

Precursors of Typical and Atypical Roasted Peanut Flavor

Jon A. Newell,¹ Michael E. Mason, and Ralph S. Matlock

Gross analysis of a soluble portion of raw peanuts before and after heating implicated amino acids and carbohydrates as precursors of typical peanut flavor. Quantitative analysis showed that amino acids and monosaccharides in raw peanuts changed in concentration during roasting. The amount of amino acid degraded during roasting appeared to be proportional to its initial concentration over a broad range of concentrations. Chemical analyses of peanuts of known organoleptic quality resulted in the derivation of a relationship which related flavor precursor concentration to subjectively measured

flavor. Calculations indicated that aspartic acid, glutamic acid, glutamine, asparagine, histidine, and phenylalanine were associated with the production of typical peanut flavor; threonine, tyrosine, lysine, and an unknown amino acid were considered to be precursors of atypical flavor. Previous knowledge of the compounds produced during roasting, coupled with the data presented in this paper, permitted the postulation of a mechanism for the production of flavor components from amino acids and carbohydrates.

Earlier work from this laboratory described the isolation of a flavor precursor fraction of raw peanuts which consisted of low molecular weight compounds rather than proteins or polysaccharides. Paper chromatography of the fraction containing the flavor precursors indicated further the presence of ninhydrin-positive and basic compounds (Mason and Waller, 1964).

Any compound that is a flavor precursor must, by nature, be a substance of low volatility which can be converted to a more volatile one during heating. The authors' approach to the peanut flavor precursor problem was to analyze the heated and unheated flavor precursor fraction or extracts of raw and roasted peanuts. Knowing the volatile compounds produced (Johnson, 1966; Mason *et al.*, 1966, 1967; Pattee *et al.*, 1965) and the nonvolatile material degraded allowed the postulation of a mechanism to explain the decrease in flavor precursor concentration during roasting and the production of compounds which exhibit typical roasted peanut flavor. A similar approach has been employed in cocoa flavor precursor work (Pinto and Chichester, 1966; Rohan and Stewart, 1966a, b).

PROCEDURES

Determination of Peanut Maturity. Peanuts having dark-colored interior pericarp surfaces and thin pink-colored testa were classed as mature; those having light-colored interior pericarp surfaces and fleshy white testa were classed as immature. Peanuts falling between these extremes were classified as intermediate in maturity. The peanuts from the two maturity classes used in the work presented here were large enough to be retained on a $15/64 \times 3/4$ inch screen.

Subjective Analysis of Peanut Flavor. A flavor panel consisting of five members was instructed to rate the flavor of four coded samples of ground roasted peanuts plus coded and uncoded standards of Argentine Spanish peanuts. The Argentine Spanish standard has consistently proved to have superior organoleptic properties

over several years of testing. The organoleptic evaluation was reported on rating sheets like that shown in Figure 1.

Mean preference rank, an estimate of peanut flavor in numerical terms as compared to a standard, was obtained by taking the average of the preference rank given by each panel member to a particular sample. The mean preference ranks reported represent an average of two determinations. In each replication, the sample in question was roasted immediately before it was presented to the panel. Because of variations in the roasting process and the inability of the panel to detect subtle flavor differences, the two replications of the mean preference rank were seldom exactly the same—for example, sample 2 (Table II) had a mean preference rank of 2.4; sample 1 had a mean preference rank of 2.2. The former sample was considered to have better flavor because the panel rated it, with respect to flavor, superior—or equal—to the standard (Figure 1) more consistently than the latter.

According to taste panel results, samples 1 and 3 had flavor somewhat inferior to samples 2 and 4. The difference in flavor of the peanut samples used was due to their degree of maturity. All samples were of the same variety, grown at the same location, and processed in the same manner. Samples 1 and 3 were harvested Sept. 18, 1965, and were more immature; samples 2 and 4 were harvested Oct. 9, 1965. The mean preference ranks for samples 1, 2, 3, and 4 were 2.2, 2.4, 3.6, and 2.4, respectively.

Preparation of Peanuts for NaCl or Perchloric Acid Extraction. Raw peanuts ground with a food grinder or ground roasted peanuts were extracted with redistilled *n*-hexane in a Soxhlet extractor. After the solvent was removed by evaporation, the dry peanuts were ground to a fine powder, and the fat-free meal was stored in tightly stoppered bottles at room temperature prior to further extraction.

Preparation of a Peanut Flavor Precursor Fraction. The flavor precursor fraction from 2 kg. of raw fat-free peanuts was obtained by extraction with 15 liters of 1M NaCl solution. The extract was concentrated to 1 liter by rotary evaporation and the evaporated extract was subjected to gel filtration on a 10.8-liter column of Sephadex G-25. The flavor precursor fraction was collected from the Sephadex column as described by Mason and Waller (1964).

Agricultural Experiment Station, Oklahoma State University, Stillwater, Okla. 74074.

¹ Present address, Anheuser-Busch, Inc., St. Louis, Mo. 63118.

CODE NO.	ODOR			FLAVOR			COMMENTS					
	Superior to Standard	Equal to Standard	Inferior to Standard	Better than Standard	Equal to Standard	Poorer than Standard	ODOR	FLAVOR	TASTE	ROAST	DRYNESS	Pref. Rank No. One Best
1												
2												

	<u>Odor</u>	<u>Flavor</u>	<u>Taste</u>	<u>Roast</u>	<u>Dryness</u>
1.	None	1. Lacks	1. Rancid	1. Under	1. Very Dry
2.	Weak	2. Low	2. Bitter	2. Good	2. Moderate
3.	Moderate	3. Undesirable	3. Salty	3. Excellent	3. Moist
4.	Strong	4. Good	4. Sweet	4. Over	4. Oily

Figure 1. Sample of an organoleptic evaluation sheet

Perchloric Acid Extraction. Ground fat-free meal was stirred with 3*N* perchloric acid (25 ml. of 3*N* HClO₄ per gram of fat-free meal) on a magnetic stirrer for 1 hour at 4° C. The acidic extract was centrifuged at 10,000 × *G* in the cold to remove insoluble material. The pH of the supernatant liquid was adjusted to 7.0 with saturated KOH; the KClO₄ formed was removed by high speed centrifugation at 4° C. The clear supernatant liquid was lyophilized to dryness and redissolved in a minimum volume of 0.2*N* citrate buffer at pH 2.2. Hydrolysis of amide nitrogen was not a problem as judged by the absence of hydrolysis of glutamine and asparagine standards which were treated in the same manner.

Preparation of Samples for Carbohydrate Analysis. Fat-free meal (0.5 gram) was extracted for 24 hours with 100 ml. of 80% ethanol in a Soxhlet extractor. The volume of the extract was reduced to about 15 ml. by rotary evaporation and placed on a 0.8 × 20 cm. column of Amberlite CG-120 (100- to 200-mesh) in the sodium form. Neutral compounds were eluted from the column with 50 ml. of deionized water, and the eluate was lyophilized to a solid residue. The residue was dissolved in 2.0 ml. of *N,N*-dimethylformamide and allowed to stand at room temperature for about 1 hour to achieve dissolution. The following additions were made to the dimethylformamide solution in the order: 0.5 ml. of pyridine, 0.4 ml. of hexamethyldisilazane, and 0.2 ml. of trimethylchlorosilane. One milliliter of a standard solution containing 8 μmoles each of ribose, fructose, glucose, inositol, and sucrose was treated in the same manner as the samples from peanuts. Sugar concentrations were calculated by comparison of sample peak areas with corresponding peak areas of the standard.

Gas Chromatography of Trimethylsilyl Ethers. Gas chromatography was conducted on a Perkin-Elmer Model 801 gas chromatograph equipped with a hydrogen flame ionization detector. A 6-foot × 1/4-inch O.D. glass column packed with 5% (w./w.) SE-52 on 100- to 110-mesh Gas Chrom Q operated at a nitrogen flow rate of 60 ml. per minute and temperature-programmed at 4° C. per minute from 120° to 250° C. was used to separate the trimethylsilyl derivatives.

Amino Acid Analyses. Amino acid contents of perchloric acid extracts obtained as previously described were determined with a Beckman 120-C amino acid analyzer using Beckman PA-28 and PA-35 resins.

Gross Changes in Flavor Precursor Fraction during Heating. A NaCl solution (saturated at room tempera-

ture) of the flavor precursor fraction obtained in the manner previously described which contained 13.5 grams of total organic solids was refluxed for 15 hours at 105° C. Total ninhydrin positive material (Gilpin and McLafferty, 1957), pentoses (Mejbaum, 1939), carbohydrates (Colvin *et al.*, 1961), reducing sugars (Nelson, 1944), and organic solids (Johnson, 1948) were determined before and after refluxing using published procedures.

RESULTS AND DISCUSSION

Effect of Heating on Flavor Precursor Fraction. The heated and unheated flavor precursor fractions were analyzed as previously described. Table I shows that total carbohydrates and amino acids decreased, pentose sugars and total organic solids remained relatively constant, and reducing activity increased sharply during refluxing. The biuret test (Robinson and Hogden, 1940) indicated that the flavor precursor fraction contained only traces of peptides after residual protein was precipitated.

The results of the analysis for ninhydrin positive material and total sugars indicated that amino acids and carbohydrates had reacted in some manner and that both were modified during the process. The observed increase in reducing power was explained by hydrolysis of sucrose or by a process in which carbohydrates were converted to reductones (Hodge, 1953). The fact that total organic solids decreased only slightly during the heating process meant that most of the material produced during heating was of low volatility.

The formation of large amounts of polymeric material was evidenced by formation of considerable insoluble dark-colored material in the flavor precursor fraction dur-

Table I. Changes in Composition of the Flavor Precursor Fraction during Refluxing

Treatment	Total, Mg.			% Change
	Before heating	After heating	Change during heating	
Ninhydrin (as leucine)	517	263	-254	49.1
Orcinol (as ribose)	16	15	-1	6.3
Anthrone (as glucose)	8,915	6,360	-2555	28.6
Alkaline copper (as glucose)	470	6,400	+5930	1261.9
Total organic solids	13,500	12,750	-750	5.6

ing heating. When a portion of the heated saline solution was dialyzed against deionized water, the brown material remained inside the dialysis tubing. The nondialyzable material was lyophilized to dryness, redissolved in a minimum of water, and subjected to gel filtration on a 20 × 3 cm. column of Sephadex G-25. The brown material which was completely excluded from the gel was collected, lyophilized, and analyzed for carbon, nitrogen, hydrogen, and ash. The analysis (C 37.86, H 5.01, N 3.97, ash 12.70, and O by difference 40.46) corresponded to an empirical formula of C₁₁H₁₈O₉N. The results of these experiments indicated that amino acids and carbohydrates of the flavor precursor fraction were undergoing chemical changes.

Changes in Individual Amino Acid Concentration during Roasting. Amino acids can give rise to aldehydes by Strecker degradation and can serve as the source of nitrogen for the formation of pyrazine compounds (Hodge, 1953; Dawes and Edwards, 1966). That these compounds are produced during roasting of peanuts was indicated by recently published results (Johnson, 1966; Mason *et al.*, 1966, 1967) in which pyrazines and aldehydes were shown to represent the major classes of organic compounds evolved from peanuts during roasting. Data presented in Tables II and III indicated very strongly that amino acids and sugars were the precursors of these volatile flavor components in roasted peanuts.

Table II. Amino Acid Concentrations (μ Moles/Gram of Fat-Free Meal) and Raw/Roasted Ratios in Fully Mature and Intermediate Maturity Peanuts

Amino Acid	Fully Mature						Intermediate Maturity					
	Sample 1			Sample 2			Sample 3			Sample 4		
	Raw	Roasted	Ratio	Raw	Roasted	Ratio	Raw	Roasted	Ratio	Raw	Roasted	Ratio
Aspartic acid	0.58	0.73	0.79	0.88	0.58	1.52	0.58	0.44	1.33	1.02	0.88	1.16
Threonine	0.73	0.58	1.26	0.29	0.12	2.42	0.88	0.58	1.52	0.44	0.29	1.52
Serine	1.17	0.88	1.33	0.58	0.44	1.32	1.61	1.02	1.58	1.75	0.88	1.99
Asparagine and glutamine	2.19	1.32	1.66	2.92	0.88	3.32	2.49	1.02	2.44	4.53	1.46	3.10
Proline	1.32	1.17	1.13	1.02	0.58	1.76	1.02	0.88	1.17	2.19	1.02	1.98
Glutamic acid	7.02	3.95	1.78	7.89	2.34	3.37	7.02	3.36	2.09	11.26	3.07	3.67
Glycine	1.17	1.02	1.15	0.44	0.44	1.00	1.75	1.17	1.50	1.61	0.73	2.21
Alanine	4.68	3.22	1.45	2.05	1.32	1.55	8.19	5.41	1.51	5.56	3.36	1.65
Valine	1.32	1.02	1.29	0.73	0.29	2.52	1.75	1.02	1.72	1.90	0.88	2.16
Unknown	2.92	1.32	2.21	4.09	0.44	9.30	1.90	0.73	2.60	1.46	0.29	5.03
Methionine	0.29	0.15	1.93	0.29	0.15	1.93	0.15	0.15	1.00	0.29	0.15	1.93
Isoleucine	0.73	0.58	1.27	0.44	0.29	1.52	0.88	0.44	2.00	0.88	0.44	2.00
Leucine	0.58	0.44	1.32	0.44	0.15	2.93	0.73	0.44	1.66	0.73	0.44	1.66
Tyrosine	0.44	0.44	1.00	0.15	0.15	1.00	0.73	0.44	1.66	0.29	0.15	1.93
Phenylalanine	2.19	2.63	0.83	2.34	1.61	1.46	2.05	1.32	1.55	1.75	1.46	1.20
β -Alanine	Trace	Trace	...	0.15	Trace	...	Trace	Trace	...	Trace	0.15	...
Lysine	0.88	0.58	1.52	0.44	0.15	2.93	0.88	0.73	1.21	0.73	0.29	2.52
Histidine	0.44	0.29	1.52	0.29	0.15	1.93	0.58	0.29	2.00	0.58	0.29	2.00
Ammonia	1.75	4.09	0.43	0.73	0.58	1.26	2.34	4.97	0.47	2.63	6.43	0.41
Arginine	1.46	1.17	1.25	1.46	1.32	1.11	1.32	2.19	0.60	1.61	1.17	1.38
Tryptophan	0.29	0.29	1.00	0.44	0.29	1.52	0.73	0.44	1.66	0.58	0.29	2.00

Table III. Gas Chromatographic Analysis of Trimethylsilyl Ethers of Carbohydrates from Raw and Roasted Peanuts

Sample Designation	Carbohydrate	Raw, μ Mole/Gram	Roasted, μ Mole/Gram	Change, μ Mole/Gram	% Change
Mature Sample 1	Fructose	6.22	11.42	+5.20	45.5
	Glucose	6.90	15.72	+8.82	56.1
	Unknown	5.87	2.96	-2.91	49.6
	Inositol	2.48	3.34	+0.86	25.7
	Sucrose	312	262	-50	16.0
Sample 2	Fructose	4.18	4.62	+0.44	9.5
	Glucose	4.00	5.72	+1.72	31.1
	Unknown	3.36	1.22	-2.14	63.7
	Inositol	1.78	1.44	-0.34	19.1
	Sucrose	266	266	...	0.0
Intermediate Sample 3	Fructose	4.38	4.76	+0.38	8.0
	Glucose	3.27	3.64	+0.37	10.2
	Unknown	1.39	1.18	-0.21	15.1
	Inositol	5.30	3.98	-1.32	24.9
	Sucrose	299	188	-111	37.1
Sample 4	Fructose	6.24	5.36	-0.88	14.0
	Glucose	3.82	5.74	+1.92	33.4
	Unknown	2.36	1.08	-1.28	54.2
	Inositol	3.02	2.46	-0.56	18.5
	Sucrose	236	232	-4	1.7

Table II shows amino acid concentrations (expressed in micromoles per gram of fat-free peanut meal) in raw and roasted peanuts and the ratio: micromoles per gram raw per micromoles per gram roasted. Several conclusions were drawn from examination of these data. First, regardless of the maturity category studied, glutamic acid, asparagine-glutamine, the unknown amino acid, phenylalanine, and alanine made up most of the total free amino acids and probably were the most important as flavor precursors. Secondly, with the exception of the underroasted sample (sample 1), the raw-roasted ratios for a given amino acid in different samples were fairly consistent. The raw-roasted ratios of the underroasted sample were consistently lower than the average of the other three samples with the exception of the very minor components: methionine, lysine, and arginine. This result would be predicted if destruction of amino acids were a function of the duration of roasting.

These two facts show that free amino acids were destroyed during roasting to a degree approximately proportional to their original concentration. Further, although initial concentrations of some free amino acids appeared to be a function of maturity, the proportion of each degraded during heating was fairly constant from sample to sample.

These observations prompted the authors to consider kinetic control as the control mechanism in the conversion of amino acids to flavor compounds during roasting. If kinetic control were independently operative—i.e., if available energy were not a limiting factor—one would expect the raw-roasted ratios for a given amino acid in different samples to remain relatively constant, provided the samples were roasted to the same extent.

Breakdown of all carbohydrates in the better flavored peanuts (Table III) in each maturity class was of the order of 4 to 10 μ moles per gram, assuming that all sucrose lost was converted to fructose and glucose; breakdown of amino acids was roughly twice that of the carbohydrates. This fact suggested that two classes of compounds reacted in a 2-to-1 stoichiometric ratio during roasting. However, under the conditions of roasting (210° C. in a nonaqueous medium), glutamine and glutamic acid can readily self-condense to form pyrrolidone carboxylic acid (Greenstein and Winitz, 1961) and thus may not have reacted in the same manner as other amino acids.

With the thought in mind that the initial concentration of each amino acid controlled the extent to which it was degraded during roasting (kinetic control), the authors derived an equation which related the concentration of amino acid flavor precursor in the raw peanut with subjectively measured flavor. As a first approximation, based on the evidence, the assumption was made that typical flavor was directly proportional to the concentration of each amino acid flavor precursor, Flavor $\propto C_p$, where C_p was the measured flavor precursor concentration in the raw peanut. Since mean preference rank, M , decreased as typical flavor increased (i.e., M was a smaller number for a better tasting sample or Flavor $\propto \frac{1}{M}$) it followed from these proportionalities that another could be written, $C_p \propto \frac{1}{M}$ or $M \propto \frac{1}{C_p}$. Insertion of the constant K_f (the flavor func-

tion constant) into the second proportionality yielded.

$$M = K_f/C_p \quad (1)$$

which was rearranged to give:

$$K_f = MC_p \quad (2)$$

If the assumption that typical flavor was proportional to flavor precursor concentration was justified, the proportionality constant, K_f , for any given precursor in one peanut sample, should be equal within experimental error of determining M and C_p , to K_f for that precursor in any other sample regardless of the flavor of the two samples. If, however, the flavor precursor in question produced compounds associated with atypical or off-flavor, then K_f values for a given precursor in two different samples would not agree, since the assumption that typical flavor was proportional to flavor precursor concentration would not be satisfied. These statements would apply only to those samples which were roasted to the same extent. Since the raw-roasted ratio would increase with heaviness of roast and would decrease with lighter roasting, the inclusion of the raw-roasted ratio, R , in Equation 2 reduced all samples to an identical heaviness of roast. Division of the right side of Equation 2 by R yielded:

$$K_f = MC_p/R \quad (3)$$

K_f values calculated from Equation 3 using the data in Table II, ratios of K_f values, and average K_f ratios for the amino acids occurring in peanuts of two maturity classes were calculated (Table IV). Ratios near 1.0 indicated amino acids which contributed to typical flavor; those which departed sharply from 1.0 indicated precursors of atypical or off-flavor. The amino acid concentration data are much more precise by nature than the mean preference rank data. Therefore the agreement of the K_f values can be no better than the precision of values for the least precise measurement—namely, the mean preference rank. The arbitrary limits set for average K_f values of precursors of typical flavor were $K_f = 1.0 - 1.7$; K_f values greater than 2.5 were considered to indicate that the amino acid was a precursor of atypical flavor.

On the basis of these calculations, aspartic acid, asparagine-glutamine, glutamic acid, phenylalanine, and histidine were considered to be precursors of typical peanut flavor; threonine, the unknown, tyrosine, and lysine were precursors of off-flavor. In Table IV, precursors of typical flavor are designated as T whereas precursors of atypical flavor are designated as A . A few average K_f value ratios in Table IV were anomalous, in that they had large standard deviations and could have been classified as either precursors of typical or atypical flavor. Some of the average K_f values in Table IV fell between the arbitrary limits set for precursors of typical flavor and precursors of atypical flavor. No predictions were made concerning these amino acids.

Equation 3 predicts that K_f values for precursors of atypical flavor should be higher in poorer flavored peanuts than the corresponding value in good flavored peanuts, since for a given M , C_p should be higher in poorer flavored peanuts. Table IV shows that K_f values for threonine, the unknown, tyrosine, and lysine were indeed higher in peanuts which had poorer flavor. The fact that in very im-

Table IV. K_f Values, Ratio of K_f Values, and Average Ratios of K_f Values in Intermediate Maturity and Fully Mature Peanuts

Amino Acid	Mature			Intermediate			Av. Ratio \pm Std. Dev.	Interpretation
	Sample 1	Sample 2	Ratio	Sample 3	Sample 4	Ratio		
Aspartic acid	1.6	1.4	1.1	1.6	2.1	1.3	1.2 \pm 0.1	T ^a
Threonine	1.3	0.3	4.3	2.1	0.7	3.0	3.7 \pm 0.7	A ^b
Serine	1.9	1.1	1.7	3.7	2.1	1.8	1.8 \pm 0.1	X ^c
Asparagine and glutamine	2.9	2.1	1.4	3.7	3.5	1.1	1.3 \pm 0.1	T
Proline	2.6	1.4	1.9	3.1	2.4	1.3	1.6 \pm 0.2	^d
Glutamic acid	8.7	5.6	1.6	12.1	7.4	1.6	1.6 \pm 0.0	T
Glycine	2.2	1.1	2.0	4.2	1.7	2.5	2.3 \pm 0.2	X
Alanine	7.1	3.2	2.2	19.5	8.1	2.4	2.3 \pm 0.1	X
Valine	2.2	0.7	3.1	3.7	2.1	1.8	2.5 \pm 0.6	^d
Unknown	2.9	1.1	2.6	2.6	0.7	3.7	3.2 \pm 0.5	A
Isoleucine	1.3	0.7	1.9	1.6	1.1	1.5	1.7 \pm 0.2	X
Leucine	1.0	0.4	2.5	1.6	1.1	1.5	2.0 \pm 0.5	^d
Tyrosine	1.0	0.4	2.5	1.6	0.4	4.0	3.3 \pm 0.7	A
Phenylalanine	5.8	3.9	1.5	4.8	3.5	1.4	1.5 \pm 0.1	T
Lysine	1.3	0.4	3.3	2.6	0.7	3.7	3.5 \pm 0.2	A
Histidine	0.6	0.4	1.5	1.0	0.7	1.4	1.5 \pm 0.1	T
Ammonia	9.0	1.4	6.4	17.9	15.4	1.2	3.8 \pm 2.6	^d
Arginine	2.6	3.2	1.2	7.9	2.8	2.8	2.0 \pm 0.8	^d
Tryptophan	0.6	0.7	1.2	1.6	0.7	2.3	1.8 \pm 0.3	X

^a T = Precursor of typical flavor.
^b A = Precursor of atypical flavor.
^c X = Intermediate ratio, no prediction.
^d Anomalous ratios.

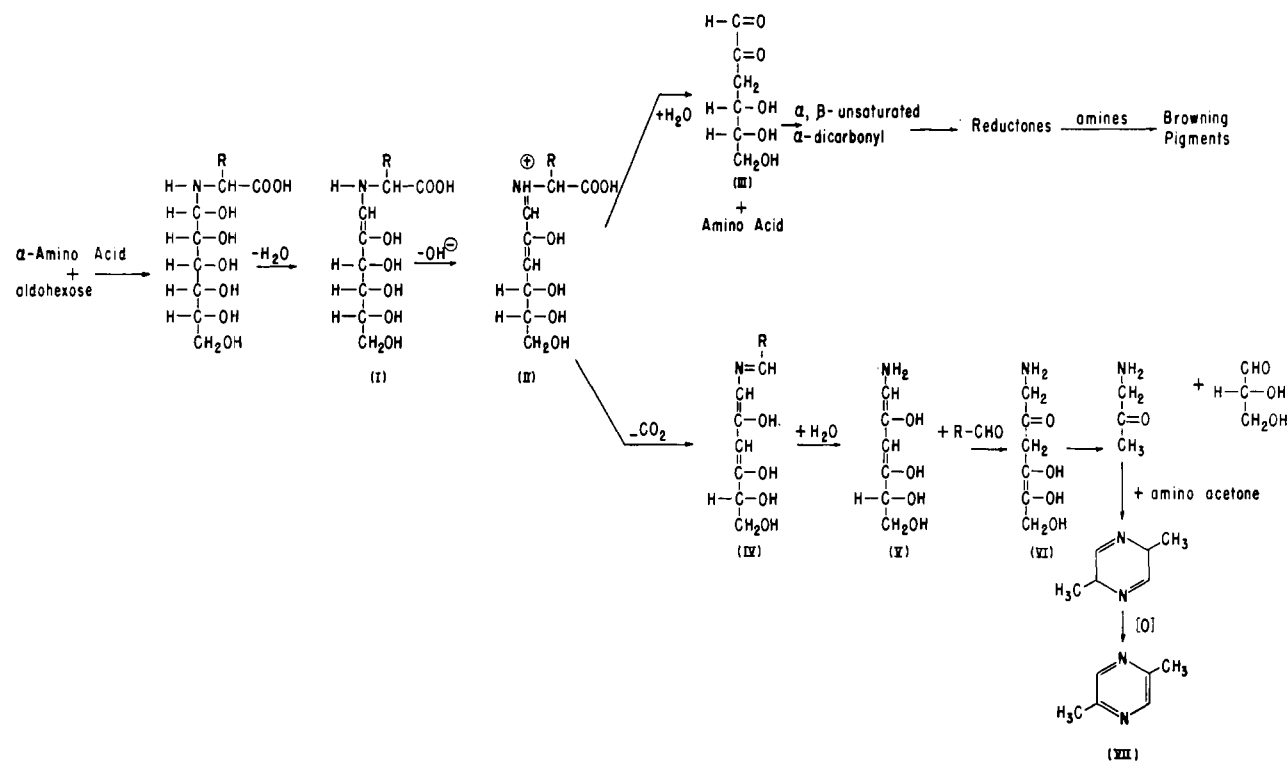


Figure 2. Postulated mechanism for conversion of amino acids and sugars to volatile compounds

mature peanuts, which have a very high level of off flavor, the amino acids which were predicted to be precursors of atypical flavor occur at very high concentrations, tends to support the conclusions drawn from K_f values concerning precursors of atypical flavor.

Similarly, the amino acids which contributed to typical peanut flavor according to calculation of K_f values were the

same ones which made up about 50% of the total free amino acids in the fully mature peanuts.

Changes in Carbohydrates during Roasting. The data in Table III showed that sucrose underwent only small decreases in concentration during roasting of peanuts having good flavor (samples 2 and 4). The results might have been interpreted to mean that sucrose per se was not

involved in the production of flavor. This interpretation agreed with the results of El'ode *et al.* (1966), who showed that sucrose was much less reactive in the browning reaction than monosaccharides.

Glucose and fructose must have been consumed during roasting, since the increase in concentration of these sugars was less than the amount which could have been produced from the hydrolysis of sucrose.

Evidently, fructose was utilized in the reactions to produce volatile compounds to a greater extent than glucose, since the increase in fructose concentration during roasting of peanuts was less than that of glucose. This result was reasonable in light of the work of Casey *et al.* (1965), who showed that fructose exhibited much higher rates of production of volatiles than glucose in model hexose-amino acid systems.

Monosaccharides are extremely important in the formation of pyrazine compounds which have been implicated as the character impact compounds of roasted peanuts. Wiggins (1956) observed that ammonia heated with an acid-hydrolyzed (inverted sucrose) sample of molasses gave a variety of pyrazine compounds; unhydrolyzed molasses took up only about one-half as much ammonia. Unpublished evidence obtained in the authors' laboratories with model glucose-amino acid systems showed that qualitatively the same volatile pyrazine compounds were produced regardless of the amino acid employed as the nitrogen source.

Hypothetical Mechanism for the Conversion of Amino Acids and Carbohydrates to Volatile Compounds. Consideration of the results obtained in this work led the authors to postulate a plausible mechanism, shown in Figure 2, for the conversion of amino acids and sugars to volatile compounds associated with peanut flavor. The mechanism, which includes ideas set forth by Hodge (1953, 1965) and Rohan and Stewart (1966a), involves the initial addition of an amino acid to the anomeric carbon atom of an aldose followed by dehydration to the 1,2-eneaminol (I) and elimination of hydroxyl ion to give the Schiff base cation (II). The Schiff base cation can undergo hydrolysis to an α -dicarbonyl compound (III) which is converted to browning pigments by a series of steps. Alternatively, the Schiff base cation could decarboxylate to the imine (IV) which would rapidly hydrolyze to yield an

aldehyde and a dieneamine (V). Enolization of the 1,2 double bond and migration of the 3,4 double bond yields the unsaturated ketoamine (VI). This compound then could undergo retro-aldol condensation to yield amino acetone and glyceraldehyde. Condensation of two molecules of amino acetone yields 2,5-dimethylpyrazine (VII) which was one of the major pyrazine compounds found in roasted peanuts (Mason *et al.*, 1966; Johnson, 1966).

ACKNOWLEDGMENT

The senior author was the recipient of a 1966 Nestlé Fellowship in Food Science.

LITERATURE CITED

- Casey, J. C., Self, F., Swain, T., *J. Food Sci.* **30**, 33 (1965).
Colvin, H. W., Atteberry, J. T., Ivy, J. T., *J. Dairy Sci.* **44**, 2081 (1961).
Dawes, I. W., Edwards, R. A., *Chem. Ind. (London)* **1966**, p. 2203.
El'ode, T. E., Dornseifer, T. P., Keith, E. S., Powers, J. J., *J. Food Sci.* **31**, 351 (1966).
Gilpin, J. A., McLafferty, F. W., *Anal. Chem.* **29**, 990 (1957).
Greenstein, J. P., Winitz, M., "Chemistry of the Amino Acids," p. 1933, Wiley, New York and London, 1961.
Hodge, J. E., *J. Agr. Food Chem.* **1**, 928 (1953).
Hodge, J. E., 4th Symposium on Foods: Chemistry and Physiology of Flavors, Corvallis, Ore., 1965.
Johnson, B., "Isolation and Identification of Some Volatile Constituents of Roasted Peanuts," M.S. dissertation, Oklahoma State University, 1966.
Johnson, M. J., *J. Biol. Chem.* **181**, 707 (1948).
Mason, M. E., Johnson, B., Hamming, M., *J. Agr. Food Chem.* **14**, 454 (1966).
Mason, M. E., Johnson, B., Hamming, M., *J. Agr. Food Chem.* **15**, 66 (1967).
Mason, M. E., Waller, G. R., *J. Agr. Food Chem.* **12**, 274 (1964).
Mejbaum, W., *Z. Physiol. Chem.* **258**, 117 (1939).
Nelson, N., *J. Biol. Chem.* **153**, 375 (1944).
Pattee, H. E., Beasley, E. O., Singleton, J. A., *J. Food Sci.* **30**, 388 (1965).
Pinto, A., Chichester, C. O., *J. Food Sci.* **31**, 726 (1966).
Robinson, H. W., Hogden, C. G., *J. Biol. Chem.* **135**, 727 (1940).
Rohan, T. A., Stewart, T., *J. Food Sci.* **31**, 202 (1966a).
Rohan, T. A., Stewart, T., *J. Food Sci.* **31**, 206 (1966b).
Wiggins, L. F., *Proc. Congr. Intern. Soc. Sugar Cane Technologists (9th) British West Indies* **1956**, p. 525.

Received for review January 9, 1967. Accepted July 18, 1967. Division of Agricultural and Food Chemistry, 152nd Meeting, ACS, New York, N.Y., September 1966. Work supported in part by the Oklahoma State University Agricultural Experiment Station and the Corn Products Institute of Nutrition.