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Acrylamide in French Fries: Influence of Free Amino Acids and Sugars

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The free amino acid profile and sugar (fructose, glucose, and sucrose) composition were determined in potato samples selected to give a large range of variation (a total of 66 samples). From these samples French fries were produced in a laboratory-scale simulation of an industrial process followed by a finish fry at 180 °C for 3.5 min using a restaurant fryer. The final product was blast frozen and analyzed for acrylamide. Acrylamide was detected in all samples, but its concentration varied significantly from 50 to 1800 ng/g. For isotope dilution ($^{13}C_3$) acrylamide analysis, samples were extracted with water, cleaned up on HLB Oasis polymeric and Accucat mixed mode anion and cation exchange SPE columns, and analyzed by LC-MS/MS. Statistical analysis of the data indicates that the effect of sugars and asparagine on the concentration of acrylamide in French fries is positive and significant ($p < 0.001$). It appears that one of the ways acrylamide formation in French fries can be effectively controlled is by the use of raw products with low sugar (and to a lesser degree, asparagine) content.

KEYWORDS: Acrylamide; potato; glucose, fructose, sucrose; asparagine; Maillard reaction, LC-MS/MS

INTRODUCTION

The discovery of acrylamide in foods for human consumption (*1*−*4*) initiated many subsequent investigations related to the issue of its presence in foodstuffs, toxicity, and possible precursors. Taking into consideration that acrylamide is a rodent carcinogen and a human neurotoxin and is classified as a probable human carcinogen (*5*), and notwithstanding two preliminary studies indicating the absence of a *substantial* link between acrylamide and human cancer (*6*, *7*), there is an urgent need to investigate the possibilities of reducing the acrylamide content in foods. We have chosen French fries as a matrix for the investigation of the relationship between possible precursors and final acrylamide content as it appears that fried potato products are an important source of acrylamide in the group of people with a high intake of acrylamide. Recently, several groups have announced findings that point to the Maillard reaction as a likely acrylamide source and implicated asparagine and sugars as possible precursors under model conditions (*8*−*14*). One of the preferred approaches would therefore focus on selective reduction of acrylamide—through control of these plausible precursors, particularly asparagine, if feasible—while allowing the Maillard reaction to proceed, at least to a certain extent, because that reaction is largely responsible for the desirable aroma and taste of food and also produces beneficial compounds (*15*).

The levels of acrylamide found by us in a limited survey of available (Ottawa, Canada) commercial French fries fluctuated widely from 60 to 1800 ng/g ($n = 8$), further indicating a possibility of reducing the acrylamide content by modification of the starting material and/or the process (it was very likely that the differences in acrylamide concentration were due to both factors).

To understand the relationship between sugars and amino acids in the formation of acrylamide, we selected 66 potato samples having a large variability of sugars and free amino acids contents. We obtained data on the three most common sugars, fructose, glucose, and sucrose (these sugars usually constitute >90% of all sugars in a potato tuber) and the complete amino acid composition, including asparagine content, of each sample.

These potato samples were cut into French fries and subjected to an identical two-step process [a preliminary fry (also known

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as a par-fry process) followed by a finish fry at 180 °C], and the final product was analyzed for acrylamide.

Analysis of French fries was done by an isotope dilution ($^{13}C_3$-acrylamide) LC-MS/MS method (*13*), which was modified and optimized for the assay of fried potato products.

To our knowledge, this is the first study in which influences of both amino acid and sugar composition were evaluated in a large set of samples (amenable to statistical analysis) for the formation of acrylamide in fried potato products. When the experimental part of our investigation was completed, reports by Haase et al. and Chuda et al. of the influence of sugars on acrylamide formation during potato chip processing were published (*16*, *17*). In the latter publication, the effects of asparagine and total free amino acids are discussed but only for a very small number of samples ($n = 3$).

MATERIALS AND METHODS

Chemicals. Dichloromethane (pesticide grade) and methanol (HPLC grade) were obtained from EM Science (Gibbstown, NJ). Water was obtained from a purification system (Millipore, MilliQ Gradient A10). Acrylamide, 99+% (14,866-0), was from Aldrich, and $^{13}C_3$ (98%) labeled standard of acrylamide, (CLM-813) was from Cambridge Isotope Laboratories (Andover, MA) (catalog numbers are given in parentheses). All stock acrylamide solutions (400 and 250 μg/mL) and calibration solutions were prepared in water. Working quantities of standards were stored at 4 °C, whereas the stock was kept at −18 °C.

Foods. To maximize variation in the raw material (sugar and amino acids), tubers from commercial varieties and advanced breeding lines grown for experimental, processing, and seed purposes were selected. A number of samples were subjected to conditions that encourage sugar formation. All fried food samples used in this study were stored at −18 °C before analysis.

Equipment/materials included the following: a high-pressure liquid chromatograph, model 1100, consisting of an autosampler, a binary pump, a degasser, and a column oven (Agilent, Palo Alto, CA); a triple-quadrupole tandem mass spectrometer, Quattro-Ultima (Micromass Inc., Manchester, U.K.); a data system, MassLynx version 3.5 (Micromass, U.K.); an analytical column, 2.1 mm i.d. × 250 mm, 5 μm Aquasil C18, 77505-252130 (Thermo Hypersil-Keystone, Bellefonte, PA), with a C18 2 × 4 mm guard column, AJO-4286 (Phenomenex, Torrance, CA); a food processor, Blend Master (Proctor-Silex, Picton, Canada); centrifuge tubes, FEP, 50 mL, 3114-0050 (Nalgene, Rochester, NY); a shaker, horizontal (Eberbach, Ann Arbor, MI); a centrifuge, fixed-angle rotor, RC-2B (Sorvall, Asheville, NC); a centrifuge, swinging bucket rotor, RC-3B (Sorvall); a centrifuge filter, 15 mL, 5 kDa cutoff, Centricon Plus-20, UFC2BCC08 (Millipore, Bedford, MA); an Oasis HLB polymeric cartridge, 6 mL, 200 mg, 106202 (Waters, Milford, MA); and an Accucat anion and cation exchange cartridge, 3 mL, 200 mg, 1228-2003 (Varian, Walnut Creek, CA).

Determination of Glucose, Fructose, and Sucrose in Raw Potato. Sugars (sucrose, glucose, and fructose contents) of freeze-dried potato tuber tissue were measured in duplicate, using an enzyme-based assay and an Ultraspec 3000 spectrophotometer (Pharmacia Biotech, Cambridge, U.K.). The procedure was modified from that of Viola and Davies (*18*) in that sucrose hydrolysis was carried out separately from the glucose and fructose reactions, and the aliquots were scaled up from the microplate quantities for measurement in spectrophotometer cuvettes as described by Daniels-Lake et al. (*19*).

Determination of Free Amino Acids in Raw Potato. The free amino acids were determined in duplicate according to the modified method suitable for use with the commercially available EZ:fast amino acid kit (*20*). Freeze-dried potato sample (150 mg) was weighed into an 8 mL flat-bottom glass vial, and 4 mL of 64% ethanol in 0.5 M HCl and 200 μL of 4 mM norleucine (internal standard) were added. After a stir bar had been inserted, the vial was sealed with a screw-top cap and placed in a Reacti-Therm III heating block (Pierce, Rockford, IL), and the mixture was stirred at high speed for 1 h at 40 °C. The mixture was then centrifuged at 3000*g*, and 100 μL of the supernatant was transferred into sample preparation vials included in the EZ:fast GC-FID free amino acid kit (Phenomenex, Torrance, CA; catalog no. 90501-1430). The samples were prepared as recommended by the manufacturer and quantified using GC-FID (3400 gas chromatograph, Varian).

Preparation of French Fries. Potato samples were processed using a laboratory simulation of an industrial process followed by a finish fry. A known amount of raw material was peeled, cut into 9.5 × 9.5 mm wide strips, blanched for 15 min at 75 °C, dipped in 1.0% sodium acid pyrophosphate solution (pH 5.1), dried to a set weight loss, prefried (Frymaster H17, LO, USA) in partially hydrogenated soybean oil at 180 °C for 75 s, chilled to 10 °C, blast frozen (Gram KPS 30, Swanley, U.K.), and stored in polyethylene bags at −25 °C. To simulate final preparation, frozen prefried strips were fried at 180 °C for 3.5 min and subsequently chilled and blast frozen to facilitate preparation for analysis.

Liquid chromatograph mass spectrometer operating conditions (MS/MS mode): mobile phase, 16% methanol in 1 mM aqueous ammonium formate (isocratic); flow rate, 0.175 mL/min; injection volume, 10−20 μL; column temp, 28 °C; autosampler temp, 10 °C; ionization mode, positive ion electrospray; desolvation gas temperature, 250 °C; source temperature, 120 °C; desolvation gas flow, 525 L/h; cone gas flow, 150 L/h; collision gas pressure, 2.9×10^{-3} mbar (argon); resolution settings, ∼80% valley separation for both quadrupoles; ion energies, 0.5 and 1.0 V for quadrupoles 1 and 3; precursor ion → product ion transitions in multiple reaction monitoring (MRM): *m/z* 75 → 58 (collision energy 11 eV); *m/z* 72 → 55 (11 eV); *m/z* 72 → 54 (11 eV); *m/z* 72 → 44 (14 eV) eV; *m/z* 72 → 27 (16 eV); cone voltage, 34 V for all MRM transitions; dwell time for each MRM transition, 0.3 s; mass span, 0.1 Da; interchannel delay, 0.05−0.1 s.

Typical Food Sample Preparation and Extraction for Acrylamide Analysis. A sample (100 g) was homogenized in a blender at a maximum speed with water (500 mL) for 1 min. The homogenate (24 g) was transferred to a 50 mL centrifuge tube, and 32 μL of 25 μg/mL isotopically labeled acrylamide spiking solution and 10 mL of dichloromethane were added. The mixture was shaken at high speed on a horizontal shaker for 15 min and centrifuged at 15000 rpm (∼24000*g*) in an RC-2B centrifuge for 2 h at 4 °C. The top (water) centrifugate layer (∼10 mL) was promptly transferred to a 5 kDa centrifuge filter and centrifuged at 3500 rpm (∼4000*g*) in an RC-3B centrifuge for 4 h at 4 °C or longer if necessary.

Typical Food Sample Cleanup. Oasis HLB cartridges were conditioned with 1 × 5 mL of methanol followed by 2 × 5 mL of water, and Accucat cartridges were conditioned with 1 × 3 mL of methanol and 2 × 3 mL of water, respectively. The filtrate from the RC-3B centrifuge (2 mL) was passed through an Oasis HLB cartridge, and the cartridge was rinsed with water (1 mL) and then eluted with water (1 mL). That eluate was loaded onto an Accucat cartridge, the first 0.5 mL of eluate was discarded, and the remaining portion was collected in a vial. The cartridge was further eluted with 1 mL of water into the same vial, and the combined eluates were analyzed by LC-MS/MS.

Our modified LC-MS/MS procedure was validated for repeatability using an in-house reference material made from potato chips and with a French fry sample containing acrylamide at 800 and 60 ng/g levels, respectively. For recovery experiments, 4 g subsamples of French fry sample containing 60 ng/g of acrylamide were spiked in triplicate with acrylamide at 500, 1000, and 10000 ng/g levels.

Statistical Analysis of Data. Data were processed using SigmaStat software ver. 2.0, SigmaPlot software ver. 7.101 (SPSS, Chicago, IL).

The various models used in this paper were fitted to the data using least-squares linear regressions. The data for variables used in the generation of **Figure 4** were transformed using the log transformation in order to stabilize the variances, that is, to make the variances homogeneous across all levels of the variable. This also had the effect of making the model additive, that is, without a significant interaction.

RESULTS AND DISCUSSION

Before analysis of products, we conducted an investigation of the optimization of an SPE cleanup procedure step (results of which will be published elsewhere). For cleanup of fried

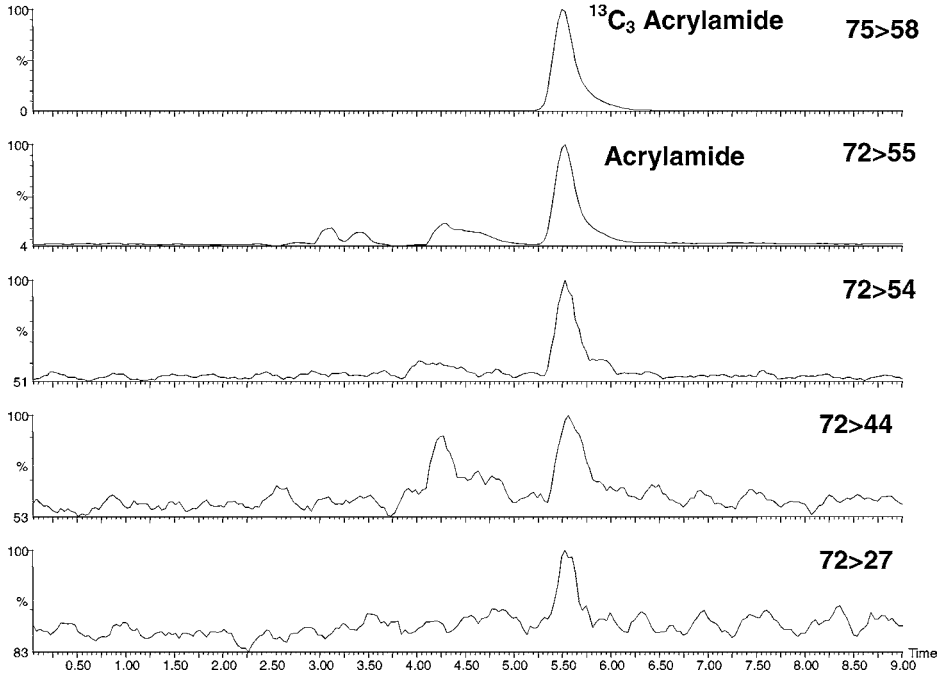

Figure 1. MRM chromatograms of a French fry sample (acrylamide concentration = 60 ng/g).

potato matrix we chose a procedure similar to that used by the U.S. FDA (*21*) with a modification step consisting of a wash of the Oasis cartridge by 1 mL of water. We found that the wash removed most inorganic and polar organic interferents and that the losses of acrylamide in the washing step were offset by a much cleaner extract.

MRM chromatograms of a French fry sample—with a 60 ng/g concentration of acrylamide—are shown in **Figure 1**. An ion transition of *m*/*z* 72 → 55 was used for the quantification of native acrylamide, whereas an ion transition of *m*/*z* 75 → 58 was used for the isotopically labeled $^{13}C_3$ acrylamide. Using a criterion of a signal-to-noise ratio of 3:1, (peak-to-peak noise definition) at the *m*/*z* 72 → 55 transition, the limit of detection was calculated as ~6 pg of standard injected on-column.

The relative standard deviation (RSD) for repeated injections (6 days over a 14 day period) of the extract of the potato chip sample (in-house reference material) containing 800 ng/g of acrylamide was 2.3% ($n = 9$). A RSD of 3.4% was obtained when replicates of the same potato chip sample were analyzed (on different days over a 14 day period) ($n = 4$). The RSD for the French fry sample containing acrylamide at a 60 ng/g level was 2.6% ($n = 6$). For samples ($n = 3$) of a mixture of the above French fry sample spiked at 500, 1000, and 10000 ng/g levels, the respective blank-corrected concentrations found (ng/g) and % RSD were, respectively, as follows: 555, 3.3%; 1090, 2.6%; and 11000, 1.5%. The five-point calibration curve (concentration of native acrylamide = 10, 25, 50, 100, and 500 ng/mL; concentration of $^{13}C_3$-acrylamide = 50 ng/mL) was linear with $r^2 = 0.9999$.

Levels of asparagine, total free amino acids and sugar (in this study defined and calculated as a sum of the three most abundant sugars, glucose, fructose, and sucrose) (mg/g of wet weight) varied in raw potato tubers from 1.5 to 11.4, from 11 to 31.5, and from 0.86 to 23, respectively. All data referred to in this paper are expressed in wet weight. The water content of potato tuber was relatively stable, with an average dry matter of 24.2% and standard deviation of 1.9%.

The procedure for extracting amino acids from potato was similar to that of Toulouee et al. (*20*). When dry potato samples ($n = 4$; an average weight of 153 mg) were fortified before extraction with a solution of asparagine (0.2 mL of 1 mg/mL), the recoveries were >95%.

Acrylamide was detected in all samples after frying at 180°C, but its concentration significantly varied from 50 to 1800 ng/g.

The relationships between the concentration of acrylamide in the final product and the concentrations of sugars and asparagine in starting materials are shown in **Table 1** and **Figure 2**.

Levels of sugars correlate well with levels of acrylamide, whereas asparagine levels alone were not strong predictors of potential levels of acrylamide in fried products. This is in agreement with the initial findings of Chuda et al. (*17*), which were based on only three samples that contained relatively low amounts (2−3 mg/fresh weight) of total free amino acids. Our results indicate a similar trend even with potatoes up to 10 times richer in amino acids. The following linear regression of sugar versus acrylamide concentrations was obtained from our experiments:

$$\text{acrylamide ng/g} = 15 + (74.1 \times \text{sugar mg/g}) \qquad (r^2 = 0.83,\ P < 0.001)$$

The levels of the three sugars were correlated ($P < 0.001$ for all, glucose − fructose, $r = 0.994$, glucose − sucrose, $r = 0.977$, sucrose − fructose, $r = 0.988$) so the linear regression data of individual sugars is listed for comparison only as the slopes are also affected by sugar ratios.

$$\text{acrylamide ng/g} = 27.1 + (241 \times \text{glucose mg/g}) \qquad (r^2 = 0.80,\ P < 0.001)$$

$$\text{acrylamide ng/g} = 50.0 + (263 \times \text{fructose mg/g}) \qquad (r^2 = 0.82,\ P < 0.001)$$

$$\text{acrylamide ng/g} = -7.9 + (176 \times \text{sucrose mg/g}) \qquad (r^2 = 0.82,\ P < 0.001)$$

The multiple linear regression of acrylamide as a function of

Table 1. Concentrations of Acrylamide in French Fries and of Asparagine and Sugars in Raw Potatoes (Wet Weight)

acrylamide (ng/g)	asparagine (mg/g)	glucose (mg/g)	fructose (mg/g)	sucrose (mg/g)
50	3.46	0.27	0.22	0.79
54	5.36	0.07	0.07	0.72
60	7.23	0.22	0.15	0.61
61	7.06	0.23	0.21	1.04
69	6.36	0.15	0.15	0.94
84	8.04	0.12	0.12	0.69
102	1.58	1.92	1.37	2.33
105	7.65	0.42	0.36	0.61
112	11.37	0.43	0.41	0.88
114	6.45	0.55	0.45	0.99
115	5.01	1.03	0.84	1.56
131	8.41	0.23	0.17	0.57
137	8.29	0.27	0.21	0.70
145	5.71	1.16	0.76	1.32
160	1.72	1.41	1.10	2.00
161	2.99	0.60	0.46	1.07
172	4.03	0.92	0.86	1.72
176	4.88	1.18	0.83	1.38
179	8.08	0.28	0.24	0.78
187	6.90	0.54	0.47	1.35
188	5.76	0.76	0.54	0.96
208	2.97	1.40	1.06	1.94
211	9.61	1.05	0.91	1.76
213	3.35	0.94	0.82	1.55
218	5.75	0.94	0.77	1.47
221	5.28	0.97	0.82	1.37
221	3.70	2.37	1.56	2.60
229	7.85	0.49	0.43	0.82
231	4.02	0.75	0.64	1.21
246	4.41	1.04	0.84	1.69
252	7.98	1.08	0.87	1.27
255	1.49	2.29	1.63	2.66
266	4.76	1.03	0.79	1.52
271	6.41	0.92	0.72	1.44
276	3.84	0.90	0.80	1.85
288	3.38	1.50	1.34	2.13
291	3.34	2.67	2.23	3.20
292	5.48	1.39	1.16	1.96
304	4.41	1.19	0.90	1.54
315	4.27	0.72	0.57	1.07
329	3.54	0.88	0.69	1.24
330	5.95	1.17	0.94	1.75
345	6.67	1.08	0.87	1.60
354	3.74	2.09	1.65	2.76
358	5.07	0.69	0.56	1.05
413	2.68	1.16	0.95	1.65
422	6.41	1.38	1.04	1.82
459	5.65	1.52	1.17	1.93
557	8.35	2.66	2.52	4.25
564	7.38	1.41	1.32	2.65
623	6.27	1.55	1.45	3.34
737	8.30	1.84	1.66	2.44
765	7.94	1.89	1.78	3.02
925	6.00	3.53	3.24	5.16
934	3.53	4.32	3.88	5.90
999	7.12	1.78	1.69	3.92
1002	3.37	5.39	4.84	7.76
1030	4.37	4.27	4.04	5.37
1062	9.16	3.99	3.78	5.99
1118	5.56	3.51	3.37	5.13
1150	4.92	4.06	3.90	5.52
1242	5.85	5.66	5.21	7.40
1320	3.26	6.28	6.11	10.60
1382	3.12	4.29	4.14	6.66
1485	4.64	5.37	4.39	6.43
1823	8.62	4.82	4.22	6.58

asparagine (Asn) and total sugars was

$$\text{acrylamide ng/g} = -196 + (35.3 \times \text{Asn mg/g}) + (76.7 \times \text{sugar mg/g})$$

($r^2 = 0.86$, $P = 0.001$, both Asn mg/g and sugar mg/g)

(sugar = glucose + fructose + sucrose)

It thus appears that asparagine (over the range of asparagine levels observed in this study) had a considerable positive effect (but not as significant as sugars) on acrylamide production.

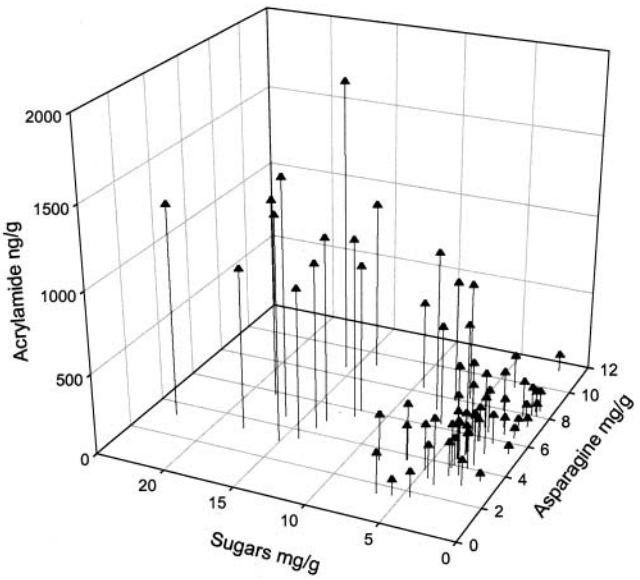

Figure 2. Concentration of acrylamide in French fries as a function of concentration of sugars and asparagine in potato tubers (wet weight).

Our single linear regression data (French fry matrix) can be compared with the data of Haase et al. (*16*) obtained from experiments on frying potato chips at 170 °C in peanut oil. Estimation of the slope of the regression lines from their diagrams was approximately 400, 2300, and 4000 ng/g of acrylamide versus mg/g of the respective sugars, sucrose, glucose, and fructose. The above values are higher than obtained in this study but the relative order is the same. We similarly calculated the slope of the regression line from Chuda's diagram (obtained from experiments at 180 °C, frying in cottonseed oil, potato chip matrix) and arrived at a slope of 4700 ng/g of acrylamide versus mg/g of glucose. A possible explanation for the much greater yield of acrylamide, as compared to our data, could be the more efficient utilization of sugars in a Maillard reaction during the frying of potato chips, which have a much greater ratio of surface/weight (and thus more reagents are available) than is found in the French fry matrix.

In our initial model experiments (*9*) (done at 175 °C) and in the model experiments of Biedermann et al. (*22*, *23*) (done at 150 °C), fructose generates more acrylamide than glucose (relative yield of fructose/glucose 1.8 ÷ 1.9), at least at these temperatures. At a temperature of 180 °C Stadler et al. (*11*) reported approximately equal activities of fructose, glucose, and sucrose in model reactions with asparagine. That might indicate influence of the temperature on the relative activities of sugars, toward the production of acrylamide, at least in some systems. Such findings can be rationalized, in part, by the fact that sucrose, a nonreducing sugar, cannot react with asparagine directly, as it needs to first undergo decomposition to reactive carbonyl compounds [sucrose has a melting point of 190−192 °C (with decomposition) but starts to undergo decomposition at temperatures >150 °C]. Perhaps the ratio of 1.03 of relative activities of fructose/glucose, obtained by Weishaar and Gutsche (*12*) in a model reaction done at 170 °C, might be skewed to a lower value due to the long heating time (60 min) used in the study.

The influence of asparagine, the other necessary component implicated in a Maillard reaction leading to the formation of acrylamide, is less obvious from **Figure 2**.

However, the influence of asparagine on the formation of acrylamide can be seen in **Figure 3**, which depicts a molar yield

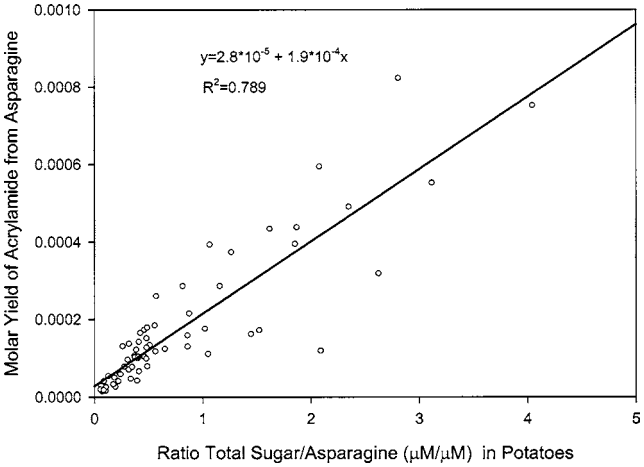

Figure 3. Molar yield of acrylamide from asparagine in French fries as a function of molar ratios of sugars and asparagine in potato tubers.

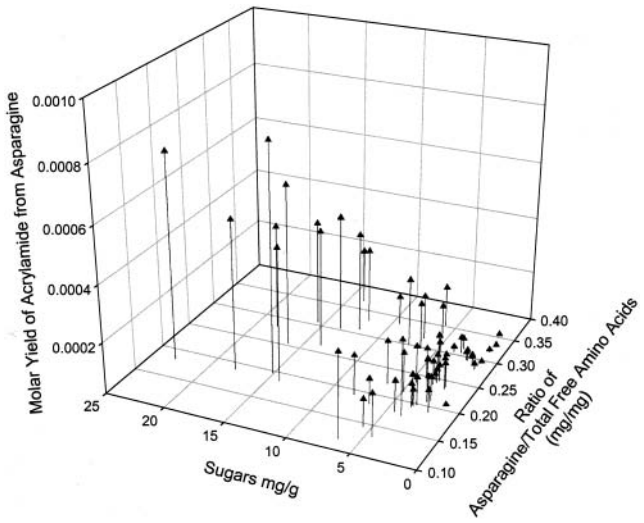

Figure 4. Molar yield of acrylamide from asparagine in French fries as a function of the ratio of asparagine to total free amino acids and sugars (wet weight).

of acrylamide from asparagine as a function of molar ratios of sugars and asparagine in starting materials. It appears that the formation of acrylamide is favored by an excess of sugars. We have seen a similar relationship in our previous model study (*9*) when acrylamide formation was enhanced when the ratio of glucose to asparagine was ≥ 1.

With the current emphasis on raw material quality for market requirements, French fry processors today invest considerable effort in obtaining material low in reducing sugars through the selection of varieties and development of growing and storage management profiles. These data suggest that existing agronomy and processing practices that minimize reducing sugars and standardize finish fry color, are in a positive way, favoring the production of finished potato products low in acrylamide.

In general, asparagine content was correlated with levels of total free amino acids in raw potatoes with a resulting ratio of ~0.3 (mg/g per mg/g). However, in a number of samples this ratio was diminished, reaching a low of 0.12. The three-dimensional relationship between acrylamide level, ratio of asparagine to total free amino acids, and sugars is shown in **Figure 4**. The plot shows a lack of a significant association between the excess of other amino acids, as compared to asparagine, and a reduced molar yield of acrylamide over the range of amino acid levels observed in this study. After logarithmic transformation (to stabilize the variance) the following equation was obtained:

$$\log \text{mol yield} = -5.06 + 1.06 \times \log \text{sugars} - 0.74 \times \log \text{ratio Asn/TAAs}$$

$$(r^2 = 0.86,\ P < 0.001,\ \log \text{sugars},\ P = 0.0003,\ \log \text{ratio Asn/TAAs})$$

Also, there was no significant correlation between any of the variables (sugars and total amino acids).

Conclusion. Our results are in agreement with earlier findings from model systems in which acrylamide formation was strongly influenced by the presence of sugars and asparagine. We have shown that by selecting potato material low in sugars (and to a lesser extent low in asparagine), acrylamide content can be substantially reduced when using an industry standard procedure and a frying temperature of 180 °C. Even if the full extent of the reduction could not be achieved for commercial reasons (e.g., organoleptic properties, availability of cultivars on a commercial scale), our study shows the importance of controlling the precursors of acrylamide. We are currently investigating other variables linked to acrylamide formation, as there are reports (*24*, *25*) that indicate temperature and/or time or process condition (soaking, additives) affect the yield of acrylamide in fried potato products. We also intend to further examine the influences of individual amino acids on the yield of acrylamide in the French fry matrix.

NOTE ADDED IN PROOF

Two relevant publications related to the "potential" of formation of acrylamide (at 120 °C, though) from precursors present in potatoes were published while the manuscript was under review (*26*, *27*).

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