	0.3	0.3	0.1	0.1	0.0	0.0
2	8	1	6.4	6.7	3.5	3.8	2.6	1.7	0.2	0.2	0.0	0.0
2	8	2	7.3	6.8	4.6	4.2	0.3	0.3	0.2	0.1	0.0	0.0
2	9	1	6.8	6.9	4.3	4.4	0.3	0.3	0.2	0.1	0.3	0.2
2	9	2	6.8	6.8	4.4	4.5	0.3	0.3	0.1	0.1	0.3	0.4
3	1	1	6.8	7.3	4.1	5.0	0.2	0.2	0.1	0.1	0.2	1.4
3	1	2	7.1	6.8	4.3	4.6	0.3	0.2	0.1	0.1	0.3	0.9
3	2	1	6.8	6.7	3.9	4.0	0.3	0.3	0.1	0.1	0.0	0.0
3	2	2	6.9	6.4	4.3	3.8	0.3	0.3	0.1	0.1	0.0	0.0
3	3	1	7.1	7.3	4.1	4.3	0.4	0.3	0.1	0.1	0.0	0.0
3	3	2	7.2	7.2	4.5	4.4	0.3	0.3	0.1	0.1	0.0	0.0
3	4	1	7.1	6.4	4.5	4.3	0.2	0.4	0.2	0.2	1.6	2.8
3	4	2	6.8	6.3	4.3	3.8	0.6	0.6	0.3	0.2	4.1	3.8
3	5	1	6.7	6.3	3.8	3.9	0.3	0.3	0.1	0.1	0.0	0.8
3	5	2	6.9	6.9	4.2	4.2	0.3	0.3	0.1	0.1	0.0	0.0
3	6	1	7.0	6.6	4.3	3.9	0.0	0.8	0.1	0.0	0.0	0.0
3	6	2	6.8	6.8	4.2	4.0	0.3	0.3	0.2	0.1	0.0	0.0
3	7	1	7.1	7.1	4.3	4.3	0.3	0.3	0.1	0.1	0.0	0.0
3	7	2	7.1	6.8	4.3	4.1	0.3	0.4	0.1	0.1	0.0	0.0
3	8	1	6.5	6.9	4.2	4.2	0.3	0.3	0.1	0.2	0.0	0.0
3	8	2	6.8	6.9	4.1	4.2	0.3	0.3	0.1	0.1	0.0	0.0
4	1	1	6.7	7.0	4.4	4.3	0.3	0.3	0.1	0.1	0.2	0.2
4	1	2	7.3	7.1	4.3	4.3	0.3	0.3	0.2	0.1	0.5	0.2
4	2	1	6.9	6.9	4.0	4.2	0.3	0.3	0.1	0.1	0.3	0.2
4	2	2	6.9	6.9	4.1	4.0	0.3	0.3	0.1	0.1	0.2	0.2
4	3	1	7.3	6.9	4.3	4.5	0.3	0.3	0.1	0.1	2.2	2.0
4	3	2	6.5	6.8	3.8	4.0	0.3	0.3	0.1	0.1	2.8	2.3
4	4	1	7.1	6.8	4.3	4.1	0.2	0.4	0.1	0.2	0.8	1.5
4	4	2	6.8	6.8	3.7	4.0	0.4	0.4	0.2	0.4	1.8	1.4
4	5	1	6.9	6.9	4.2	3.8	0.3	0.3	0.1	0.1	0.0	0.4
4	5	2	6.4	6.5	3.8	3.9	0.3	0.3	0.1	0.1	0.8	0.8
4	6	1	6.9	6.8	4.3	4.0	0.3	0.4	0.1	0.1	0.3	1.0

4	6	2	7.1	6.1	4.2	4.0	0.2	0.4	0.0	0.2	1.4	4.3
4	7	1	7.1	6.9	4.3	4.1	0.3	0.4	0.1	0.1	0.3	0.4
4	7	2	7.1	6.9	4.5	4.2	0.3	0.3	0.1	0.1	0.5	0.0
4	8	1	6.9	7.1	4.2	4.3	0.3	0.3	0.1	0.2	0.0	0.3
4	8	2	7.1	6.9	4.3	4.5	0.3	0.3	0.1	0.1	0.4	0.4
4	9	1	6.7	6.6	4.4	4.4	0.4	0.4	0.1	0.2	0.5	0.4
4	9	2	6.8	6.9	4.3	4.2	0.4	0.3	0.1	0.1	0.2	0.0
5	1	1	7.1	7.1	4.7	4.4	0.3	0.3	0.0	0.0	0.0	0.0
5	1	2	6.8	7.1	4.5	4.2	0.4	0.3	0.0	0.0	0.3	0.2
5	2	1	6.9	6.8	4.4	4.3	0.3	0.3	0.1	0.1	0.4	0.2
5	2	2	6.9	7.1	4.0	4.4	0.3	0.3	0.1	0.1	0.3	0.4
5	3	1	6.6	6.9	4.1	4.3	0.3	0.3	0.1	0.1	2.3	1.8
5	3	2	7.1	6.9	4.3	4.1	0.3	0.6	0.1	0.1	0.8	2.6
5	4	1	6.7	7.7	4.5	4.6	0.5	0.2	0.3	0.2	4.0	1.1
5	4	2	7.5	6.4	4.4	4.1	0.2	0.6	0.1	0.4	1.0	2.8
5	5	1	6.4	6.9	3.8	4.1	0.3	0.3	0.1	0.2	1.4	0.0
5	5	2	6.6	6.7	4.0	3.9	0.3	0.3	0.1	0.1	0.6	0.4
5	6	1	7.0	7.0	4.3	4.4	0.2	0.3	0.0	0.1	4.2	1.6
5	6	2	7.0	6.8	4.3	4.3	0.2	0.4	0.0	0.1	4.6	1.3
5	7	1	7.1	7.1	4.3	4.4	0.3	0.3	0.1	0.1	0.3	0.3
5	7	2	7.1	7.0	4.5	4.3	0.3	0.3	0.1	0.1	0.4	0.2
5	8	1	6.9	6.4	4.2	4.0	0.3	0.9	0.1	0.1	0.0	1.3
5	8	2	6.7	6.9	4.2	4.2	0.3	0.3	0.2	0.1	0.8	0.0
5	9	1	6.5	6.6	4.5	4.4	0.3	0.3	0.2	0.1	0.8	0.6
5	9	2	6.2	6.6	4.7	4.4	0.3	0.3	0.2	0.1	1.0	0.5
6	1	1	6.8	6.8	4.1	4.3	0.3	0.3	0.1	0.1	0.2	0.2
6	1	2	7.0	6.8	4.3	4.3	0.3	0.3	0.1	0.1	0.2	0.2
6	2	1	6.9	6.9	4.4	4.3	0.3	0.3	0.1	0.1	0.3	0.3
6	2	2	6.9	6.9	4.3	4.3	0.3	0.3	0.1	0.2	0.4	0.3
6	3	1	6.8	7.1	4.1	4.3	0.3	0.3	0.1	0.1	1.1	1.8
6	3	2	7.1	6.6	4.3	3.7	0.3	0.9	0.1	0.1	1.8	2.9
6	4	1	6.7	6.8	4.1	4.1	0.3	0.5	0.1	0.1	0.7	1.0
6	4	2	6.8	6.8	4.1	4.1	0.4	0.4	0.2	0.1	1.4	1.0
6	5	1	6.7	6.9	3.8	4.2	0.3	0.3	0.1	0.1	0.4	0.0
6	5	2	6.9	6.8	4.2	4.0	0.3	0.3	0.1	0.1	0.0	0.3
6	6	1	6.9	6.8	4.1	4.1	0.4	0.3	0.1	0.1	0.4	0.2
6	6	2	6.9	6.7	4.2	3.9	0.3	0.4	0.1	0.1	0.0	1.6
6	7	1	7.1	6.8	4.3	4.2	0.3	0.3	0.1	0.2	0.5	0.2
6	7	2	6.8	6.8	4.0	4.1	0.3	0.3	0.1	0.1	0.6	0.4
6	8	1	6.9	6.8	4.2	4.2	0.3	0.3	0.1	0.1	0.0	0.2
6	8	2	7.1	6.9	4.2	4.2	0.3	0.3	0.1	0.1	0.3	0.5
8	1	1	6.8	6.8	4.1	4.4	0.3	0.3	0.1	0.1	0.2	0.2
8	1	2	6.8	6.9	4.4	4.1	0.3	0.4	0.1	0.2	0.2	0.2
8	2	1	6.9	6.9	4.3	4.3	0.3	0.3	0.1	0.1	0.2	0.3
8	2	2	6.8	6.8	4.1	4.2	0.3	0.3	0.1	0.1	0.4	0.2
8	3	1	7.2	7.2	4.4	4.5	0.3	0.3	0.1	0.1	1.5	1.2
8	3	2	7.1	6.9	4.3	4.3	0.3	0.3	0.1	0.2	1.8	0.8
8	4	1	6.6	6.6	4.5	4.0	0.8	0.5	0.2	0.2	1.1	0.7
8	4	2	7.2	6.2	4.6	3.9	0.2	0.4	0.2	0.6	1.4	4.8
8	5	1	6.7	6.9	3.8	4.2	0.5	0.3	0.1	0.1	0.8	0.0

8	5	2	6.5	6.8	3.9	3.8	0.3	0.3	0.1	0.1	0.4	0.6
8	6	1	7.0	6.4	4.2	4.4	0.3	0.7	0.1	0.1	0.4	2.7
8	6	2	6.6	6.8	4.0	4.2	0.5	0.4	0.1	0.2	2.3	3.5
8	7	1	6.9	6.8	4.2	4.1	0.3	0.3	0.1	0.1	0.0	0.8
8	7	2	7.1	7.1	4.3	4.3	0.3	0.3	0.1	0.1	0.4	0.5
8	8	1	6.7	6.7	4.0	4.1	0.8	0.6	0.2	0.2	0.5	1.1
8	8	2	6.7	6.8	4.0	4.2	0.3	0.5	0.2	0.1	0.6	0.5
8	9	1	6.4	6.6	4.4	4.2	0.3	0.3	0.1	0.1	0.6	0.8
8	9	2	6.6	6.6	4.3	4.3	0.3	0.3	0.1	0.2	0.5	0.7
10	1	1	6.8	6.8	4.0	4.0	0.4	0.4	0.1	0.1	0.2	0.2
10	1	2	6.8	6.5	4.0	3.9	0.4	0.4	0.1	0.2	0.2	0.4
10	2	1	6.9	6.9	4.3	4.4	0.3	0.3	0.1	0.2	0.4	0.0
10	2	2	6.9	6.6	3.8	3.8	0.4	0.7	0.1	0.1	1.0	2.0
10	3	1	7.2	6.8	4.5	4.1	0.3	0.8	0.1	0.1	2.5	1.7
10	3	2	6.9	6.9	4.5	4.5	0.3	0.3	0.1	0.1	3.1	2.5
10	4	1	6.4	5.9	4.1	3.7	0.8	1.0	0.3	0.4	3.1	3.8
10	4	2	6.7	6.0	4.0	3.2	0.6	0.9	0.2	1.0	1.2	4.1
10	5	1	6.5	6.6	3.7	3.8	0.8	0.5	0.2	0.1	1.5	1.0
10	5	2	6.9	6.8	4.2	4.0	0.3	0.3	0.1	0.1	0.0	0.6
10	6	1	6.7	6.6	3.8	3.9	0.4	0.4	0.2	0.1	1.7	3.2
10	6	2	6.9	6.4	4.2	3.8	0.3	0.6	0.1	0.2	0.0	5.3
10	7	1	6.8	6.8	4.2	4.1	0.3	0.3	0.1	0.1	0.0	0.7
10	7	2	6.8	6.7	3.8	4.0	0.3	0.3	0.2	0.1	1.5	1.1
10	8	1	6.6	6.4	3.8	3.1	0.3	1.0	0.1	0.1	1.4	2.6
10	8	2	6.7	6.9	4.2	4.2	0.3	0.3	0.1	0.1	0.7	0.0
10	9	1	6.7	6.6	3.9	3.9	0.3	0.4	0.1	0.2	0.4	0.5
10	9	2	6.5	6.6	3.8	3.8	0.6	0.4	0.2	0.2	0.9	0.5
13	1	1	6.5	6.6	3.9	4.5	0.5	0.3	0.2	0.1	0.5	0.4
13	1	2	7.3	6.6	3.8	4.5	0.3	0.3	0.1	0.2	0.4	0.4
13	3	1	6.9	6.0	4.5	3.5	0.3	0.6	0.1	0.1	2.0	2.5
13	3	2	6.4	6.5	3.5	3.9	0.3	0.5	0.1	0.1	2.6	2.8
13	4	1	6.6	6.6	4.3	3.8	0.3	0.6	0.2	0.2	2.7	2.7
13	4	2	7.1	6.1	4.4	3.5	0.5	0.8	0.2	0.2	1.7	4.1
13	5	1	6.1	6.4	3.6	3.8	2.4	0.3	0.1	0.1	2.3	1.5
13	5	2	6.7	6.5	3.8	3.8	0.3	0.3	0.2	0.2	0.6	1.0
13	6	1	7.0	7.1	4.4	4.2	0.3	0.3	0.1	0.1	2.7	1.4
13	6	2	6.8	6.7	4.2	4.2	0.4	0.4	0.2	0.1	5.4	2.7
13	7	1	6.5	6.6	3.8	4.0	0.8	0.6	0.1	0.1	2.5	0.8
13	7	2	6.9	6.8	4.2	4.0	0.3	0.4	0.1	0.1	0.0	0.7
13	8	1	6.7	6.4	4.2	3.5	0.3	0.4	0.1	0.1	0.3	0.9
13	8	2	6.7	6.7	4.0	3.9	0.3	0.3	0.1	0.1	0.3	0.3
13	9	1	6.8	6.7	4.5	4.5	0.3	0.3	0.1	0.1	0.6	0.4
13	9	2	6.8	6.8	4.2	4.2	0.4	0.3	0.1	0.1	0.4	0.2
16	1	1	7.1	7.3	3.9	4.4	0.4	0.3	0.2	0.2	0.3	0.4
16	1	2	6.6	6.6	3.8	3.8	0.4	0.4	0.2	0.2	0.4	0.3
16	3	1	7.1	6.7	4.5	3.8	0.3	0.6	0.1	0.1	2.4	2.3
16	3	2	6.8	6.7	3.9	3.9	0.3	0.7	0.1	0.1	1.3	1.9
16	4	1	7.0	6.6	3.8	4.2	0.5	0.4	0.7	0.2	1.5	0.8
16	4	2	6.8	6.3	4.4	4.1	0.4	0.8	0.2	1.1	0.6	2.2
16	6	1	6.8	6.9	4.2	4.2	0.4	0.3	0.1	0.2	2.4	5.1

16	6	2	6.9	6.9	4.2	4.0	0.3	0.6	0.1	0.1	0.0	5.5
16	7	1	6.6	6.4	3.9	3.8	0.3	0.3	0.2	0.2	0.8	1.1
16	7	2	7.1	6.9	4.3	4.2	0.0	0.3	0.1	0.1	1.1	0.0
16	9	1	6.7	6.7	4.4	4.5	0.3	0.3	0.1	0.1	0.5	0.6
16	9	2	6.7	6.5	4.5	4.4	0.3	0.6	0.2	0.1	0.4	0.9
19	3	1	6.7	6.1	3.9	3.2	0.3	1.5	0.1	0.1	0.9	4.1
19	3	2	6.5	4.5	3.8	2.7	0.6	2.3	0.1	0.1	1.6	4.8
19	4	1	6.5	6.6	3.8	3.9	0.5	0.6	0.3	0.4	1.7	0.9
19	4	2	6.4	6.3	3.6	4.1	1.1	1.1	0.6	0.7	1.6	2.5
19	5	1	6.9	6.6	4.4	3.8	0.3	0.6	0.1	0.2	0.4	1.0
19	5	2	6.9	6.8	4.2	4.0	0.3	0.3	0.1	0.2	0.0	0.4
19	6	1	7.1	6.8	4.2	4.1	0.3	0.4	0.1	0.2	0.8	5.8
19	6	2	6.7	6.9	3.9	4.3	0.4	0.4	0.1	0.1	4.4	3.3
19	7	1	6.7	4.9	3.9	2.7	0.3	2.1	0.1	1.0	0.5	5.6
19	7	2	6.4	4.8	4.0	2.7	0.4	2.0	0.1	1.3	1.0	5.0
19	9	1	6.8	6.3	4.4	4.6	0.3	0.3	0.1	0.1	0.3	1.3
19	9	2	6.6	6.4	4.6	4.6	0.3	0.3	0.2	0.1	0.8	1.0
22	1	1	6.2	6.6	3.8	3.7	0.6	0.6	0.2	0.3	0.5	0.5
22	1	2	6.7	6.6	4.3	3.9	0.3	0.4	0.2	0.2	0.2	0.3
22	3	1	5.1	6.2	3.7	3.5	0.8	1.2	0.1	0.1	3.4	3.0
22	3	2	6.9	3.8	4.2	2.5	0.3	2.1	0.1	0.3	0.0	5.0
22	4	1	6.4	6.2	3.8	3.6	0.8	1.0	0.2	0.5	0.9	2.7
22	4	2	6.4	5.8	3.9	3.8	1.0	1.2	0.4	0.8	1.9	4.1
22	5	1	6.9	6.4	4.2	3.6	0.3	0.3	0.1	0.0	0.0	1.6
22	5	2	6.9	6.9	4.4	3.9	0.3	0.7	0.1	0.1	0.5	0.6
22	6	1	6.9	6.7	4.2	4.2	0.3	0.4	0.1	0.5	0.0	5.7
22	6	2	6.5	5.8	4.0	3.8	0.3	0.4	0.2	0.6	4.3	7.0
22	7	1	6.6	5.2	3.9	3.2	0.3	1.3	0.1	0.1	0.6	4.5
22	7	2	6.7	5.9	3.9	3.7	0.3	0.3	0.1	2.0	0.5	5.0
22	8	1	6.9	6.9	4.2	3.8	0.5	1.3	0.1	0.4	0.4	1.7
22	8	2	6.7	6.4	4.0	3.7	0.3	1.2	0.1	0.1	0.7	1.4
22	9	1	6.8	6.6	4.3	4.5	0.3	0.3	0.1	0.1	0.2	0.6
22	9	2	6.7	6.6	4.5	4.6	0.3	0.3	0.1	0.1	0.5	0.7

Table A.11 The raw sensory data of peanut butter samples treated with cocoa powder.

			Peanutty		**Roast/Toast**		**Cardboard**		**Painty**		**DoD**	
Weeks	**Panelist**	**Reps**	**0**	**90**	**0**	**90**	**0**	**90**	**0**	**90**	**0**	**90**
1	1	1	3.6	3.6	2.5	2.4	0.0	0.0	0.0	0.0	1.4	1.5
1	1	2	4.3	4.1	3.1	2.6	0.0	0.0	0.0	0.0	2.2	2.4
1	3	1	4.4	4.7	2.1	3.2	0.0	0.0	0.0	0.0	1.4	1.4
1	3	2	4.5	4.6	3.0	3.2	0.0	0.7	0.0	0.0	2.6	3.2
1	4	1	3.1	2.6	2.2	2.8	0.0	0.0	0.0	0.0	2.5	2.6
1	4	2	3.8	2.6	2.3	2.0	0.0	0.0	0.0	0.0	4.2	4.7
1	5	1	3.8	4.0	2.4	2.7	0.0	0.0	0.0	0.0	0.7	0.2
1	5	2	3.7	3.5	2.0	2.0	0.0	0.0	0.0	0.0	1.4	1.6
1	6	1	4.6	3.8	2.8	2.5	0.0	0.0	0.0	0.0	0.6	0.4
1	6	2	3.8	3.9	2.9	3.1	0.0	0.0	0.0	0.0	2.0	1.5
1	7	1	4.6	4.3	2.8	2.8	0.0	0.0	0.0	0.0	0.4	0.2
1	7	2	4.7	4.5	2.8	2.7	0.0	0.0	0.0	0.0	0.2	0.2
1	8	1	5.0	4.7	3.4	3.0	0.0	0.0	0.0	0.0	1.2	0.2

1	8	2	4.9	4.9	3.5	3.5	0.0	0.0	0.0	0.0	0.8	0.9
2	1	1	4.1	4.1	3.1	3.1	0.0	0.0	0.0	0.0	1.0	1.0
2	1	2	4.2	4.4	3.0	2.8	0.0	0.0	0.0	0.0	0.4	0.2
2	2	1	4.3	4.1	2.7	2.5	0.0	0.0	0.0	0.0	0.0	0.0
2	2	2	4.3	4.7	3.2	2.8	0.0	0.0	0.0	0.0	0.0	0.0
2	3	1	4.7	4.5	3.2	3.0	0.0	0.0	0.0	0.0	2.4	1.5
2	3	2	4.4	4.4	3.0	3.0	0.0	0.0	0.0	0.0	1.2	1.0
2	4	1	3.9	4.2	3.2	2.8	0.0	0.0	0.4	0.0	2.4	0.2
2	4	2	4.2	4.1	3.1	2.5	0.2	0.0	0.3	0.3	2.7	1.2
2	5	1	4.1	3.7	2.7	2.4	0.0	0.0	0.0	0.0	0.4	1.6
2	5	2	4.3	4.3	2.8	2.6	0.0	0.0	0.0	0.0	0.0	0.4
2	7	1	4.5	4.1	2.9	2.7	0.0	0.0	0.0	0.0	0.0	0.0
2	7	2	4.0	4.1	2.7	2.7	0.0	0.0	0.0	0.0	0.0	0.0
2	8	1	4.3	3.9	2.8	2.7	0.0	0.0	0.0	0.0	0.7	2.3
2	8	2	3.8	4.9	3.8	3.4	0.0	0.0	0.0	0.0	2.0	2.2
2	9	1	4.3	4.3	2.9	2.8	0.0	0.0	0.0	0.0	0.0	0.0
2	9	2	4.3	4.2	2.8	2.8	0.0	0.0	0.0	0.0	0.0	0.1
3	1	1	4.1	4.1	3.1	3.1	0.0	0.0	0.0	0.0	0.7	0.6
3	1	2	4.2	4.5	2.7	3.1	0.0	0.0	0.0	0.0	0.3	0.4
3	2	1	4.3	4.1	2.7	2.8	0.0	0.0	0.0	0.0	0.0	1.6
3	2	2	4.3	4.1	3.1	2.8	0.0	0.0	0.0	0.0	0.3	0.4
3	3	1	4.5	4.5	3.2	3.0	0.0	0.0	0.0	0.0	0.0	0.0
3	3	2	4.1	4.6	2.7	3.2	0.3	0.0	0.0	0.0	1.5	1.0
3	4	1	4.5	4.3	2.7	2.7	0.1	0.0	0.1	0.0	2.2	1.0
3	4	2	4.4	4.4	3.0	2.8	0.0	0.0	0.3	0.0	2.3	0.1
3	5	1	3.9	4.3	2.6	2.6	0.6	0.0	0.0	0.5	1.1	0.9
3	5	2	3.9	4.3	2.5	3.2	0.0	0.0	0.0	0.0	1.0	1.0
3	6	1	3.1	3.8	2.5	3.1	1.5	0.3	0.7	0.2	0.0	0.0
3	6	2	3.0	3.6	4.3	2.5	0.9	0.4	0.5	0.2	6.4	4.7
3	7	1	4.2	4.3	2.8	2.8	0.0	0.0	0.0	0.0	0.0	0.0
3	7	2	4.4	4.5	3.0	3.1	0.0	0.0	0.0	0.0	0.2	0.4
3	8	1	4.3	4.6	2.9	2.9	0.0	0.0	0.0	0.0	0.0	0.0
3	8	2	4.1	4.1	2.8	2.8	0.0	0.0	0.0	0.0	0.2	0.2
4	1	1	4.2	4.1	3.0	3.2	0.0	0.0	0.0	0.0	0.2	0.3
4	1	2	4.4	4.3	3.0	2.9	0.0	0.0	0.0	0.0	0.2	0.0
4	2	1	4.5	4.3	2.8	2.6	0.0	0.0	0.0	0.0	0.3	0.3
4	2	2	4.3	4.3	3.1	2.5	0.0	0.0	0.0	0.0	0.4	0.4
4	3	1	4.1	3.5	2.7	2.4	0.0	0.0	0.0	0.0	2.0	3.2
4	3	2	4.5	4.6	3.2	3.1	0.0	0.2	0.0	0.0	2.1	2.7
4	4	1	4.3	4.0	2.8	3.4	0.0	0.0	0.1	0.3	0.2	2.6
4	4	2	4.1	4.1	2.9	2.5	0.0	0.0	0.2	0.0	0.5	1.8
4	5	1	4.0	4.3	2.8	2.8	0.0	0.4	0.0	0.0	0.4	0.4
4	5	2	4.3	4.0	2.8	2.8	0.0	0.4	0.0	0.0	0.0	0.6
4	6	1	4.1	3.8	2.7	3.0	0.3	0.5	0.1	0.2	2.2	4.1
4	6	2	4.0	3.8	2.5	2.8	0.6	0.4	0.4	0.4	4.8	4.3
4	7	1	4.4	4.5	3.0	3.1	0.0	0.0	0.0	0.0	0.2	0.2
4	7	2	4.5	4.5	3.0	3.1	0.0	0.0	0.0	0.0	0.4	0.5
4	8	1	4.3	4.3	3.2	2.8	0.0	0.0	0.0	0.0	0.3	0.0
4	8	2	4.5	4.7	2.9	3.2	0.0	0.0	0.0	0.0	0.4	0.8
4	9	1	4.3	4.2	2.8	2.8	0.0	0.0	0.0	0.0	0.0	0.2

4	9	2	4.3	4.1	2.8	2.9	0.0	0.0	0.0	0.0	0.0	0.2
5	1	1	4.1	4.4	3.1	3.0	0.0	0.0	0.0	0.0	0.2	0.2
5	1	2	4.5	4.2	3.0	3.0	0.0	0.0	0.0	0.0	0.2	0.2
5	2	1	4.1	4.1	2.5	2.4	0.2	0.3	0.0	0.0	1.3	0.9
5	2	2	3.9	4.1	2.6	2.5	0.0	0.2	0.0	0.0	1.5	1.5
5	3	1	4.4	3.9	3.0	2.5	0.0	0.6	0.0	0.0	1.8	3.0
5	3	2	4.3	4.8	3.2	3.2	0.0	0.0	0.0	0.0	1.4	2.3
5	4	1	4.1	4.7	2.4	3.1	0.0	0.0	0.4	0.1	2.5	1.9
5	4	2	4.6	4.6	3.1	2.8	0.0	0.0	0.1	0.2	0.4	0.8
5	5	1	4.3	3.8	2.8	2.4	0.0	0.0	0.0	0.0	0.0	1.7
5	5	2	3.9	4.3	2.8	2.9	0.0	0.0	0.0	0.0	0.6	0.0
5	6	1	3.7	3.5	2.0	2.4	1.4	0.4	0.6	0.4	8.4	7.1
5	6	2	3.8	3.0	2.9	3.2	0.2	2.3	0.3	1.6	5.4	10.4
5	7	1	4.3	4.3	2.8	3.0	0.0	0.0	0.0	0.0	0.0	0.4
5	7	2	4.5	4.3	3.1	3.0	0.0	0.0	0.0	0.0	0.8	0.2
5	8	1	4.1	4.3	2.8	2.9	0.0	0.0	0.0	0.0	0.7	0.0
5	8	2	4.3	4.1	2.7	2.7	0.0	0.0	0.2	0.0	0.6	0.8
5	9	1	4.3	4.3	2.9	2.8	0.0	0.0	0.0	0.0	0.0	0.0
5	9	2	4.3	4.3	2.9	2.8	0.0	0.0	0.0	0.0	0.0	0.0
6	1	1	4.4	4.5	3.1	3.1	0.0	0.0	0.0	0.0	0.2	0.2
6	1	2	4.5	4.1	3.0	2.7	0.0	0.0	0.0	0.0	0.2	0.2
6	2	1	4.1	4.3	2.9	2.5	0.4	0.3	0.0	0.0	0.9	1.0
6	2	2	4.1	3.9	2.8	2.4	0.0	0.5	0.0	0.0	0.5	2.0
6	3	1	4.5	4.1	3.1	2.6	0.0	0.3	0.0	0.0	1.5	2.5
6	3	2	4.4	4.2	3.0	2.8	0.0	0.0	0.0	0.0	1.6	0.9
6	4	1	4.4	4.4	2.5	3.0	0.0	0.1	0.0	0.0	1.1	0.7
6	4	2	3.8	4.5	2.4	2.7	0.2	0.0	0.2	0.0	2.0	2.0
6	5	1	4.3	4.3	2.9	2.8	0.0	0.0	0.8	0.0	0.9	0.0
6	5	2	4.1	4.1	2.8	2.8	0.0	0.0	0.0	0.5	0.3	0.4
6	6	1	4.3	3.2	3.2	2.5	0.3	1.4	0.2	0.2	2.5	3.9
6	6	2	3.6	2.8	2.8	3.3	0.2	0.3	0.2	0.4	4.0	5.0
6	7	1	4.3	4.1	2.8	2.7	0.0	0.0	0.0	0.0	0.0	0.4
6	7	2	4.2	4.1	2.7	2.7	0.0	0.0	0.0	0.0	0.5	0.4
6	8	1	4.5	4.1	3.2	2.7	0.0	0.0	0.0	0.0	0.6	0.5
6	8	2	4.3	4.3	2.8	2.8	0.0	0.0	0.0	0.0	0.0	0.0
8	1	1	4.2	4.2	3.0	2.8	0.0	0.0	0.0	0.0	0.2	0.2
8	1	2	4.3	4.2	3.0	2.8	0.0	0.0	0.0	0.0	0.2	0.2
8	2	1	4.0	4.1	2.4	2.3	1.3	0.4	0.0	0.0	3.3	3.3
8	2	2	3.9	3.8	2.8	2.2	1.6	1.7	0.0	0.0	3.5	3.4
8	3	1	4.2	4.1	2.7	2.5	0.0	0.8	0.0	0.0	1.6	2.5
8	3	2	4.2	4.1	2.8	2.7	0.0	0.0	0.0	0.0	1.0	1.4
8	4	1	4.2	4.5	3.1	2.7	0.0	0.0	0.0	0.0	0.8	0.6
8	4	2	4.1	4.2	2.7	2.8	0.0	0.0	0.0	0.0	0.2	0.3
8	5	1	4.3	4.3	2.9	2.5	0.0	0.0	0.0	0.0	0.0	0.8
8	5	2	4.3	3.9	2.8	2.5	0.0	0.0	0.0	0.5	0.0	0.9
8	6	1	4.3	4.1	2.8	2.9	0.3	0.2	0.2	0.1	3.0	2.4
8	6	2	4.1	3.8	3.1	2.7	0.3	0.0	0.2	0.2	4.1	3.8
8	7	1	4.1	4.1	2.6	2.8	0.0	0.0	0.0	0.0	0.4	0.2
8	7	2	4.3	4.1	2.7	2.5	0.0	0.0	0.0	0.0	0.2	0.4
8	8	1	4.3	4.5	2.7	2.7	0.0	0.0	0.0	0.0	0.4	0.4

8	8	2	4.2	4.3	3.6	2.5	0.0	0.0	0.0	0.0	1.1	0.4
8	9	1	4.3	4.3	2.8	2.9	0.0	0.0	0.0	0.0	0.0	0.0
8	9	2	4.3	4.3	2.8	2.9	0.0	0.0	0.0	0.0	0.0	0.0
10	1	1	4.1	4.1	2.8	2.7	0.0	0.0	0.0	0.0	0.2	0.3
10	1	2	4.1	4.2	2.7	3.1	0.0	0.0	0.0	0.0	0.3	0.2
10	2	1	3.9	3.5	2.3	2.5	1.0	1.2	0.0	0.0	4.1	3.8
10	2	2	4.2	3.7	2.5	2.4	1.6	1.4	0.1	0.0	3.2	3.9
10	3	1	4.1	3.9	2.8	2.2	0.0	0.4	0.0	0.0	1.7	3.1
10	3	2	4.3	4.1	2.8	2.6	0.0	0.0	0.0	0.0	0.0	1.5
10	4	1	4.2	4.1	2.7	2.7	0.0	0.2	0.8	0.4	1.2	2.3
10	4	2	3.8	4.1	2.7	2.5	0.3	0.3	0.3	0.8	3.3	4.4
10	5	1	4.3	4.3	2.8	3.1	0.0	0.0	0.0	0.5	0.0	0.9
10	5	2	3.9	4.0	2.5	2.6	0.6	0.8	0.0	0.0	1.6	1.4
10	6	1	4.1	4.1	2.9	2.7	1.4	0.4	0.2	0.1	7.0	5.5
10	6	2	4.3	4.1	2.8	3.0	0.2	0.3	0.0	0.2	5.6	4.2
10	7	1	4.1	4.3	2.8	2.8	0.0	0.0	0.0	0.0	0.4	0.0
10	7	2	4.4	3.9	3.0	2.4	0.0	0.4	0.0	0.0	0.4	1.1
10	8	1	4.1	4.3	2.8	2.9	0.0	0.0	0.0	0.0	0.4	0.0
10	8	2	4.6	4.0	3.3	2.5	0.0	0.8	0.0	0.0	1.1	1.0
10	9	1	4.3	4.1	2.9	2.8	0.0	0.0	0.0	0.0	0.0	0.2
10	9	2	4.3	4.3	2.9	2.9	0.0	0.0	0.0	0.0	0.0	0.0
13	3	1	4.3	3.8	3.2	2.2	0.0	1.3	0.0	0.0	2.5	2.3
13	3	2	3.9	3.9	2.7	2.6	0.6	1.0	0.0	0.0	1.9	2.5
13	4	1	4.3	4.2	3.0	2.8	0.0	0.0	0.0	0.2	0.2	1.6
13	4	2	4.0	4.5	2.7	3.1	0.0	0.0	0.4	0.2	2.0	0.7
13	5	1	4.3	4.3	2.6	2.5	0.0	0.0	0.0	0.7	0.3	0.8
13	5	2	4.1	4.3	2.6	2.9	0.0	0.0	0.9	0.0	0.9	0.0
13	6	1	3.6	3.3	2.7	2.8	0.4	0.9	0.4	0.2	6.6	5.3
13	6	2	3.2	3.4	3.5	2.7	0.5	0.3	0.2	0.2	7.6	5.6
13	7	1	4.1	4.4	2.5	3.0	0.0	0.0	0.0	0.0	1.0	0.6
13	7	2	4.1	4.5	2.7	3.0	0.0	0.0	0.0	0.0	0.8	0.6
13	8	1	4.3	4.3	2.8	2.7	0.0	0.0	0.0	0.0	0.0	0.4
13	8	2	4.3	4.3	2.8	2.8	0.0	0.0	0.0	0.0	0.0	0.0
13	9	1	4.3	4.3	2.8	2.8	0.0	0.0	0.0	0.0	0.0	0.0
13	9	2	4.3	4.3	2.9	2.8	0.0	0.0	0.0	0.0	0.0	0.0
16	1	1	3.8	3.8	2.3	2.1	0.2	0.0	0.0	0.0	1.0	0.9
16	1	2	3.3	3.5	2.0	2.2	0.1	0.0	0.0	0.0	1.2	0.9
16	3	1	3.4	4.1	2.3	2.7	1.0	0.0	0.0	0.0	2.7	0.8
16	3	2	4.0	3.7	2.8	2.5	0.4	0.6	0.0	0.0	1.4	2.3
16	4	1	4.3	4.3	2.8	2.8	0.0	0.2	0.1	0.2	0.6	0.8
16	4	2	3.4	4.1	2.1	2.8	0.6	0.2	0.5	0.2	3.6	1.2
16	6	1	3.9	3.7	3.2	3.2	0.4	0.4	0.2	0.2	8.5	8.1
16	6	2	3.3	1.4	2.7	2.3	0.0	0.6	0.2	0.2	5.6	9.6
16	7	1	4.3	3.9	2.9	2.5	0.0	0.0	0.0	0.0	0.0	2.3
16	7	2	4.1	3.8	2.6	2.5	0.0	0.0	0.0	0.0	0.8	1.6
16	9	1	4.3	4.3	2.8	2.9	0.0	0.0	0.0	0.0	0.0	0.0
16	9	2	4.3	4.3	2.8	2.8	0.0	0.0	0.0	0.0	0.0	0.0
19	3	1	4.1	2.3	2.9	1.4	0.0	2.5	0.0	0.0	2.1	4.9
19	3	2	3.9	1.5	2.8	1.1	0.0	2.3	0.0	0.0	1.1	5.0
19	4	1	4.2	3.7	3.1	2.5	0.8	0.2	0.3	0.4	2.8	2.0

19	4	2	4.1	3.4	2.5	2.5	0.2	0.8	0.8	0.6	2.4	3.8
19	5	1	4.0	3.9	2.6	2.5	1.0	0.8	0.0	0.0	1.6	1.5
19	5	2	4.3	4.3	2.8	2.5	0.0	0.7	0.0	0.0	0.0	1.0
19	6	1	3.8	3.3	3.6	2.5	1.1	0.9	0.2	0.2	9.1	11.0
19	6	2	2.8	1.7	2.5	3.2	0.6	2.9	0.2	0.6	9.1	13.8
19	7	1	4.2	4.1	2.7	2.7	0.0	0.0	0.0	0.0	0.5	0.6
19	7	2	4.2	3.6	2.7	2.1	0.0	1.0	0.0	0.4	0.9	3.6
19	9	1	4.3	4.3	2.9	2.8	0.0	0.0	0.0	0.0	0.0	0.0
19	9	2	4.3	4.3	2.8	2.8	0.0	0.0	0.0	0.0	0.0	0.0
22	1	1	3.8	4.0	3.3	3.2	0.0	0.0	0.0	0.0	0.5	0.0
22	1	2	4.1	4.0	3.3	3.3	0.0	0.2	0.0	0.2	0.5	0.5
22	3	1	4.5	2.0	3.0	1.8	0.0	2.0	0.0	0.4	2.2	5.2
22	3	2	3.8	2.7	2.7	1.3	0.0	1.9	0.0	0.0	1.6	3.6
22	4	1	4.1	3.8	2.4	2.3	0.7	0.3	0.2	0.3	2.5	0.9
22	4	2	3.9	3.1	2.7	2.3	1.0	1.2	0.8	0.9	4.0	4.3
22	5	1	4.1	4.0	2.7	2.7	0.7	0.5	0.0	0.6	0.6	1.2
22	5	2	4.3	4.0	2.9	2.6	0.7	0.0	0.0	0.6	0.9	0.9
22	6	1	4.0	4.0	2.7	2.8	0.0	1.4	0.2	0.3	4.3	8.6
22	6	2	3.8	3.5	2.6	2.5	1.5	0.4	0.5	1.7	9.6	10.8
22	7	1	4.3	4.1	2.9	2.6	0.0	0.0	0.0	0.0	0.0	0.7
22	7	2	4.1	3.5	2.7	2.1	0.4	2.0	0.0	0.4	1.0	4.2
22	8	1	4.0	4.3	2.7	2.9	0.0	0.0	0.0	0.0	1.0	0.0
22	8	2	3.8	4.0	2.5	2.9	0.9	0.0	0.0	0.0	1.5	0.6
22	9	1	4.3	4.3	2.9	2.9	0.0	0.0	0.0	0.0	0.0	0.0

Table A.12 The raw sensory data of peanut butter samples treated with tocopherols.

			Peanutty		**Roast/Toast**		**Cardboard**		**Painty**		**DoD**	
Weeks	**Panelist**	**Reps**	**0**	**90**	**0**	**90**	**0**	**90**	**0**	**90**	**0**	**90**
1	1	1	7.1	7.1	4.9	4.9	0.0	0.0	0.0	0.0	1.4	1.6
1	1	2	7.1	7.1	4.3	5.0	0.0	0.0	0.0	0.1	0.8	2.3
1	2	1	6.8	7.3	4.2	4.3	0.0	0.0	0.0	0.0	0.8	0.5
1	2	2	6.8	6.9	4.5	4.5	0.0	0.0	0.0	0.0	0.6	0.4
1	3	1	7.8	7.7	4.3	5.0	0.0	0.0	0.0	0.0	1.2	2.9
1	3	2	7.1	7.4	4.9	5.0	0.0	0.0	0.0	0.0	1.7	1.6
1	4	1	7.3	6.8	5.0	3.9	0.0	0.0	0.0	0.0	2.8	4.6
1	4	2	6.6	7.6	3.9	3.8	0.0	0.2	0.0	0.0	4.5	3.2
1	5	1	6.8	7.1	4.1	4.5	0.0	0.0	0.0	0.0	0.7	0.0
1	5	2	7.4	7.5	4.2	4.7	0.0	0.0	0.0	0.0	0.5	0.2
1	6	1	6.8	6.8	4.7	4.3	0.0	0.0	0.0	0.0	0.2	0.5
1	6	2	6.8	7.1	4.5	4.1	0.0	0.0	0.0	0.0	0.4	1.4
1	7	1	7.1	6.9	4.9	4.6	0.0	0.0	0.0	0.0	0.4	0.2
1	7	2	6.9	7.1	4.3	4.4	0.0	0.0	0.0	0.0	0.4	0.1
1	8	1	6.6	7.0	3.8	4.5	0.0	0.0	0.0	0.0	2.0	0.0
1	8	2	7.3	6.5	5.1	5.2	0.0	0.0	0.0	0.0	2.0	2.1
1	9	1	7.0	6.4	4.3	4.1	0.0	0.0	0.0	0.0	0.2	0.5
1	9	2	7.0	6.4	4.5	4.1	0.0	0.0	0.0	0.0	0.4	0.8
2	1	1	7.3	7.3	4.8	4.5	0.0	0.0	0.0	0.0	0.0	0.0
2	1	2	6.9	7.4	4.7	4.7	0.0	0.0	0.0	0.0	0.0	0.0
2	2	1	7.1	6.8	4.7	4.5	0.0	0.0	0.0	0.0	0.0	0.0

2	2	2	6.9	7.1	4.5	4.1	0.4	0.0	0.0	0.0	0.0	0.0
2	3	1	7.3	7.3	4.7	4.7	0.0	0.0	0.0	0.0	1.7	1.5
2	3	2	7.5	7.3	4.7	4.7	0.0	0.0	0.0	0.0	2.3	1.7
2	4	1	6.9	7.3	4.3	4.2	0.2	0.2	0.0	0.2	1.1	0.8
2	4	2	7.4	7.2	4.7	4.9	0.2	0.2	0.3	0.2	2.3	2.4
2	5	1	7.1	6.8	4.8	4.1	0.0	0.6	0.0	0.0	0.9	1.2
2	5	2	7.1	7.1	4.1	4.5	0.0	0.0	0.0	0.0	0.4	0.0
2	7	1	7.3	7.3	4.8	4.7	0.0	0.0	0.0	0.0	0.0	0.0
2	7	2	7.2	7.2	4.7	4.7	0.0	0.0	0.0	0.0	0.0	0.0
2	8	1	7.2	7.4	4.7	4.8	0.0	0.0	0.0	0.0	0.0	0.0
2	8	2	7.1	7.3	4.9	5.2	0.0	0.0	0.0	0.0	0.0	0.0
2	9	1	7.3	7.1	4.3	4.5	0.0	0.0	0.0	0.0	0.4	0.0
2	9	2	7.3	7.1	4.3	4.5	0.0	0.0	0.0	0.0	0.4	0.0
3	1	1	7.2	6.8	4.9	4.2	0.0	0.0	0.0	0.0	0.7	0.5
3	1	2	6.8	7.0	4.9	4.7	0.0	0.0	0.0	0.0	0.4	0.4
3	2	1	7.1	6.8	4.5	4.5	0.0	0.0	0.0	0.0	0.0	0.0
3	2	2	6.7	6.7	4.1	3.9	0.0	0.0	0.0	0.0	0.0	0.0
3	3	1	7.3	6.8	4.8	4.5	0.0	0.0	0.0	0.0	0.0	0.0
3	3	2	7.4	7.3	4.7	4.8	0.0	0.0	0.0	0.0	0.0	0.0
3	4	1	6.8	7.1	4.3	4.4	0.0	0.2	0.0	0.0	2.8	0.4
3	4	2	6.9	7.0	4.3	4.7	0.2	0.4	0.0	0.2	3.5	4.0
3	5	1	7.1	7.1	4.5	4.3	0.0	0.0	0.0	0.0	0.0	0.3
3	5	2	6.8	6.7	4.2	4.1	0.0	0.0	0.0	0.0	0.4	0.7
3	6	1	6.6	7.1	4.3	4.7	0.0	0.2	0.0	0.0	0.0	0.0
3	6	2	6.9	6.9	4.3	4.3	0.2	0.0	0.0	0.1	0.0	0.0
3	7	1	7.3	7.3	4.7	4.7	0.0	0.0	0.0	0.0	0.0	0.0
3	7	2	7.3	7.1	4.8	4.5	0.0	0.0	0.0	0.0	0.0	0.4
3	8	1	6.9	7.1	4.5	4.5	0.0	0.0	0.0	0.0	0.0	0.0
3	8	2	7.1	7.3	4.7	4.7	0.0	0.0	0.0	0.0	0.0	0.0
4	1	1	7.5	6.8	4.7	4.8	0.0	0.0	0.0	0.0	0.4	0.3
4	1	2	6.8	7.0	4.3	4.7	0.0	0.0	0.0	0.0	0.0	0.2
4	2	1	6.9	7.1	4.5	4.5	0.0	0.0	0.0	0.0	0.2	0.2
4	2	2	6.8	7.1	4.3	4.2	0.0	0.0	0.0	0.0	0.9	0.4
4	3	1	6.8	6.7	4.3	4.3	0.0	0.0	0.0	0.0	2.4	1.7
4	3	2	7.5	7.3	4.9	4.7	0.0	0.0	0.0	0.0	3.0	1.5
4	4	1	6.8	6.2	4.3	3.9	0.1	0.3	0.0	0.1	0.9	2.8
4	4	2	6.8	6.5	4.2	4.3	0.0	0.2	0.1	0.0	1.5	1.9
4	5	1	6.7	7.1	4.0	4.5	0.0	0.0	0.0	0.0	0.6	0.0
4	5	2	7.1	6.6	4.5	4.1	0.0	0.0	0.0	0.0	0.0	1.0
4	6	1	6.8	7.0	4.3	4.3	0.0	0.0	0.0	0.0	1.0	0.4
4	6	2	7.0	7.1	4.3	4.1	0.2	0.0	0.0	0.0	2.1	1.0
4	7	1	7.2	6.9	4.8	4.3	0.0	0.0	0.0	0.0	0.6	0.4
4	7	2	7.1	7.2	4.5	4.7	0.0	0.0	0.0	0.0	0.0	0.3
4	8	1	7.1	7.1	4.5	4.5	0.0	0.0	0.0	0.0	0.0	0.0
4	8	2	7.3	7.4	4.8	4.7	0.0	0.0	0.0	0.0	0.8	0.8
4	9	1	6.8	6.8	4.5	4.5	0.0	0.0	0.0	0.0	0.3	0.4
4	9	2	6.8	6.8	4.5	4.5	0.0	0.0	0.0	0.0	0.2	0.3
5	1	1	6.8	6.9	4.3	4.9	0.0	0.0	0.0	0.0	0.2	0.4
5	1	2	7.2	7.2	4.7	4.6	0.0	0.0	0.0	0.0	0.2	0.2
5	2	1	7.1	7.1	4.5	4.5	0.0	0.0	0.0	0.0	0.0	0.0

5	2	2	6.9	6.8	4.5	4.3	0.0	0.0	0.0	0.0	0.5	1.0
5	3	1	7.2	6.8	4.9	4.2	0.0	0.0	0.0	0.0	1.4	1.6
5	3	2	7.3	6.4	4.7	4.1	0.0	0.4	0.0	0.0	1.6	2.5
5	4	1	7.3	7.4	4.9	4.6	0.0	0.2	0.0	0.3	0.5	1.7
5	4	2	7.1	6.3	4.6	4.0	0.0	0.1	0.0	0.0	0.2	2.7
5	5	1	7.2	7.1	4.7	4.2	0.0	0.0	0.0	0.0	0.4	0.4
5	5	2	7.1	6.8	4.5	4.1	0.0	0.0	0.0	0.0	0.0	0.8
5	6	1	7.3	6.9	4.5	4.3	0.2	0.2	0.0	0.0	2.0	4.3
5	6	2	6.8	6.8	4.7	4.3	0.0	0.4	0.0	0.1	4.3	5.1
5	7	1	7.0	7.0	4.3	4.3	0.0	0.0	0.0	0.0	0.4	0.5
5	7	2	6.9	7.0	4.3	4.3	0.0	0.0	0.0	0.0	0.4	0.4
5	8	1	7.1	7.1	4.5	4.5	0.0	0.0	0.0	0.0	0.0	0.0
5	8	2	6.8	7.1	4.3	4.5	0.0	0.0	0.0	0.0	0.5	0.0
5	9	1	6.8	6.9	4.7	4.7	0.0	0.0	0.0	0.0	0.3	0.2
5	9	2	6.9	7.0	4.7	4.6	0.0	0.0	0.0	0.0	0.2	0.2
6	1	1	7.0	7.0	4.4	4.3	0.0	0.0	0.0	0.0	0.1	0.2
6	1	2	7.2	6.9	4.7	4.3	0.0	0.0	0.0	0.0	0.2	0.2
6	2	1	7.1	6.9	4.5	4.5	0.0	0.2	0.0	0.0	0.0	0.6
6	2	2	6.8	6.9	4.5	4.7	0.4	0.4	0.0	0.0	8.1	1.2
6	3	1	7.0	6.9	4.3	4.3	0.0	0.0	0.0	0.0	1.7	1.6
6	3	2	7.0	6.8	4.4	4.3	0.0	0.0	0.0	0.0	1.6	1.1
6	4	1	7.2	7.3	4.6	4.5	0.1	0.0	0.0	0.0	0.3	0.2
6	4	2	6.8	6.7	4.2	4.3	0.3	0.2	0.0	0.1	1.6	1.5
6	5	1	7.3	7.1	4.7	4.5	0.0	0.0	0.0	0.0	0.3	0.0
6	5	2	7.1	6.8	4.5	4.5	0.0	0.0	0.0	0.0	0.0	0.3
6	6	1	7.0	6.8	4.7	4.3	0.0	0.2	0.0	0.0	1.0	2.5
6	6	2	7.0	7.0	4.3	4.6	0.2	0.2	0.0	0.0	2.7	0.5
6	7	1	7.3	7.2	4.7	4.7	0.0	0.0	0.0	0.0	0.4	0.4
6	7	2	6.9	7.3	4.3	4.7	0.0	0.0	0.0	0.0	0.4	0.6
6	8	1	6.8	6.8	4.2	4.2	0.0	0.0	0.0	0.0	0.4	0.5
6	8	2	6.8	6.8	4.2	4.2	0.0	0.0	0.0	0.0	0.5	0.0
8	1	1	6.9	7.0	4.3	4.3	0.1	0.0	0.0	0.0	0.2	0.2
8	1	2	7.0	6.9	4.4	4.6	0.0	0.0	0.0	0.0	0.1	0.2
8	2	1	6.8	6.8	4.5	4.5	0.4	0.4	0.0	0.0	0.7	0.6
8	2	2	6.8	6.3	4.3	3.6	0.4	2.1	0.0	0.0	0.9	5.2
8	3	1	7.0	7.0	4.5	4.1	0.0	0.4	0.0	0.0	1.6	2.3
8	3	2	7.3	7.2	4.8	4.6	0.0	0.0	0.0	0.0	1.6	2.1
8	4	1	7.2	7.3	4.3	4.2	0.0	0.0	0.0	0.0	0.4	0.4
8	4	2	7.0	7.2	4.4	4.3	0.0	0.0	0.0	0.0	0.2	0.4
8	5	1	7.1	7.1	4.5	4.5	0.0	0.4	0.0	0.0	0.0	0.4
8	5	2	6.8	7.1	4.2	4.7	0.0	0.0	0.0	0.0	0.4	0.2
8	6	1	7.0	7.0	4.3	4.3	0.0	0.0	0.0	0.0	0.4	0.5
8	6	2	7.1	6.8	4.5	4.7	0.0	0.0	0.0	0.0	0.2	0.9
8	7	1	7.1	7.1	4.4	4.5	0.0	0.0	0.0	0.0	0.3	0.0
8	7	2	7.1	6.9	4.5	4.3	0.0	0.0	0.0	0.0	0.0	0.6
8	8	1	6.9	6.8	4.5	4.3	0.3	0.2	0.0	0.0	0.4	0.8
8	8	2	6.7	6.8	4.2	4.5	0.4	0.0	0.0	0.0	0.8	0.4
8	9	1	7.2	6.9	4.5	4.7	0.0	0.3	0.0	0.2	0.2	0.4
8	9	2	7.3	7.2	4.7	4.5	0.0	0.0	0.0	0.0	0.2	0.2
10	1	1	6.8	6.8	4.3	4.3	0.0	0.0	0.0	0.0	0.3	0.2

10	1	2	6.8	6.7	4.3	4.3	0.0	0.2	0.0	0.0	0.3	0.4
10	2	1	6.2	6.8	4.5	4.1	1.1	0.3	0.0	0.0	2.6	1.0
10	2	2	6.8	5.5	4.5	3.9	0.6	2.4	0.0	0.0	1.2	5.0
10	3	1	7.1	6.7	4.7	4.3	0.0	0.4	0.0	0.0	2.1	2.3
10	3	2	7.1	6.8	4.5	4.2	0.0	0.9	0.0	0.0	0.0	3.4
10	4	1	6.8	6.6	3.8	4.2	0.4	0.8	0.4	0.4	2.8	3.7
10	4	2	7.2	6.0	4.7	4.1	0.2	0.7	0.0	0.6	0.6	4.8
10	5	1	6.9	7.1	4.2	4.3	0.4	0.0	0.0	0.0	0.4	0.2
10	5	2	7.1	7.1	4.5	4.5	0.0	0.0	0.0	0.0	0.0	0.0
10	6	1	7.1	6.4	4.5	4.5	0.0	0.0	0.2	0.0	1.0	1.4
10	6	2	7.0	7.1	4.2	4.7	0.4	0.4	0.0	0.2	1.6	5.8
10	7	1	6.8	7.1	4.3	4.5	0.0	0.0	0.0	0.0	0.8	0.5
10	7	2	7.1	6.8	4.5	4.2	0.0	0.3	0.0	0.0	0.0	1.6
10	8	1	7.1	7.1	4.5	4.5	0.0	0.0	0.0	0.0	0.2	0.3
10	8	2	7.1	6.8	4.5	4.2	0.0	0.2	0.0	0.0	0.0	0.4
10	9	1	6.8	6.7	4.3	4.1	0.4	0.4	0.0	0.0	0.4	0.9
10	9	2	6.8	6.6	4.2	4.1	0.4	0.4	0.0	0.0	0.7	0.8
13	3	1	7.2	4.7	4.7	2.7	0.0	1.1	0.0	0.0	1.1	4.8
13	3	2	7.2	7.1	4.7	4.7	0.0	0.4	0.0	0.0	1.1	1.4
13	4	1	7.2	6.8	4.4	4.7	0.2	0.2	0.2	0.2	2.2	2.3
13	4	2	6.8	6.8	4.7	4.3	0.3	0.1	0.0	0.2	2.6	3.1
13	5	1	6.8	6.7	4.7	4.1	0.0	0.8	0.0	0.0	0.6	0.9
13	5	2	7.1	7.1	4.5	4.5	0.0	0.0	0.0	0.0	0.0	0.0
13	6	1	7.1	7.0	4.5	4.3	0.0	0.0	0.0	0.0	0.0	5.3
13	6	2	7.2	7.2	4.3	4.5	0.0	0.0	0.0	0.0	1.8	1.1
13	7	1	6.6	6.9	4.1	4.3	0.4	0.4	0.0	0.0	1.2	0.6
13	7	2	6.7	7.1	4.1	4.5	0.4	0.0	0.0	0.0	1.4	0.0
13	8	1	6.8	6.7	4.3	3.6	1.1	1.2	0.0	0.0	1.0	1.7
13	8	2	6.8	6.8	3.8	4.1	0.0	1.4	0.0	0.0	0.8	1.0
13	9	1	6.8	6.8	4.7	4.8	0.0	0.0	0.0	0.0	0.2	0.4
13	9	2	6.2	6.6	4.8	4.7	0.4	0.6	0.0	0.0	0.7	0.8
16	1	1	6.7		4.1		0.0		0.0		0.3	
16	1	2	6.6	6.7	4.2	3.8	0.2	0.0	0.0	0.0	0.7	0.8
16	3	1	6.9	6.1	4.2	3.5	0.4	0.9	0.0	0.0	1.2	2.9
16	3	2	6.8	6.3	4.5	3.6	0.4	1.3	0.0	0.0	1.4	2.4
16	4	1	7.0	6.6	4.3	4.3	0.4	0.6	0.2	0.3	0.8	3.5
16	4	2	7.2	6.7	4.7	4.1	0.3	0.6	0.0	0.6	0.5	2.8
16	6	1	7.1	7.0	4.2	4.5	0.0	0.0	0.0	0.2	2.5	5.1
16	6	2	6.8	7.0	4.3	4.5	0.1	0.0	0.0	0.0	5.5	1.1
16	7	1	6.7	6.9	4.3	4.5	0.2	0.0	0.0	0.0	0.5	0.4
16	7	2	6.9	7.2	4.3	4.6	0.0	0.0	0.0	0.0	0.3	0.5
16	9	1	6.8	6.5	4.8	4.8	0.4	0.7	0.0	0.0	0.8	1.0
16	9	2	6.5	6.5	4.8	4.8	0.6	0.4	0.0	0.0	0.8	1.0
19	3	1	6.8	7.0	4.3	3.9	0.0	1.4	0.0	0.0	2.0	2.5
19	3	2	6.6	6.6	4.5	3.8	0.0	1.3	0.0	0.0	1.7	2.8
19	4	1	6.5	6.5	4.3	4.3	0.2	0.5	0.1	0.3	0.5	3.3
19	4	2	5.7	5.7	4.0	3.8	0.7	0.6	1.3	0.4	3.3	3.5
19	5	1	7.1	6.8	4.1	4.7	0.9	0.7	0.0	0.0	1.1	1.0
19	5	2	6.8	6.6	4.1	4.1	0.8	0.0	0.0	0.0	1.0	1.2
19	6	1	7.0	6.6	4.5	4.6	0.2	0.8	0.0	0.3	1.0	9.5

19	6	2	6.8	6.3	4.3	4.3	0.2	0.2	0.0	0.0	6.1	9.6
19	7	1	7.1	4.9	4.5	2.8	0.0	2.2	0.0	0.0	0.0	5.1
19	7	2	7.3	5.1	4.7	2.7	0.0	2.3	0.0	0.4	0.7	5.3
19	9	1	6.8	6.7	4.7	4.8	0.0	0.8	0.0	0.0	0.7	1.0
19	9	2	6.6	6.7	4.9	4.9	0.7	0.8	0.0	0.0	0.9	1.0
22	1	1	6.7	6.7	3.9	4.3	0.2	0.2	0.0	0.0	0.6	0.4
22	1	2	6.7	6.7	4.8	4.1	0.0	0.0	0.0	0.0	0.3	0.4
22	3	1	7.1	5.5	4.7	3.6	0.0	1.2	0.0	0.0	1.3	2.8
22	3	2	7.1	5.2	4.7	3.0	0.0	1.8	0.0	0.0	1.5	4.4
22	4	1	6.7	6.7	4.2	4.4	0.4	0.2	0.2	0.0	1.0	0.2
22	4	2	6.6	6.1	4.1	4.0	0.8	0.8	0.2	0.7	2.5	3.7
22	5	1	7.1	7.1	4.5	4.3	0.0	1.0	0.0	0.0	0.0	1.3
22	5	2	7.1	7.1	4.7	4.5	0.0	0.6	0.0	0.0	0.4	0.7
22	6	1	6.9	5.6	4.5	4.1	0.2	0.3	0.0	1.6	1.6	9.4
22	6	2	7.1	5.8	4.5	4.5	0.0	0.4	0.0	1.6	0.0	10.3
22	7	1	7.1	5.0	4.5	2.7	0.0	1.3	0.0	1.8	0.0	4.9
22	7	2	7.2	4.9	4.7	2.9	0.0	1.9	0.0	0.5	0.5	4.7
22	8	1	6.8	6.8	4.5	4.2	0.0	0.0	0.0	0.0	0.8	0.8
22	8	2	7.1	7.1	4.2	4.5	0.0	1.0	0.0	0.0	0.7	0.8
22	9	1	6.5	6.5	4.8	4.9	0.7	0.7	0.0	0.0	1.2	1.0
22	9	2	6.5	6.3	4.8	4.9	0.7	1.2	0.0	0.0	1.2	1.6