Effect of Roasting Time and Temperature on the Generation of Nonvolatile (Polyhydroxyalkyl)pyrazine Compounds in Peanuts, As Determined by High-Performance Liquid Chromatography

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A high-performance liquid chromatographic (HPLC) method was used for the determination of (polyhydroxyalkyl)pyrazine (PHAP) compounds in peanuts roasted to different levels as part of a 3×3 time/temperature study. The content of volatile alkylpyrazine compounds generated at each point was determined by headspace gas chromatography−mass spectrometry (GC−MS) and compared to the PHAP content. In general, results showed that the levels of both PHAP and alkylpyrazine compounds increased with both time and temperature, reaching a maximum at the longest roast time and highest temperature. Formation rates for both types of compounds showed a strong dependence on temperature, giving linear Arrhenius plots with similar slopes. There was no indication that the PHAP compounds formed during roasting decomposed to form alkylpyrazines.

Keywords: *Roast peanuts; (polyhydroxyalkyl)pyrazines; alkylpyrazines; LC-MS; flavor generation; headspace GC−MS*

INTRODUCTION

Much work has been done to isolate and identify the volatile components formed during the roasting of peanuts. Various techniques of isolation including solvent extraction, fractional distillation, static headspace, and purge and trap have been used; separation and identification of the volatile compounds was done primarily by GC−MS. Among the most important volatile flavor compounds found in roasted peanuts are the alkylpyrazines. Very little work has been done, however, on the isolation and identification of nonvolatile pyrazine compounds such as (polyhydroxyalkyl)-pyrazines (PHAPs). One proposed formation mechanism of PHAPs is shown in Figure 1 (Tsuchida et al., 1973). The PHAP compound shown is fructosazine, or 2,5-bis(tetrahydroxybutyl)pyrazine, which may be formed from ketosamine precursors formed during the Maillard reaction.

Previous workers have investigated PHAP formation in caramel colors (Tsuchida et al., 1986) and soy sauce (Tsuchida et al., 1990). The caramel color and soy sauce work used cellulose membrane dialysis, preparative column chromatography, paper chromatography, and thin-layer chromatography to isolate and separate the various PHAPs. Off-line UV/vis, infrared and NMR were used for compound identification. PHAPs were identified by their UV absorbance at ∼275 nm, which is characteristic of disubstituted pyrazines (Linnell et al., 1961; Mason, 1959) or at 295 nm, which is characteristic of disubstituted pyrazines conjugated with a vinyl group, their IR spectrum, which showed the presence of hydroxy groups, and their NMR spectrum, which was used to identify the number of protons and their environment. Compounds identified included fructosazine and other related compounds containing shorter side chains and/or fewer hydroxyl groups. In addition, GC−MS has been performed on the trimethylsilyl and butaneboronate trimethylsilyl ethers of PHAPs (Tsuchida et al., 1978).

Hardt and Baltes (1988) performed Curie-point pyrolysis−capillary GC−MS on eight PHAPs, resulting in the identification of 44 compounds including 32 pyrazine derivatives. Pyrolysis was performed at 600 °C for 10 s, after which time the pyrolyzate was introduced to the GC−MS. It was found that thermal decomposition of PHAPs resulted in the formation of dozens of pyrazine compounds, which included several alkylpyrazines. This work showed that PHAP compounds could decompose thermally into alkylpyrazines, which had already been shown to be important flavor and aroma compounds in peanuts. Koehler and Odell (1970) proposed that PHAP compounds could decompose to produce alkylpyrazines at temperatures commonly encountered in food systems. They considered this an alternate pathway to the traditional view that sugars first fragment then react with amines to form pyrazines.

In a previous publication (Magaletta et al., 1996) the authors described a solid-phase extraction/HPLC method which was useful for the isolation and separation of PHAP compounds from peanuts. Using diode array and mass spectrometric detectors, the authors were able to identify eight PHAPs present in a roasted peanut extract. In this paper, the above method is used to determine the PHAP content of peanuts roasted in a 3×3 experiment and to determine some of the key kinetic parameters involved in PHAP formation. In addition, the alkylpyrazine content of these peanuts is determined by headspace GC−MS and the findings compared to the PHAP data in an attempt to determine whether the decomposition of PHAPs is contributing to the formation of alkylpyrazines in peanuts.

EXPERIMENTAL PROCEDURES

Solvents and Chemicals. Authentic fructosazine (MW = 320), purchased from Sigma Chemical Corporation, was used as a standard for the HPLC work. Authentic 2-methylpyrazine (MW = 94), purchased from Bedoukian Research, Inc., was used as a standard for the headspace GC−MS work. All

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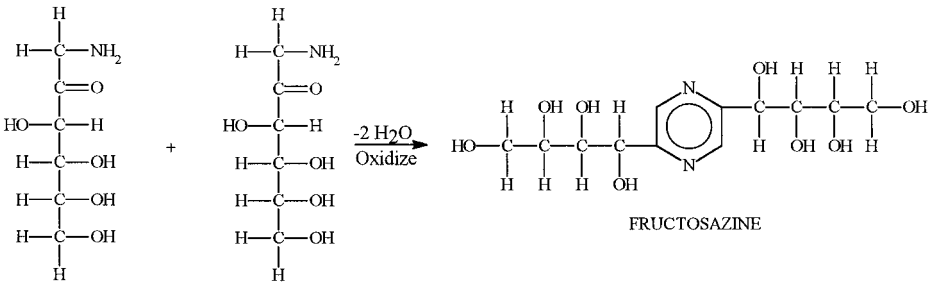

Figure 1. Proposed formation mechanism of fructosazine.

solvents and chemicals used were of analytical reagent grade except for ultrapure water, which was generated as needed using a Milli-Q system from Millipore Corporation. Peanuts were fresh, whole extra-large Virginia peanuts.

Color Measurement Equipment and Conditions. Color of the various peanut samples was determined using an Agtron model M-45 colorimeter, using the green scale. Calibration to a reading of 0 was done using the no. 12 standard tile and calibration to a reading of 100 was accomplished with the no. 33 tile. In this measurement system, a higher number corresponds to a lighter color and therefore to a less dark roast.

HPLC Equipment and Conditions. The equipment and conditions used were the same as in the previous publication (Magaletta et al., 1996). Detection was accomplished by UV absorption at 275 nm, with a bandwidth of 5 nm. For the higher PHAP concentration samples (samples I and F), sensitivity was set at 0.05 AUFS, and an injection volume of 50 μL was used. A sensitivity of 0.02 AUFS and an injection volume of 100 μL were used for all the other samples.

Headspace GC−MS Equipment and Conditions. Headspace analysis was performed using a Perkin-Elmer HS-40 automated headspace sampler interfaced to a Finnigan Magnum ion trap GC−MS. The GC−MS was equipped with a septum programmable injector (SPI) programmed temperature inlet, cooled with liquid nitrogen.

The headspace sampler conditions were as follows. Thermostat time was 15 mins at 75 °C, helium pressure was 12 psi, pressurizing time was 1.0 min, withdrawal time was 0.2 min, and injection time was 2.0 min. HS-40 sampling needle and transfer line temperature were each set at 120 °C.

The GC column used was a Nukol 30 meter capillary, with a 0.25 mm i.d. and a 0.25 μm film thickness, purchased from Supelco, Inc.

The GC conditions were as follows. The SPI was initially held at −40 °C for 3 min, then ramped to 80 °C over 0.75 min, and held for the duration of the analysis. The column oven was held at −40 °C for 5 min, then ramped to 200 °C at 5 °C/min, and held 10 min. The transfer line from the GC to the MS was held at 200 °C.

Seven grams of roasted peanuts were sealed in a 22 mL headspace vial with a Teflon-lined butyl rubber septum and crimp capped, then transferred to the HS-40 for analysis in duplicate.

HPLC Calibration. To take into account losses of PHAPs due to less than 100% recovery during cleanup, a fructosazine standard was taken through the entire cleanup procedure as if it was a sample. This prepared standard was then injected into the HPLC (50 or 100 μL injection volume), and the resulting peak height was used to calculate the amounts of each PHAP present. Fifteen milliliters of a 10 ppm solution of fructosazine was passed through the entire cleanup procedure, resulting in 1.0 mL of a solution which would be 150 ppm in concentration if 100% recovery was achieved. The calculation used for determination of PHAP content in parts per million (ppm) is as follows:

$$\frac{h_{\text{sample}}(\text{standard})\ V_{\text{f}}\ V_{\text{iMeOH}}(100 - \%\text{fat})}{h_{\text{standard}} w_{\text{sample}}\ V_{\text{MeOH used}}\ 100}$$

where h_{sample} height of sample peak; V_{f}, final volume; V_{iMeOH}, initial volume of MeOH extract; h_{standard}, height of standard peak; w_{sample}, sample weight(g); $V_{\text{MeOH used}}$, volume of methanol extract used. Substituting the appropriate terms, the calculation becomes

$$\frac{h_{\text{sample}}(150)(1.0)(30)(53)}{h_{\text{standard}}(6.0)(15)(100)} = \text{ppm of each PHAP in peanuts}$$

The percentage fat term is necessary because the roasted peanuts were defatted with hexane prior to extraction and 6.0 g of the defatted meal was used in the analysis. The peanuts were found to be 47.0% fat by Soxhlet extraction in triplicate. This procedure is only semiquantitative because of the changes in peak height due to differing elution volumes and because of the differences in molar absorptivities of the different PHAP compounds.

Table 1. Roasting Conditions and Resulting Agtron Color Values

temperature (°C)	roast time (min)		
	3	7	11
152	A (113)	D (75)	G (48)
163	B (103)	E (40)	H (25)
174	C (63)	F (3)	I (−12)

GC Calibration. A standard of 2-methylpyrazine in fresh corn oil was prepared at a concentration of 100 ppm. Seven grams of this standard was sealed in five 22 mL headspace vials which were run along with the samples. All alkylpyrazine concentrations were determined by comparison of the average standard peak area to sample peak area, using an external standard calculation. This approach is valid because previous work showed the calibration curve to be linear between 0 and 100 ppm, with a correlation coefficient of 0.9988. Peak areas were integrated from the total ion chromatograms for the mass range between 35 and 140 amu.

Peanut Roasting Equipment and Conditions. Fresh, whole extra-large Virginia peanuts were blanched in a forced air oven for 1 h at 95 °C and the skins manually removed. Agtron color values for the peanuts were identical at 122.4 both before and after blanching. Only intact whole blanched peanuts were used in the roasting study. One-half kilogram quantities of these peanuts were roasted in a Pitco Frialator commercial fryer using fresh peanut oil according to a 3×3 experimental design. After roasting, the peanuts were cooled for 5 min on a vacuum cooler and sealed in glass jars. The times and temperatures used appear in Table 1, along with the letter code assigned to each condition. The resulting Agtron color readings are displayed in parentheses next to the letter designations.

Sample Preparation and Cleanup. Sample preparation for HPLC analysis was performed exactly as stated in the previous article except that a 15.0 mL aliquot of the initial methanol extract was taken and dried down under nitrogen instead of the entire liquid layer, in order to allow more accurate quantitation. All samples were run in duplicate, and the average of the two results was used for data analysis.

Fructosazine Decomposition Study. One hundred milligrams of authentic fructosazine standard was sealed in a 1 mL reaction vial with a Teflon septum and heated in a commercial fryer to 174 °C for 11 min in order to determine whether this compound decomposed to alkylpyrazines at the conditions which produced the darkest peanut roasting in the study. The entire headspace volume above the sample was

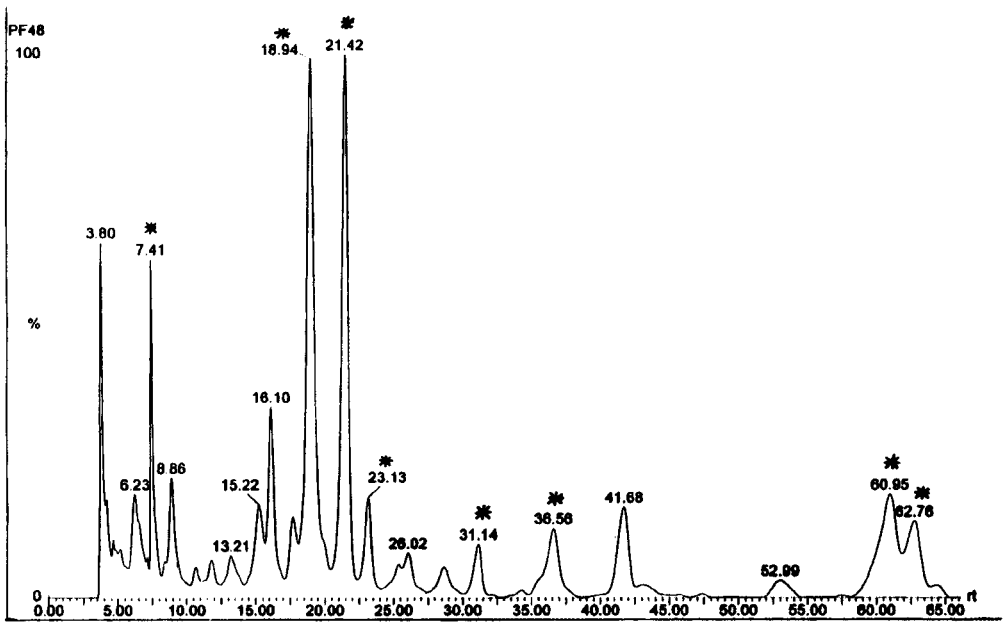

Figure 2. Typical HPLC chromatogram of roasted peanut extract.

Table 2. Retention Times, Molecular Weights, and Identification of Peanut Extract Peaks

retention time (min)	peak no.	MW	identified pyrazine compound
7.41	1	304	2-(tetrahydroxybutyl)-5 (or 6)-(2′,3′,4′-trihydroxybutyl)
18.94	2	184	2-(2′,3′,4′-trihydroxybutyl)
21.42	3	288	2,6-bis(2′,3′,4′-trihydroxybutyl)
23.13	4	288	2,5-bis(2′,3′,4′-trihydroxybutyl)
31.14	5	258	2-(2′,3′,4′-trihydroxybutyl)-5 (or 6)-(2′,3′-dihydroxypropyl)
36.56	6	228	2-(tetrahydroxybutyl)-5 (or 6)-ethyl
60.95	7	272	2-(2′,3′,4′-trihydroxybutyl)-6-(2′,3′-dihydroxybutyl)
62.76	8	272	2-(2′,3′,4′-trihydroxybutyl)-5-(2′,3′-dihydroxybutyl)

then withdrawn using a gas-tight syringe, injected in the GC−MS injection port (set at −40 °C) and run using the same conditions as for the peanut alkylpyrazine analysis.

RESULTS AND DISCUSSION

Recovery of PHAP during Cleanup. A recovery study was performed in triplicate on the entire procedure, using a fructosazine standard in place of the peanut methanol extract. Recovery was low but consistent, averaging 28.7% with a standard deviation of 0.58% and a coefficient of variation of 2.0%. Because of this fact, a standard which had been run through the cleanup procedure was used for calibration purposes.

The precision of the HPLC method was determined via a pooled standard deviation of eight duplicate analyses from five different roast samples (E, F, G, H, and I) on individual peaks which averaged ∼3 ppm in concentration. The standard deviation at this level was found to be 0.30 ppm, giving a relative standard deviation of 10.4%.

HPLC Analysis of Roasted Peanuts. Duplicate samples of the raw, blanched, and A−I peanut samples above were prepared as described and analyzed for PHAP content via HPLC. A typical chromatogram of peanut extract appears in Figure 2, and the identification of the peaks labeled appears in Table 2 (Magaletta et al., 1996).

Table 3. Content of Each PHAP Peak (in ppm) at Each Time/Temperature Point[a]

roast peak no.	A	B	C	D	E	F	G	H	I
1	nd	nd	nd	nd	0.38	3.74	nd	2.07	14.79
2	nd	nd	0.61	0.61	1.69	16.90	1.08	3.03	39.56
3	nd	nd	0.92	1.00	3.03	16.71	2.69	7.14	34.76
4	nd	nd	nd	nd	0.17	2.50	nd	0.50	4.61
5	nd	nd	nd	nd	nd	1.44	nd	0.38	2.88
6	nd	nd	nd	nd	nd	1.34	nd	nd	1.34
7	nd	nd	nd	0.23	0.81	3.26	0.56	0.92	4.80
8	nd	nd	nd	0.44	0.84	4.13	0.81	1.04	5.38
total	nd	nd	1.53	2.28	6.92	50.02	5.14	15.08	108.11

[a] nd = not detected (<0.2 ppm).

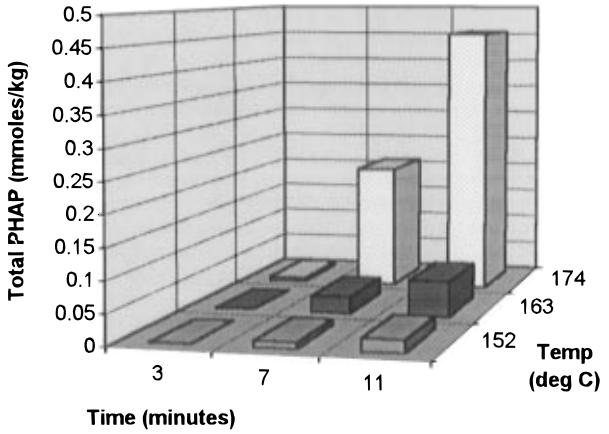

Figure 3. 3D plot of PHAP formation as a function of time and temperature.

Only samples F and I (the two most darkly roasted samples) contained all eight of the peaks identified in Table 2. The raw and blanched samples and roasted samples A and B contained no detectable PHAP compounds. In general, as the degree of roast increased, so did the PHAP content. A summary of the results for each peak at each time/temperature point is contained in Table 3. The data for total PHAP content in Table 3 was converted to units of millimoles/kilograms of peanuts and plotted as a 3D graph in Figure 3.

Table 4. Content of Each Alkylpyrazine Peak (in ppm) at Each Time/Temperature Point[a]

roast peak no.	A	B	C	D	E	F	G	H	I
1	nd	0.1066	1.7193	0.7724	3.0222	13.1873	1.3040	6.0409	17.4177
2	nd	0.4311	2.8041	1.8810	4.6059	13.8460	3.51952	8.7507	12.2619
3	nd	nd	nd	0.1937	0.7755	4.6622	0.3695	1.6915	5.2404
4	nd	nd	nd	nd	0.2166	1.4803	0.0617	0.6339	1.6156
5	nd	nd	0.2281	nd	0.3864	1.4221	0.0880	0.7722	1.3365
6	nd	0.06020	0.4968	0.2291	0.7550	1.7649	0.2818	1.3326	1.3381
7	nd	nd	0.0691	0.3810	1.0904	3.4861	0.6790	1.7651	2.9548
8	nd	0.03517	0.4819	0.1855	0.7303	2.1094	0.4728	1.3628	1.7855
total	nd	0.6331	5.7993	3.6427	11.5824	41.9582	6.7764	22.3499	43.9504

[a] nd = not detected (<0.05 ppm).

Table 5. Experimentally Determined Kinetic Data for PHAP and Alkylpyrazine Compounds

parameter	PHAP compounds			Alkylpyrazines		
temp (°C)	152	163	174	152	163	174
k (mmol kg^{-1} min^{-1})	0.002525	0.007313	0.05605	0.007816	0.02534	0.08532
k (mol kg^{-1} s^{-1})	$4.21E-8$	$1.22E-7$	$9.34E-7$	$1.3E-7$	$4.22E-7$	$1.42E-6$
E_a (kJ/mol)		222			172	
A(mol kg^{-1} s^{-1})		$6.71E+19$			$1.56E+14$	

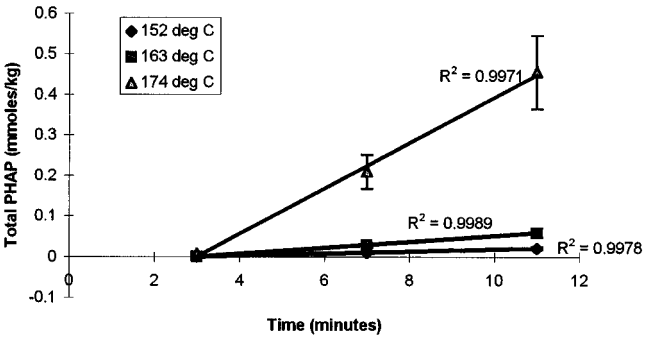

Figure 4. Relationship between total PHAP content and time at the three roasting temperatures. Error bars represent ± twice the method relative standard deviation at each point.

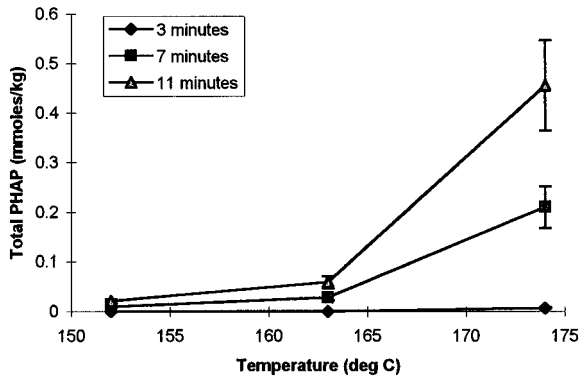

Figure 5. Relationship between total PHAP content and temperature at the three roasting times. Error bars represent ± twice the method relative standard deviation at each point.

As can be seen, PHAP content increases with time at each roasting temperature and also increases as roasting time is held constant and roasting temperature is increased. A similar effect was seen for all the individual PHAP compounds; the following analysis is based on the total PHAP content.

The dependence of total PHAP content on time at each temperature is shown graphically in Figure 4. It is readily apparent that there is a linear relationship between roasting time and PHAP content at all three temperatures studied, with PHAP content increasing as roasting time is increased. The linearity of the plots indicate that the reaction is zero order with respect to product under these conditions, and the formation rate may be described by [PHAP] = kt, where k = the rate constant and t = time. The rate constant for formation of PHAPs at each temperature may be calculated as the slope of the respective line. Rate constants at each temperature have been calculated and appear in Table 5.

Figure 5 illustrates the dependence of PHAP formation on temperature, when the roasting time is held constant. This plot shows that the PHAP formation rate is strongly dependent upon temperature.

GC Analysis of Roasted Peanuts. The relative standard deviation of the GC method was found to be 2.63%. A typical headspace GC−MS total ion chromatogram appears in Figure 5, along with the selected ion chromatograms and peak identifications for each compound.

The headspace GC results show a similar trend to the HPLC results in that the volatile pyrazine levels continue to increase during the course of the roasting. No alkylpyrazines were detected in either the raw or blanched peanuts. All quantitation is vs 2-methylpyrazine alone, so volatility differences between the pyrazines are not accounted for. Also, the vapor pressure of each pyrazine over peanuts may not be identical to that over pure oil, introducing further error. For these reasons, the absolute amounts shown may be seriously in error, but a comparison of relative amounts between each roasting condition is still valid. A summary of the results for each peak at each time/temperature point is contained in Table 4. Peak numbers correspond to the elution order in Figure 6, hence methyl pyrazine is peak no. 1 and 3-ethyl-2,5-dimethylpyrazine is peak no. 8.

Figures 7 and 8 illustrate that, in general, alkylpyrazine formation shows similar dependence on time and temperature to PHAP formation. Each individual alkylpyrazine exhibited a time/temperature dependence similar to the total. The formation rate constants for each temperature were calculated as for the PHAP results and also appear in Table 5. As shown in Figure 7, there is the same type of linear relationship between roasting time and alkylpyrazine formation as seen for PHAP formation, with the exception of the 174 °C roasting temperature, where the R^2 value is much lower than at the other temperatures. This deviation from linearity may be caused by breakdown of the alkylpyra-

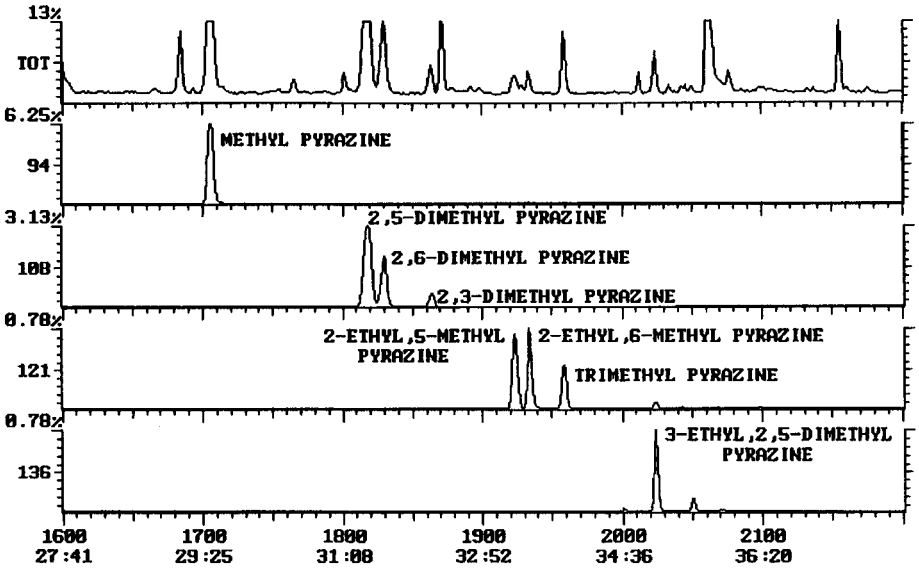

Figure 6. Total and selected ion chromatograms of typical roasted peanut sample.

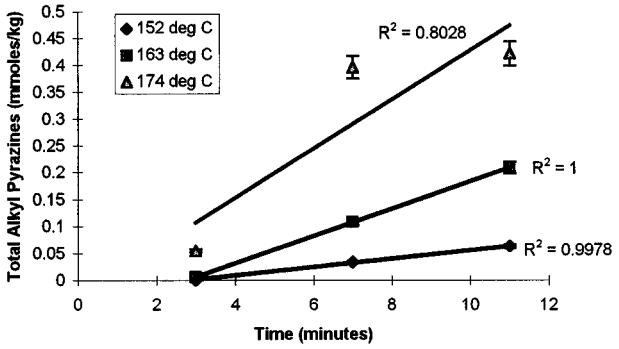

Figure 7. Relationship between total alkylpyrazine content and time at the three roasting temperatures. Error bars represent ± twice the method relative standard deviation at each point.

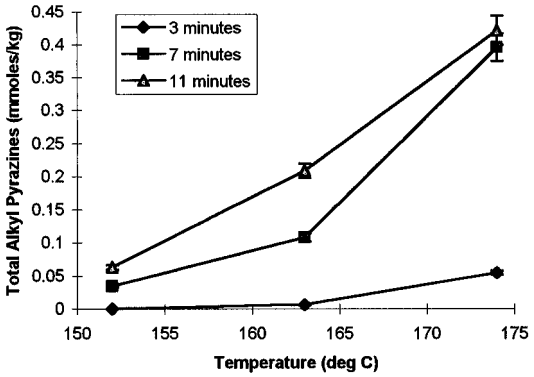

Figure 8. Relationship between total alkylpyrazine content and temperature at the three roasting times. Error bars represent ± twice the method relative standard deviation at each point.

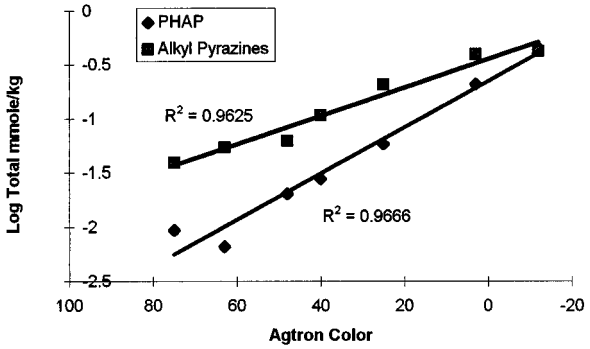

Figure 9. Correlation between color and pyrazine formation in peanuts.

zine compounds, saturation of the headspace in the sample vial, or volatilization from the peanut matrix. Koehler and Odell (1970) reported a similar effect in their study of sugar−amino acid model systems, wherein yields of volatile pyrazines became variable above 150 °C. Since breakdown is not seen for the PHAP compounds, which may reasonably be expected to be less stable than alkylpyrazines, volatilization of the alkylpyrazines, especially at the longest roasting times, seems the more likely cause of the nonlinearity. The fact that the pyrazines formed in this study were entrapped in the peanut matrix could explain why the effect was not seen until the 174 °C temperature was reached. Saturation of the headspace in the vial is unlikely because a methylpyrazine standard was shown to give a linear response up to 100 ppm, while 44 ppm is the maximum found in a sample. In order to minimize this effect in the kinetic calculations to follow, the rate constant for the 174 °C temperature was calculated using only the 3 and 7 min data.

Correlation between Color and Pyrazine Levels. Figure 9 relates PHAP and alkylpyrazine formation to the development of color, which is commonly used as a measure of the degree of roasting. The results for samples A and B were not included on the graph because the log of 0 is not a meaningful quantity. In both cases, a linear relationship is seen between the Agtron color value and the log of the total concentration. As roast level increases, the molar quantities of PHAPs approach and eventually surpass those of alkylpyrazines, probably because of volatilization of the alkylpyrazines at the longer roast times and higher temperatures.

Comparison of PHAP and Alkylpyrazine Formation Kinetics. From examination of the data in Table 5, it is apparent that PHAP formation rates in peanuts are several times slower than those of alkylpyrazines at the three temperature points studied.

By using the data from Table 5, an Arrhenius plot showing the dependence of PHAP and alkylpyrazine formation rates on roasting temperature was constructed and is shown in Figure 10. A more rigorous

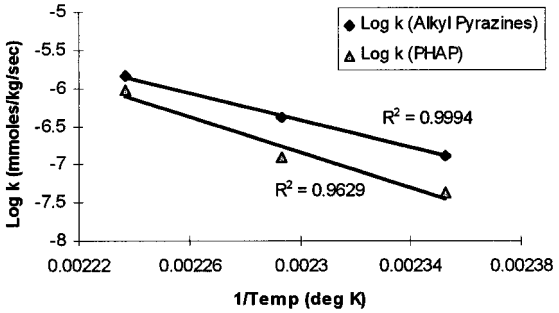

Figure 10. Arrhenius plots relating the formation rate constants of PHAP and alkylpyrazine compounds to roasting temperature. Rate constants are derived from the total concentrations of PHAP and alkylpyrazine compounds at each temperature.

Table 6. Experimentally Determined Kinetic Data for Four of the Individual PHAP Compound Peaks

PHAP peak no.	E_a (kJ/mol)	A (mol kg^{-1} s^{-1})
2	257	$3.25E + 23$
3	182	$3.74E + 14$
7	154	$3.04E + 10$
8	135	$2.10E + 08$

examination of the kinetics involved in these reactions would require many more data points to be collected; the purpose of this analysis is only to determine whether PHAP and alkylpyrazine formation have a similar dependence on temperature. The nonlinearity seen for the alkylpyrazine data at 174 °C, which is most likely attributable to volatilization of the pyrazines from the peanut matrix, brings the data at this temperature into question, since the k values derived from the slope of the line may be significantly in error. Because of this fact, only the data points for 3 min and 7 min at 174 °C were used to calculate the k value. A linear plot is obtained for both PHAP and alkylpyrazine formation, indicating that there are no significant side reactions or decompositions occurring to either species under the conditions shown on the graph. Formation of both types of compounds seems to have a similar dependence on temperature, indicating that similar mechanisms may be involved. Since the slope of the plot is equal to $-E_a/2.303R$, an approximation of the activation energy for each species may be determined. E_a for PHAP formation was found to be 222 kJ/mol, while that for alkylpyrazine formation was 172 kJ/mol. The fact that these energies are relatively close is to be expected, since both of the compound types are thought to be formed in similar reactions. Due to the small data set involved in these calculations, it is not possible to say with confidence whether the difference in activation energies is significant. Table 6 shows the variation in E_a and A between four of the PHAP peaks, illustrating that the variation between individual PHAPs is greater than that between total PHAP and total alkylpyrazine. The y intercepts of the plot correspond to log A, the preexponential factor, and thus the Arrhenius equations (Figure 10) for PHAP and alkylpyrazine formation are as follows:

$$\text{PHAP:} \quad k\ (\text{mol kg}^{-1}\ \text{s}^{-1}) = 6.71E + 19\text{e}^{-26698/T}$$

$$\text{alkyl:} \quad k\ (\text{mol kg}^{-1}\ \text{s}^{-1}) = 1.56E + 14\text{e}^{-20636/T}$$

Results of Fructosazine Decomposition Study. After 11 min at 174 °C, the fructosazine standard showed no visible signs of decomposition or discoloration. GC−MS analysis failed to detect any alkylpyrazine compounds in the headspace above the material.

On the basis of the kinetics and decomposition study data, it does not appear that PHAP compounds are decomposing during peanut roasting to form alkylpyrazines, but rather are increasing steadily during the course of roasting. The work of Hardt and Baltes (1988) demonstrated that PHAP compounds do decompose to alkylpyrazines, but it is apparent from the work herein that very high temperatures are needed to cause this decomposition. It appears from this work that the hypothesis that PHAP compounds thermally decompose to alkylpyrazines at temperatures commonly encountered in peanut roasting is false. PHAP and alkylpyrazine formation rates show a similar dependence on temperature, as would be expected since each are products of the Maillard reaction.

CONCLUSIONS

(Polyhydroxyalkyl)pyrazine compounds are formed during the roasting of peanuts and may be isolated from the peanut matrix using a procedure consisting of defatting with hexane, methanol extraction, and solid-phase extraction with anion and cation exchange cartridges. HPLC may be used to separate the extracted PHAP compounds from the remaining interferences and from each other.

The HPLC procedure may be used to quantitate the amounts of PHAP compounds formed during roasting and thus provides a means of monitoring their formation rates at different times and temperatures. Eight PHAP compounds were detected in the most highly roasted peanut samples, while the concentration and number of peaks detected decreased as roasting time and temperature were decreased.

Alkylpyrazines were separated, identified, and quantitated using the GC−MS technique and also showed an increase in concentration as the roasting time and temperature were increased. For both the PHAP and alkylpyrazine compounds, the log of the total molar concentration is linearly proportional to the peanut color on the Agtron green color scale.

The total concentrations of PHAP and alkylpyrazine compounds increased linearly with time and exponentially with temperature. Arrhenius plots of total PHAP and total alkylpyrazine content yielded straight lines, indicating no significant decompositions occurring during the roasting. The activation energies of the two compound types were shown to be similar (222 kJ/mol for PHAP, 172 kJ/mol for alkylpyrazines), indicating that similar mechanisms may be at work in their formation; molar formation rate constants are approximately three times higher for the alkylpyrazines than the PHAPs. Activation energies calculated for four of the individual PHAP compounds varied from 135 to 257 kJ/mol.

NEXT STEPS

Further research in this area might involve the exploration of the differences between oil roasting and dry roasting, since dry roasting conditions are very different in terms of time and temperature from those employed in this study. If quantities of pure PHAP standards other than fructosazine are obtained or synthesized, further decomposition study work could be carried out to determine whether some of the less

substituted PHAP compounds will decompose to alkylpyrazines under roasting conditions. Finally, studies using heavy isotope-labeled sugars or amino acids could be carried out to determine the exact formation mechanisms of PHAP compounds and whether PHAP compounds formed will decompose to produce heavy isotope-labeled alkylpyrazines under roasting conditions.

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