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Food Chemistry 89 (2005) 77–84
Food Chemistry
www.elsevier.com/locate/foodchem

Polyphenolic and antioxidant changes during storage of normal, mid, and high oleic acid peanuts

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Received 17 June 2003; received in revised form 6 February 2004; accepted 6 February 2004

Abstract

The quality of dry roasted peanuts is highly dependent on storage conditions for preventing oxidation of fatty acids; however, changes in polyphenolics affecting antioxidant capacity due to co-oxidative reactions are unknown. The objective of this work was to evaluate oxidative stability of polyphenolics in peanut kernels with naturally varying rates of lipid oxidation. Three peanut varieties containing varying levels of oleic acid (normal, mid, and high) were dry roasted and evaluated for phytochemical changes over four months of storage at 20 and 35 °C; analyses included peroxide value, total and individual phenolics and antioxidant capacity. The normal oleic acid peanuts suffered up to 2.6-fold and mid-oleic acid peanuts 2-fold more lipid oxidation than the high-oleic acid peanuts stored at 35 °C. Changes in total soluble phenolics were initially similar among cultivars, but antioxidant capacity was found to decrease by 62%, on average, during storage at 35 °C, independently of rates of lipid oxidation. Free *p*-coumaric acid, three esterified derivatives of *p*-coumaric, and two esterified derivatives of hydroxybenzoic acid were the predominant polyphenolics present and their rates of change were similar among cultivars and independent of storage time or temperature. The high-oleic acid content was essential for prevention of lipid oxidation, but data indicated that co-oxidative reactions, affecting polyphenolic content during storage, were not great enough to significantly alter antioxidant capacity.

Keywords: Peanuts; Storage; Antioxidants; Polyphenolics; Lipid oxidation

1. Introduction

Increased interest in peanut cultivars with the high-oleic acid trait have centred on their low degree of lipid oxidation during storage and on factors influencing organoleptic quality. The high oleic trait was initially reported by Norden, Gorbet, and Knauft (1987) and has since been incorporated into many new peanut varieties with greater stability against oxidation. A low incidence of oxidation is associated with more desirable flavours in these peanuts following roasting. Also, research has shown that the consumption of high-oleic acid peanuts has potential health benefits, such as lowered blood cholesterol levels in hypercholesterolemic women (O'Byrne, Knauft, & Shiremen, 1997). The concentration of oleic acid in high-oleic acid peanuts is similar to that of olive oil (Cabrini et al., 2001), which is known for its heart-healthy characteristics. Studies with roasted peanuts have shown variation in organoleptic properties of peanuts among cultivars, oleic acid content, and roasting conditions (Anderson, Hill, Gorbet, & Brodbeck, 1998; Braddock, Sims, & O'Keffe, 1995; Mugundi, Sims, Gorbet, & O'Keefe, 1998; O'Keefe, Wiley, & Knauft, 1993; Pattee et al., 2002a; Pattee, Isleib, Moore, Gorbet, & Giesbrecht, 2002b; Reed, Sims, Gorbet, & O'Keffe, 2002). However, data on polyphenolic composition and its relative changes during storage does not exist for roasted peanut kernels as a function of lipid oxidation.

Lipid oxidation is usually implicated as the primary cause of decreased shelf life, adverse tastes, and

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0308-8146/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2004.02.020

generation of undesirable aromas during extended storage of roasted peanuts (Braddock et al., 1995; Mugundi et al., 1998; O'Keefe et al., 1993; Pattee et al., 2002a; Reed et al., 2002). Oxidative processes are typically accelerated by conditions of light, oxygen, water activity, or exposure to high temperatures and food processors attempt to control many of these factors by nitrogen-filled headspaces, vacuum packaging, and barriers to light. However, oxidation of polyunsaturated fatty acids, specifically linoleic (18:2) and linolenic (18:3) acids, still occurs, even following strict handling practices. Since rates of lipid oxidation are directly proportional to the degree of fatty acid unsaturation, peanut cultivars with higher than normal oleic acid (18:1) should have greater stability against lipid oxidation and potentially a reduced incidence of co-oxidation of phytochemicals compared to normal oleic acid varieties.

Naturally-occurring phytochemicals in peanuts and other oilseeds, such as tocopherols, carotenoids, and polyphenolics, may have a role in slowing or preventing lipid oxidation, due to their antioxidative nature. In model systems, the exogenous addition of phenolic compounds, such as catechin and rosemarinic acid, were shown to enhance oxidative stability during storage of peanut oil (Chu & Hsu, 1999) and were as effective as common synthetic antioxidants. Numerous polyphenolics have been identified in peanuts (Duke, 1992; Seo & Morr, 1985) but their stability over time and their combined role in augmenting lipid oxidation is unknown. Phenolic compounds, such as *p*-coumaric, ferulic acid, and other hydroxy and methoxyl-substituted benzoic acids, are not highly regarded as effective antioxidants in a lipophilic environment (Herraiz, Galisteo, & Chamorro, 2003; Huang, Yen, Chang, Yen, & Duh, 2003; Reed et al., 2002; Rice-Evans & Bourne, 1998), but their possible existence in esterified or protein-bound forms may augment their radical-scavenging properties in vivo. Other compounds potentially present in roasted peanuts, such as Maillard-derived compounds, were shown to be effective suppressants of rancidity in model and food systems, while proteins and protein hydrolysates were also reported to be antioxidants in model systems (Hatate, 1996; Herraiz et al., 2003; Huang et al., 2003; Taguchi, Iwami, Kawabata, & Ibuki, 1988; Tanaka, Sugita, Wen-kui, Nagashima, & Taguchi, 1990).

It is hypothesized that a lowered incidence of lipid oxidation in roasted peanuts would relate to higher retention of soluble phytochemicals with antioxidant capacity. Lipid oxidation of foods typically generates hydroperoxides or other reactive oxygen species which, unless prevented from propagation, may simultaneously destroy native antioxidant compounds. It is unknown how phenolic compounds in peanuts are altered under peroxidative conditions during variable storage conditions. Therefore, this study investigated polyphenolics and antioxidant capacities of three peanut cultivars, each with varying oleic acid contents, stored under normal (20 °C) and accelerated storage conditions (35 °C).

2. Materials and methods

2.1. Materials and processing

Shelled kernels from three peanut cultivars, with varying oleic acid content, were obtained from the University of Florida Agricultural Research Center in Marianna, Florida and were stored frozen under a blanket of nitrogen. All three cultivars were runner-type peanuts with good disease resistance and included 'Georgia Green', a normal-oleic acid peanut with a long production history, containing ca. 50–53% oleic acid and 27–29% linoleic acid, 'Florida MDR 98', a mid-oleic acid peanut containing ca. 59–64% oleic acid and 15–20% linoleic acid (Anderson & Gorbet, 2002), and 'ANorden', a recent cultivar developed with high-oleic acid content (>80%) and low linoleic acid content (<4%). Peanut seeds were removed from frozen storage, warmed to room temperature, and 500 g from each cultivar were roasted at 170 °C for 10 min in a Pyrex forced air convection oven (Aroma AeroMatic Oven, San Diego, CA, USA). Peanuts were agitated every 3 min to ensure uniform roasting and the temperature was monitored, using a digital thermocouple, to ±3 °C (Component Design, Portland, OR, USA). Peanuts were cooled, their skins (testa) manually removed and subsequently divided into two equal portions for storage at 20 or 35 °C. For storage, 50 g of peanuts were individually sealed into plastic bags to be removed at each sampling time, 0, 1, 2, 3, and 4 months later.

2.2. Physicochemical analyses

Peanut kernels were blended in a kitchen-scale food processor to the smallest obtainable particle size and 5 g were homogenized in 20 ml of 80% methanol using a tissuemizer (PT-10, Brinkman Instruments, Westbury, NY). Samples were filtered through Whatman #4 filter paper and measurements of phenolics and antioxidant capacity taken directly from the extract. Total soluble phenolics, including contributions from phenolic amino acids, were measured using the Folin–Ciocalteu assay, with data expressed in gallic acid equivalents (mg/kg). Individual polyphenolics were separated and characterized by HPLC, by first diluting the extracts with an equal volume of water, and run according to the conditions of Talcott, Brenes, and Howard (2000) using a Waters 2690 Alliance HPLC system. Separation was conducted on a Waters Spherisorb ODS-2 (4.6×250

mm) column with detection at 280 nm using a Waters 996 PDA detector, scanning from 200 to 400 nm. The addition of water prior to sample injection, which diluted extracts to 40% methanol, was critical to facilitate partitioning from the reversed phase column. Concentrations of individual polyphenolics were expressed as equivalents of *p*-hydroxybenzoic acid, tryptophan, or *p*-coumaric acid, based on spectral similarities to each standard.

Antioxidant capacity was determined using the ORAC (oxygen radical absorbance capacity) assay, as previously described for a microplate reader (Talcott, Percival, Pitter-Moore, & Celoria, 2003). Peanut isolates were diluted, from 50- to 100-fold, in pH 7 phosphate buffer, prior to pipetting into a 96-well microplate. All values were background-corrected for methanol content by using a solvent blank of the same dilution and quantified in μmoles trolox equivalents per gramme of peanut.

The remainder of each ground peanut was non-quantitatively extracted with hexane for 24 h at 4 °C, filtered through Whatman #1 filter paper, and the solvent removed under reduced pressure at 35 °C to recover crude lipids. Peroxide value was then determined on 5 g of oil, using 0.01 N sodium thiosulfate at the titrant (AOAC, 1990), and data were expressed as milliequivalents of peroxide per kilogramme of oil.

2.3. Statistical analysis

Data was analyzed as a $3 \times 5 \times 2$ full factorial that included three peanut cultivars analyzed at five sampling times and at two storage temperatures. Data represent the means of duplicate determinations. Multiple linear regression, Pearson correlation coefficients and analysis of variance, were conducted, using JMP software Version 5 (SAS Institute, 2002), with mean separation performed by the LSD test ($P < 0.05$).

3. Results and discussion

3.1. Lipid oxidation

Trends observed for lipid oxidation in each peanut variety were dependent on storage temperature and natural differences in fatty acid composition during storage. Normal-oleic acid peanuts (Georgia Green) experienced peroxide accumulations that were twice the level of mid-oleic acid peanuts (Florida MDR98) at both 20 and 35 °C (Table 1). Normal- and mid-oleic acid peanuts stored at 35 °C (see Fig. 1) were also 2-fold higher in peroxides than those at 20 °C, and, despite these differences, the high-oleic peanuts (ANorden) did not exhibit an appreciable change in peroxide formation at either storage temperature for the duration of the study. Peroxide values for each cultivar were in agreement with previous studies evaluating lipid oxidation rates in peanuts with varying oleic acid contents, and data further accentuated the enhanced shelf life characteristics of high-oleic peanuts. Although polyphenolics present in natural lipid systems are known to suppress oxidation (Onyeneho & Hettiarachchy, 1992), the stability of such compounds present in peanut kernels and their inhibitory properties against lipid oxidation are generally unknown.

3.2. Polyphenolics and antioxidant capacity

Inherent differences in individual polyphenolic compounds and antioxidant capacities existed among the three peanut cultivars that were not necessarily related to their fatty acid composition. Compositional differences may be due to background genetics, disease resistance, growth conditions, post-harvest handling, or response to roasting conditions. Total soluble phenolics, measured as metal ion reducing equivalents by the Folin–Ciocalteu assay, were initially similar between cultivars (1.36 mg/kg) and steadily decreased during storage in a temperature-independent manner that was also independent of fatty acid oxidation (Table 1). However, initial differences in antioxidant capacity (μmoles trolox equivalents per kg) were observed for normal-(57.4), mid-(58.7), and high-(50.8) oleic acid peanuts that may be attributed to natural antioxidant variation among cultivars or due to their respective changes during roasting. When data were subsequently normalized to reflect relative changes in antioxidant capacity over time, it was evident that resultant decreases were similar among cultivars and therefore independent of their rate of lipid oxidation. A significant decrease in antioxidant capacity was also observed between samples stored at different temperatures, since peanuts stored at 35 °C were 6.6% lower, on average, than counterparts stored at 20 °C (Fig. 2) and concentration changes over time were similar between temperatures. Only modest correlations existed between total phenolics and antioxidant capacity ($r = 0.53$ and $r = 0.70$ at 20 and 35 °C, respectively,) but their respective decreases during storage were a good indication that soluble (80% methanol) phytochemicals with antioxidant capacity, most likely polyphenolics and/or protein–polyphenolic complexes, were altered during storage.

Changes in specific polyphenolics during storage were investigated by separating individual soluble polyphenolics by HPLC monitored at 280 nm. The predominant compounds separated had characteristic spectra similar to that of *p*-hydroxybenzoic acid (257.3 nm), tryptophan (280.3 nm), or *p*-coumaric acid (309.3 nm) with eight distinctive compounds quantified in equivalents of these standards. An additional compound, 5-hydroxymethylfurfural (285.5 nm), was also separated but not quantified, and was a result of reducing sugar degradation at

Table 1
Effect of storage time (0–4 months) and temperature (20 and 35 °C) on the concentration (mg/kg) of total soluble phenolics, *p*-coumaric acid and esterified derivatives of *p*-coumaric acid present in peanut cultivars with varying oleic acid content

Attribute	Oleic acid content[a]	20 °C					35 °C				
		Day 0	Month 1	Month 2	Month 3	Month 4	Day 0	Month 1	Month 2	Month 3	Month 4
Total Soluble Phenolics[b]	Normal	1,380 a[c]	1,300 a	1,280 a	984 b*[d]	1,000 a	1,380 a	1,270 a	1,210 a	1,280 a†[e]	901 a*
	Mid	1,320 a	1,160 a	1,020 a	1,160 b	1,000 a	1,320 a	1,280 a	1,090 a	1,090 a	935 a
	High	1,390 a	1,180 a	1,110 a	1,320 a*	819 a*	1,390 a	1,230 a	1,080 a	1,270 a	759 a*
p-Coumaric acid ester (Peak 3)[f]	Normal	141 a	138 a	149 a	136 a	146 a	141 a	127 a	144 a*	143 a	135 a
	Mid	62.9 c	68.1 b	69.7 c	69.6 b	76.0 b	62.9 c	54.2 c	63.6 c	70.2 c	65.2 b
	High	89.7 b	77.4 b	88.3 b	83.0 b	85.7 b	89.7 b	79.1 b	89.4 b	86.3 b	86.8 b
p-Coumaric acid ester (Peak 4)	Normal	32.7 a	25.5 a	32.3 a	31.3 a	24.3 a*	32.7 a	32.4 a†	32.1 a†	32.4 a	23.1 a*
	Mid	11.8 b	12.6 b	15.4 b	18.8 b	17.9 a	11.8 b	9.5 b	14.4 b	16.0 b	15.6 b
	High	11.1 b	9.5 b	11.2 b	13.4 b	18.8 a*	11.1 b	11.8 b	10.7 b	12.3 b	14.2 b
p-Coumaric acid (Peak 5)	Normal	88.2 a	81.9 a	85.0 a	78.1 a	81.5 a	88.2 a	79.2 a	81.5 a	77.8 a	79.9 a
	Mid	60.4 b	61.9 b	57.3 b	57.1 b	54.0 b	60.4 b	50.6 b†	54.3 b	52.3 b	49.5 b
	High	55.8 b	57.3 b	60.5 b	55.8 b	54.5 b	55.8 b	50.2 b	54.7 b	56.3 b	50.1 b
p-Coumaric acid ester (Peak 8)	Normal	4.4 ab	3.8 a	4.6 a	3.0 ab*	2.8 a	4.4 a	3.6 a	3.7 a	3.1 a	3.3 a
	Mid	5.1 a	3.8 a*	3.3 b	3.9 a	3.8 a	5.1 ab	3.4 ab*	2.9 a	2.8 a†	2.9 ab†
	High	3.7 b	2.3 a*	2.3 b	2.8 b	3.3 a	3.7 b	2.4 b*	2.7 a	2.9 a	1.9 b

[a] Georgia Green (normal-oleic acid), Florida MDR98 (mid-oleic acid), and ANorden (high-oleic acid).
[b] Total soluble phenolics measured by the Folin–Ciocalteu assay and quantified in gallic acid equivalents.
[c] Values with different letters within columns are significantly different (LSD test, $P < 0.05$), and indicate the effect of oleic acid content.
[d] Means with an asterisk (*) within each peanut cultivar indicate a significant difference (LSD test, $P < 0.05$) between two consecutive months of storage.
[e] Means with a dagger (†) indicate a significant difference (LSD test, $P < 0.05$) due to storage temperature within each peanut cultivars at corresponding storage times.
[f] Peak identifications correspond to Fig. 3.

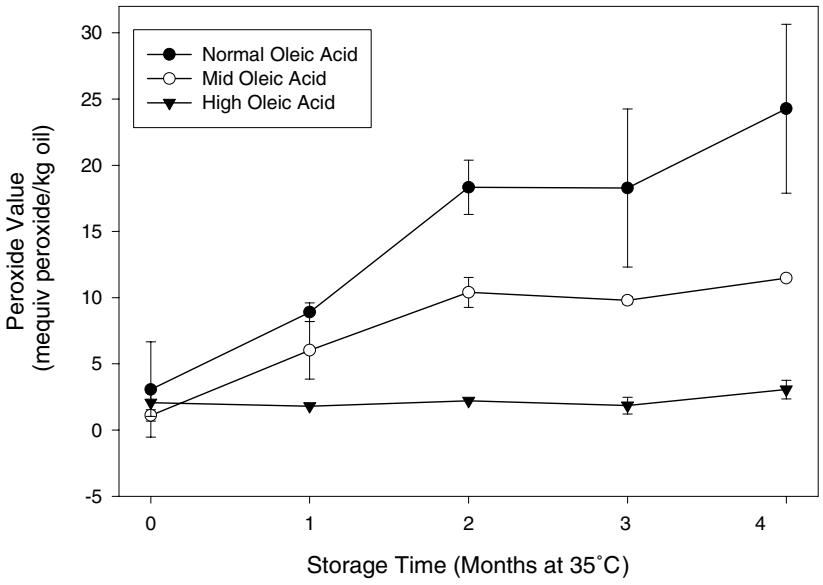

Fig. 1. Peroxide value of normal-, mid-, and high-oleic acid peanuts during storage at 35 °C. Bars represent the standard error of the mean ($n = 2$).

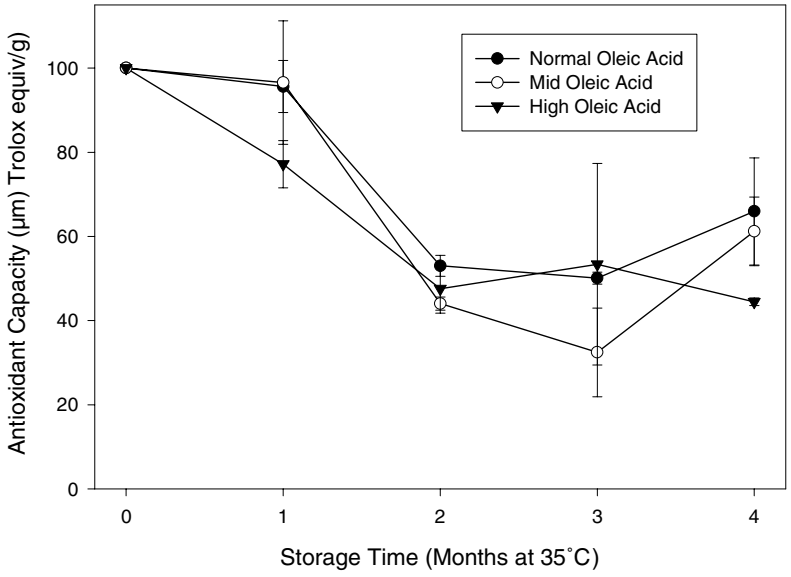

Fig. 2. Percent relative change in antioxidant capacity of normal-, mid-, and high-oleic acid peanuts during storage at 35 °C for up to 4 months. Bars represent the standard error of the mean ($n = 2$).

the high temperatures of roasting. Previous studies have identified soluble forms of both free and bound polyphenolics in peanuts and defatted peanut flours, with bound phenolics representing up to 90% of the total present (Dabrowski & Sosulski, 1984; Fajardo, Waniska, Cuero, & Pettit, 1995; Seo & Morr, 1985). Bound phenolics, with similar spectral properties to *p*-coumaric acid and hydroxybenzoic acid, were tentatively characterized in all three cultivars, and likely represented ester-linkages with carbohydrates or protein–polyphenolic complexes.

Overall, the normal-oleic acid peanut had higher concentrations of individual polyphenolics than mid-or high-oleic acid peanuts. Despite varying phenolic concentrations, the relative changes in individual polyphenolics during storage were similar among the three cultivars and changes were independent of storage temperature. The small changes observed in overall polyphenolic concentrations were an indication that these compounds did not have an appreciable impact on prevention of lipid oxidation and were generally poorly correlated with antioxidant capacity over time.

Free *p*-coumaric acid (Peak 5), along with three tentatively identified esterified derivatives of *p*-coumaric (Peaks 3, 4, and 8), was the predominant soluble

polyphenolic that likely contributed to the antioxidant capacity of peanuts (Table 1; Fig. 3). Derivatives of *p*-coumaric acid were also found in malted barley and contributions to antioxidant capacity were found in a methyl linoleate system for both *trans*- and *cis*-*p*-coumaric acid (Maillard & Berset, 1995). Insignificant changes in *p*-coumaric acid were observed at 20 °C and for the normal-oleic cultivar held at 35 °C, while mid- and high-oleic acid cultivars experienced a small decline after 4 months storage (10.9 and 5.7 mg/kg, respectively). The three esters of *p*-coumaric acid, despite initial concentration differences among cultivars, all demonstrated small variations in concentration throughout storage. These differences were mostly attributed to raw kernel diversity, such as kernel maturity, within the peanuts themselves. On average, concentrations of *p*-coumaric acid and its derivatives were mostly constant at both storage temperatures and did not reflect hydrolysis or oxidative changes.

Two compounds that shared UV spectral characteristics with *p*-hydroxybenzoic acid were also observed in all three cultivars (Table 2), but were tentatively characterized as an esterified form of hydroxybenzoic acid, since free *p*-hydroxybenzoic acid was not detected in the peanuts, even after a mild acid hydrolysis (data not shown). Hydroxybenzoic acids, such as protocatechuic

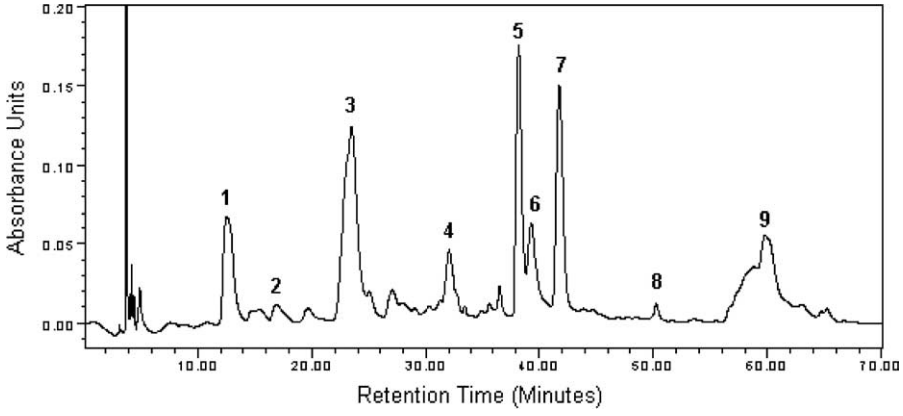

Fig. 3. Typical reversed phase HPLC chromatograms of 40% methanol-soluble phytochemicals in dry-roasted peanuts. Peak 1 is 5-hydroxymethylfurfural (not quantified), with remaining peak assignments found in Tables 1 and 2.

Table 2
Effect of storage time (0–4 months) and temperature (20 and 35 °C) on the concentration (mg/kg) of hydroxybenzoic acid esters and protein/amino acid (tryptophan) present in peanut cultivars with varying oleic acid content

	Oleic acid content[a]	20 °C					35 °C				
		Day 0	Month 1	Month 2	Month 3	Month 4	Day 0	Month 1	Month 2	Month 3	Month 4
Hydroxybenzoic acid ester (Peak 2)[e]	Normal	29.4 b[b]	29.4 a	25.2 ab	24.0 ab	19.4 a	29.4 b	24.4 ab[†c]	25.1 ab	22.0 a	19.9 ab
	Mid	27.4 b	28.9 a	20.8 b*[d]	17.9 b	24.2 a	27.4 b	20.8[†]	23.2 b	17.2 a	15.6 b[†]
	High	45.5 a	31.0 a*	30.9 a	28.8 a	24.7 a	45.5 a	31.5 a*	33.2 a	23.0 a*	25.9 a
Hydroxybenzoic acid ester (Peak 9)	Normal	113 a	116 a	101 a	184 a*	263 a*	114 a	100 a	57.6 b	222 a*	207 a
	Mid	103 a	109 a	62.4 a	126 a*	158 b	103 a	58.5 a*[†]	49.8 b	159 b*	130 b
	High	78.1 a	81.1 a	88.6 a	143 a	164 b	78.1 a	74.6 a	109 a	131 b	131 b
Tryptophan (Peak 6)	Normal	187 a	210 a	235 a	172 a*	186 a	187 a	176 a	198 a	170 a	197 a
	Mid	99.2 b	90.7 b	105 b	78.2 b	84.3 b	99.2 b	85.1 b	93.1 b	80.5 b	74.8 b
	High	56.9 b	68.2 b	63.3 b	55.5 b	74.7 b	56.9 b	58.4 b	38.1 c*	53.3 b	46.9 b
Soluble protein[f] (Peak 7)	Normal	388 a	411 a	362 a*	365 a	343 a	388 a	376 a	341 a	379 a	320 a
	Mid	160 c	141 b	143 b	142 c	138 b	160 c	152 b	128 c	132 c	136 c
	High	228 b	199 b	224 b*	220 b	170 b	228 b	194 b	192 b	221 b	196 b

[a] Georgia Green (normal-oleic acid), Florida MDR98 (mid-oleic acid), and ANorden (high-oleic acid).

[b] Values with different letters within columns are significantly different (LSD test, $P < 0.05$), and indicate the effect of oleic content.

[c] Means with a dagger (†) indicate a significant difference (LSD test, $P < 0.05$) due to storage temperature, within each peanut cultivars, at corresponding storage times.

[d] Means with an asterisk (*) within each peanut cultivar indicate a significant difference (LSD test, $P < 0.05$) between two consecutive months of storage.

[e] Peak identifications correspond to Fig. 3.

[f] Soluble protein with spectral properties of free tryptophan.

and *p*-hydroxybenzoic acid, were shown to be relatively good inhibitors of lipid peroxidation in vitro (Onyeneho & Hettiarachchy, 1992). Similar to the trends observed with *p*-coumaric acid esters, concentrations of the hydroxybenzoic acid esters varied between cultivars and did not appreciably change with an increase in storage temperature. However, changes in concentration were noted during storage that were not considered oxidative in nature, due to their temperature independence. The more polar hydroxybenzoic acid ester (Peak 2) decreased during storage by 39% at its lowest level, while the second, less polar ester (Peak 9) was present in considerably higher concentrations in each cultivar and significantly increased after the second month of storage at both temperatures. After four months of storage, concentrations of Peak 9 increased nearly 2-fold at 20 °C and 1.6-fold at 35 °C for each cultivar, its low polarity potentially indicating a natural hydrolysis compound that formed independent of storage temperature.

The last two compounds quantified were identified as free tryptophan (Peak 6) and a soluble protein with a tryptophan residue (Peak 7), as indicated by their identical spectral characteristics. Normal-oleic acid peanuts had appreciably higher concentrations of these compounds than mid- and high-oleic peanuts, but concentrations were not related to antioxidant capacity during storage. As observed with the phenolic acids, these compounds did not demonstrate a temperature-dependent change in concentration over time and the minor changes in concentration were attributable to normal variations over time within each subset of peanuts.

Overall, changes in polyphenolics were poorly related to antioxidant capacity and were generally independent of lipid oxidation or storage temperature. Initial concentrations of individual polyphenolics quantified by HPLC were 984, 530, and 568 mg/kg for normal-, mid-, and high-oleic acid peanuts, respectively, but concentrations were only 409, 270, and 284 mg/kg when tryptophan and the soluble protein were eliminated. These values were appreciably lower than values obtained by the Folin–Ciocalteu assay (1.36 mg/kg on average) and reflected by high level of interference in the assay. Since the antioxidant capacity of peanuts changed significantly over time and in a temperature-dependent manner, whereas individual polyphenolics did not, data suggest that other compounds soluble in 80% methanol, such as unidentified or co-eluting polyphenolics not specifically quantified in this study, may be responsible for some of the antioxidant changes. Despite their poor overall correlations with antioxidant capacity, high concentrations of *p*-coumaric acid and its esterified derivatives were likely contributors to the total antioxidant capacity of peanuts, since appreciable activity exists for *p*-coumaric acid in vitro (Pellegrini, Visioli, Buratti, & Brighenti, 2002; Rice-Evans, Miller, & Paganga, 1996). Previous studies have also isolated other potential contributors to antioxidant capacity in peanuts, such as an ethyl ester of protocatechuic acid isolated from peanut testa (Huang et al., 2003), luteolin in peanut hulls (Duh, Yeh, & Yen, 1992), Maillard-derived compounds and protein hydroylsates (Hwang, Shue, & Chang, 2001), tocopherols (Hashim, Koehler, & Eitenmiller, 1993), and resveratrol (Ibern-Gonzalez, Roig-Perez, Lameula-Raventos, & Torre-Boronat, 2000; Sobolev & Cole, 1999) in peanuts and peanut derivatives. However, identifications of compounds, initially soluble in 80% methanol, responsible for losses in antioxidant capacity in stored peanuts were not elucidated in this study, yet the relatively high antioxidant capacity exhibited by the peanuts kernels was good evidence to support their potential health benefits.

Acknowledgements

This research was supported in part by the Florida peanut producers through the Florida Department of Agriculture and Consumer Services and the Florida Agricultural Experiment Station, and approved for publication as Journal Series No. R-09663.

References

Anderson, P. C., Hill, K., Gorbet, D. W., & Brodbeck, BV. (1998). Fatty acid and amino acid profiles of selected peanut cultivars and breeding lines. *Journal of Food Composition and Analysis, 9*, 100–111.

Anderson, P. C., & Gorbet, D. W. (2002). Influence of year and planting date on fatty acid chemistry of high-oleic acid and normal peanut genotypes. *Journal of Agricultural and Food Chemistry, 50*, 1298–1305.

Association of Official Analytical Chemists. (1990). Peroxide value of oils and fats (965.33). In K. Helrich (Ed.), *Official methods of analysis* (15th ed., pp. 956–957) AOAC Inc., Arlington, VA.

Braddock, J. C., Sims, C. A., & O'Keffe, S. F. (1995). Flavor and oxidative stability of roasted high-oleic acid peanuts. *Journal of Food Science, 60*, 489–493.

Cabrini, L., Barzanti, V., Cipollone, M., Fiorentini, D., Grossi, G., Tolomelli, B., Zambonin, L., & Landi, L. (2001). Antioxidants and total peroxyl radical-trapping ability of olive and seed oils. *Journal of Agricultural and Food Chemistry, 49*, 6026–6032.

Chu, Y. H., & Hsu, H. F. (1999). Effect of antioxidants on peanut oil stability. *Food Chemistry, 66*, 29–34.

Dabrowski, K. J., & Sosulski, F. W. (1984). Composition of free ad hydrolyzable phenolics acids in defatted flours of ten oilseeds. *Journal of Agricultural and Food Chemistry, 32*, 128–130.

Duh, P. D., Yeh, D. B., & Yen, G. C. (1992). Extraction and identification of an antioxidative component of peanut hulls. *Journal of American Oil Chemistry Society, 69*, 814–818.

Duke, J. A. (1992). *Handbook of phytochemical constituents of GRAS herbs and other economic plants*. Boca Raton, FL: CRC Press.

Fajardo, J. E., Waniska, R. D., Cuero, R. G., & Pettit, R. E. (1995). Phenolic compounds in peanut seeds: Enhanced elicitation by chitosan and effects on growth and aflatoxin B1 production by *Aspergillus flavus*. *Food Biotechnology, 9*, 59–78.

Hashim, I. B., Koehler, P. E., & Eitenmiller, R. R. (1993). Tocopherols in runner and Virginia peanut cultivars at various maturity stages. *Journal of the American Oil Chemists' Society, 70*, 633–635.

Hatate, H. (1996). Antioxidative activity of ovalbumin hydrolysates and their synergistic effects with α-tocopherol. *Nippon Shokuhin Kagaku Kogaku Kaishi, 43*, 719–722.

Herraiz, T., Galisteo, J., & Chamorro, C. (2003). L-tryptophan reacts with naturally occurring and food-occurring phenolic aldehydes to give phenolic tetrahydro-β-carboline alkaloids: Activity as antioxidants and free radical scavengers. *Journal of Agricultural and Food Chemistry, 51*, 2168–2173.

Huang, S. C., Yen, G. C., Chang, L. W., Yen, W. J., & Duh, P. D. (2003). Identification of an antioxidant, ethyl protocatechuate, in peanut seed testa. *Journal of Agricultural and Food Chemistry, 51*, 2380–2383.

Hwang, J. Y., Shue, Y. S., & Chang, H. M. (2001). Antioxidative activity of roasted and defatted peanut kernels. *Food Research International, 34*, 639–647.

Ibern-Gonzalez, M., Roig-Perez, S., Lameula-Raventos, R. M., & Torre-Boronat, M. C. (2000). Resveratrol and piceid levels in natural and blended peanut butters. *Journal of Agricultural and Food Chemistry, 48*, 6352–6354.

Mugundi, J. B., Sims, C. A., Gorbet, D. W., & O'Keefe, S. F. (1998). Flavor stability of high-oleic peanuts stored at low humidity. *Journal of the American Oil Chemists' Society, 75*, 21–25.

Maillard, M. N., & Berset, C. (1995). Evolution of antioxidant activity during kilning: Role of insoluble bound phenolic acids of barley and malt. *Journal of Agricultural and Food Chemistry, 43*, 1789–1793.

Norden, A. J., Gorbet, D. W., & Knauft, D. A. (1987). Variability in oil quality amomg peanut genotypes in the Florida breeding program. *Peanuts Science, 14*, 7–11.

O'Byrne, D. J., Knauft, D. A., & Shiremen, R. B. (1997). Low fat-monounsaturated rich diets containing high-oleic peanuts improve serum lipoprotein profiles. *Lipids, 32*, 687–695.

O'Keefe, S. F., Wiley, V. A., & Knauft, D. A. (1993). Comparison of oxidative stability of high- and normal-oleic peanut oils. *Journal of the American Oil Chemists' Society, 70*, 489–492.

Onyeneho, S. N., & Hettiarachchy, N. S. (1992). Antioxidant activity of durum wheat bran. *Journal of Agricultural and Food Chemistry, 40*, 1496–1500.

Pattee, H. E., Isleib, T. G., Gorbet, D. W., Moore, K. M., Lopez, Y., Baring, M. R., & Simpson, C. E. (2002a). Effect of the high-oleic trait on roasted peanut flavor in backcross-derived breeding lines. *Journal of Agricultural and Food Chemistry, 50*, 7362–7365.

Pattee, H. A., Isleib, T. G., Moore, K. M., Gorbet, D. W., & Giesbrecht, FG. (2002b). Effect of high-oleic trait and paste storage variables on sensory attribute stability of roasted peanuts. *Journal of Agricultural and Food Chemistry, 50*, 7366–7370.

Pellegrini, N., Visioli, F., Buratti, S., & Brighenti, F. (2002). Direct analysis of total antioxidant activity of olive oil and studies on the influence of heating. *Journal of Agricultural and Food Chemistry, 49*, 2532–2538.

Reed, K. A., Sims, C. A., Gorbet, D. W., & O'Keffe, S. F. (2002). Storage water activity affects of flavor fade in high- and normal-oleic peanuts. *Food Research International, 35*, 769–774.

Rice-Evans, C., & Bourne, L. (1998). Considerations for the efficacy of phenolic phytochemicals as nutritional antioxidants. *Pathophysiology, 5*, 267.

Rice-Evans, C. A., Miller, N. J., & Paganga, G. (1996). Structure-antioxidant activity relationships of flavonoids and phenolic acids. *Free Radical Biological Medicine, 20*, 933–956.

SAS Institute, Inc. (2002). JMP Software Version 5, Cary, NC.

Seo, A., & Morr, C. V. (1985). Activated carbon and ion exchange treatments for removing phenolics and phytate from peanut protein products. *Journal Food Science, 50*, 262–263.

Sobolev, V. S., & Cole, R. J. (1999). *trans*-Resveratrol content in commercial peanuts and peanut products. *Journal of Agricultural and Food Chemistry, 47*, 1435–1439.

Taguchi, K., Iwami, K., Kawabata, M., & Ibuki, F. (1988). Antioxidative effects of wheat gliadin and hens' egg white in powder model systems: Protection against oxidative deterioration of safflower oil and sardine oil. *Agricultural Biological Chemistry, 52*, 539–545.

Talcott, S. T., Brenes, C. H., & Howard, L. R. (2000). Contribution of periderm material and blanching time to the quality of pasteurized peach puree. *Journal Agricultural and Food Chemistry, 48*, 4590–4596.

Talcott, S. T., Percival, S. S., Pitter-Moore, J., & Celoria, C. (2003). Phytochemical composition and antioxidant stability of fortified yellow passion fruit (*Passiflora edulis*). *Journal Agricultural and Food Chemistry, 51*, 935–941.

Tanaka, M., Sugita, S., Wen-kui, C., Nagashima, Y., & Taguchi, T. (1990). Influence of water activity on the development of antioxidative effect during the Maillard reaction between histidine and glucose. *Nippon Suisan Gakkaishi, 56*, 525–530.