Formation of Strecker Aldehydes and Pyrazines in a Fried Potato Model System

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Sugars and amino acids were removed from potato slices by soaking in water and ethanol. They were then infused with various combinations of sugars (glucose and/or fructose) and amino acids (asparagine, glutamine, leucine, isoleucine, phenylalanine, and/or methionine) and fried. Volatile compounds were trapped onto Tenax prior to gas chromatography−mass spectrometry. Relative amounts of compounds (relative to the internal standard) and relative yields (per mole of amino acid infused into the slices) were determined. Amounts of 10 pyrazines, 4 Strecker aldehydes, and 4 other compounds were monitored. Relative amounts and relative yields of compounds varied according to the composition of the system. For the single amino acid−glucose systems, leucine gave the highest relative amount and relative yield of its Strecker aldehyde. Asparagine and phenylalanine gave the highest total relative amount and total relative yield, respectively, of pyrazines. In the system containing all of the amino acids and glucose, the relative amount of 3-methylbutanal was higher, whereas the amounts of the other monitored Strecker aldehydes were lower. Most of the relative amounts of individual pyrazines were lower compared to the glucose−asparagine system, whereas the total relative yield of pyrazines was lower, compared to all of the single amino acid−glucose mixtures. Addition of fructose to the mixed amino acid−glucose model system generated Strecker aldehydes and pyrazines in ratios that were more similar to those of untreated potato chips than to those from the same system but without fructose. Both the sugars and the amino acids present in potato are crucial to the development of flavor compounds in fried potato slices.

Keywords: *Potato chips; potato crisps; flavor; aroma; model system; Strecker aldehydes; pyrazines*

INTRODUCTION

Potato chips (also known as potato crisps) are prepared by deep-fat frying potato slices. Flavor is an important quality attribute of chips and is affected by various factors including the composition of the raw tuber, composition of the frying oil, temperature and time of frying, and packaging and storage of the chips (*1*).

Reports of the flavor components of potato chips have been reviewed by Whitfield and Last (*3*) and Maga (*4*). In summary, ∼150 volatile compounds have been identified, including various aldehydes, ketones, pyrazines, and sulfur compounds. The Maillard reaction and lipid degradation are their main sources. Important aroma components are considered to include methional, phenylacetaldehyde, 3-ethyl-2,5-dimethylpyrazine, 3-methylbutanal, and 2,4-decadienal (*4*). Surprisingly, only two compounds formed by Maillard−lipid interactions, that is, 2-butyl- and 2-pentylthiophene, have been identified (*5*).

Free amino acids and sugars in the potato tuber are important precursors of chip flavor components (*5*). Potato tuber composition varies according to agronomic factors, including cultivar, soil, climate, irrigation, and fertilizer application, as well as poststorage conditions (*6*). Typical levels of sugars and amino acids in Saturna, a chipping potato cultivar, at the point of use are given in Table 1. Glucose and fructose are the most abundant reducing sugars, and asparagine and glutamine are the amino acids present in the highest amounts.

Table 1. Concentrations of Sugars and Amino Acids in a Potato Cultivar Used for Chipping (Saturna) (United Biscuits, Personal Communication)

sugar	concn (g/100 g)		
glucose	0.1		
fructose	0.08		
sucrose	1.07		
amino acid	**concn (mg/100 g)**	**amino acid**	**concn (mg/100 g)**
Ala	4.7	Lys	4.7
Arg	16.4	Met	4.7
Asn	93.9	Phe	4.7
Asp	4.7	Pro	4.7
Gln	28.2	Ser	4.7
Glu	9.4	Thr	18.8
Gly	0	Trp	0
His	7	Tyr	7
Ile	7	Val	9.4
Leu	4.7		

Model system studies have been conducted, which aid understanding of the role played by individual sugars and amino acids in the development of chip flavor. They have included heated aqueous solutions (*7*−*9*), fried filter paper presoaked with either aqueous solutions of amino acids and sugars (*10*) or potato extracts (*8*, *11*), and fried cotton wool balls presoaked in aqueous amino acid solutions (*12*). The role of the food matrix is frequently overlooked when a model system for the investigation of flavor formation is designed, although matrix−flavor component interactions can affect the

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Table 2. Composition and Codes of the Model Systems

component	initial concn[a] (mg/100 mL)	uptake[b] (mg/100 g)	W[c]	A	Gn	L	I	P	M	G	GA	GGn	GL	GI	GP	GM	X	F	FA	GFA	Y	Z
glucose	500	258.7								x	x	x	x	x	x	x	x			x	x	x
fructose	500	218.2																x	x	x	x	x
asparagine	475	210		x							x						x		x	x	x	x
glutamine	150	82.3			x							x					x				x	x
leucine	25	11.6				x							x				x				x	x
isoleucine	35	15					x							x			x				x	x
phenylalanine	25	11.9						x							x		x				x	x
methionine	25	13.7							x							x	x				x	x
threonine	100	46.9																				x

[a] Initial concentration of components in the steeping solution. [b] Concentration of components in potato slices. Average of three experiments. Average standard deviation <15%. [c] Blank. Steeped in water only.

release of volatile compounds and hence perceived flavor (*13*). A model potato system, based on sliced raw potato tubers, has been used to study color development in potato chips (*14*, *15*).

The aim of the current study was to develop a model potato chip system based on raw potato slices and to apply it to the investigation of the role of selected amino acids and sugars in the formation of potato chip flavor.

EXPERIMENTAL PROCEDURES

Materials and Reagents. Potatoes, *Solanum tuberosum* cultivar Saturna, specific gravity range of 1.086−1.096, palmolein, and metalized laminate chip bags were provided by United Biscuits (Billingham, U.K.). Ethanol, copper(II) sulfate 5-hydrate, ammonium hydroxide, and methanol (all 99+% grade), and phenylalanine (minimum purity = 99%) were from BDH (Poole, U.K.). Asparagine, glutamine, and leucine (all minimum purity = 99%), and isoleucine, methionine, and threonine (all minimum purity = 98%) were from Sigma (Poole, U.K.). Fructose (98+%) and glucose (99+%) were from Acros Organics (Loughborough, U.K.). Borate buffer, 50 mM, pH 9.3, was from Hewlett-Packard (Bracknell, U.K.). Sodium hydroxide, 1.0 and 0.1 M, was from Fluka (Gillingham, U.K.). 1,2-Dichlorobenzene (minimum purity = 98%) was from Aldrich (Gillingham, U.K.). High-purity water was produced in-house using a Purite (High Wycombe, U.K.) Labwater RO50 unit and was used throughout.

Preparation of Potato Slices. The procedures used to prepare potato slices for frying were developed from those described by Khanbari and Thompson (*14*). Potatoes were washed, peeled, and sliced (1.4 ± 0.1 mm). Slices were rinsed in cold water for 2 min and stored in water at room temperature (for a maximum of 5 h) before further use. They were blotted on paper towels, to remove excess surface water, prior to weighing. For system U, slices were fried without further treatment.

Removal of Sugars and Amino Acids. Potato slices (100 g) were added to water (500 mL) at 60 °C, stirred, and kept for 5 min before transferring to 50% ethanol (500 mL) at 45 °C, stirring, and keeping for 15 min. The slices were rinsed thoroughly with four 1 L aliquots of cold water before storage in water overnight at 4 °C, prior to further use. The removal of glucose from slurried soaked slices was checked using glucose reagent strips, which had a detection limit of ~0.5 mM, equivalent to ~0.1 mg/mL (Clinistix, Bayer plc, Newbury, U.K.).

Infusion of Sugars and Amino Acids. Slices (100 g) were infused with predetermined amounts of amino acids and/or sugars by placing them in the steeping solution (200 mL) at 40 °C for 10 min. Slices were then removed, drained, blotted on paper towels, and immediately fried. The compositions of the various model systems and their codes are given in Table 2. All systems were prepared in triplicate.

Frying Procedure. Palmolein (3 L) was heated to 180 °C for 20 min, before use, in a Séléction (Magimix, France) professional system deep-fat fryer. As the slices (25 g) were placed in the oil, the fryer was switched off and remained off throughout frying (2 min), to ensure reproducible conditions on each frying occasion. After frying, slices were drained and cooled on paper towels before sealing in chip bags. Fresh palmolein was used each day (maximum of 30 batches per day).

Capillary Electrophoresis (CE). The concentrations of amino acids and sugars in the steeping solutions were determined before and after use. Analyses were performed using a Hewlett-Packard ^{3D}capillary electrophoresis system equipped with a built-in diode array detector, a Hewlett-Packard ChemStation for system control, data collection and data analysis, and an uncoated fused silica capillary of extended light path (bubble factor of 3), 50 μm i.d., 48.5 cm total length, 40 cm to the detector (Hewlett-Packard). All samples were filtered through a 0.2 μm PVDF filter (Whatman, Maidstone, U.K.) before injection onto the anionic end of the capillary by pressure (5 s at 50 mbar). Significant operating parameters were: capillary temperature, 25 °C; maximum current threshold, 120 A; voltage, 25 kV for 10 min.

For amino acids, 50 mM, pH 9.3, borate buffer was used, and the detector wavelength was 200 nm. New capillaries were conditioned with 1 M sodium hydroxide (30 min), 0.1 M sodium hydroxide (20 min), and water (15 min). Between-run conditioning was with 0.1 M sodium hydroxide (3 min) and running buffer (3 min), with buffer renewal every four runs.

The method for sugars was based on the procedure reported by Bazzanella and Bachmann (*16*). The electrolyte was 6 mM copper sulfate solution prepared by dissolving copper(II) sulfate (75 mg) in 500 mM ammonium hydroxide (50 mL) and adjusting the pH to 11.6 with 25% ammonium hydroxide. New capillaries were conditioned with water (2 min), 0.1 M sodium hydroxide (10 min), water (2 min), 0.1 M sodium hydroxide (10 min), water (2 min), and copper electrolyte (20 min). The capillary was conditioned between runs with copper electrolyte (5 min), and fresh electrolyte was used for every run. The detector wavelength was 245 nm.

The detector response was linear for all of the chosen amino acids and sugars over relevant concentration ranges of standard solutions [$R^2 = 0.914-0.999$ (*17*)]. The uptake of amino acids and sugars by the potato slices was calculated as

$$\text{uptake (per 100 g of potato slices)} = (CV_1) - (\text{area}_2 \times CV_2/\text{area}_1)$$

where C = the concentration of the amino acid or sugar in the steeping solution before use (mg/mL), V_1 and V_2 are the volumes of the steeping solution before and after use, respectively (mL), and area_1 and area_2 are the average peak areas obtained for the steeping solution before and after use, respectively, (mAU·s).

Preparation of Flavor Isolates. Crushed chips (10 g) and water (40 mL) were placed in a 250 mL conical flask fitted with a Dreschel head and located in a water bath at 37 °C. 1,2-Dichlorobenzene in methanol (130.6 μg/mL, 1 μL) was injected onto a Tenax trap (155 mm long, 3 mm i.d.), containing 85 mg of Tenax TA (SGE, Milton Keynes, U.K.) and fitted at the exit of the conical flask. Volatile compounds were collected by passing nitrogen at 40 mL/min over the sample for 1 h.

The Tenax trap was then connected directly to the nitrogen supply for 5 min to remove any residual water. Control isolates were prepared using water (40 mL) in the sample flask.

Gas Chromatography—Mass Spectrometry (GC-MS). Analyses were performed using a Hewlett-Packard HP 5890 series II gas chromatograph connected to an HP 5972 series mass selective detector. System control and data acquisition and analysis were achieved using an HP ChemStation. The fused silica column (60 m long, 0.25 mm i.d.) was coated with a 0.25 μm film thickness of CP-SIL8 (Chrompak, London, U.K.). Helium at 1.5 mL/min was the carrier gas. With the GC oven switched off, the first 0.5 m of the column was cooled in solid CO_2 for 4 min. The Tenax trap was placed into the CHIS thermal desorption port (SGE) of the GC (heated to 280 °C), and the desorbed volatiles were cryofocused onto the front of the column. After 5 min, the CO_2 was removed and the GC oven temperature was raised to 40 °C and held for 2 min, followed by a 4 °C/min increase to 200 °C, a 10 °C/min increase 250 °C, and holding at 250 °C for 15 min. The inlet purge came on when the temperature program began and backflushed the Tenax trap. Mass spectra were recorded in the electron impact (EI) mode, with a voltage of 70 eV, a source temperature of 165−175 °C, and a mass scan range of *m/z* 32−450 with 1.82 scans/s. Linear retention indices (RI) for the volatile compounds were calculated with reference to a standard mixture of *n*-alkanes (C_6−C_{22}), run under the same conditions. Identifications of components were made by comparing mass spectra and RI with those of authentic compounds held on laboratory databases and reported in the literature (*18*−*20*). When both mass spectra and RI data agreed with those in the literature, identities were considered to be positive. When only mass spectral data were available, identities were considered to be tentative. Relative amounts of volatile compounds were calculated by reference to the internal standard (1,2-dichlorobenzene).

Statistical Analysis. One-way analysis of variance (ANOVA) and multiple-range tests (Statgraphics Plus version 4.1) were used to indicate significant differences in the levels of volatile compounds among the model chip samples.

RESULTS AND DISCUSSION

Preparation of the Model System. The use of reagent strips indicated that glucose was present in soaked potato slices below the detection limit (~0.5 mM). Fructose and the amino acids all have solubilities similar to that of glucose (*21*) and, therefore, it was assumed that all of these components were also removed from the potato slices or were present at very low levels. The potato cell wall network and starch were not removed by the soaking procedure. These components are responsible for the generation of the typical crisp potato chip texture during frying (*22*).

Glucose and fructose were selected for study because they are the most abundant reducing sugars in the raw potato tuber (United Biscuits, personal communication). The amino acids were chosen for various reasons. Asparagine and glutamine are the most abundant in raw potato (United Biscuits, personal communication); methionine yields methional, which possesses a potato-like odor (*23*); and the Strecker aldehydes of leucine, isoleucine, and phenylalanine are reported to be important chip flavor compounds (*4*). The concentration of each amino acid and sugar used in the steeping solutions and their average uptakes by the potato slices are shown in Table 2. The presence of more than one component in the steeping solution did not significantly affect uptake by the slices, and Figure 1 compares the uptake of glucose in the absence and presence of different amino acids. The model potato slices contained selected amino acids and sugars at concentrations that were proportional to levels in a potato cultivar used for chipping (United Biscuits, personal communication), although the absolute concentrations were ~2-fold higher. More details concerning the development of the model system are available (*17*).

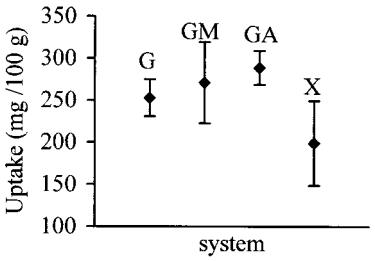

Figure 1. Uptake of glucose by potato slices steeped in aqueous solutions of glucose with and without amino acids. No significant difference in uptake of glucose was observed among the systems. Codes of model systems and glucose and amino acid concentrations of steeping solution are given in Table 2.

Frying Procedure. To achieve reproducible frying conditions, the fryer was switched off for the duration of frying immediately after the potato slices were placed in the oil. This resulted in the temperature falling from 180 to ~165 °C over the first 30 s of frying, followed by a further fall of 5 °C, to 160 °C, between 30 and 150 s (*17*). This temperature decrease was similar to that expected in most commercial continuous crisp fryers.

Frying potato slices that had been soaked to remove sugars and amino acids and steeped in water (W) gave a product with a crisp texture and a translucent, oily appearance. All of the other models gave chips with the same texture as W but the color was yellow/brown and varied according to the sugars and/or amino acids present. The texture and color were similar to those of untreated chips (U), that is, chips prepared from slices without steeping in water or infusion with selected sugars and amino acids.

Volatile Flavor Compounds from the Glucose Systems. Relative amounts of 18 compounds were monitored in the model systems containing either a single amino acid or glucose or glucose−amino acid mixtures (Tables 3 and 4). All of the monitored pyrazines were identified in model U. The Strecker aldehydes of leucine, isoleucine, phenylalanine, and methionine were monitored, together with benzaldehyde (formed from phenylacetaldehyde) (*24*) and three sulfides (formed from methionine) (*25*). Low levels of four compounds, that is, 2- and 3-methylbutanal, dimethyl disulfide, and benzaldehyde, were identified in model W. The presence of 2- and 3-methylbutanal, in particular, indicates that not all of the amino acids (and possibly not all of the sugars) were removed from the potato slices during steeping because these compounds are formed from isoleucine and leucine, respectively (*26*). However, their levels in W were at least 275−385-fold lower than in the models infused with these amino acids (Table 3).

Strecker Aldehydes and Their Degradation Products. Table 3 shows that all of the models containing leucine, isoleucine, methionine, and phenylalanine produced their respective Strecker aldehydes, even in the absence of sugar. By definition, Strecker aldehydes are produced by the Strecker degradation of an amino acid with an α-dicarbonyl compound (*27*). The dicarbonyl compound may come from sugar degradation, that is, glucose in these models, and the inclusion of glucose significantly increased the levels of Strecker aldehydes. The forma-

Table 3. Relative Amounts[a,b] of Strecker Aldehydes and Their Selected Degradation Products Formed in Model Potato Chips

	RI		model system[e]											
compound	exptl[c]	lit.[d]	W	U	L	I	P	M	G	GL	GI	GP	GM	X
3-methylbutanal	671	655	2[a]	940[c]	770[b]	3[a]	4[a]	4[a]	30[a]	4500[d]		30[a]	33[a]	5600[e]
2-methylbutanal	680	665	2[a]	840[c]	9[a]	550[b]	3[a]	2[a]	15[a]	55[a]	4600[e]	31[a]	18[a]	1900[d]
phenylacetaldehyde	1063	1066		89[b]			69[b]		2[a]	2[a]	4[a]	490[d]	2[a]	180[c]
benzaldehyde	981	983	13[ab]	26[bc]	6[a]	4[a]	14[ab]	5[a]	7[a]	8[a]	16[abc]	85[d]	7[a]	30[c]
methional		924		6[a]				6[a]					110[c]	21[b]
dimethyl sulfide				6				3					4	1
dimethyl disulfide	753	744	6[a]	290[cd]	6[a]	5[a]	7[a]	100[b]	19[a]	8[a]	7[a]	17[a]	330[d]	240[c]
dimethyl trisulfide	989	990		8				7	1				7	6

[a] Amounts of components are quoted in relative GC peak area units to two significant figures (see Experimental Procedures). Figures quoted are the means of triplicate analyses. CV < 25%. [b] Means with different superscript letters within a row are significantly different ($P < 0.05$). [c] Calculated RI values for identified components. [d] Linear retention indices obtained for authentic compounds analyzed on the same GC column or from the literature (*19*, *20*). [e] See Table 2 for explanation of codes other than U. Model system U was prepared by frying potato slices without removal of or infusion with sugars and amino acids.

Table 4. Relative Amounts[a,b] of Selected Pyrazines Formed in Model Potato Chips

	RI		model system[e]										
pyrazine	exptl[c]	lit.[d]	U	A	Gn	G	GA	GGn	GL	GI	GP	GM	X
pyrazine			6[ab]		1[a]	1[a]	57[d]	38[c]	5[ab]	6[ab]	11[b]	6[ab]	38[c]
methylpyrazine	836	833	97[b]	3[a]	3[a]	6[a]	130[c]	120[bc]	13[a]	10[a]	26[a]	17[a]	91[b]
2,5(6)-dimethylpyrazine	924	925	80[d]			6[a]	32[c]	22[abc]	7[a]	6[a]	11[ab]	13[ab]	25[bc]
ethylpyrazine	927	930	45[b]			1[a]	91[c]	43[b]	4[a]	5[a]	8[a]	4[a]	82[c]
2,3-dimethylpyrazine	930	932	15[d]			1[a]	19[e]	6[b]	1[a]	1[a]	1[a]	1[a]	10[c]
vinylpyrazine	946	948	9[b]				62[e]	22[c]	2[ab]	2[ab]	3[ab]	2[ab]	33[d]
2-ethyl-6-methylpyrazine	1009	1010	29[b]				8[a]	6[a]					9[a]
2-ethyl-3(5)-methylpyrazine	1014	1016	27[d]			1[a]	15[c]	5[ab]				3[a]	12[bc]
2-vinyl-6-methylpyrazine	1033	1034	11				12	10					14
3-ethyl-2,5-dimethylpyrazine	1086	1086	40[b]				3[a]						3[a]
total			359[bc]	3[a]	4[a]	16[a]	429[c]	272[b]	32[a]	30[a]	60[a]	46[a]	317[b]

[a] Amounts of components are quoted in relative GC peak area units to two significant figures (see Experimental Procedures). Figures quoted are the means of triplicate analyses. CV < 25%. [b] Means with different superscript letters within a row are significantly different ($P < 0.05$). [c] Calculated RI values for identified components. [d] Linear retention indices obtained for authentic compounds analyzed on the same GC column or from the literature (*19*, *20*). [e] See Table 2 for explanation of codes other than U. Model system U was prepared by frying potato slices without removal of or infusion with sugars and amino acids.

tion of these aldehydes in model systems L, I, P, and M (amino acid alone models, see Table 2) may be due to the presence of low levels of residual sugar, or the required α-dicarbonyl may come from the frying oil (*28*). Alternatively, they may form in the absence of a dicarbonyl compound via the Shigematsu reaction (*29*).

Dividing the relative amount values for the Strecker aldehydes in model systems GL, GI, GP, and GM (amino acid plus glucose models, see Table 2) by the number of moles of each amino acid infused into the potato slices gave relative yield values. Rates of reaction of amino acids with various carbonyl compounds have been investigated (*30*−*32*), and the order of reactivity varies according to the reaction conditions, including the nature of the carbonyl compound. Hofmann et al. (*32*) showed that leucine generated twice the amount of its Strecker aldehyde, compared to phenylalanine and alanine, on heating with glucose at 100 °C for 30 min, supporting the results of the current study.

The relative amount of each Strecker aldehyde in the systems infused only with amino acid was ∼12% of that in the corresponding system containing glucose; that is, the relative rate of reaction with and without glucose was independent of the amino acid. Model system X contained all of the examined amino acids plus glucose, with each reactant being present at the same initial concentration as in the simpler models. The relative amount of 3-methylbutanal in X was ∼120% of that in GL. In contrast, relative amounts of 2-methylbutanal, phenylacetaldehyde, and methional were 60−80% lower than those in GI, GP, and GM, respectively. Glucose may be present at a level that limits the formation of Strecker aldehydes in X, with the exception of 3-methylbutanal, the rate of formation of which is relatively high (*32*). The participation of 2-methylbutanal (*33*), 3-methylbutanal (*34*), phenylacetaldehyde (*24*, *35*), and methionine (*9*) in subsequent reactions may also account for differences in yields observed here.

Relative amounts of benzaldehyde and phenylacetaldehyde were higher in P, GP, and X, compared to the other model systems. Benzaldehyde forms from linoleic acid (*36*) and was identified as a volatile component of heated palmolein (*17*). However, the levels identified in P, GP, and X indicate that phenylalanine was its main source. Arnoldi et al. (*24*) established benzaldehyde as an important degradation product of phenylacetaldehyde.

Three sulfides were identified in the methionine-containing systems (Table 3). Dimethyl disulfide was produced in the highest amounts, relative amounts being higher than those of methional by factors of 17, 3, and 11, respectively, in M, GM, and X. Sulfides, including methionine, are readily oxidized to their sulfoxides (*37*), and components of the frying oil, such as linoleic acid, may facilitate this process (*38*). Yu and Ho (*9*) heated either methionine sulfoxide or methionine with glucose at 180 °C for 1 h. They postulated that methional sulfoxide was primarily formed from methionine sulfoxide by the Shigematsu reaction and that it degraded mainly to methanethiol (which subsequently oxidized to dimethyl disulfide), with only a small proportion being transformed to methional. In contrast,

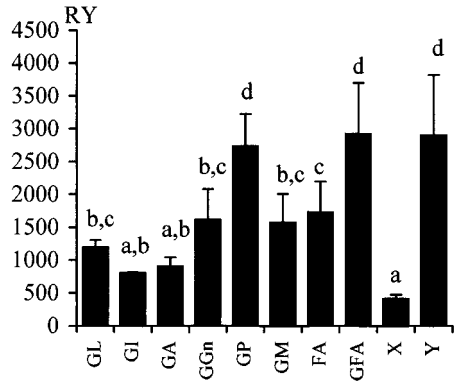

Figure 2. Total relative yield of pyrazines in model systems. Bars with different letters indicate significantly different ($P < 0.05$) relative yield values. Codes of model systems and glucose and amino acid concentrations of steeping solution are given in Table 2.

only a small amount of methional formed from methionine was degraded to methanethiol, giving methional as the main product, rather than dimethyl disulfide. It is suggested that, in the current study, the oxidation of methionine to its sulfoxide by components of the frying oil or potato lipid, as proposed by Mandin et al. (*38*), results in higher amounts of dimethyl disulfide than methional.

Pyrazines. Relative amounts of the 10 pyrazines identified in the model systems are listed in Table 4. No pyrazines were identified in I, L, P, and M, and only low levels were detected in A and Gn. Dicarbonyl compounds are required for pyrazine formation from isoleucine, leucine, phenylalanine, and methionine (*26*), and they appear to come mainly from glucose rather than from palmolein. Levels of total and individual pyrazines in GA and GGn were always significantly higher than levels in other models containing one amino acid and glucose (GI, GL, GP, and GM), but asparagine and glutamine were infused into the potato slices at higher levels than the other amino acids (Table 2). The total relative yields of pyrazines in the models are shown in Figure 2. GP gave a total relative yield of pyrazines that was significantly higher than those for the other models containing glucose as the only sugar, and this is in line with previous reports comparing yields of pyrazines in various sugar−amino acid systems (*24*, *33*).

The total relative yield of pyrazines in GGn was higher than that in GA, but not significantly so. Koehler et al. (*39*) heated glucose−amino acid systems at 120 °C for 24 h and obtained higher yields of pyrazines for asparagine than glutamine. However, Chun and Ho (*40*) used conditions that more closely resembled those applied in the current study, that is, frying in corn oil at 180 °C for 1 min, to show that glutamine gave higher pyrazine yields. Amino acids provide nitrogen for pyrazine formation. For glutamine and asparagine, nitrogen may be released as ammonia by deamination (loss of the α-amino group) or by deamidation (loss of the amide group). Deamidation appears to be the more important mechanism in oil media (*41*), with more ammonia being released from glutamine than asparagine. For glutamine, deamidation can occur by intramolecular cyclization involving the amide group and either the carboxyl or α-amino group, whereas, for asparagine, intramolecular cyclization involving the amide and α-amino groups does not occur due to steric hindrance (*41*).

With the exception of 3-ethyl-2,5-dimethylpyrazine, the relative amount of each individual pyrazine in model system X was lower than the sum of its relative amounts in the single amino acid−glucose systems, the total relative amount of pyrazines in X being 38% of the sum of the values in the single amino acid−glucose systems (Table 4). Glucose may limit pyrazine formation in system X, but unexpected yields of pyrazines have been reported from mixed amino acid model systems, including lower amounts of pyrazines than were anticipated when more than one amino acid was heated with glucose (*33*, *42*). Pyrazines may act as precursors for subsequent reactions which are favored in X. Also, pathways leading to compounds other than pyrazines may be favored in X. The kinetics of formation of flavor compounds, including pyrazines, formed by the Maillard reaction is a neglected area, and only limited work has been published for complex mixtures of amino acids and sugars (*43*). Further kinetics studies are required to fully understand the data presented here.

To facilitate comparison of systems giving very different relative amounts for pyrazines, Table 5 gives the relative amount of each pyrazine as a percentage of the total relative amount for pyrazines. The most noticeable variation in percentage relative amounts for pyrazines among the systems is the ratio of methylpyrazine to 2,5-(6)-dimethylpyrazine. This ratio is <3 for GL, GI, GP, and GM but >4 for GA and GGn. Previous studies have reported variations in yields and ratios of different pyrazines according to the amino acid used (*24*, *33*, *40*, *42*).

Percentage relative amounts of 8 of the 10 pyrazines were significantly different between X and untreated chips (U) (Table 5). Because glucose was the main source of carbonyl compounds for pyrazine formation, further model systems were prepared incorporating fructose, the second most abundant reducing sugar in raw potato.

Volatile Flavor Compounds from the Fructose Systems. *Strecker Aldehydes.* Percentage relative amounts for the Strecker aldehydes in Y are compared to those in U and X in Table 6. The percentage relative amount ratio: 3-methylbutanal:2-methylbutanal is 1.1, 3.0 and 2.2, respectively, in U, X and Y. The addition of fructose to the model (Y) has brought the ratio closer to those for untreated chips (U), although differences in percentage relative amounts for 2- and 3-methylbutanal among all three systems were not significant.

Pyrazines. Percentage relative amounts for each pyrazine in the fructose-containing systems are listed in Table 5. Percentage relative amounts for 2,5(6)-dimethylpyrazine, 2-ethyl-6-methylpyrazine, and 3-ethyl-2,5-dimethylpyrazine were significantly higher in model systems F and FA, compared to G and GA, whereas amounts of pyrazine, ethylpyrazine, vinylpyrazine, and 2-vinyl-6-methylpyrazine were significantly lower. Previous studies (*44*−*47*) have established that when amino acids are heated with either glucose or fructose, yields of pyrazines vary with the amino acid and temperature and time of heating. In line with the current study, Leahy and Reineccius (*45*) found that asparagine gave greater relative yields of pyrazine and methylpyrazine and lower relative yields of 2,5- and 2,6-dimethylpyrazine on heating with glucose than with fructose. Pyruvaldehyde is important for the formation of dimethylpyrazines, which were formed at higher levels in FA compared to GA. Thus, it appears that pyruvaldehyde is formed in greater amounts from fructose than glucose

Table 5. Percentage RA Values for Pyrazines[a,b]

component	model system[c] U	G	GA	GGn	GL	GI	GP	GM	X	F	FA	GFA	Y	Z
pyrazine	1.8[a]	8.4[c]	13[de]	14[ef]	16[f]	12[d]	18[g]	13[de]	12[d]	1.4[a]	0.6[a]	5.4[b]	4.8[b]	4.5[b]
methylpyrazine	27[a]	34[bcd]	30[ab]	44[gh]	40[ef]	37[de]	43[fg]	36[d]	29[a]	37[de]	32[bc]	47[h]	35[cd]	33[bcd]
2,5(6)-dimethylpyrazine	22[cd]	37[g]	7.3[a]	7.5[a]	23[d]	23[de]	18[bc]	29[f]	8.0[a]	55[i]	45[h]	17[b]	26[def]	28[ef]
ethylpyrazine	13[de]	8.3[b]	21[g]	16[f]	12[de]	18[fg]	13[e]	9.4[bc]	26[h]	3.6[a]	4.7[a]	10[bcd]	12[de]	12[cde]
2,3-dimethylpyrazine	4.1[de]	2.8[bcd]	4.5[e]	1.8[ab]	1.9[ab]	2.2[abcd]	2.3[bcd]	3.1[bcde]	3.2[bcde]	1.8[ab]	1.2[a]	2.6[bcd]	3.8[cde]	2.1[abc]
vinylpyrazine	2.4[a]	1.5[a]	14[f]	7.7[d]	6.6[cd]	7.7[cd]	5.9[bc]	4.7[b]	11[e]		1.2[a]	7.0[cd]	4.6[b]	4.8[b]
2-ethyl-6-methylpyrazine	8.0[f]		1.9[a]	2.0[ab]					2.9[d]		2.6[c]	2.2[b]	3.1[d]	4.4[e]
2-ethyl-3(5)-methylpyrazine	7.3[ef]	7.6[f]	3.6[abcde]	1.8[abc]				5.5[cdef]	3.6[abcd]		7.3[ef]	6.0[def]	4.6[bcdef]	6.5[def]
2-vinyl-6-methylpyrazine	3.2[cd]		2.7[bc]	3.7[de]					4.3[f]		2.0[a]	2.3[ab]	4.2[ef]	3.8[e]
3-ethyl-2,5-dimethylpyrazine	11[f]		0.4[a]						0.9[ab]	2.3[d]	3.5[e]	0.8[ab]	1.1[b]	1.8[c]

[a] Percentage of the sum of the relative amount (RA) for all monitored pyrazines. Figures quoted are the means of triplicate analyses. CV < 25%. [b] Means with different superscript letters within a row are significantly different ($P < 0.05$). [c] See Table 2 for explanation of codes other than U. Model system U was prepared by frying potato slices without removal of or infusion with sugars and amino acids.

Table 6. Percentage RA Values for Strecker Aldehydes[a,b]

compound	model system[c] U	X	Y
3-methylbutanal	50	73	67
2-methylbutanal	45	25	30
phenylacetaldehyde	4.7[b]	2.3[a]	2.8[a]
methional	0.3	0.3	0.5

[a] Percentage of the sum of the relative amount (RA) for all monitored Strecker aldehydes. Figures quoted are the means of triplicate analyses. CV < 25%. [b] Means with different superscript letters within a row are significantly different ($P < 0.05$). [c] See Table 2 for explanation of codes other than U. Model system U was prepared by frying potato slices without removal of or infusion with sugars and amino acids.

when potato slices are fried using the conditions applied in the current study, and it is suggested that the kinetics and relative importance of mechanisms, including retroaldolization, by which these sugars degrade differ under frying conditions.

Percentage relative amounts of pyrazines in GFA were between those obtained for GA and FA, with the exception of methylpyrazine, which was significantly higher in GFA than in the other systems. This is probably due to its apparent ease of formation in both GA (most abundant pyrazine) and FA (second most abundant pyrazine). The significantly higher total relative yield for pyrazines in GFA compared to both GA and FA (Figure 2) confirms that sugar was limiting pyrazine formation in both GA and FA.

When fructose was added to the model containing glucose and all of the examined amino acids (Y), the percentage relative amounts of all pyrazines, except the methyl derivative, were closer than those of X to the untreated chips (U) (Table 5). However, the improvement was very small for some compounds and was significant ($P < 0.05$) only for the parent compound and the 2,5(6)-dimethyl, ethyl, and vinyl derivatives. The total relative yield of pyrazines in Y was significantly higher than in X (Figure 2), confirming that the level of reducing sugar was limiting pyrazine formation in the latter system.

3-Ethyl-2,5-dimethylpyrazine was the only pyrazine in Y with a percentage relative amount that was well out of line with that of the untreated chips (U), amounts being ~10-fold lower in Y (Table 5). Wang and Odell (*48*) demonstrated that alkylpyrazines could be produced from hydroxyamino acids (serine and threonine) in the absence of sugar. More recently, Shu (*49*) proposed a mechanism, involving decarbonylation and dehydration, to explain this observation and described 3-ethyl-2,5-dimethylpyrazine as one of the major products from threonine heated to 300 °C. Percentage relative amounts of pyrazines in model system Z, which contained all of the flavor precursors present in Y plus threonine, are shown in Table 5. The percentage relative amount increased from 1.1% in system Y to 1.8%, and this is a significant increase. The other monitored pyrazines had percentage relative amounts that did not differ significantly between Y and Z, with the exception of 2-ethyl-6-methylpyrazine, which also increased significantly in Z. Nevertheless, the percentage relative amount for 3-ethyl-2,5-dimethylpyrazine in Z was still quite different from that in U (11.1%), and the heating conditions encountered during frying may not have been sufficient to form substantial amounts of 3-ethyl-2,5-dimethylpyrazine from threonine.

In conclusion, a model system, based on potato slices, has been developed to successfully study the formation of Strecker aldehydes and pyrazines in potato chips. The examined amino acids gave different yields of their Strecker aldehydes, and yields varied in the mixed amino acid−glucose system, compared to single amino acid−glucose mixtures. The higher observed yields of dimethyl disulfide, compared to methional, in the methionine systems suggest that methionine is oxidized to its sulfoxide prior to undergoing the Strecker degradation. Phenylalanine gave the highest total relative yield of pyrazines on heating with glucose. Glutamine gave a higher total relative yield than asparagine, and this was attributed to its greater ability to undergo deamidation. Amounts of pyrazines were lower in the mixed amino acid−glucose model compared to single amino acid−glucose mixtures. Use of fructose in place of, or in addition to, glucose increased the total relative yield of pyrazines and lowered the methylpyrazine/2,5(6)-dimethylpyrazine ratio. This suggests that greater amounts of pyruvaldehyde, which is important for dimethylpyrazine formation, are formed from fructose than from glucose during frying. A model system containing glucose, fructose, asparagine, glutamine, leucine, isoleucine, phenylalanine, and methionine resulted in the generation of Strecker aldehydes and pyrazines with percentage relative amounts that were more similar to those of untreated potato chips than those from a system containing all of these flavor precursors apart from fructose.

Previous model system studies aimed at understanding flavor development in potato chips have generally used equimolar amounts of a single sugar and a single amino acid (*7*−*12*). Also, the reaction medium, and sometimes the temperature and time of heating, differed from those used in the present study. Further work is

needed to understand the specific effects of the potato matrix on chip flavor.

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