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Polyphenolic content and sensory properties of normal and high oleic acid peanuts

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Abstract

Peanuts are an important food crop with many health benefits of their consumption realized by consumers worldwide. Limited information is available on non-nutrient phytochemical composition of peanuts and their relative antioxidant values, knowledge that may serve to increase overall marketability of the crop. Shelled peanuts from eight cultivars and four experimental genotypes with either high or normal oleic acid contents were evaluated for phytochemical, antioxidant, and sensory properties (roasted only) before and after dry roasting under constant time and temperature conditions. Peanuts were evaluated for color, total and individual phenolics, and antioxidant capacity while a trained sensory panel evaluated the peanuts for roasted and burnt peanut flavor and aroma, sweetness, and bitterness. Overall, no meaningful differences were observed for phytochemical and antioxidant properties between high and normal oleic acid peanuts, but differences were present among cultivars. However, high oleic acid varieties had higher burnt peanut aroma and burnt peanut flavor compared to normal oleic peanuts but were not necessarily independent from roasted peanut aroma and flavor. Numerous polyphenolics were separated and characterized based on spectral similarities to *p*-hydroxybenzoic acid, tryptophan, and *p*-coumaric acid in both free and bound (esterified) forms. Peanuts were found to be a good source of antioxidant polyphenolics, such as *p*-coumaric acid, that may be contributing factors to potential health benefits of their consumption.

Keywords: Peanut; Antioxidant; Roasting; Polyphenolic; Sensory

1. Introduction

Quality and stability characteristics associated with peanuts and peanut products can now be better maintained due to an adaptation of the high oleic acid (>80%) trait into several new peanut cultivars. Peanuts with high oleic acid contents were determined to have improved stability against lipid oxidation that could lead to adverse flavors (Mugendi, Sims, Gorbet, & O'Keefe, 1998; O'Keefe, Wiley, & Knauft, 1993), and exhibited nearly twice the shelf life of peanuts with normal (50% oleic) oleic acid content (Braddock, Sims, & O'Keefe, 1995). Organoleptic properties of peanuts vary among cultivars, with oil content, and roasting conditions; yet other than differences in their fatty acid content, the high oleic varieties are generally difficult to distinguish from normal oleic varieties despite reported differences in certain sensory attributes relating to roasted characteristics (Baker, Sims, Gorbet, Sanders, & O'Keefe, 2002; Pattee et al., 2002; Reed, Sims, Gorbet, & O'Keefe, 2002).

Agronomic and postharvest factors have been shown to influence chemical composition and sensory properties of roasted peanuts (Buckholtz, Daun, Stier, & Trout, 1980; Chiou, Chang, Tsai, & Ho, 1991; Chung, Eiserich, & Shibamoto, 1993; Smyth et al., 1998), while lipid oxidation rates logically influence storage stability. The degree of roasting also influenced quality and antioxidant parameters of peanut kernels (Hwang, Shue, & Chang, 2001), creating a complex environment for peanut quality assessment. Peanut kernels are not typically considered a good source of antioxidant

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phytochemicals, other than tocopherols, and contain approximately 50% lipid, 25% protein, and 16% carbohydrate making them a nutritious alternative to meat products. However, more than 15 polyphenolics have been identified in peanuts (Duke, 1992) and, along with 80–140 mg/kg total tocopherols (Hashim, Koehler, & Eitenmiller, 1993), these compounds may contribute to purported health benefits of peanuts. Seo and Morr (1985) identified six polyphenolics in defatted peanut protein isolates that may be responsible for adverse color and flavor development when used as a food ingredient, while Fajardo, Waniska, Cuero, and Pettit (1995) demonstrated a stress-elicited synthesis of free and bound phenolics in peanuts, with *p*-coumaric and ferulic acid the major compounds identified. Hydroxycinnamic acids such as *p*-coumaric acid are ubiquitous in higher plants and are found with various hydroxyl and methoxyl substitutions and may exist in esterified forms or bound to proteins (Bartolome & Gomez-Cordoves, 1999; Herraiz, Galisteo, & Chamorro, 2003; Niwa, Doi, Kato, & Osawa, 2001). As an antioxidant, *p*-coumaric acid is an effective radical inhibitor in vitro (Rice-Evans, Miller, & Paganga, 1996; Rice-Evans, Miller, & Paganga, 1997) but contains only moderate inhibitory properties against lipid peroxidation (Kikuzaki, Hisamoto, Hirose, Akiyama, & Taniguchi, 2002; Rice-Evans & Bourne, 1998).

The objective of this work was to assess physicochemical and organoleptic properties of high and normal oleic acid peanuts since no quantitative studies comparing polyphenolic content and antioxidant capacity have been conducted for raw and roasted peanut kernels. Most peanuts are consumed following a mild or medium roast at high temperatures (whole peanuts or peanut butter), but since peanuts may also be consumed raw or boiled (Sobolev, 2001) a chemical distinction was also made between raw and roasted peanuts in this study.

2. Materials and methods

2.1. Materials and processing

Eight cultivars and four experimental genotypes of raw, shelled peanut kernels (*Arachis hypogaea* L.) were obtained from the University of Florida Agricultural Research Center in Marianna, Florida and were frozen under a blanket of nitrogen for 10 weeks at −20 °C prior to roasting. Cultivars included the high oleic acid peanuts 'Hull', 'ANorden', 'Andru II', 'GP-1' and 'SunOleic 97R' and the normal oleic acid peanuts 'Carver', 'Georgia Green', and 'DP-1'. Additional developmental genotypes included 'UF98515' and 'UF00620' (high oleic) and the normal oleic acid peanuts 'UF00324' and 'UF98116'. Peanuts were removed from storage, warmed to room temperature, and 500 g from each cultivar/genotype roasted at 175 °C for 10 min in a Pyrex forced air convection oven (Aroma AeroMatic Oven, San Diego, CA, USA). This time-temperature combination was determined in preliminary studies to give a medium roast with a lightness value near 50. Peanuts were agitated every 3 min to insure uniform roasting and the temperature was monitored using a digital thermocouple (Component Design, Portland, OR, USA) surrounded by peanuts with temperature variations ca. ±3 °C. Peanuts were cooled, testa (outer skin) manually removed, and then placed into plastic bags under a blanket of nitrogen and kept frozen at −20 °C for an additional eight weeks prior to physicochemical evaluations on both raw (not roasted; testa removed) and roasted peanuts and for sensory evaluations on roasted peanuts.

2.2. Physicochemical analyses

Objective peanut color was determined using a Colorguard colorimeter (BYK-Gardner, Columbia, MD, USA) and measurement of Hunter L (lightness) determined on 75 g of whole peanuts. A commercially available brand (Kraft Foods: Planters dry roasted, unsalted) of peanuts was also evaluated for comparison in physicochemical and sensory analyses. For chemical analysis, peanuts were ground in a kitchen-scale food processor (ca. 30 s) to the smallest obtainable particle size and 10 g homogenized for 1 min in 20 ml of 80% methanol. Samples were allowed to extract for 24 h at room temperature and the supernatant collected after centrifugation to remove insoluble matter. Total soluble phenolics were measured using the Folin–Ciocalteu assay (Swain & Hillis, 1959) and data expressed in gallic acid equivalents. Individual polyphenolics were separated and characterized by HPLC according to the conditions of Talcott, Brenes, and Howard (2000) using a Waters 2690 Alliance HPLC system, a Waters Spherisorb ODS-2 (4.6×250 mm) column, and a Waters 996 PDA detector monitored at 280 nm. Concentrations of separated compounds were expressed in equivalents of either *p*-hydroxybenzoic acid, tryptophan, or *p*-coumaric acid (Sigma Chemical Company, St. Louis, MO, USA) based on spectral similarities to each standard.

Antioxidant capacity was determined using the ORAC (oxygen radical absorbance capacity) assay and the modifications of Ou, Hampsch-Woodill, and Prior (2001) using fluorescein as the fluorescent probe. Peroxyl radicals were generated by 2,2′-azobis (2-amidinopropane) dihydrochloride and fluorescence loss monitored on a Molecular Devices fmax® 96-well fluorescent microplate reader (485 nm excitation and 538 nm emission). Each peanut isolate was diluted 50-fold in pH 7 phosphate buffer prior to pipetting into a 96-well mi-

croplate and all values background corrected for methanol content by using a solvent blank of the same dilution. A 4-fold dilution factor was used in the actual assay that corresponded to an in-well standard concentration ranging from 6.25 to 50 μM Trolox.

Soluble polyphenolics were also isolated from a subset of roasted peanuts by homogenizing with 80% methanol and filtering through Whatman #4 filter paper. Insoluble residues in the filtrate were washed twice with 20 ml of 100% methanol, the solvents pooled, and removed by rotary evaporation at 45 °C. The remaining residue was dissolved in a known volume of water and placed in a sonic water bath for 5 min to further facilitate solubilization. Following centrifugation to remove insoluble matter, an aliquot of this aqueous isolate was loaded onto a pre-conditioned Waters Sep-Pak C_{18} cartridge and two fractions collected, C_{18} non-retained and C_{18} retained. Both isolates were analyzed for individual polyphenolics by HPLC and antioxidant activity as compared to the initial isolate prior to fractionation.

2.3. Sensory analysis

A 10 person (four male, six female) trained sensory panel comprised of staff and students at the University of Florida's Department of Food Science and Human Nutrition were used quantify roasted peanut sensory properties. Panelists were trained in three, one-hour sessions for roasted peanut aroma, burnt peanut aroma, roasted peanut flavor, burnt peanut flavor, sweetness, and bitterness using peanuts that were roasted to different intensities. Ballot scoring was based on a 15 cm line scale using sensory attributes common only to whole peanuts, with 0 cm representing none and 15 cm representing the most intense peanut displaying a given attribute. Panelists were also trained with and employed the use of anchor points on each ballot, which represented sensory intensities for the commercial brand of dry roasted peanuts. These anchor points allowed for more uniform comparisons of each peanut variety and served as a benchmark for ballot scoring. Following the first two training sessions, panelists were asked to reach a consensus on sensory attributes for the commercial brand of dry roasted peanuts (roasted peanut aroma = 5 cm; burnt peanut aroma = 2 cm; roasted peanut flavor = 4 cm; burnt peanut flavor = 1 cm; sweetness = 10 cm; and bitterness = 5 cm) and these values were included on each ballot for their respective sensory attribute. After the training sessions, panelists were evaluated under actual testing conditions simulating normal peanut consumption and were found to have an overall standard error of ±0.88 cm on the 15-cm structured line scale. For each evaluation session, panelists were given 25 g of peanuts sealed in plastic sampling cups from four peanut cultivars/genotypes, each randomly selected and coded. Panelists were instructed to initially evaluate aroma characteristics prior to the remaining attributes. A second set of four randomly selected samples was then presented after a 15 min break for a maximum of eight samples presented daily. Evaluations were conducted under normal lighting conditions and water was provided for palate rinsing between samples. Each sample was evaluated twice over a four week period.

2.4. Statistical analysis

Data represents the mean and standard error of duplicate determinations of both physicochemical and sensory evaluations. Multiple linear regression, analysis of variance, and Pearson correlations were conducted using JMP5 software (SAS Institute, 2002), and mean separation using the LSD test ($P < 0.05$).

3. Results and discussion

3.1. General

Lipids from a typical normal oleic peanut may be expected to contain approximately 50% oleic acid as compared to high oleic varieties that can exceed 80% oleic acid (Knauft, Gorbet, & Norden, 2000). Although high oleic peanuts were conclusively proven to have an increased shelf life through reduced lipid oxidation, little data are available on phytochemical characteristics that may distinguish these varieties from normal oleic peanuts. Average values for measured physicochemical attributes (color, individually quantified phenolics, and antioxidant capacity) were found to be insignificant between high and normal oleic acid cultivars with the exception of total soluble phenolics by the Folin–Ciocalteu assay (Table 1), which were slightly higher for normal oleic acid varieties. Roasting conditions were optimized to give an L-value near 50 (Sanders, Vercellotti, Crippen, & Civille, 1989) with an actual mean of 49.2 for all varieties (Table 2). This roast color was considerably darker than the commercially available peanut used for comparison ($L = 58.2$). Lightness values varied among varieties and ranged from 44.5 to 53.7 following roasting under identical time-temperature conditions with insignificant differences in lightness found for raw peanuts (data not shown). Average moisture content of unroasted peanuts were 3.50% compared to 0.66% for roasted peanuts, which served to slightly concentrate phytochemical constituents in the latter on a fresh weight basis.

3.2. Polyphenolic characterization

The conditions of roasting served to alter physicochemical attributes among cultivars, since individual

Table 1
The average (avg) and standard error (err) for antioxidant capacity (μM Trolox equivalents/g) and polyphenolic content (mg/kg) of raw and roasted peanuts (fresh weight) as affected by cultivar/genotype and oleic acid concentration

Cultivar or genotype	Oil[a]	Antioxidant capacity				Total soluble phenolics[b]				*p*-Coumaric acid				Total phenolics by HPLC[c]				Total phenolics without proteins[d]			
		Raw		Roasted		Raw		Roasted		Raw		Roasted		Raw		Roasted		Raw		Roasted	
		Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err
Carver	NO	28.8	1.1	36.9	0.1	1100	2.0	1080	0.5	24.8	0.4	40.5	0.4	103	14.7	142	18.5	40.2	0.7	53.2	1.3
DP-1	NO	25.0	2.8	23.9	0.4	1110	40	1080	14	13.0	0.5	42.1	0.1	72.2	1.4	210	14.5	27.5	1.1	151	10.2
Ga. Green	NO	26.9	1.3	32.3	0.6	913	39	949	8.5	25.5	2.4	115	0.2	175	1.5	394	0.3	48.1	1.8	223	5.1
UF00324	NO	33.8	1.0	37.2	0.1	1040	22	986	9.5	57.9	3.6	112	0.7	175	3.4	360	5.0	81.8	3.7	214	9.0
UF98116	NO	33.1	3.2	40.0	1.2	1140	45	1040	77	20.2	0.1	82.7	1.0	138	0.4	283	15.5	37.4	0.3	201	14.1
Retail brand[e]	NO	NA[f]		28.1	0.8	NA		1040	1.5	NA		28.2	0.4	NA		119	0.0	NA		64.6	0.0
Anorden	HO	24.1	0.2	29.7	0.4	980	24	1000	13	18.4	1.2	19.5	0.1	155	4.7	119	3.6	33.2	2.2	35.8	1.2
GP-1	HO	30.1	2.2	35.2	0.6	1020	63	1000	3.0	12.9	0.6	80.7	0.5	125	20.8	235	26.8	27.4	0.8	176	15.9
Hull	HO	27.9	1.1	31.7	0.4	948	2.5	1000	8.0	8.33	1.3	30.6	0.5	110	1.2	141	19.3	23.6	1.4	47.5	2.5
Andru II	HO	20.2	0.1	26.3	0.1	908	9.5	839	21	13.5	7.0	56.7	0.3	218	13.3	291	30.7	43.0	7.1	127	10.7
SunOleic & 97R	HO	34.4	3.0	37.3	1.0	992	45	981	22	12.2	9.8	54.0	2.2	176	23.8	247	4.7	28.5	9.9	165	0.0
UF98515	HO	18.4	2.3	29.6	0.4	916	81	968	34	31.4	1.0	80.7	0.3	161	1.4	366	4.5	50.1	1.2	215	9.3
UF00620	HO	29.8	3.5	41.2	0.6	1090	25	1050	7.5	65.9	0.9	117	3.2	204	2.3	352	8.7	89.8	0.9	227	11.0
Average[g]	NO	29.5	2.7	34.1	1.9	1060	39	1030	25	28.3	7.7	78.5	12	132	20	278	36	47.0	9.3	168	28
Average	HO	26.4	2.1	33.0	2.9	979	23	977	22	23.2	7.6	62.7	17	164	14	250	50	42.2	8.7	142	29

[a] Oleic acid content: NO = normal oleic acid (~50%) and HO = high oleic acid (>80%).
[b] Measured using the Folin–Ciocalteu metal reduction assay.
[c] Measured as the sum of individually quantified polyphenolics, tryptophan, and soluble proteins.
[d] Measured as the sum of individually quantified polyphenolics only.
[e] Planters dry roasted peanuts.
[f] NA = Raw peanuts not available.
[g] Reflects the average of NO and HO varieties, not including the retail brand.

Table 2
The average (avg) and standard error (err) for objective lightness (*L*-value) and sensory descriptive analysis of roasted peanuts as affected by oleic acid concentration

Cultivar or genotype	Oil[a]	Lightness		Roasted peanut aroma		Burnt peanut aroma		Roasted peanut aroma		Burnt peanut aroma		Sweet		Bitter	
		Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err	Avg	Err
Carver	NO	53.7	0.1	8.91	0.7	4.88	0.9	6.64	0.6	2.68	0.5	4.59	0.7	6.46	0.8
DP-1	NO	48.1	0.6	9.01	0.6	6.75	0.7	8.10	0.7	7.27	0.8	3.71	0.6	8.33	0.7
Ga. Green	NO	48.2	0.6	9.20	0.6	6.22	0.8	8.26	0.8	4.81	0.8	5.36	0.8	6.41	0.7
UF00324	NO	51.6	0.1	9.34	0.5	5.33	0.6	8.23	0.6	5.13	1.0	2.96	0.4	7.31	0.9
UF98116	NO	51.0	0.2	9.92	0.6	6.49	0.8	8.00	0.4	6.45	1.0	4.31	0.9	7.99	0.9
Retail brand[b]	NO	58.2	0.3	5.00	0.0	1.00	0.0	4.00	0.0	1.00	0.0	10.0	0.0	4.00	0.0
Anorden	HO	46.5	0.7	8.67	0.5	6.77	0.9	9.53	0.4	6.59	0.9	3.58	0.4	7.87	0.6
GP-1	HO	44.5	0.4	9.61	0.8	8.65	0.7	8.87	0.6	7.21	0.9	5.07	0.6	6.80	0.8
Hull	HO	51.0	0.1	9.65	0.5	8.41	0.9	9.19	0.5	7.92	0.9	3.74	0.7	8.53	0.8
Andru II	HO	53.7	1.2	8.61	0.4	5.42	0.9	7.23	0.2	4.40	0.9	5.38	0.7	7.07	0.6
SunOleic 97R	HO	44.9	0.7	10.3	0.5	7.93	0.9	9.02	0.5	8.93	0.8	2.83	0.5	9.60	0.8
UF98515	HO	44.5	1.4	8.74	0.6	5.56	0.5	7.91	0.9	5.88	0.8	4.37	0.6	5.74	0.6
UF00620	HO	53.0	0.1	9.19	0.7	5.95	0.7	8.28	0.5	5.69	1.0	4.23	0.5	7.42	0.7
Average[c]	NO	50.5	1.5	9.28	0.2	5.93	0.4	7.85	0.3	5.27	0.8	4.19	0.4	7.30	0.5
Average	HO	48.3	1.8	9.26	0.2	6.96	0.5	8.58	0.3	6.66	0.6	4.17	0.3	7.58	0.5

[a] Oleic acid content: NO = normal oleic acid (~50%) and HO = high oleic acid (>80%).
[b] Planters dry roasted peanuts.
[c] Reflects the average of NO and HO varieties, not including the retail brand.

and total polyphenolics quantified by HPLC were generally higher for roasted compared to raw peanuts. Numerous polyphenolics were separated at 280 nm and characterized and quantified based on spectral properties of *p*-hydroxybenzoic acid (257.3 nm), tryptophan (280.3 nm), and *p*-coumaric acid (309.3 nm). These compounds were common to both raw and roasted peanuts, however free *p*-hydroxybenzoic acid was not detected in the peanuts (Fig. 1; Table 3). Various studies have reported the diversity of polyphenolics present in peanuts and Dabrowski and Sosulski (1984) demonstrated that over 90% of these compounds were present in a bound form. Experimentally, these bound, most likely esterified forms, were also evident based on the diversity of compounds present with spectral characteristics resembling hydroxy-substituted benzoic acids (i.e. Compound 5), but most of these compounds were not further characterized due to their low concentrations.

The predominant phenolic acid present with antioxidant potential was *p*-coumaric acid. Previously identified in peanuts, *p*-coumaric acid was reported to account for 40–68% of the 1760–2033 mg/kg total phenolics present in defatted peanut flour (Seo & Morr, 1985) compared to 83% of the total phenolics reported by Dabrowski and Sosulski (1984). Whole raw peanuts contained an average of 25 mg/kg of *p*-coumaric acid that ranged from 8 to 66 mg/kg among cultivars. Concentrations appreciably increased following roasting with an average of 69 mg/kg that ranged from 19 to 117 mg/kg among cultivars. Two experimental genotypes (UF00324 and UF00620) were found to contain exceptionally high levels of *p*-coumaric acid (>100 mg/kg), similar to Georgia Green, a well established and commonly consumed peanut variety. Concentration differences following roasting were attributed to esterified and/or bound forms of *p*-coumaric acid present in both raw and roasted peanuts, with identity based on their closely related spectral properties to free *p*-coumaric acid. These compounds (compounds 3 and 8) were hypothesized to be hydrolyzed and released under roasting conditions and may have originated from glycosides (*p*-coumaric acid-β-D-glycosides), protein–phenolic complexes, lignin, or from cell wall materials (Lu & Ralph, 1999; Sosulski, 1979).

Other polyphenolics also increased after roasting, specifically three compounds (compounds 3, 9, and 10) that shared similar UV spectral characteristics to *p*-hydroxybenzoic acid that were initially present in low concentrations in raw peanuts (0.40, 1.8, and 16.7 mg/kg) on average. Following roasting these same compounds increased to 52.3, 8.71 and 24.5 mg/kg, respectively on average, presumably due to similar heat-catalyzed changes that seemed to occur with *p*-coumaric acid. However, these compounds were not considered as actual derivatives of *p*-hydroxybenzoic acid itself, only sharing similar spectral properties, since the free acid form was not found in these peanuts neither before or after roasting nor following acid hydrolysis (1 N HCl at 100 °C for 15 min).

Although not typically considered a compound with appreciable antioxidant potential, tryptophan and other

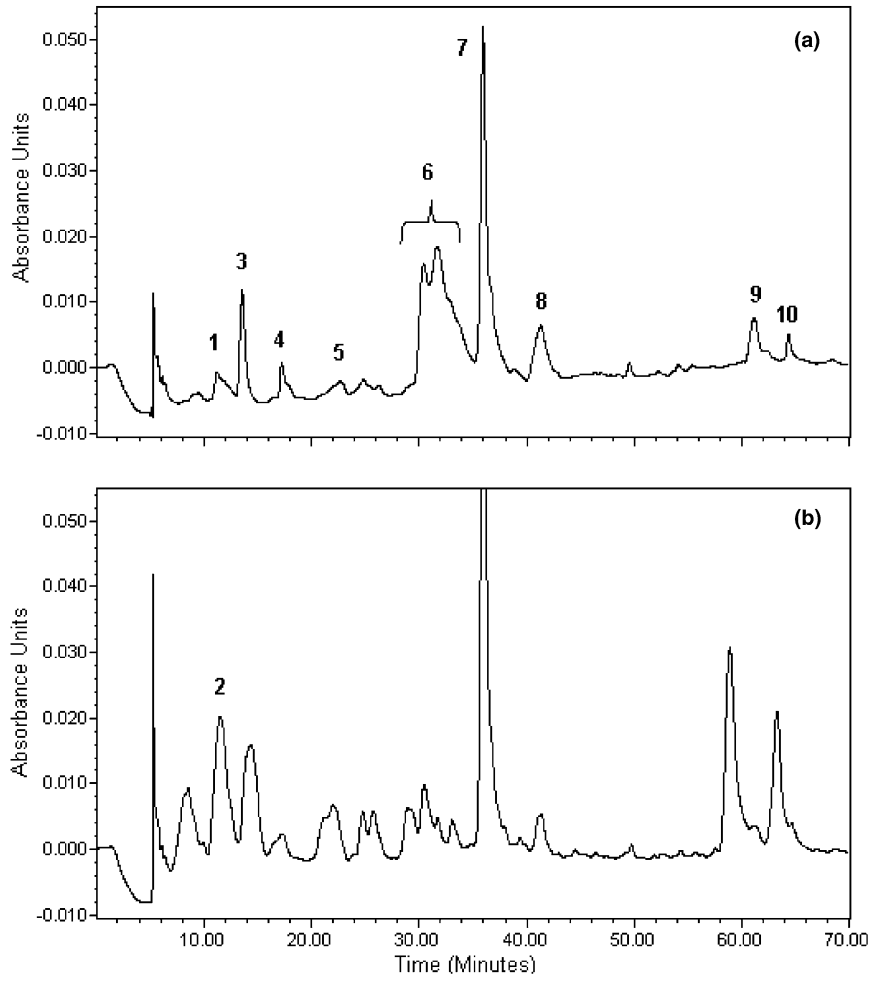

Fig. 1. Reversed phase HPLC chromatograms of 80% methanol-soluble polyphenolics and unidentified proteins in peanuts before (a) and after (b) roasting. Compounds are tentatively identified in Table 3.

Table 3
Tentative identification and spectral characteristics of selected polyphenolics and proteins present in peanuts separated by reversed phase HPLC

Peak no.	Tentative identification	Retention time (min)	λ_{max} (nm)
1	Soluble protein (tryptophan)	11.25	276.1
2	5-hydroxymethyl furfural	11.29	285.5
3	*p*-hydroxybenzoic acid ester	13.61	257.2
4	Soluble protein (tryptophan)	17.26	276.1
5	Hydroxybenzoic acid ester	22.68	266.6
6	Soluble proteins (with free tryptophan)	25.35	276.1
7	*p*-Coumaric acid	35.96	309.3
8	*p*-Coumaric acid ester	41.36	314.0
9	*p*-hydroxybenzoic acid ester	58.88	257.2
10	*p*-hydroxybenzoic acid ester	63.24	261.9

Peak numbers correspond to Fig. 1.

soluble proteins containing tryptophan were simultaneously separated at 280 nm with other peanut polyphenolics and represented the majority of compounds separated by HPLC based on peak area. However, Hwang et al. (2001) reported that peanut protein hydrolysates could inhibit the oxidation of low-density lipoprotein oxidation. The soluble proteins and free tryptophan detected in raw peanuts were altered appreciably following roasting (Fig. 1, Table 3) and several of these compounds exhibited spectral properties similar to both tryptophan and *p*-coumaric acid, potentially indicating protein–polyphenolic complexation. Chromatographically, these compounds were detected as four or more peaks (varied among cultivars) with a retention time from 25 to 35 min including the compound representing free tryptophan ($t_r = 30.4$ min). Following

roasting, these complexes were disrupted in response to the high temperature of roasting, revealing several co-eluting compounds in roasted peanuts not previously identified that were characterized as either soluble proteins or hydroxybenzoic acid derivatives. Changes in tryptophan or other soluble proteins were difficult to link to any specific function, such as changes in antioxidant activity, due to the high variation present among cultivars and other reactions involving tryptophan such as Maillard browning. Subsequent acid hydrolysis revealed that many soluble proteins with tryptophan residues were still present after roasting (data not shown), leaving behind free tryptophan which was reported to vary from 2540 to 3320 mg/kg in fresh peanuts (Duke, 1992, USDA Handbook, 2002).

3.3. Protein interferences

For additional insight as to compositional changes in peanut polyphenolics as influenced by roasting, total phenolics were measured and calculated in two ways. The first as the sum of the predominant chromatographic peaks (Table 3) separated by HPLC (with and without contributions from soluble proteins) and secondly as a measure of metal ion reducing capacity with the Folin–Ciocalteu assay. Concentrations among cultivars for all discernable compounds quantified by HPLC ranged from 72 to 394 mg/kg, which was appreciably lower than values obtained from the Folin–Ciocalteu assay (840–1140 mg/kg). The concentration range for the latter was in agreement with Seo and Morr (1985) in peanut flours when lipid removal is accounted for. However, these values were poorly correlated to antioxidant capacity due in part to variable contributions from soluble proteins that resulted in an overestimation of actual phenolic concentrations. By eliminating contributions from compounds spectrally identified as protein and/or amino acid residues the resultant concentrations (24–227 mg/kg) were then moderately correlated to the antioxidant capacity of peanuts ($r = 0.50$, $P = 0.004$). Overall, roasting did not alter the concentration of total phenolics by the Folin–Ciocalteu assay, but levels were statistically higher for normal (+67 mg/kg) compared to high oleic acid peanuts. However, this concentration difference was not considered practically significant and concentrations may have been influenced by factors not specifically analyzed for such as varying levels of protein or reducing sugars.

3.4. Antioxidant capacity

The cinnamic acid derivative *p*-coumaric acid is a secondary metabolite with appreciable antioxidant activity, 2.2× that of Trolox (Rice-Evans et al., 1996), and along with other polyphenolics in peanuts may have a role in plant disease resistance and/or oxidative protection. The antioxidant content of peanuts increased overall following roasting in response to moisture loss, heat-catalyzed changes in phenolics or soluble proteins, or even the development of radical scavenging compounds generated during Maillard browning. Values ranged from 18.4 to 34.4 μM Trolox equivalents in raw peanuts and increased to 23.9–41.2 μM following roasting. The antioxidant capacity of roasted peanuts was moderately related to *p*-coumaric acid ($r = 0.55$, $P = 0.001$) in roasted peanuts but no such correlation existed for raw peanuts, potentially indicating that esterified or bound forms of *p*-coumaric acid were less efficient radical scavenging agents. Despite the predominance of macromolecules in peanuts, the concentrations of phytochemicals found in peanut kernels had a moderately high antioxidant capacity in relation to other fruits and vegetables. Additionally, these compounds may be contributing factors towards their purported health benefits, such as the reported link between consumption of high oleic acid peanuts and decreased LDL/HDL cholesterol ratios (O'Byrne, Knauft, & Shiremen, 1997).

3.5. Fractionation of polyphenolics

Separation of polyphenolics on reversed phase C_{18} cartridges was beneficial for characterizing specific polyphenolics responsible for the antioxidant properties of raw and roasted peanuts. This simple fractionation allowed for division of polar compounds (non-retained on C_{18}) from less polar or higher molecular weight species (retained on C_{18}). The resultant fractions were subsequently assessed for antioxidant capacity and phenolic profiles by HPLC as compared to the original isolate. Isolates from each peanut resulted in similar fractionation characteristics and on average the non-retained fraction contained 51.8% of the total antioxidant activity of the original isolate (Fig. 2) compared to only 35.3% in the C_{18} retained fraction, leaving 12.9% unaccounted for. Subsequent HPLC separation of each fraction revealed a remarkable similarity between chromatograms of the initial isolate and the non-retained fraction (data not shown), yet a 2-fold difference in antioxidant capacity existed between them for each cultivar evaluated. Additionally, the non-retained fraction contained 95% of the free *p*-coumaric acid present in peanuts and even after acid hydrolysis of each fraction to release esterified or bound phenolic forms, the polar fraction still contained nearly 90% of the total *p*-coumaric. The small difference in concentration was due to esterified or bound forms of *p*-coumaric acid present in the C_{18} retained fraction. Many of the compounds in the non-retained fraction were characterized as soluble proteins, thus their relatively low antioxidant capacity, while the C_{18} retained fraction revealed numerous compounds that were not previously elucidated

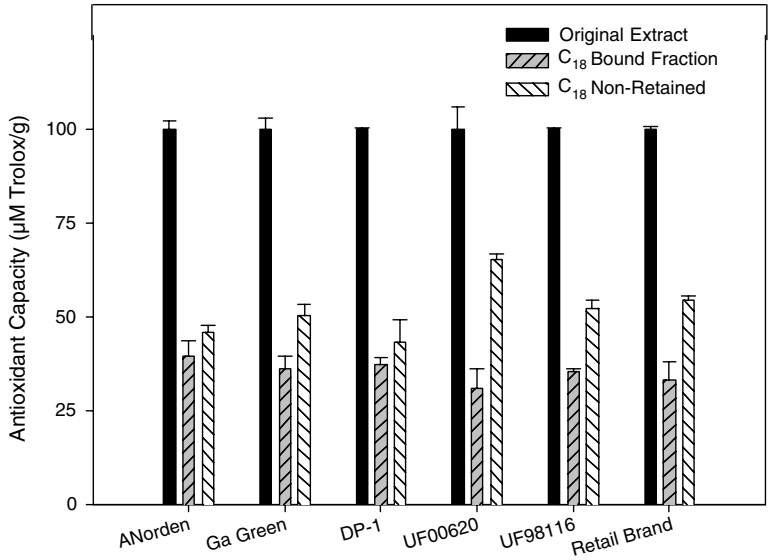

Fig. 2. Antioxidant capacity of water-soluble antioxidants in peanuts partitioned from a reversed phase C_{18} cartridges. Samples included the original extract and those compounds with (bound) and without (unbound) affinity to the C_{18} cartridge. Retail brand represents a commercially available dry roasted peanut. Bars represent standard error of the mean ($n = 2$).

in the original isolate. These additional compounds, though present in small quantities, were co-eluting with the predominant polyphenolics detected as found previously between raw and roasted peanuts, and contributed to antioxidant properties of the peanuts.

3.6. Sensory evaluations

Significant differences existed for roasted peanut sensory characteristics as influenced by cultivar and designation as high or normal oleic acid (Table 2). On average, high oleic acid peanuts had higher burnt peanut aroma and burnt peanut flavor than normal oleic acid varieties, but no differences were found for roasted peanut aroma, roasted peanut flavor, sweetness, or bitterness. No chemical differentiation could be made among varieties that were related to sensory attributes, specifically burnt peanut characteristics, and no previous studies have specifically evaluated burnt peanut attributes. The closest variable to burnt peanut aroma and/or flavor may be the roasted peanut descriptors that are typically attributed to aroma-active compounds, carbohydrates, or pyrazines (Baker et al., 2003; Mason, Johnson, & Hamming, 1966; Pattee, Isleib, Giesbrecht, & McFeeters, 2000). To distinguish between burnt and roasted attributes, panelists were trained to differentiate using peanuts that were roasted from medium to dark by varying roast times at a constant temperature. The consensus of the panelists was that peanuts could smell or taste roasted but not burnt, yet burnt peanuts typically had high roasted attributes. These specific distinctions helped to differentiate high and normal oleic acid peanut cultivars in this study. A significant relationship was found between burnt and roasted peanut attributes ($r = 0.88$ each, for aroma and flavor scores) and were inversely related ($r = -0.54$ to -0.61) to lightness values for burnt peanut flavor, burnt peanut aroma, and roasted peanut flavor. High oleic acid peanuts were reported to have higher roasted peanut intensities that persist longer during storage compared to normal oleic acid peanuts (Braddock et al., 1995; Pattee et al., 2002; Reed et al., 2002). All sensory attributes, except for sweetness, were appreciably higher than the commercially available dry roasted peanuts used for reference. This difference was due to its relatively low degree of roasting (L-value = 58.23) compared to the cultivars evaluated in these studies.

4. Conclusions

Peanuts contain a diverse array of compounds that contribute to peanut sensory and antioxidant properties, but few differences in phytochemical profiles between normal and high oleic acid varieties were found in this study. The predominant phenolic acid with antioxidant potential was *p*-coumaric acid, which increased following roasting due to heat-catalyzed hydrolytic reactions from its native esterified or bound forms. Total soluble phenolics were assessed by both HPLC and the Folin–Ciocalteu assay and were poorly correlated to antioxidant activity since concentrations were generally overestimated due to contributions from soluble proteins. Only when phenolic concentrations detected by HPLC were corrected for protein interference did a statistically significant correlation to

antioxidant capacity exist. The antioxidant capacity of peanuts were found to be relatively high in raw and roasted peanuts and increased by 22% on average following roasting. High oleic acid peanuts where found to have higher burnt flavor and aroma compared to normal oleic lines, attributes that were seemingly unrelated to individual or total polyphenolic composition. However, peanut taste attributes are a complexity of physicochemical reactions that take place during roasting, and details on the role of polyphenolics contributing to sensory attributes of individual peanut cultivars were not elucidated.

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