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Changes in Free Amino Acids and Sugars of Peanuts During Oil Roasting[1]

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ABSTRACT

Changes in free amino acids and sugars during oil roasting of peanuts at a temperature of 147C (9-14 min) were investigated. While a majority of the free amino acids decreased as a result of the roasting treatment, glutamic acid and peptide-cysteine showed the largest percent decreases (59.5% and 83.5% respectively). Alanine, isoleucine, phenylalanine, unknown (4)-tyrosine showed only small changes. Typical flavor precursors (the sum of aspartic acid, glutamic acid, peptide, phenylalanine, and histidine) decreased about 57% during roasting while atypical flavor precursors (the sum of threonine, tyrosine, lysine, and arginine) dercreased slightly. The sugar data were variable, but on the average significantly decreased 8%.

Key Words: Peanuts, *Arachis hypogaea* L., roasting, free amino acids, sugars.

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Roasting is a cooking process applied to peanuts for development of a unique, desirable flavor. The first studies of this flavor development were conducted by Pickett and Holley (11). They observed a decrease of free amino nitrogen and total sugars, development of a brown color, and evolution of carbon dioxide, aldehydes, and ammonia.

Later research showed pyrazine compounds to be responsible for the "roasted-nutty" character of roasted peanuts (3). Newell et al. (7) confirmed the role of free amino acids and sugars as flavor precursors of roasted peanut flavor and postulated the mechanisms whereby these components were converted to pyrazine compounds via Maillard sugar-amine type reactions.

The free amino acid content of raw peanuts varies among varieties, planting locations, and maturation (9,10,18,19). The sugar content of raw peanuts (1), peanut flour (14), and raw and roasted peanuts (15) has also been examined. Newell et al. (7) analyzed four Argentine spanish peanut samples for changes in amino acid and monosaccharide concentrations during roasting, while Young et al. (20) measured the changes in amino acids during dry, oil, and microwave roasting of peanuts.

The purpose of this study was to measure the changes in free amino acids and sugars that result from roasting of peanuts containing variable amounts of these flavor precursor components.

Materials and Methods

Initially, 30 samples of raw peanuts (Table 1) were subjectively selected (8) from the combined 150 samples from two studies of Oupadissakoon et al. (9,10). The roasting of peanut samples is described in detail by Oupadissakoon (8). Peanut oil (420 mL) (Galanide, Inc., Norfolk, VA) was poured into a deep fryer (Presto Fry Baby) and heated to 147C. Samples of peanuts (200g) were roasted 9-14 min. to obtain an acceptable uniform medium roast color, drained 1 min., cooled 5 min. in a bin equipped with a small fan, and then blanched by hand to remove the skins and hearts. A 25 g sample of each was ground using a Krups KM-45 grinder (Robert Krups) and stored (-18C) until analyzed.

Table 1. List of peanut samples.

Peanut sample no.	Variety	Location (county)	Planting period (days)	AMI[a]
1	Florigiant	Northampton, NC	137	35.0
3	NC 17922	Northampton, NC	137	43.0
11	NC 6	City of Suffolk, VA	129	37.0
17	NC 17922	City of Suffolk, VA	129	37.5
23	Florigiant	Northampton, NC	137	42.0
40	NC 6	Martin, NC	129	34.5
46	NC 17922	Martin, NC	129	23.0
53	Florigiant	Sussex, VA	138	55.0
67	Florigiant	Bertie, NC	149	34.5
68	Florigiant	Bertie, NC	156	25.0
71	Florigiant	Chowan, NC	114	39.5
73	Florigiant	Chowan, NC	128	45.0
76	Florigiant	Northampton, NC	107	68.0
77	Florigiant	Northampton, NC	114	63.0
79	Florigiant	Northampton, NC	128	40.5
81	Florigiant	Northampton, NC	142	30.0
82	Florigiant	Northampton, NC	149	30.0
83	Florigiant	Northampton, NC	156	31.5
84	Florigiant	Halifax, NC	114	57.5
88	Florigiant	Halifax, NC	142	42.5
89	Florigiant	Halifax, NC	149	48.5
93	Florigiant	Hertford, NC	121	54.0
98	Florigiant	Hertford, NC	156	38.0
103	Florigiant	Nash, NC	135	52.0
104	Florigiant	Nash, NC	142	54.0
111	NC 6	City of Suffolk, VA	141	35.5
122	Florigiant	Northampton, NC	145	38.5
149	NC 17976	Martin, NC	140	20.5
156	NC 6	Sussex, VA	152	30.5
164	NC 17976	Sussex, VA	152	37.0

[a]AMI = Arginine maturity index(8).

The methods for free amino acid and sugar determinations on these roasted peanut samples were the same as previously reported on the raw peanut samples (10). Extractions were in duplicate with a single analysis of each.

The amino acids were analyzed using a Durrum D-500 amino acid analyzer, and eluted in the following order: unknown (1), unknown (2), unknown (3), aspartic acid (ASP), threonine-serine-asparagine-glutamine (TSER) which eluted as a single peak, glutamic acid (GLU), glycine (GLY), alanine (ALA), peptide-cystine (PC) which eluted together, valine (VAL), isoleucine (ILE), unknown (4)-tyrosine (U4T) which often eluted together, phenylalanine (PHE), histidine (HIS), lysine (LYS), ammonia (NH_3), and arginine (ARG).

Data were evaluated statistically by analysis of variance procedure (13) and the Waller-Duncan test (17). The change in concentration of a component during roasting was obtained as a ratio of the concentration before and after roasting. The roasted peanut data have not been shown in Tables 2 and 3 but can be calculated by dividing the raw value by its ratio.

Table 2. Effect of roasting on content of selected free amino acids of peanuts.

	TF			AF			Glutamic acid			Peptide + Cysteine			Arginine		
Sam	Conc	W-D	Ratio	Conc	W-D	Ratio	Conc	W-D	Ratio	Conc	W-D	Ratio	Conc	W-D	Ratio
76	18.39	a	2.30	6.38	a	0.67	8.58	bc	1.98	1.30	defghij	3.99	5.55	a	0.95
3	17.56	ab	3.24	2.75	def	1.32	8.06	cd	2.82	1.76	a	6.47	2.14	fgh	2.30
23	17.42	ab	2.81	2.99	de	0.98	9.01	ab	2.68	1.51	abcdef	7.06	2.33	ef	1.47
93	17.04	b	2.60	5.18	b	1.43	9.25	ab	2.67	1.27	defghij	6.25	4.45	b	2.84
89	16.84	b	2.82	4.41	c	2.23	9.38	a	3.13	1.01	ijklmn	6.30	3.77	cd	5.15
71	15.30	c	2.61	3.30	d	1.86	6.93	efg	2.41	1.54	abcdef	4.72	2.70	e	5.10
84	15.17	c	2.04	4.25	c	0.78	8.05	cd	2.06	1.23	fghijk	4.97	3.60	cd	1.47
1	15.00	cd	2.42	2.94	de	1.01	7.92	cd	2.33	1.05	hijklm	4.24	2.32	ef	1.54
53	14.03	cde	2.56	3.99	c	1.51	7.70	de	2.96	0.88	lmn	3.95	3.32	d	2.19
77	13.66	def	2.26	4.55	c	0.88	6.96	efg	2.18	1.25	efghijk	4.31	3.91	c	1.39
104	13.37	efg	2.01	1.81	hijk	0.71	6.29	ghi	2.04	1.52	abcdef	8.37	1.43	ijk	1.12
81	13.17	efg	2.65	2.58	efg	1.36	7.32	def	2.97	0.81	mn	5.46	2.18	efg	3.26
88	13.07	efg	2.14	1.54	ijklm	0.66	6.67	fgh	2.46	0.88	lmn	5.44	1.14	jklm	1.12
156	13.06	efg	2.06	1.77	hijkl	1.01	6.47	ghi	2.38	1.65	abc	6.39	1.34	ijkl	1.58
98	12.91	efg	2.13	1.26	klmno	0.70	7.90	cd	2.67	1.36	cdefgh	8.39	0.90	lmno	1.47
164	12.66	fgh	1.85	1.75	hijkl	0.75	6.09	hi	2.12	1.26	defghijk	5.75	1.32	ijkl	1.13
122	12.50	fghi	1.67	1.98	ghij	0.64	6.76	fgh	1.76	0.99	jklmn	4.43	1.50	ijk	1.39
103	12.33	fghi	2.28	1.83	hijk	0.88	6.70	fgh	2.52	1.17	ghijkl	5.79	1.45	ijk	1.70
11	12.21	ghi	2.19	2.13	ghi	0.47	6.39	ghi	2.01	1.55	abcde	7.39	1.64	hij	0.54
149	11.47	hij	2.24	0.81	o	0.56	7.01	efg	2.32	1.78	a	7.87	0.52	no	1.10
17	11.31	ijk	2.03	2.18	fgh	0.96	6.08	hi	2.05	1.08	hijklm	3.08	1.71	ghi	1.53
73	11.29	ijkl	1.66	1.24	klmno	0.68	6.35	ghi	2.02	1.32	defghi	5.27	0.86	lmno	1.32
111	10.64	jklm	1.73	1.44	jklmn	0.84	5.30	jk	1.85	1.41	bcdefg	4.18	1.00	klmn	1.39
46	10.09	klmn	2.66	0.93	no	0.54	5.24	jk	2.59	1.70	ab	8.05	0.61	no	0.74
68	9.95	lmn	2.52	0.76	o	0.82	4.80	kl	2.70	1.55	abcde	7.81	0.40	o	1.34
79	9.88	mn	2.74	1.32	klmno	0.77	5.82	ij	2.82	0.88	lmn	6.94	1.02	klmn	1.30
67	9.76	mn	2.57	1.66	hijkl	1.41	4.94	kl	2.86	1.40	bcdefg	8.39	1.24	ijklm	2.57
82	9.47	mn	2.59	1.06	mno	0.94	6.41	ghi	3.10	0.72	n	6.57	0.76	mno	2.05
40	9.12	n	2.70	1.17	lmno	1.36	4.42	l	2.79	1.57	abcd	5.58	0.82	lmno	2.51
83	9.12	n	2.64	0.81	o	0.74	4.97	kl	2.88	0.95	klmn	8.59	0.54	no	1.63
G.M.	12.93		2.36	2.36		0.98	6.79		2.47	1.28		6.05	1.88		1.84
C.V.	5.63		5.42	13.9		5.90	6.13		5.95	12.6		15.5	15.0		11.1

Sam = Sample number is identified in Table 1.
Conc = Concentration of amino acid is in micro moles/g of raw peanuts. The micro moles/g in roasted peanuts can be calculated by dividing the raw value by its Ratio.
W-D = Comparison is made down a column. Those with the same letter are not significantly different at the 5% level according to the Waller-Duncan K ratio t-test.
Ratio = Ratio of amino acid concentrations in raw to roasted peanuts.
TF = Typical flavor precursors. AT = Atypical flavor precursors.
G.M. = Grand mean. C.V. = Coefficient of variation.

Results and Discussion

The free amino acid profile of the roasted peanut samples differed from that reported for the raw peanut samples (9,10). Unknowns 1, 2, 3, and 4, previously found in the raw peanuts, were not observed in these roasted samples. Threonine (THR) and serine (SER) were separated in the roasted samples due to the loss of ASN and GLN, but are combined so as to calculate ratios for the TSER component. Proline (PRO), methionine (MET), and leucine (LEU) were determined in the roasted peanuts, but lack of quantitation in the raw samples made it impossible to calculate ratios. This quantitation problem only occurred in freshly cured virginia type peanuts grown in the North Carolina/Virginia peanut growing area. Since the alanine value of raw peanuts included both glycine and alanine due to poor separation, the two peaks in the roasted data were combined for the ratio calculation.

The Waller-Duncan (W-D) comparison and rank of the free amino acid contents of raw peanuts (μ mol/g) among all samples are shown in Table 2. The changes are shown as ratios. Ratios greater than 1.00 (or actually about 0.95 since there is a loss of about 5-6% moisture during roasting) indicate a decrease in the component during roasting.

Based on available literature (4,7), 12 components were selected as those probably having the greatest contribution to either good (typical flavor precursors which include ASP + GLU + PC + PHE + HIS) or off-flavor (atypical flavor precursors which include TSER + U4T + LYS + ARG) of roasted peanuts. Amino acid total (ATOT) was obtained from the combined total of all free amino acids. Typical and atypical flavor precursors (Table 2) were classified as suggested by Newell et al. (7) and Cobb and Johnson (2). Analysis showed ATOT were highly correlated with 9 of these 11 components: TSER, 0.921; GLU, 0.867; HIS, 0.743; ARG, 0.911; TF, 0.970;

AF, 0.922; sucrose (SUC) 0.612; Sugar total (STOT), 0.666; and arginine maturity index (AMI) 0.703.

GLU (Table 2) predominated and generally comprised about 35% of the toal amino acids (ATOT) or slightly over 50% of the typical flavor precursor group. The concentrations of GLU in raw peanut samples (9,10) varied significantly (4.42-9.38 μ mol/g of peanuts) and decreased with roasting to give an average ratio of 2.47. This average ratio is in agreement with the average ratio of 2.73 reported by Newell et al. (7). It was not possible to establish a pattern for these changes as supported by the nonsignificant correlation coefficient between GLU content and its ratio. Newell (6) studied a model system and reported that dimethylethyl pyrazine was higher in the GLU-glucose system than the other amino acid-sugar systems. The dimethylethyl pyrazine compound was one of the compounds which contributed to the "roasted-nutty" sensory note (3).

The PC component (Table 2) had a mean value of 1.28 μ mol/g of raw peanuts and gave the largest percent decrease (ratio of 6.05). In earlier studies, this component was shown to increase with increasing maturity (4,6). A recent study (9), from which a portion of these 30 samples was taken, suggests the peptide does not always increase with increasing maturity. The peptide has been reported to be hydrolyzed to produce free amino acids which serve as flavor precursors (4,7). The composition of this peptide, which is referred to as peptide-2 by Mason et al. (4), is primarily GLU, ASP, PHE, GLY, and SER. The large ratio indicating a decrease in the peptide during roasting supports the observations by Mason et al. (4).

ARG (Table 2) on the average decreased (ratio 1.84) during roasting but showed a large range of ratios (0.54 for sample 11 to 5.15 for sample 89). This variability among the ratios is surprising and not yet understood. In this study, AMI and ARG are significantly correlated in both raw peanuts (0.793) and roasted peanuts (0.738).

The average concentration of HIS was 0.156 μ mol/g. This along with a low average ratio (1.27) indicates that there are small consistent decreases in HIS content during roasting. HIS has been associated with the typical flavor precursors (7).

The changes in PHE due to roasting were variable, showing a range of ratios from 0.22 to 2.40 with an average of 0.926. The variation in the PHE data in this study may be due to variation in the roasting time (7) of these samples and the release of PHE from the peptide during roasting.

TSER, with a mean value of 2.02 μ mol/g, showed a decrease (ratio 1.90) during roasting. ASN and GLN were shown to be in the TSER peak of the raw peanuts, but, for the most part, disappeared in the roasted peanuts. They may have been partially deaminated during the roasting treatment as well as reacting as flavor precursors. Since the quantitation of each of these four components of the TSER peak was not made in this study, an interpretation of the changes in the TSER peak is not possible. ASN and GLN have been shown to be typical flavor precursors with THR being classified as an atypical flavor precursor (7).

Even though there was no correlation between the raw/roast ratios (mean 1.34 μmol/g) and initial concentrations of ASP, (mean 1.47 μ mol/g) there was a tendency for ASP to decrease during roasting except for a few samples. This agrees with the results of Newell et al. (7), who also, noted that the ratio for ASP in the under-roasted sample was lower than the average. Additionally, ASP can be generated from both ASN and peptide giving a total of three factors affecting the ASP ratio values.

ALA, ILE, and U4T on the average changed very little during roasting (ratios 0.954, 0.809, and 0.988, respectively). VAL and LYS were present in small amounts (0.569 and 0.156 μ mol/g) and free LYS decreased about 40% upon roasting. McOsker (5) had reported that toal lysine (which also includes the LYS from the protein) decreased about 15% upon roasting. LYS is an atypical flavor precursor (7). VAL, which has not been associated with typical or atypical flavor decreased about 47%. ATOT for all samples decreased on the average about 40% (ratios ranged from 1.24 to 2.46).

The decrease in the content of NH_3 in all peanut samples due to roasting was of an appreciable magnitude (average ratio 3.17). The decrease in ratios for NH_3 was highly correlated with the decreasing levels of NH_3 in the raw peanut samples (0.634). Sample 71 had the highest NH_3 concentration (3.26 μ mol/g), and decreased the most (ratio of 8.05) during roasting. Sample 149, which was close to the average ratio, had the lowest NH_3 concentration (1.18 μmol/g). Ammonia, when reacted with sugars, has been shown to yield roasted flavor related pyrazine compounds (12, 16).

The effect of roasting on STOT was an 8% decrease (Table 3). fructose (FU), glucose (GLC), inositol, sucrose (SUC), raffinose, and stachyose average concentrations decreases ranged from 3.6% for raffinose to 35.1% for inositol and the average ratios were 1.06, 1.34, 1.54, 1.09, 1.04, and 1.11 respectively. Ribose increased about 80% during roasting with an average ratio of 0.184.

Table 3. Effect of roasting on content of major sugars of peanuts.

	Fructose			Glucose			Sucrose			Total sugars		
Sam	Conc	W-D	Ratio	Conc	W-D	Ratio	Conc	W-D	Ratio	Conc	W-D	Ratio
76	1.65	bcd	0.66	0.57	defgh	0.85	145.0	a	1.10	156.3	a	1.06
3	1.65	bcde	1.37	0.82	bcd	1.23	105.0	cdef	1.28	118.0	de	1.36
23	1.21	defghijk	1.06	0.54	efgh	1.10	99.2	defgh	1.32	110.0	ef	1.34
93	1.41	cdefg	1.16	0.89	ab	1.89	132.0	b	1.38	143.6	b	1.32
89	1.30	cdefghij	1.67	0.47	efgh	2.24	96.3	efghij	1.26	107.5	efg	1.21
71	2.03	ab	1.29	0.84	bc	2.27	146.2	a	1.46	158.6	a	1.46
84	1.30	cdefghij	0.79	0.48	efgh	0.93	130.6	b	1.13	142.1	b	1.07
1	1.33	cdefghi	1.36	0.67	bcdef	1.76	87.3	ijkl	1.12	100.0	fghi	1.24
53	1.37	cdefgh	1.83	0.66	bcdef	1.81	90.5	ghijk	1.03	101.4	fghi	1.02
77	1.01	ghijklm	0.39	0.43	fgh	0.95	127.7	b	1.05	137.8	bc	1.03
104	1.38	cdefgh	1.19	0.52	efgh	1.12	101.5	defg	1.11	109.1	efg	1.09
81	0.83	klm	0.66	0.42	fgh	0.87	74.4	mn	0.86	83.6	l	0.87
88	0.92	hijklm	0.81	0.38	gh	1.18	89.7	hijk	1.25	101.2	fghi	1.25
156	0.86	jklm	0.52	0.61	cdefgh	1.00	113.1	c	1.09	122.4	d	1.05
98	1.42	cdefg	0.89	0.58	cdefgh	1.18	98.6	defghi	1.09	109.4	ef	1.07
164	0.87	jklm	0.68	0.49	efgh	1.46	80.5	klmn	1.00	89.7	ijkl	0.98
122	1.19	fghijkl	1.14	0.55	efgh	1.15	82.8	klmn	1.08	92.7	hijkl	1.04
103	1.24	cdefghijk	1.56	0.42	fgh	1.25	94.4	fghij	1.14	102.7	fgh	1.13
11	1.41	cdefg	1.07	0.59	cdefgh	1.01	116.0	c	0.98	126.4	cd	0.97
149	1.13	fghijkl	1.02	0.38	gh	1.06	75.3	mn	0.97	82.1	l	0.96
17	1.51	cdef	1.09	0.64	bcdefg	1.47	85.3	jklm	0.93	97.1	ghijk	0.98
73	1.69	bc	1.03	0.35	h	0.95	101.1	defgh	0.95	109.5	ef	0.92
111	1.25	cdefghijk	0.72	0.89	abc	1.21	107.2	cde	0.96	117.5	de	0.97
46	1.23	cdefghijk	1.28	0.54	efgh	1.50	77.8	lmn	1.09	84.9	kl	1.04
68	2.37	a	1.97	1.12	a	2.56	109.6	cd	1.04	118.3	de	1.03
79	0.88	ijklm	0.70	0.37	h	0.80	77.2	lmn	0.91	86.5	jkl	0.93
67	1.57	bcdef	0.98	0.73	bcde	1.49	109.5	cd	1.08	119.3	de	1.36
82	0.64	m	0.83	0.35	h	1.63	71.5	n	1.09	81.0	l	1.10
40	0.99	ghijklm	1.17	0.49	efgh	0.94	90.4	ghijk	1.12	98.4	fghij	1.10
83	0.74	lm	0.96	0.52	efgh	1.45	73.0	n	1.01	81.2	l	0.96
G.M.	1.28		1.06	0.58		1.34	99.6		1.09	109.6		1.09
C.V.	17.5		15.2	21.5		19.5	6.16		2.86	5.96		3.38

Sam = Sample number is identified in Table 1.
Conc = Concentration of sugar is in micro moles/g of raw peanuts. The micro moles/g in roasted peanuts can be calculated by dividing the raw value by its Ratio.
W-D = Comparison is made down a column. Those with the same letter are not significantly different at the 5% level according to the Waller-Duncan K ratio t-test.
Ratio = Ratio of sugar concentrations in raw to roasted peanuts.
G.M. = Grand mean. C.V. = Coefficient of variation.

In raw virginia type peanuts, the FRU content (1.28 μ mol/g) may be twice that of GLC (0.50 μ mol/g). Using spanish peanuts, Newell et al. (7) found FRU and GLC concentrations to be about equal (5.26 and 4.50 μ mol/g) and several times greater than the levels found in this study. FRU and GLU concentrations generally decreased, but not in all cases, which could be anticipated since these compounds can be formed as well as degraded during roasting. SUC was present in the highest concentration (average 99.6 μmol/g), and accounted for about 87% of total sugars. Newell (6) reported about 278 μ mol/g of SUC in spanish peanuts. SUC has previously been reported to be hydrolysed during roasting to give GLC and FRU which serve as sugar reactants in the nonenzymatic browning reaction for roasted peanut flavor formation (1). The majority of the samples in this study showed decreases in sucrose but a few had unexplainable increases. In addition to its role as a source of flavor precursors, sucrose levels are no doubt important as a source of sweetness in the flavor of roasted peanuts.

In summary, changes in free amino acids and sugars during oil roasting of peanuts were investigated. Large decreases in glutamic acid and a peptide (both typical flavor precursors) were noted. Small but significant decreases in sugars occurred during roasting.

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