Characteristics of Heat-Treated Aqueous Extracts of Peanuts and Cashews

W. M. Coleman, III,* J. L. White, Jr., and T. A. Perfetti

Bowman Gray Technical Center, R. J. Reynolds Tobacco Company,
Winston-Salem, North Carolina 27102-1487

The characteristics of the aqueous extracts of cashews and two varieties of peanuts in terms of their total and free amino acid profiles are described. When the aqueous extracts of these natural products are "heat-treated" in a sealed reaction vessel, selected types of volatile organic compounds are produced. The various types and yields of compounds produced are described. Additionally, theories based on (1) free and total amino acid pools, (2) Maillard chemistries, and (3) sugar degradation processes are advanced to account for their origin. On the basis of differences in the free amino acid pools of the aqueous extracts of each natural product, quantitative differences in the distribution of volatile materials can be explained. The findings are compared to results on other components of peanuts and other processing techniques.

INTRODUCTION

The perceived aroma and flavor of a food are in large part determined by the types and levels of volatile organic compounds present in a specific food item (Whitfield, 1992; Mauron, 1981; Buckholz, 1988). Three types of reactions are generally responsible for the formation of these aromas and flavors: (1) Maillard reactions between amino acids and sugars, (2) lipid degradations (thermal and oxidative), and (3) thermal degradation of sugars. The products of the Maillard reactions often yield many types of nitrogen heterocyclic compounds, i.e., pyrazines. Many of the Maillard reaction products have distinctive aromas and very low odor thresholds. Lipid degradation reactions can produce either deterioration or improvements, as judged sensorially, in food quality by yielding a variety of oxygen-containing compounds, such as aldehydes, ketones, and alcohols. Thermal degradation reactions of sugars generally produce low molecular weight open-chain oxygen-containing compounds, as well as heterocyclic oxygen-containing species such as furan derivatives. The flavor and aroma quality of these compounds again vary dependent upon the types and levels of each odorant or flavorant produced.

The volatile flavor and aroma components of roasted peanuts, an important agricultural product, have been studied by many groups since 1965 when Pattee (1965) first reported carbonyl compounds as products from this source. Soon thereafter, Mason et al. (1969) made the first confirmed reported of the presence of pyrazines in roasted peanuts. Since these first works, a wide variety of papers have appeared (Walradt et al., 1971; vanStraten, 1977; Buckholz, 1979; Buckholz et al., 1980a,b; Ho et al., 1982, 1983; Rodriguez et al., 1989; Chiou et al., 1991; Shyu, 1992). All of these works have shown that the major volatile components formed during roasting were consistent with the three reaction types described above. These papers have described the effects of reaction time, temperature, percent moisture, amino acid levels, percent sugar, maturity, seed size, and storage on potential quality of whole and selected nut component parts. It has been clearly established, from these studies, that precursor levels of amino acids and sugars have important bearing on the

final quality of the roasted nut (Rodriguez et al., 1989), regardless of the portion of the nut employed.

To date, however, no paper has appeared describing the chemical characteristics of aqueous extracts of whole peanuts and the resultant volatile compounds that are produced when these extracts are heated in a closed container. The importance of and rationale for investigating such a heating of aqueous extracts lie with the potential of producing aqueous extracts having some of the unique characteristics of the roasted starting materials. These naturally prepared aqueous extracts would then be translocated to other different natural product substrates thereby, for example, imparting the aroma and flavor characteristics of peanuts to other materials.

The objectives of this paper were to describe the characteristics of (1) the aqueous extracts of two varieties, NCV11 and NC7, of peanuts, legumes, and cashew nuts and (2) the volatile materials produced when the aqueous solutions are roasted and (3) to compare these findings with those from studies on other components of the peanut.

MATERIALS AND METHODS

Materials. Peanuts and cashews were obtained from the Research and Development Division of Planters Life Savers Corp. The shells and testa were removed prior to extraction with the warm water.

Methods. *Amino Acid Analyses.* Total and free amino acid levels were determined by AAA Labs, Inc., Mercer Island, WA, using the following procedure: a 20-h 6 N HCl/0.05% mercaptoethanol hydrolysis at 150 °C with one crystal of phenol added before acid hydrolysis. Serine was increased by 10% and threonine was increased by 5% to compensate for destruction by acid hydrolysis. For cystine, performic acid was used for oxidation prior to acid hydrolysis.

Volatile Compounds. The headspace measurements and compound identifications were determined as previously described by Coleman (1992). This procedure is based on the hyphenated technique, purge and trap/gas chromatography/flame ionization detection/mass selective detection (P&T/GC/FID/MSD). The volatile materials are swept from the sample and concentrated onto a Tenax trap. The trapped materials are then thermally desorbed onto a capillary GC column, followed by separation and quantitative analysis by FID coupled with qualitative analysis by MSD.

Heat-Treated Aqueous Extracts. The aqueous extracts were prepared in a 3-L Erlenmeyer flask by gently warming (45–90

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°C) approximately 400 g of whole nuts (peanuts or cashews) in 1.5 L of water for 3–4 h. The extracted nuts were separated from the solution by a simple filtration employing a fritted filter and allowed to dry. The filtrate of the aqueous extract was placed in a 2-L steam jacketed pressure vessel (Parr Instrument Co., Model 4522) fitted with an external motorized stirrer. The pressure vessel was sealed, and high-pressure steam was circulated through the outer jacket of the vessel. Within minutes (3–5 min) the internal temperature of the vessel was brought to 175–180 °C. This temperature was maintained for 30 min. The contents of the vessel were continuously stirred. An internal pressure of 150–300 psig was reached within the first 10 min of the reaction and maintained for the remainder of the reaction time. After 30 min, the steam was removed and cool water was circulated through the jacket of the pressure vessel. Within approximately 40–50 min the internal temperature of the vessel and extract had reached 30–40 °C and the pressure had returned to atmospheric. The pressure vessel was unsealed, and the warm extract was removed and placed in a sterile 4-L glass jar and sealed. The heat-treated extracts were then stored in a freezer at –20 °C until ready for examination.

RESULTS AND DISCUSSION

Two of the more important and abundant chemical classes common to all natural products are amino acids and sugars. In nature, it is well-known that amino acids and sugars react slowly with one another to produce low yields of a wide variety of chemical species. On the other hand, when man purposefully combines and heats these two classes of compounds in each other's presence, with adequate moisture and controlled pH, larger levels of selected unique classes of volatile and semivolatile compounds as well as nonvolatile compounds are produced (Teranishi et al., 1981). The volatile aroma and flavor compounds produced by this reaction include aldehydes, ketones, pyrazines, pyridines, and furans. These types of compounds have been linked to positive sensory attributes in selected natural products such as coffee, tobacco, and peanuts after roasting (Teranishi et al., 1981). It should be noted that the major products of these nonenzymatic browning reactions are polymeric nonvolatile melanoidins with volatile and semivolatile portions of the products being less than or equal to around 1% by weight of the total initial reacting species. Nonetheless, this 1% yield has significant impact on sensory responses (Leahy, 1985).

Aqueous solutions of natural products are known to contain among other components sugars and amino acids (Young and Hovie, 1990). Thus, it seemed plausible that Maillard-type chemistries could be performed on aqueous extracts of natural products to produce materials with desired sensory attributes. In addition, it was reasoned that differences in variety and type of peanut could be recognized from the aqueous extracts. It also seemed reasonable that the profile of the volatile compounds produced by heating the aqueous extracts would be unique for each variety and type of peanut. Therefore, aqueous extracts of two varieties of peanuts, NCV11 and NC7, as well as an aqueous extract of cashews were prepared, and each was heated separately at 180 °C for 30 min in a closed Parr bomb. After cooling, the headspace above the dark brown extracts of each peanut or cashew was examined using dynamic headspace techniques (Coleman, 1992).

The major components of the headspace above the samples are listed in Table 1. From a qualitative perspective, the types of compounds found were all consistent with (1) Maillard-type chemistries or (2) thermal degradation of sugars. The furans and ketones were produced by thermal degradation of the sugars. The pyrazines and aldehydes were produced by Maillard chemistries. These types of compounds were very similar to those previously

**Table 1. Comparison of Headspace Volatile FID Area Percentages of Aqueous Extracts**

| compound	NCV11	NC7	cashew
furan	BDL[a]	BDL	7.59
propanal	BDL	BDL	1.69
acetone	19.51	14.91	30.48
2-methylpropanal	14.03	12.65	13.95
2-methylfuran	2.60	1.00	1.62
butanone	1.34	1.50	2.16
2-pentanone	4.89	4.83	7.62
3-methylbutanal	20.17	24.07	11.49
2-methylbutanal	9.99	10.80	8.08
2,3-pentanedione	1.94	4.67	BDL
1-hydroxy-2-propanone	0.52	0.54	1.90
3-hydroxy-2-butanone	0.09	0.07	BDL
hexanal	1.22	0.21	0.35
methylpyrazine	0.38	0.59	0.68
dihydro-2-methyl-3(2H)furanone	0.43	0.51	0.45
furfural	2.72	3.98	7.44
dimethylpyrazines	0.46	0.74	0.44
acetylfuran	0.45	0.22	0.49
benzaldehyde	1.09	1.03	0.24
5-methylfurfural	0.31	0.43	0.42
benzeneacetaldehyde	9.43	6.07	0.46
3-phenylfuran	2.15	1.23	BDL
total FID area	674.57	988.81	1738.23

[a] BDL, below detection limit.

documented in the headspace above roasted peanuts (Coleman, 1992; Young and Hovie, 1990). The aroma of all of the heated extracts was consistent with roasted peanuts. Consequently, the reagents necessary to produce Maillard chemistries and sugar degradation processes were present in sufficient quantities in the aqueous extracts to produce the expected compounds and aroma notes.

The quantitative data in Table 1 indicated that some headspace volatiles were unique to the sample type, and in some cases, the amounts found could be used to indicate the sample type. The total FID area counts, which is a measure of the total amount of volatile material, was particular to each sample. For example, the total FID area counts for the NCV11, NC7, and cashew samples were 719.8, 988.81, and 1738.23, respectively. The RSD (standard deviation divided by the average, times 100) values for these experiments were ±10%; thus, the differences in these numbers were statistically significant. It has been demonstrated (Buckholz et al., 1980a) that the sensory attributes of peanut materials can be correlated with the carbonyl and pyrazine content of the peanuts. For example, a decrease in carbonyls with a subsequent increase in pyrazines was noted to be an important indication for good quality peanut flavor (Buckholz et al., 1980a). Close examination of the percent distribution data in Table 1 indicated that the quality of the NC7 should be better than that of the NCV11 because of the increased amounts of pyrazines coupled with similar carbonyl content. Independent sensory evaluation of these two heated aqueous extract products would be required before the NC7 extract could be confidently judged the superior product.

It was somewhat surprising to find that the qualitative description of the headspace volatiles from the cashew nut was very similar to that of the two peanut samples (Table 1). On the other hand, if amino acids and sugars were responsible for the reactions, then the qualitative aspects of the headspace volatiles could be somewhat similar. This was the case in that the types of compounds found for the two peanuts were very similar to those found for the cashews. The uniqueness of the cashew was found
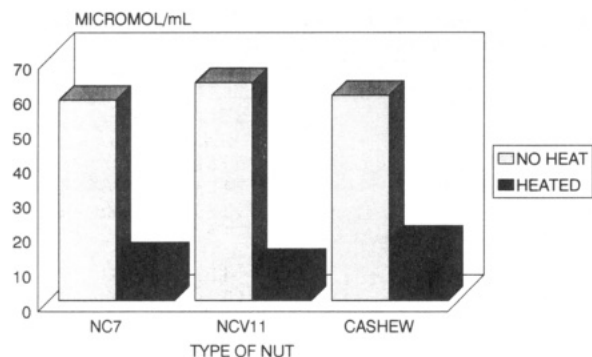
Figure 1. Total amino acid levels of aqueous extracts, with and without heat, as a function of type of nut.
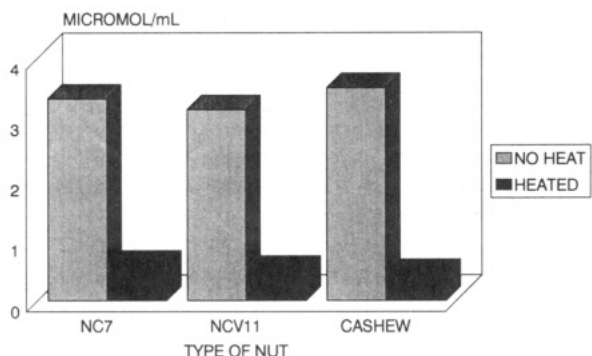
Figure 2. Free amino acid levels of aqueous extracts, with and without heat, as a function of type of nut.

in the quantitative aspects of the headspace volatiles when compared to the two peanut samples. For example, the total FID area counts for the cashew were 1738.23, almost twice the amount for the peanut samples. In addition, the percent distribution of volatile materials was very different. For example, acetone accounted for approximately 30% of the volatile material in the cashew and less than 20% in the peanut samples, while furfural accounted for approximately 7% of the volatile material in the cashew and only 3–4% in the two peanut samples. Interestingly, however, the percent contributions from pyrazine-type compounds were similar for each sample at around 1%.

Some leading indicators that the amino acid/sugar reaction chemistries may be responsible for the general trend in the headspace volatiles for these peanuts and cashews could be found in the characteristics of other aqueous extracts of other natural products. For example, the types of volatile materials found with coffee, tea, cocoa, fruits, vegetables, and baked goods were very similar to those found in these heated extracts (Teranishi et al., 1981, 1992). The major volatile aromatic compounds from this wide range of natural products would suggest a strong common thread in their makeup, that being the amino acids and sugar pool.

An underlying cause for the presence of the volatile compounds, as well as differences in their distribution, must rest in part with differences in the total (Figure 1) and free amino acid (Figure 2) concentration and distribution of each within a prepared aqueous extract (Rodriguez et al., 1989; Chiou et al., 1991; Teranishi et al., 1981, 1992; Woodroff, 1983). Tables 2 and 3 contain information on the total and free amino content of the aqueous extracts, respectively, prior to heat treatment for both the peanuts and the cashew. The total amino acid contents of all three extracts were very similar. For example, the values for NC7, NCV11, and cashew were 57.8794, 62.897, and 59.2271

Table 2. Total Amino Acids in Aqueous Extracts

amino acid	NC7	NCV11	cashew
alanine	2.76	2.72	3.16
arginine	6.01	6.74	5.79
aspartic acid	7.13	7.61	4.07
cystine/2	1.42	1.53	2.02
glutamic acid	12.60	13.80	15.90
glycine	4.48	5.88	3.67
histidine	1.07	1.16	0.90
isoleucine	1.30	1.30	1.62
leucine	3.27	3.62	3.30
lysine	1.61	1.72	2.30
methionine	0.77	0.76	0.85
phenylalanine	2.34	2.67	1.77
proline	5.14	3.70	3.29
serine	3.90	4.32	4.10
threonine	0.49	1.61	1.52
tryptophan	ND[a]	ND	ND
tyrosine	1.58	1.85	1.28
valine	1.79	1.79	2.58
GABU[b]	0.05	ND	0.88
glucosamine	0.12	0.12	0.09
sum	57.88	62.90	59.23

[a] ND, not detected. [b] γ-Aminobutyric acid.

Table 3. Free Amino Acids in Aqueous Extracts

amino acid	NC7	NCV11	cashew
alanine	0.278	0.17	0.405
arginine	ND[a]	ND	ND
aspartic acid	0.0609	0.0243	0.0784
cystine/2	0.0124	ND	ND
glutamic acid	1.16	1.14	1.18
glycine	ND	ND	ND
histidine	0.0783	0.0644	0.027
isoleucine	0.0832	0.09	ND
leucine	0.185	0.16	0.127
lysine	0.0354	0.073	ND
methionine	0.152	0.152	0.0765
phenylalanine	0.585	0.619	0.142
proline	0.129	0.0514	0.214
serine	0.0472	0.0066	ND
threonine	0.0184	0.0066	ND
tryptophan	ND	ND	0.139
tyrosine	0.115	0.0822	0.185
valine	0.21	0.298	0.142
asparagine	ND	ND	ND
GABU[b]	0.0641	0.06	0.8
glucosamine	0.0034	0.0007	ND
sum	3.3313	3.1512	3.5159

[a] ND, not detected. [b] γ-Aminobutyric acid.

μmol/mL, respectively. In contrast, the distribution within each aqueous extract was unique. A case in point was the arginine levels. The values were 6.01, 6.74, and 5.79 μmol/mL for NC7, NCV11, and cashew, respectively. Arginine has been associated with bitter taste in peanut products (Woodroff, 1983) and as such should have an impact on aroma and flavor characteristics of these aqueous extracts. It was interesting to note that the NCV11 product had the highest level of arginine, while the cashew had the lowest amount of arginine.

The free amino acids can be expected to react much faster than those bound in the protein form and as such could yield some important information that would differentiate between the two varieties of peanuts and the cashew (Woodroff, 1983). Table 3 contains the data on the free amino acid content of the samples. As seen with the total amino acids, a sum of the values indicated no significant differences in the sample. In contrast, however, the distribution within the mix of amino acids was different for each extract. For example, the amount of leucine varied from 0.127 to 0.185 μmol/mL. It seems plausible to

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Table 4. Total Amino Acids in Aqueous Extracts after Heat Treatment

amino acid	NC7	NCV11	cashew
alanine	0.903	0.718	1.24
arginine	0.134	0.133	ND[a]
aspartic acid	0.924	0.79	0.542
cystine/2	0.104	0.0955	0.219
glutamic acid	3.35	2.83	6.27
glycine	2.12	2.11	1.89
histidine	0.22	0.164	0.299
isoleucine	0.294	0.198	0.412
leucine	0.657	0.494	0.878
lysine	0.189	0.161	0.219
methionine	0.143	0.12	0.301
phenylalanine	0.426	0.31	0.517
proline	0.778	0.621	0.947
serine	0.953	0.778	1.26
threonine	0.356	0.265	0.574
tryptophan	ND	ND	ND
tyrosine	0.362	0.277	0.369
valine	0.432	0.368	0.806
GABU[b]	0.081	0.0579	0.429
glucosamine	0.0561	0.0425	0.0615
sum	12.4821	10.5329	17.2335

[a] ND, not detected. [b] γ-Aminobutyric acid.

Table 5. Free Amino Acids in Aqueous Extracts after Heat Treatment

amino acid	NC7	NCV11	cashew
alanine	0.0705	0.0592	0.0403
arginine	ND[a]	ND	ND
aspartic acid	0.263	0.217	0.094
cystine/2	0.005	ND	ND
glutamic acid	0.0126	0.0091	0.0137
glycine	0.0786	0.066	0.0563
histidine	ND	ND	ND
isoleucine	0.0048	0.0039	0.0066
leucine	0.0039	0.0042	0.004
lysine	ND	ND	ND
methionine	ND	ND	ND
phenylalanine	0.0144	0.0255	ND
proline	0.0116	0.0118	ND
serine	0.0304	0.0274	0.0219
threonine	0.0108	0.0073	0.0045
tryptophan	ND	ND	ND
tyrosine	0.0117	0.0109	ND
valine	0.0157	0.0153	0.0159
asparagine	0.0035	0.0028	ND
GABU[b]	0.0338	0.0246	0.167
glucosamine	0.0047	0.0039	0.0097
sum	0.575	0.4889	0.4339

[a] ND, not detected. [b] γ-Aminobutyric acid.

attribute the differences in headspace volatile profiles to the differences in the amounts of the amino acids. Support for this conclusion was based in part on the distribution of 2-methylbutanal, 3-methylbutanal, benzeneacetaldehyde, and 2-methylpropanal. These compounds have been documented as arising from the following amino acids: isoleucine, leucine, phenylalanine, and valine, respectively (Whitfield, 1992). A general trend is evident between the amounts of volatile aldehydes and free amino acids. As the amount of free amino acid increased, so did the relative amount of the corresponding aldehyde. For example, the amounts of leucine free amino acid for NC7, NCV11, and cashew were 0.185, 0.160, and 0.127 μmol/mL, while the amounts of 3-methylbutanal were 24.07%, 20.17%, and 11.48%, respectively.

Confirmation of these findings can be found in the values for the free amino acids in the heated extracts. If amino acids, both total and free, were participating in the formation of Maillard reaction products, then measurable decreases in their concentrations should be evident in the heat-treated extracts compared to the starting extracts. Comparison of the data in Tables 2 and 4 shows the consumption of the total amino acid pool during the heat treatment of the aqueous extracts. Figure 1 displays the sum of the total amino acid levels of the aqueous extracts before and after heat treatment. It was obvious that a significant portion of the total amino acid pool was consumed during the 30-min heat treatment. For example, the total amino acid level in NC7 was 57.87 μmol/mL prior to heat and 12.48 μmol/mL after heat treatment. Thus, approximately 70–80% of the total amino acids were consumed. Similar changes were observed in the other peanut case as well as with the cashews. From a free amino acid perspective (Figure 2), matching trends were found (Tables 3 and 5). For example, the free amino acid level for the cashew sample was 3.52 μmol/mL prior to heat treatment and 0.434 μmol/mL after heat treatment. Hence, approximately 80–90% of the free amino acid pool was consumed.

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