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Effect of Citric Acid and Glycine Addition on Acrylamide and Flavor in a Potato Model System

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Acrylamide levels in cooked/processed food can be reduced by treatment with citric acid or glycine. In a potato model system cooked at 180 °C for 10−60 min, these treatments affected the volatile profiles. Strecker aldehydes and alkylpyrazines, key flavor compounds of cooked potato, were monitored. Citric acid limited the generation of volatiles, particularly the alkylpyrazines. Glycine increased the total volatile yield by promoting the formation of certain alkylpyrazines, namely, 2,3-dimethylpyrazine, trimethylpyrazine, 2-ethyl-3,5-dimethylpyrazine, tetramethylpyrazine, and 2,5-diethyl-3-methylpyrazine. However, the formation of other pyrazines and Strecker aldehydes was suppressed. It was proposed that the opposing effects of these treatments on total volatile yield may be used to best advantage by employing a combined treatment at lower concentrations, especially as both treatments were found to have an additive effect in reducing acrylamide. This would minimize the impact on flavor but still achieve the desired reduction in acrylamide levels.

KEYWORDS: Acrylamide; flavor; pH; citric acid; glycine; potato; Strecker aldehydes; pyrazines

INTRODUCTION

Much attention and research have been focused on the mechanisms underlying acrylamide formation in food. This sense of urgency was prompted by the discovery of acrylamide in cooked food, by the National Food Administration in Sweden in April 2002 (*1*). Acrylamide is a known neurotoxin and probable carcinogen, and its presence at levels in excess of 1 ppm in food is a matter for some concern (*2*), although the degree of the risk is still far from being certain (*3*). Initial research showed that the highest levels of acrylamide were found in carbohydrate-rich plant-based foods such as potatoes and cereals (*1*), with maximum levels found in potato-based foods cooked at temperatures exceeding 120 °C (as achieved in frying, grilling, roasting, or baking).

Mottram et al. (*4*) and others (*5*, *6*) have demonstrated that the Maillard reaction plays a major role in acrylamide formation, with asparagine (the main amino acid of potatoes) being the essential amino acid precursor for acrylamide. Suppressing the Maillard reaction would therefore reduce the levels of acrylamide. However, the Maillard reaction is also a major route for the generation of desirable flavors and colors in food, making it indispensable for ensuring the sensory quality expected by consumers. It is important, therefore, to study the relationship between flavor generation and acrylamide production to be able to develop a strategy to minimize acrylamide without adverse effects on the flavor of foods.

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The factors that will affect acrylamide levels in foods will be those that influence the Maillard reaction. These include reactant levels (i.e., the reducing sugar and amino acid compositions of food); processing conditions, such as cooking time, temperature, and moisture level; pH; and the presence of additives. Reactant levels are influenced not only by the type of food but also by plant cultivar, soil conditions, harvesting time, and storage conditions. Proposals based on the above have been put forward to lower acrylamide levels in food, and these include using raw products with low sugar or asparagine content; reducing cooking time and temperature; lowering the pH; and using additives, such as amino acids (e.g., glycine) or proteins. These additives may compete effectively with asparagine in the Maillard reaction or may bind acrylamide. Reviews on acrylamide and its mitigation have been published by Stadler and Scholz (*7*), Taeymans et al. (*8*), and Friedman (*9*).

The work reported here focuses on the reduction of acrylamide in a heated potato model system by lowering the pH with citric acid and using glycine as an additive. More importantly, it also elucidates the effect of these treatments on two classes of flavor compounds—the Strecker aldehydes and the alkylpyrazines—in the finished product. The Strecker aldehydes and alkylpyrazines are of great interest particularly for potato flavor. Wagner and Grosch identified and quantified the potent odorants of French fries (*10*). These included the Strecker aldehydes methylpropanal and 2- and 3-methylbutanal, as well as the alkylpyrazines 2-ethyl-3,5-dimethylpyrazine, 2-ethyl-3,6-dimethylpyrazine, and 2,3-diethyl-5-methylpyrazine. In earlier work, Guadagni et al. (*11*) used odor activity values to identify

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important odorants in potato crisp aroma. Of the eight compounds highlighted as most important, four were Strecker aldehydes (methional, phenylacetaldehyde, and 2- and 3-methylbutanal) and one was an alkylpyrazine (2-ethyl-3,6-dimethylpyrazine).

To date, little has been reported on the consequences to flavor when mitigating acrylamide formation, although there has been some evidence to show that the addition of citric acid does have a negative impact on flavor and browning. Amrein et al. (*12*) reported that the addition of citric acid negatively affected the taste, leavening, and browning in gingerbread. Gama-Baumgartner et al. (*13*) found that although a two-fold reduction of acrylamide in French fries was possible with the addition of an optimal amount of 0.75% w/w citric acid, this had a strong impact on sensory quality (i.e., taste and color). Similarly, Jung et al. (*14*) treated French fries with 1−2% w/w of citric acid and found that this affected sensory quality at the 2% w/w citric acid level. The effect of glycine addition on the flavor profile of potato products has not been reported.

MATERIALS AND METHODS

Chemicals. Glycine (99+%) and anhydrous citric acid (Sigma-Aldrich Company Ltd., Poole, United Kingdom) were used in 0.3 and 1.0% w/w solutions with deionized water for addition to potato cakes prior to cooking. The following compounds were used to prepare calibration standards for quantitation of volatiles: methylpyrazine (99+%), 2,5-dimethylpyrazine (99%), 2,3-dimethylpyrazine (99%), 2,6-dimethylpyrazine (98%), ethylpyrazine (98%), 2-ethyl-3-methylpyrazine (99%), propylpyrazine (98+%), tetramethylpyrazine (98%), 2-ethyl-3,5(6)-dimethylpyrazine (99.5+%), 2,3-diethyl-5-methylpyrazine (99%), and phenylacetaldehyde (98%) from Fisher Scientific UK Ltd. (Loughborough, United Kingdom); pyrazine (99+%), trimethylpyrazine (99%), 2,3-diethylpyrazine (98%), and isobutylpyrazine (98%) from Avocado Research Chemicals (Heysham, United Kingdom); and benzaldehyde (99.9%), 1,2-dichlorobenzene (99%), 2-ethyl-5(6)-methylpyrazine (98%), 2-methyl-3-propylpyrazine (97%), and 2-isobutyl-3-methylpyrazine (99%) from the Sigma-Aldrich Company Ltd. Solvents used were methanol (AnalaR grade), *n*-pentane (AnalaR grade), and diethyl ether (AnalaR grade) from Merck Ltd. (Poole, United Kingdom). Chemicals used for acrylamide, amino acid, and sugar analysis in our laboratory were previously described by Elmore et al. (*15*).

Preparation and Cooking of Potato Products. Model potato cakes were prepared from drum-dried potato flake (Maris Piper:Pentland Dell 1:1) provided by McCain Foods (GB) Ltd. (Scarborough, United Kingdom). For the control samples, potato flakes and deionized water were mixed in the ratio 1:1.3 w/w in a mechanical dough maker (Crypto-Peerless, Peerless Ltd., Halifax, United Kingdom). The resulting potato dough was passed through a mechanical dough roller. A pastry cutter was then used to cut out the raw potato cakes from the flattened dough. To promote even baking of the potato product and to minimize rising during cooking, indentations were made to the surface of the raw cakes. Prior to cooking, cakes were 3 mm thick, 73 mm in diameter, and weighed approximately 18 g. The potato cakes were baked at 180 °C in an electric moving-band impingement oven (Impinger II, Lincoln Foodservice Products Inc., Fort Wayne, IN) for between 10 and 60 min. The cakes were arranged in the oven in three rows of five cakes each. After they were baked, the cakes were allowed to cool and harden. Each batch of 15 cakes was then combined and milled to a fine powder for analysis, thereby representing the average heating conditions in the oven. The combined sample was subsequently divided into three portions, and each portion was analyzed separately to obtain triplicate analyses.

Other cakes were prepared by mixing potato flakes with 0.3 or 1% w/w of a solution of glycine in deionized water, 0.3% w/w of a solution of citric acid in deionized water, or a combined 0.3% w/w glycine/0.3% w/w citric acid solution, while maintaining the same ratio of potato flakes to aqueous solution (1:1.3 w/w). Potato cakes prepared using a 0.3% w/w citric acid solution had a citric acid concentration of 0.39% w/w, based on the dry weight of potato. Those prepared using 0.3 or 1.0% w/w glycine solution had an initial glycine concentration of 0.39 or 1.3% w/w (dry weight), respectively.

Table 1. Concentrations (mmol/kg Dry Weight) and Molar Ratios of Reducing Sugars and Amino Acids in Uncooked Model Potato Cakes with and without Added Glycine

	set 1	set 2
total reducing sugars (TRS)	26.9	33.0
asparagine	38.0	27.0
control		
glycine	0.42	0.54
total amino acids (AA)	106.4	83.0
AA/TRS molar ratio	3.95	2.52
with added 0.39% glycine (dry wt)		
added glycine	52.0	
total amino acids (AA)	158.3	
AA/TRS molar ratio	5.88	
with added 1.3% glycine (dry wt)		
added glycine	173.2	173.2
total amino acids (AA)	279.5	256.2
AA/TRS molar ratio	10.38	7.77

Table 2. Amount[a] of Acrylamide (μg/kg) Formed in Model Potato Cakes Cooked at 180 °C

	control		0.39% CA[b]		1.3% Gly[c]		0.39% Gly + 0.39% CA[d]	
cook time (min)	set 1	set 2	set 1	set 2	set 1	set 2	set 1	set 2
15	4040	2110	1390	1940	427	409	1480	1150
30	9300	9480	9630	7750	2330	2340	5190	4960
60	5290	5900	4490	ND[e]	1830	2790	3720	ND

[a] Amounts of acrylamide are quoted in μg/kg on a dry weight basis; values for set 1 are single point measurements; for set 2, they are the means of triplicate analyses. [b] Samples treated with 0.39% w/w (dry wt) of citric acid. [c] Samples treated with 1.3% w/w (dry wt) of glycine. [d] Samples treated with 0.39% w/w (dry wt) of glycine and 0.39% w/w (dry wt) of citric acid. [e] Not determined.

Two sets of samples were produced, with each prepared from a different batch of potato flakes. This resulted in slight differences in the molar ratios of reducing sugars and total amino acids in the potato cakes (**Table 1**). Samples in set 1 were cooked for between 10 and 60 min and were only analyzed for acrylamide at 12 time points without replication (**Table 2**). Samples in set 2 were cooked for 15, 30, or 60 min and subjected to both acrylamide and volatile analyses in triplicate (**Tables 2−4**). To limit the number of samples to be analyzed, set 2 did not include the samples prepared with 0.3% w/w glycine. For the 60 min samples, only those prepared with 1% w/w glycine solution were compared to the control. Set 2 cooking times were specifically chosen to represent key points on the acrylamide formation curve, i.e., where the level of acrylamide was similar to a commercial product (15 min), where it reached a maximum (30 min), and where the level of acrylamide dropped upon further heating but alkylpyrazine levels were highest (*16*).

Analysis of Acrylamide. Acrylamide was analyzed as the dibromo derivative by gas chromatography−mass spectrometry (GC-MS) using the method of Castle et al. (*17*), with the modifications described by Elmore et al (*15*). Labeled [1,2,3-$^{13}C_3$]acrylamide was used as the internal standard.

The brominated extracts (2 μL) were injected onto a Clarus 500 GC-MS system (PerkinElmer Inc., Boston, MA) in splitless mode at 250 °C, the splitter opening after 0.5 min. Pulsed injection was used; the helium carrier gas flow rate was 5 mL min^{-1} for 0.5 min, followed by a decrease to 1 mL min^{-1} over 0.5 min. The flow rate was maintained at 1 mL min^{-1} for 10 min and then increased over 0.5 min to 5 mL min^{-1}, until the end of the run. A DB-17 MS capillary column was used (30 m × 0.25 mm i.d., 0.15 μm film thickness; Agilent, Palo

Table 3. Relative Amounts[a] of Strecker Aldehydes and Selected Dicarbonyl Compounds Formed in Model Potato Cakes Cooked at 180 °C

	15 min of heating				30 min of heating				60 min of heating	
compound[b]	control	Gly[c]	CA[d]	Gly + CA[e]	control	Gly[c]	CA[d]	Gly + CA[e]	control	Gly[c]
					Strecker aldehydes					
2-methylpropanal	660 b	440 a	770 c	760 bc	930 c	410 a	810 c	590 b	590 b	340 a
2-methylbutanal	6500 b	4500 a	8000 c	7700 c	9700 d	4200 a	8800 c	6100 b	6800 b	3400 a
3-methylbutanal	2400 b	1400 a	3100 c	2700 b	1800 b	1000 a	1900 b	1300 ab	1100 a	840 a
benzaldehyde	5 a	4 a	8 b	8 b	31 b	17 a	28 b	21 a	56 b	31 a
phenylacetaldehyde	25 b	8 a	41 c	21 b	53 b	18 a	49 b	29 a	40 b	20 a
					dicarbonyls					
2,3-butanedione	18 a	42 c	19 a	35 b	52 b	71 c	39 a	47 b	77 b	57 a
2,3-pentanedione	20 b	9 a	21 b	14 ab	30 b	12 a	26 b	16 a	26 b	12 a

[a] Amounts of components (determined from headspace concentration) are GC-MS peak areas relative to the internal standard peak area (set to 100). Values quoted are the means of triplicate analyses; CV < 30%. Means with different letters within a row for each cooking time are significantly different ($P < 0.05$) by Fisher's LSD test. [b] Compounds identified by comparison of mass spectra and LRI with those of authentic compounds. [c] Samples treated with 1.3% w/w (dry wt) of glycine. [d] Samples treated with 0.39% w/w (dry wt) of citric acid. [e] Samples treated with 0.39% w/w (dry wt) of glycine and 0.39% w/w (dry wt) of citric acid.

Table 4. Amounts[a] of Alkylpyrazines (μmol/kg) Formed in Model Potato Cakes Cooked at 180 °C

		15 min of heating				30 min of heating				60 min of heating	
compound	ID[b]	control	Gly[c]	CA[d]	Gly + CA[e]	control	Gly[c]	CA[d]	Gly + CA[e]	control	Gly[c]
					C_1 substituted						
methyl-	A	80.6 b	30.2 a	121 b	74.4 ab	385 b	96.8 a	264 b	230 ab	395 b	182 a
					C_2 substituted						
2,5-dimethyl-	A	77. 7 a	121 a	85.5 a	109 a	327 b	277 ab	204 a	271 ab	301 a	367 a
2,6-dimethyl-	A	32.0 a	35.1 a	40.2 a	50.5 a	139 ab	117 ab	95.9 a	148 b	139 a	194 a
ethyl-	A	51.3 b	13.1 a	65.5 c	38.2 b	224 d	53.5 a	179 c	127 b	252 b	87.2 a
2,3-dimethyl-	A	10.9 a	29.4 b	11.7 a	30.5 b	57.9 a	124 b	35.8 a	105 b	61.7 a	211 b
					C_3 substituted						
2-ethyl-6-methyl-	A	33.0 b	16.2 a	38.1 b	31.7 b	148 d	53.1 a	122 c	99.5 b	156 b	71.5 a
2-ethyl-5-methyl-	A	25.6 a	27.5 a	27.0 a	30.8 a	105 c	69.5 a	80.4 b	85.4 b	107 b	80.4 a
trimethyl-	A	31.48 a	308 c	28.6 a	140 b	138 a	719 c	87.0 a	366 b	135 a	861 b
2-ethyl-3-methyl-	A	21.0 a	20.2 a	22.0 a	23.5 a	88.9 c	61.8 a	68.3 ab	70.7 b	91.0 a	82.2 a
propyl-	A	0.24 b	0.09 a	0.37 c	0.26 b	1.80 c	0.39 a	1.97 d	1.28 b	2.56 b	0.69 a
					C_4 substituted						
2,6-diethyl-	B	1.87 c	0.69 a	2.33 d	1.65 b	9.36 c	2.45 a	8.92 c	6.02 b	9.92 b	2.98 a
2-ethyl-3,6-dimethyl-	A	29.2 a	37.3 b	27.5 a	36.8 b	100 c	78.7 a	78.3 a	90.2 b	100 a	93.4 a
isobutyl-	A	0.28 c	0.08 a	0.27 c	0.14 b	2.07 d	0.46 a	1.84 c	1.09 b	2.99 b	0.87 a
2,3-diethyl-	A	0.64 c	0.21 a	0.78 d	0.54 b	2.85 c	0.76 a	2.79 c	1.84 b	3.04 b	1.04 a
2,5-diethyl-	B	0.63 a	1.08 c	0.69 a	0.92 b	2.63 ab	3.03 b	2.27 a	2.51 ab	2.75 a	3.61 b
2-ethyl-3,5-dimethyl-	A	6.40 a	37.2 c	6.38 a	19.6 b	32.9 a	104 c	25.8 a	69.1 b	34.8 a	125 b
2-methyl-6-propyl-	B	0.27 b	0.17 a	0.33 c	0.28 b	1.58 c	0.70 a	1.49 c	1.29 b	1.90 b	0.98 a
tetramethyl-	A	0.35 a	11.8 c	0.31 a	3.80 b	2.46 a	48.8 c	1.62 a	17.4 b	2.62 a	60.5 b
2-methyl-5-propyl-	B	0.09 ab	0.07 a	0.12 b	0.13 b	0.63 b	0.31 a	0.64 b	0.59 b	0.81 b	0.20 a
2-methyl-3-propyl-	A	0.16 ab	0.11 a	0.18 b	0.16 ab	0.79 b	0.47 a	0.71 b	0.75 b	0.92 a	0.85 a
					C_5 substituted						
2-methyl-6-isobutyl-	C	1.95 c	0.77 a	1.92 c	1.49 b	10.1 d	2.61 a	8.82 c	6.13 b	11.0 b	3.33 a
2,3-diethyl-5-methyl-	A	1.26 a	1.42 a	1.13 a	1.11 a	3.62 ab	2.63 a	3.92 b	3.65 ab	3.87 a	3.01 a
2,6-diethyl-3-methyl-	B	2.53 a	2.69 a	2.74 ab	3.15 b	9.16 b	6.03 a	8.77 b	8.35 b	9.11 b	6.20 a
2-methyl-5-isobutyl-	C	1.21 c	0.43 a	1.11 c	0.81 b	5.40 d	1.49 a	4.69 c	3.19 b	5.99 b	2.15 a
2-methyl-3-isobutyl-	A	0.12 d	0.06 a	0.11 c	0.08 b	0.58 b	0.21 a	0.57 b	0.29 a	0.86 b	0.25 a
2,5-diethyl-3-methyl-	B	0.20 a	0.45 c	0.23 ab	0.31 b	0.99 a	1.40 b	0.91 a	1.32 b	1.05 a	1.63 b
total alkylpyrazines		411 a	696 b	486 ab	600 ab	1800 b	1830 b	1290 a	1720 ab	1830 a	2440 a

[a] Amounts of components (determined from SDE) are in μmol/kg on a dry weight basis. Values quoted are the means of triplicate analyses; CV < 30%. Means with different letters within a row for each cooking time are significantly different ($P < 0.05$) by Fisher's LSD test. [b] A, identified and quantified by comparison with authentic compounds; B, identified by library mass spectra and LRI values from the literature (*44*) and quantified using the closest isomer available as an authentic compound; and C, identified by library mass spectra only and quantified using the closest isomer available as an authentic compound. [c] Samples treated with 1.3% w/w (dry wt) of glycine. [d] Samples treated with 0.39% w/w (dry wt) of citric acid. [e] Samples treated with 0.39% w/w (dry wt) of glycine and 0.39% w/w (dry wt) of citric acid.

Alto, CA). The oven temperature was 85 °C for 1 min, rising at 8 °C min^{-1} to 200 °C, then 30 °C min^{-1} to 280 °C for 10 min. The transfer line was held at 280 °C, and the ion source was held at 180 °C. The mass spectrometer was operated in the electron impact mode at 70 eV with selected ion monitoring. Four ions were used to characterize brominated [1,2,3-$^{13}C_3$]acrylamide (*m*/*z* 108, 110, 153, and 155), and another four ions were used to characterize brominated acrylamide (*m*/*z* 106, 108, 150, and 152). The ion *m*/*z* 155 was used to quantify brominated [1,2,3-$^{13}C_3$]acrylamide, and the ion *m*/*z* 152 was used to quantify brominated acrylamide.

Analysis of Volatiles. Dynamic headspace concentration onto Tenax and simultaneous steam distillation and solvent extraction (SDE) were used to isolate volatiles from the cooked potato cakes. Headspace concentration, a milder extraction method, was used for the Strecker aldehydes rather than SDE, because of their higher reactivity as compared to the alkylpyrazines. Unsubstituted pyrazine was found by both SDE and headspace concentration, but it could not be isolated in sufficient quantities by SDE for quantification.

For headspace concentration, the method described by Madruga and Mottram (*18*) was used but with the following modifications. The

samples (7 g) were mixed with 93 g of deionized water and extracted at 37 °C for 1 h. Volatiles were collected on a glass-lined stainless steel trap (105 mm × 3 mm i.d.) containing 85 mg of Tenax TA (Scientific Glass Engineering Ltd., Milton Keynes, United Kingdom). Following extraction, an internal standard (100 ng of 1,2-dichlorobenzene in 1 μL of methanol) was added to the trap. For SDE, the method of Mottram et al. (*19*) was used to prepare solvent extracts (30 mL of 9:1 v/v *n*-pentane/diethyl ether) from 25 g of sample in 1 L of deionized water. The concentration of internal standard used was 100 μg/mL of 1,2-dichlorobenzene in *n*-hexane.

GC-MS analyses were carried out on an HP 5972 mass spectrometer, coupled to an HP5890 gas chromatograph and a G1034C Chemstation, using a Zebron ZB-Wax column (60 m × 0.25 mm i.d., 0.25 μm film thickness; Phenomenex, United Kingdom). For the headspace samples, a CHIS injection port (Scientific Glass Engineering Ltd., United Kingdom), held at 250 °C, was used to desorb thermally the adsorbed volatiles from the Tenax trap onto the front of the column for 5 min, with a column retention gap inserted in solid CO_2. For the SDE extracts, direct injection of a 1 μL volume in the splitless mode (the splitter opening after 1 min) at 250 °C was used. For both types of injection, the temperature program employed was as follows: 5 min at 40 °C, a ramp of 4 °C min^{-1} to 250 °C, then 10 min at 250 °C. The helium carrier gas flow was 1.0 mL min^{-1}. *n*-Alkanes (C_6−C_{25}) were analyzed under the same conditions to obtain linear retention index (LRI) values for the components. The mass spectrometer was operated in the electron impact mode with source temperature of 170 °C, an ionizing voltage of 70 eV, and a scan range from *m*/*z* 29 to *m*/*z* 400 at 2.05 scans s^{-1}. Compounds were identified by comparing their mass spectra and LRI values with those for authentic compounds, published LRI data, or by comparison with spectra contained in the NIST/EPA/NIH Mass Spectral Database (MS Windows version 2.0a, 2002).

Quantitation of Volatiles. In the headspace analyses, approximate quantities of the volatiles were estimated by comparison of their peak areas, obtained from the total ion chromatograms, with that of the 1,2-dichlorobenzene standard, using a response factor of 1. For SDE, linear calibration curves were prepared for compounds where authentic standards were available; where these were unavailable, those of the closest related isomer were used. The internal standard method was employed using 10 calibration solutions of each compound containing between 3 and 500 mg/L of the compound and 20 mg/L of the internal standard 1,2-dichlorobenzene. The analytical fractional recovery was established by spiking a sample with a known amount of pure standard and comparing this to the amount recovered after extraction. Pyrazines with the same molecular mass were assumed to have the same analytical recovery, and the calculated quantities were adjusted to take into account the observed recovery.

Analysis of Amino Acids. The free amino acids were measured using the EZ-Faast amino acid derivatization technique (Phenomenex, Torrance, CA) followed by analysis on the Clarus 500 GC-MS system as described by Elmore et al. (*15*).

Analysis of Sugars. This was carried out on an 8220i Dionex ion chromatography system (Dionex Corp., Sunnyvale, CA) using the method described by Elmore et al. (*15*).

Measurement of pH for Raw Potato Cakes. A 100 g sample of the dough used to prepare the cakes was homogenized with 125 mL of distilled water in a blender to form a slurry. The slurry was separated into three portions, and the pH of each portion was measured at room temperature using a pH meter and electrode (Orion model 410A and Combo PerpHect, Thermo Electron Corporation, Beverly, MA). The mean of the three readings (which did not differ by more than 0.15 pH units) was reported as the final pH. Prior to cooking, the control potato cakes had an initial pH of 5.8−6.0 (**Table 5**). Those with added glycine had a similar pH, while those with added citric acid had an initial pH of 5.2.

Statistical Analysis. One-way analysis of variance and Fisher's least significant difference (LSD) test (Statgraphics Plus version 4.1) were used to indicate significant differences ($p \leq 0.05$) in the levels of acrylamide and volatile components between the control and the treatment means.

Table 5. Effect of Glycine and Citric Acid on the pH of Uncooked Model Potato Cakes

	set 1	set 2
control	5.78	6.00
treatment (dry weight basis)		
1.3% glycine	5.99	6.01
0.39% glycine	5.98	
0.39% citric acid	5.15	5.16
0.39% glycine + 0.39% citric acid	5.15	5.14

RESULTS AND DISCUSSION

Volatiles from Potato Cakes. Although over 80 compounds were found in the headspace volatiles and SDE extracts from the cooked potato cakes, only Strecker aldehydes and alkylpyrazines were monitored across the range of samples. These two important classes of flavor compounds are formed in significant quantities, along with acrylamide, in heated potato via the Maillard reaction. In discussing the mechanistic basis for their kinetic model describing acrylamide formation in potato/wheat/rye cakes, Wedzicha et al. (*20*) suggested that the formation of Strecker aldehydes and alkylpyrazines is in competition with acrylamide formation. Therefore, these two classes of flavor compounds are of particular interest in relating flavor generation to acrylamide formation. Moreover, several Strecker aldehydes and alkylpyrazines have been highlighted as character impact compounds of cooked potato aroma (*10*, *11*).

An attempt was made to identify the Strecker aldehyde methional, but this compound could not be readily found. Oruna-Concha et al. (*21*) were also unable to measure methional in baked potato flesh and skin. It is likely that insufficient methional was present in the samples to be measurable, either because of the low level of methionine in the raw material (1.2 mol % of total free amino acids present in potato flake) or because of the subsequent loss of methional. This loss could be due to further reactions or volatilization. Previous work in our laboratory on the kinetics of Strecker aldehyde and acrylamide formation demonstrated that methylpropanal, 2- and 3-methylbutanal, and phenylacetaldehyde displayed very similar formation kinetics (*16*). Therefore, it is likely that methional and other Strecker aldehydes would behave similarly. The results reported for the monitored Strecker aldehydes should then be representative of the class as a whole (other than formaldehyde, the Strecker aldehyde of glycine, in the case of glycine addition).

Additionally, although benzaldehyde was listed as a Strecker aldehyde, it is unlikely to have been formed through the direct Strecker degradation of phenylglycine, which was not present in measurable levels in the potato cakes. However, it is possible that its formation is related to the Strecker degradation of phenylalanine (*22*).

Effect of Citric Acid Addition. A small, but consistent, lowering of acrylamide levels in samples containing added citric acid was found (**Figure 1**). The average reduction was approximately 20%. These data were obtained from single analyses on samples cooked at 180 °C for between 10 and 60 min. Similar analyses in triplicate on samples prepared from a different batch of potato flake also showed a reduction in acrylamide in samples with added citric acid (**Table 2**). The effect of citric acid on acrylamide was less marked in this second set, with a decrease of 8% at 15 min and 18% at 30 min relative to the control samples (**Table 2**). This could be a result of using two different batches of potato flakes for the two sets of samples, although the same formulations were used. Nevertheless, the general trends were found to be very similar.

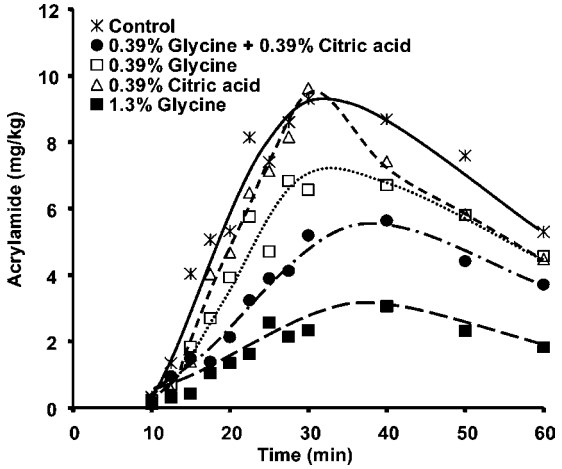

Figure 1. Formation of acrylamide in model potato cakes (set 1) cooked at 180 °C and formulated with the addition of glycine and/or citric acid.

The results obtained agree with those of other researchers, who have also observed a decrease in measured acrylamide, in potato model systems, when the pH was lowered through treatment with citric acid. The percentage reduction in acrylamide observed matched well with that of Rydberg et al. (*23*), who found that the addition of 0.1, 0.5, and 2.0% w/w of citric acid to homogenized potato slurry (heated at 180 °C for 25 min) led to a decrease in acrylamide of 18, 35, and 46%, respectively, as compared to the control. Jung et al. (*14*) dipped French-fried potatoes into 1 or 2% citric acid solutions prior to frying for 6.5 min at 190 °C and found that this lowered acrylamide levels by 73−80%, relative to the control (without dipping). However, this was probably also due to the leaching of reducing sugars and asparagine from the surface of the potato, because dipping in a solution of water without citric acid also reduced the acrylamide.

The addition of citric acid appeared to increase the net yield of Strecker aldehydes by 20−60%, relative to the control at a short cooking time of 15 min, and had no significant effect at a longer cooking time of 30 min (**Table 3**). This is contrary to the observations of Cremer and Eichner (*24*) in low moisture systems and plant powders heated at 90 °C for 60 min. They found that the amount of Strecker aldehydes produced increased linearly with pH from 3.0 to 9.0 or, conversely, that lowering the pH reduced Strecker aldehyde yields. A possible reason for this discrepancy is the difference in temperatures used. At temperatures above 100 °C, the later stages of the Maillard reaction are promoted, particularly the formation of heterocyclic compounds and melanoidins. Temperatures exceeding 100 °C are also required for acrylamide formation. The higher temperature used in the potato model system would promote such reactions, including the degradation of the Strecker aldehydes. The results suggest that decreasing the pH had a greater effect on limiting these degradation reactions than it had on Strecker aldehyde formation, thereby increasing the apparent net yield of Strecker aldehydes. Moreover, the rate of Strecker aldehyde formation can be expected to be higher at short cooking times as the concentration of reactants is still high. Chan and Reineccius (*25*) also observed higher Strecker aldehyde yields at pH 7.0 than at pH 8.0, in aqueous glucose/leucine and glucose/phenylalanine model systems heated from 75 to 115 °C. They also explained this latter observation by suggesting that the loss of aldehydes through secondary reactions was greater at pH 8.0 than at pH 7.0.

In keeping with the general observation that pyrazine formation is favored at high pH (*26*), the results obtained indicated a decrease of between 10 and 25% in alkylpyrazine yields, relative to the control, with citric acid addition at 30 min (**Table 4**). This trend was not as clear at 15 min, and this could be due to the fact that alkylpyrazines are advanced Maillard end products. At 15 min, only 22% of the total alkylpyrazine yield at 60 min was observed in the control samples, indicating that the formation of alkylpyrazines was still in its early stages, thus making it more difficult to determine the effect of citric acid addition. At 30 min, however, 96% of the total alkylpyrazine yield was observed.

Effect of Glycine Addition. Glycine has been shown to be one of the most effective amino acid additives in mitigating acrylamide formation (*23*, *27*), and the results shown in **Figure 1** demonstrate a marked decrease in acrylamide content with glycine addition. At a concentration of 0.39% w/w, glycine decreased the acrylamide content by an average of approximately 30%, relative to the control, while at a glycine concentration of 1.3% w/w, acrylamide decreased by approximately 70%. In addition, it was observed that glycine addition had a marked enhancing effect on the browning of the potato cakes. This reduction in acrylamide could be due to either competitive consumption of precursors by glycine and/or increased loss or thermal degradation of acrylamide (*23*). An example of reactions by which acrylamide would be lost is the Michael reaction of the olefinic group with the amino group of glycine (*20*), thereby covalently binding free acrylamide. Glycine was on average more effective than citric acid in reducing acrylamide levels when used at the same concentration. However, increasing the glycine concentration by approximately three-fold, from 0.39 to 1.3% w/w, only yielded an approximately two-fold increase in acrylamide reduction. Rydberg et al. (*23*) reported that the addition of 0.3 and 1.0% w/w of glycine to homogenized potato slurry, heated at 180 °C for 25 min, reduced acrylamide levels by 70 and 90%, respectively. This decrease is larger than that reported here. In contrast, Brathen et al. (*27*) blanched potato slices in water and in 0.05 M glycine solution (approximately 0.4% w/w) before frying for 4 min at 170 °C and found that this reduced the acrylamide content by 30 and 70%, respectively.

With the addition of 1.3% w/w of glycine, the levels of all of the Strecker aldehydes monitored were found to decrease by 30−70% relative to the control (**Table 3**). This decrease is very likely to be due to glycine competing with other amino acids for available Strecker reagents (e.g., dicarbonyl compounds from sugar fragmentation) in Strecker degradation reactions, resulting in lower concentrations of other Strecker aldehydes being formed. The Strecker aldehyde of glycine is formaldehyde, and its formation is likely to have increased markedly with the addition of free glycine at the expense of the other Strecker aldehydes. This formaldehyde can readily take part in other reactions including the formation of some pyrazines (see below), but it is too volatile (bp −19.3 °C) and too reactive to remain in the final product.

The addition of glycine (1.3% w/w) to the potato model system increased the total yield of the monitored alkylpyrazines by about 30% on average as compared to the control. However, glycine only increased the levels of certain pyrazines and decreased the yields of many. Those pyrazines that increased generally had methyl or ethyl substituents in both the 2- and the 3-positions (**Table 4**). In particular, the levels of 2,3-dimethylpyrazine, trimethylpyrazine, 2-ethyl-3,5-dimethylpyrazine, and tetramethylpyrazine all increased by more than 100%. Yields of 2,5-diethyl-3-methylpyrazine increased by 40−130%. Particularly dramatic increases were observed for trimethylpyra-

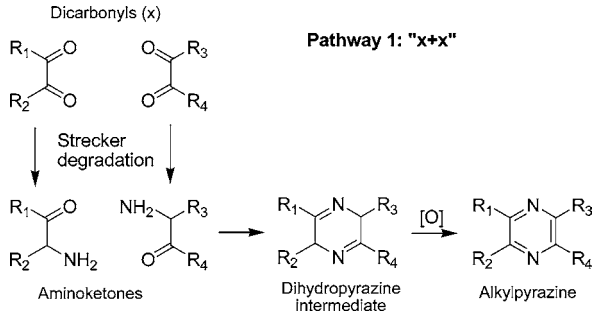

Figure 2. Pathway for alkylpyrazine formation, involving condensation of two aminoketones to form a dihydropyrazine, with direct oxidation to the corresponding alkylpyrazine, where "*x*" refers to the dicarbonyl precursor.

zine and tetramethylpyrazine, with yields increasing by as much as nine- and 33-fold, respectively. The increases in these pyrazines were at the expense of most of the others, whose levels fell by 20−80% when glycine was added.

Although tri- and tetramethylpyrazine showed the greatest increase, the odor thresholds of these pyrazines in water (0.4 and 1.0 mg/kg, respectively), and also of 2,3-dimethylpyrazine (0.4 mg/kg), are much higher than that of 2-ethyl-3,6-dimethylpyrazine (0.0004 mg/kg) (*28*), which is important for potato crisp aroma. This suggests that the effect on perceived flavor could be influenced more by the resulting decrease in 2-ethyl-3,6-dimethylpyrazine, and other such pyrazines with a low odor threshold, rather than by an increase in the mentioned pyrazines. Nevertheless, 2-ethyl-3,5-dimethylpyrazine and 2,5-diethyl-3-methylpyrazine, which do exhibit odor thresholds similar to that of 2-ethyl-3,6-dimethylpyrazine (*28*), both increased with glycine addition.

The change in alkylpyrazine profile can probably be attributed to the fact that glycine is able to participate in the Maillard reaction in several ways. Glycine can undergo Strecker degradation, giving rise to its Strecker aldehyde, formaldehyde, and α-amino carbonyls, the alkylpyrazine precursors. At the same time, formaldehyde can undergo aldol condensation type reactions with other carbonyl compounds, yielding longer chain α-dicarbonyls or α-hydroxycarbonyls. These may subsequently be involved in Strecker degradation or react with free ammonia, forming α-amino carbonyls that incorporate a glycine subunit (*29*, *30*). The latter may then condense with other α-amino carbonyls to yield dihydropyrazines, which are subsequently oxidized to the corresponding pyrazines. This pathway is referred to here as the "$x + x$" pathway, where "*x*" refers to the dicarbonyl or hydroxycarbonyl generating the aminoketone (**Figure 2**). It is often considered the most direct and important route for pyrazine formation. On the other hand, formaldehyde may react directly with dihydropyrazine intermediates to give alkylpyrazines with an additional substituent, again comprising a glycine subunit, referred to as the "$x + x + y$" pathway (**Figure 3**). Here, the "*y*" refers to the aldehyde, whose carbon skeleton is incorporated as an additional substituent on the pyrazine ring (*31*, *32*). Amrani-Hemaimi et al. (*31*) suggested this mechanism to be responsible for the incorporation of [3-^{13}C]-alanine carbon atoms as ethyl substituents in pyrazines, via interaction of acetaldehyde (the Strecker aldehyde of alanine) with dihydropyrazines.

The increase in specific alkylpyrazines suggests that glycine must be involved directly in their formation, rather than merely increasing the overall concentration of α-amino carbonyls (the alkylpyrazine precursors), through Strecker degradation reactions. If it is assumed that the "$x + x$" pathway is the main route for pyrazine formation, the key alkylpyrazines that are

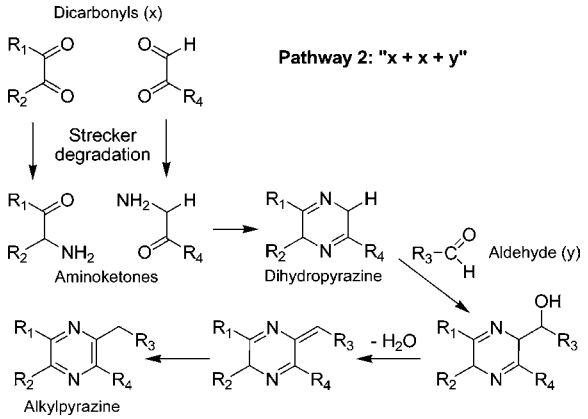

Figure 3. Pathway for alkylpyrazine formation with incorporation of an additional substituent through interaction of an aldehyde (*y*) with the dihydropyrazine intermediate formed from dicarbonyl precursors (*x*).

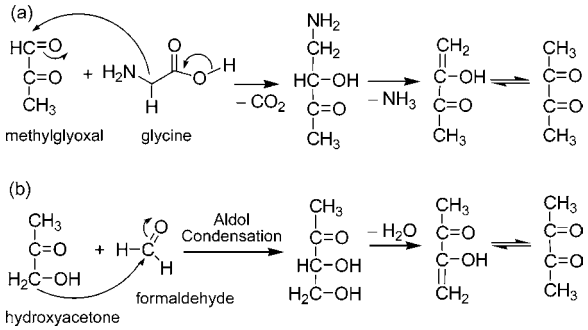

Figure 4. Formation of 2,3-butanedione by (**a**) direct interaction of glycine with methylglyoxal [derived from Keyhani and Yaylayan (*33*)] or (**b**) aldol condensation of formaldehyde with hydroxyacetone.

enhanced by glycine appear to have in common a C_4 and a C_5 α-aminoketone precursor, namely, 3-amino-2-butanone and 3(2)-amino-2(3)-pentanone, giving the 2,3-dimethyl- and 2-ethyl-3-methyl-compounds. These are likely to have been derived from corresponding C_4 and C_5 α-dicarbonyls or α-hydroxycarbonyls, specifically 2,3-butanedione or 3-hydroxy-2-butanone and 2,3-pentanedione or 3(2)-hydroxy-2(3)-pentanone, respectively. This suggests that the addition of glycine may have increased the levels of these carbonyls as compared to the others, resulting in an increase in their alkylpyrazine end products at the expense of other pyrazines. The substantial increase in tetramethylpyrazine in particular, which would require two molecules of 2,3-butanedione and/or 3-hydroxy-2-butanone to generate the necessary α-amino carbonyls for its formation, attests to the likelihood of glycine promoting the formation of either or both of these precursors.

This hypothesis is supported by the work of Yaylayan and Keyhani (*29*). They found that 70% of the 2,3-butanedione generated in [2-^{13}C]glycine/glucose systems were singly labeled, as compared to none in [2-^{13}C]alanine/glucose systems. Thus, the introduction of more glycine into the system could be expected to enhance the level of 2,3-butanedione. They proposed that this may be the result of direct interaction of glycine with methylglyoxal, leading to the chain elongation of the latter by one carbon unit originating from the C-2 atom of glycine (**Figure 4a**) (*33*). Moreover, by this pathway, methylglyoxal is consumed to produce 2,3-butanedione, thereby indirectly reducing the levels of the alkylpyrazines requiring methylglyoxal for their formation. Alternatively, an increase in glycine would have also boosted the concentration of formaldehyde, its Strecker aldehyde, and this may have promoted aldol condensation reactions between hydroxyacetone and formaldehyde, again

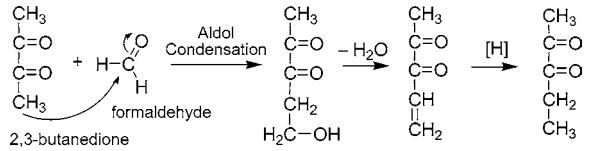

Figure 5. Formation of 2,3-pentanedione by aldol condensation of 2,3-butanedione and formaldehyde. Derived from Weenen (*34*).

leading to 2,3-butanedione formation (**Figure 4b**). Increased levels of 2,3-butanedione and formaldehyde may in turn have enhanced the level of 2,3-pentanedione. **Figure 5** illustrates a possible pathway for the formation of 2,3-pentanedione through the aldol condensation of 2,3-butanedione with formaldehyde (*34*). Similar formation pathways involving chain elongation of small rearranged sugar fragments through aldol condensation with glycine subunits can be envisaged for the α-hydroxycarbonyls.

To verify this hypothesis, the levels of 2,3-butanedione and 2,3-pentanedione in the samples with added glycine were compared to the control (**Table 3**). The α-hydroxycarbonyls could not be detected in the chromatograms and so were not monitored. It was observed that glycine addition did significantly increase 2,3-butanedione, particularly at short cooking times. There was a more than a two-fold increase at 15 min and a 36% increase at 30 min, although there was a 26% decrease at 60 min. Previously published data on sugar and amino acid precursors in similar potato cakes, cooked for 10−60 min at 180 °C, showed that the reducing sugars were completely depleted after about 25−30 min (*15*). This suggests that the rate of increase of 2,3-butanedione production with glycine addition is limited by the availability of small molecule carbonyl precursors, like methylglyoxal or hydroxyacetone, which derive from sugars. With a higher availability of precursors in the early stages of the reaction, much more 2,3-butanedione is formed from reaction with glycine, but the increased rate of depletion of these precursors lowers the rate of increase as the reaction progresses.

Although the expected increase in 2,3-butanedione was observed, it was found that the measured 2,3-pentanedione did not increase with glycine. In fact, there was a decrease of approximately 60% in 2,3-pentanedione for all three cooking times employed. Therefore, while there is fairly strong evidence to suggest that the increase in 2,3-butanedione due to glycine promoted the formation of 2,3-dimethyl, trimethyl, and tetramethylpyrazine, it is not clear how glycine is involved in 2-ethyl-3,5-dimethyl and 2,5-diethyl-3-methylpyrazine formation. It is also not clear why production of these latter two pyrazines increased, while their corresponding isomers decreased.

Because glycine produces formaldehyde through Strecker degradation, an alternative route by which glycine could promote the formation of the key pyrazines is via the "$x + x + y$" pathway, as mentioned above. The addition of formaldehyde to dihydropyrazine intermediates would result in the introduction of a methyl group. It is possible that this pathway could be more significant for these key pyrazines than for the others, thereby enhancing their formation. Amrani-Hemaimi et al. (*31*) conducted their experiments in [3-^{13}C]alanine/glucose or fructose dry model systems pyrolyzed at 210 °C. They observed some doubly labeled ethyl-substituted pyrazines. Although the "$x + x + y$" pathway is logical, it cannot account for the incorporation of more than one ethyl substituent from acetaldehyde (*29*). This suggests that to obtain doubly labeled alkylpyrazines, another mechanism, probably "$x + x$", occurs in parallel.

Combined Effect of Citric Acid and Glycine Addition. The addition of a combination of 0.39% w/w citric acid and 0.39% w/w glycine (dry weight) resulted in an additive effect in reducing acrylamide, as compared to the samples treated with either chemical alone (**Figure 1**). In parallel work with an on-line system, using the same materials, product formulations, and temperatures, Cook and Taylor (*35*) employed a response surface design to determine the effectiveness of combined treatments of citric acid and soy protein hydrolysate in lowering acrylamide in the potato model system. They reached a similar conclusion that a combined treatment of low levels of citric acid and soy protein hydrolysate was very effective in reducing acrylamide levels.

With the volatiles, it was observed that for components where the effects of citric acid and glycine were opposing, the combined effect of both additives on these components was small. This can be seen for the Strecker aldehydes at 15 min (**Table 3**). Overall, the effect of glycine addition appeared to dominate over that of citric acid for the volatiles studied, particularly for those alkylpyrazines whose yields were greatly enhanced by glycine addition (**Table 4**).

In the preceding sections, it was noted that citric acid and glycine have very different effects on the volatile profile. Citric acid, in general, reduced alkylpyrazine and total volatile yields by suppressing the Maillard reaction. Glycine, on the other hand, increased alkylpyrazine and total volatile yields but does this by preferentially promoting the formation of certain alkylpyrazines only. Yields of other pyrazines and of the Strecker aldehydes were affected negatively by glycine. This suggests that a combined treatment of lower levels of citric acid and glycine would have less impact on the flavor profile than a higher level of either treatment on its own, which would be needed to achieve the same reduction in acrylamide.

This suggestion is especially significant as the character impact compounds of cooked potato, like methional, phenylacetaldehyde, 2-methylbutanal, 3-methylbutanal, 2-ethyl-3,6-dimethylpyrazine, and 2,3-diethyl-5-methylpyrazine, are likely to be lowered in the presence of added glycine. An alternative would be to use a combination of different amino acids to boost the desired Strecker aldehydes and alkylpyrazines, while at the same time mitigating acrylamide levels. However, this may be limited by the fact that amino acids are not equally effective in mitigating acrylamide formation. Rydberg et al. (*23*) demonstrated that glycine and glutamine were almost twice as effective as alanine, lysine, and glutamic acid in suppressing acrylamide levels at low additive concentrations.

In conclusion, it is clear that acrylamide formation and flavor generation are intricately linked through the Maillard reaction and that attempts to mitigate acrylamide formation would have a significant impact on flavor. This has been demonstrated for pH modification with citric acid and for glycine addition, although similar considerations would apply equally to other acrylamide mitigation strategies. However, differences in the effect on flavor between these strategies can be exploited to minimize the overall impact on sensory quality. This can be achieved by employing a combination of treatments.

LITERATURE CITED

(1) Tareke, E.; Rydberg, P.; Karlsson, P.; Eriksson, S.; Törnqvist, M. Analysis of acrylamide, a carcinogen formed in heated foodstuffs. *J. Agric. Food Chem.* **2002**, *50*, 4998−5006.

(2) Erickson, B. E. Finding acrylamide. *Anal. Chem.* **2004**, *76*, 247A−248A.

(3) Mucci, L. A.; Dickman, P. W.; Steineck, G.; Adami, H. O.; Augustsson, K. Dietary acrylamide and cancer of the large bowel, kidney, and bladder: Absence of an association in a population-based study in Sweden. *Br. J. Cancer* **2003**, *88*, 84−89.

(4) Mottram, D. S.; Wedzicha, B. L.; Dodson, A. T. Acrylamide is formed in the Maillard reaction. *Nature* **2002**, *419*, 448−449.
(5) Stadler, R. H.; Blank, I.; Varga, N.; Robert, F.; Hau, J.; Guy, P. A.; Robert, M. C.; Riediker, S. Acrylamide from Maillard reaction products. *Nature* **2002**, *419*, 449−450.
(6) Becalski, A.; Lau, B. P. Y.; Lewis, D.; Seaman, S. W. Acrylamide in foods: Occurrence, sources, and modeling. *J. Agric. Food Chem.* **2003**, *51*, 802−808.
(7) Stadler, R. H.; Scholz, G. Acrylamide: An update on current knowledge in analysis, levels in food, mechanisms of formation, and potential strategies of control. *Nutr. Rev.* **2004**, *62*, 449−467.
(8) Taeymans, D.; Wood, J.; Ashby, P.; Blank, I.; Studer, A.; Stadler, R. H.; Gonde, P.; Van Eijck, P.; Lalljie, S.; Lingnert, H.; Lindblom, M.; Matissek, R.; Muller, D.; Tallmadge, D.; O'Brien, J.; Thompson, S.; Silvani, D.; Whitmore, T. A review of acrylamide: An industry perspective on research, analysis, formation and control. *Crit. Rev. Food Technol.* **2004**, *44*, 323−347.
(9) Friedman, M. Chemistry, biochemistry, and safety of acrylamide. A review. *J. Agric. Food Chem.* **2003**, *51*, 4504−4526.
(10) Wagner, R. K.; Grosch, W. Key odorants of French fries. *J. Am. Oil Chem. Soc.* **1998**, *75*, 1385−1392.
(11) Guadagni, D. G.; Buttery, R. G.; Turnbaugh, J. G. Odour thresholds and similarity ratings of some potato chip components. *J. Sci. Food Agric.* **1972**, *23*, 1435−1444.
(12) Amrein, T. M.; Schönbächler, B.; Escher, F.; Amadò, R. Acrylamide in gingerbread: Critical factors for formation and possible ways for reduction. *J. Agric. Food Chem.* **2004**, *52*, 4282−4288.
(13) Gama-Baumgartner, F.; Grob, K.; Biedermann, M. Citric acid to reduce acrylamide formation in French fries and roasted potatoes? *Mitt. Lebensm. Hyg.* **2004**, *95*, 110−117.
(14) Jung, M. Y.; Choi, D. S.; Ju, J. W. A novel technique for limitation of acrylamide formation in fried and baked corn chips and in French fries. *J. Food Sci.* **2003**, *68*, 1287−1290.
(15) Elmore, J. S.; Koutsidis, G.; Dodson, A. T.; Mottram, D. S.; Wedzicha, B. L. Measurement of acrylamide and its precursors in potato, wheat, and rye model systems. *J. Agric. Food Chem.* **2005**, *53*, 1286−1293.
(16) Low, M. Y.; Mottram, D. S.; Elmore, J. S. The relationship between acrylamide formation and flavour generation in heated foods. In *Flavour Science of Foods and Beverages*; Bredie, W. L. P., Petersen, M. A., Eds.; Elsevier: 2005.
(17) Castle, L.; Campos, M.-J.; Gilbert, J. Determination of acrylamide monomer in hydroponically grown tomato fruits by capillary gas chromatography−mass spectrometry. *J. Sci. Food Agric.* **1991**, *54*, 549−555.
(18) Madruga, M. S.; Mottram, D. S. The effect of pH on the formation of Maillard-derived aroma volatiles using a cooked meat system. *J. Sci. Food Agric.* **1995**, *68*, 305−310.
(19) Mottram, D. S.; SzaumanSzumski, C.; Dodson, A. Interaction of thiol and disulfide flavor compounds with food components. *J. Agric. Food Chem.* **1996**, *44*, 2349−2351.
(20) Wedzicha, B. L.; Mottram, D. S.; Elmore, J. S.; Koutsidis, G.; Dodson, A. T. Kinetic models as a route to control acrylamide formation in food. In *Chemistry and Safety of Acrylamide in Food*; Friedman, M., Mottram, D. S., Eds.; Springer: New York, 2005; pp 235−253.
(21) Oruna-Concha, M. J.; Duckham, S. C.; Ames, J. H. Comparison of volatile compounds isolated from the skin and flesh of four potato cultivars after baking. *J. Agric. Food Chem.* **2001**, *49*, 2414−2421.
(22) Baltes, W.; Mevissen, L. Model reactions on roast aroma formation. 6. Volatile reaction-products from the reaction of phenylalanine with glucose during cooking and roasting. *Z. Lebensm.-Unters. Forsch.* **1988**, *187*, 209−214.
(23) Rydberg, P.; Eriksson, S.; Tareke, E.; Karlsson, P.; Ehrenberg, L.; Törnqvist, M. Investigations of factors that influence the acrylamide content of heated foodstuffs. *J. Agric. Food Chem.* **2003**, *51*, 7012−7018.
(24) Cremer, D. R.; Eichner, K. The influence of the pH value on the formation of Strecker aldehydes in low moisture model systems and in plant powders. *Eur. Food Res. Technol.* **2000**, *211*, 247−251.
(25) Chan, F.; Reineccius, G. The reaction kinetics for the formation of isovaleraldehyde, 2-acetyl-1-proline, di(H)di(OH)-6-methylpyranone, phenylacetaldehyde, 5-methyl-2-phenyl-2-hexenal, and acetylfuran in model systems. In *Maillard Reactions in Chemistry, Food and Health*; Labuza, T. P., Ed.; Royal Society of Chemistry: Cambridge, 1994; pp 131−139.
(26) Leahy, M. M.; Reineccius, G. A. Kinetics of the formation of alkylpyrazines—Effect of pH and water activity. In *Thermal Generation of Aromas*; Parliament, T. H., McCorrin, R. J., Ho, C. T., Eds.; American Chemical Society: Washington, DC, 1989; pp 196−208.
(27) Brathen, E. B.; Kita, A.; Knutsen, S. H.; Wicklund, T. Addition of glycine reduces the content of acrylamide in cereal and potato products. *J. Agric. Food Chem.* **2005**, *53*, 3259−3264.
(28) van Gemert, L. J. *Compilations of Odour Threshold Values in Air and Water*; TNO Nutrition and Food Research Institute: Zeist, The Netherlands, 2003.
(29) Yaylayan, V. A.; Keyhani, A. Origin of 2,3-pentanedione and 2,3-butanedione in D-glucose/L-alanine Maillard model systems. *J. Agric. Food Chem.* **1999**, *47*, 3280−3284.
(30) Yaylayan, V. A.; Keyhani, A. Origin of carbohydrate degradation products in L-alanine/D-^{13}C glucose model systems. *J. Agric. Food Chem.* **2000**, *48*, 2415−2419.
(31) Amrani-Hemaimi, M.; Cerny, C.; Fay, L. B. Mechanisms of formation of alkylpyrazines in the Maillard reaction. *J. Agric. Food Chem.* **1995**, *43*, 2818−2822.
(32) Chiu, E. M.; Kuo, M. C.; Bruechert, L. J.; Ho, C. T. Substitution of pyrazines by aldehydes in model systems. *J. Agric. Food Chem.* **1990**, *38*, 58−61.
(33) Keyhani, A.; Yaylayan, V. A. Elucidation of the mechanism of pyrazinone formation in glycine model systems using labeled sugars and amino acids. *J. Agric. Food Chem.* **1996**, *44*, 2511−2516.
(34) Weenen, H. Reactive intermediates and carbohydrate fragmentation in Maillard chemistry. *Food Chem.* **1998**, *62*, 393−401.
(35) Cook, D. J.; Taylor, A. J. On-line MS/MS monitoring of acrylamide generation in potato- and cereal-based systems. *J. Agric. Food Chem.* **2005**, *53*, 8926−8933.

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