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Thermally Generated 3-Aminopropionamide as a Transient Intermediate in the Formation of Acrylamide

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On the basis of the recent findings that "biogenic amines" can also be formed during thermal food processing from their parent amino acids in a Strecker-type reaction, the formation of 3-aminopropionamide, the biogenic amine of asparagine, was investigated in model systems as well as in thermally processed Gouda cheese. The results of model studies revealed that, besides acrylamide, 3-aminopropionamide was also formed in amounts of 0.1−0.4 mol % when asparagine was reacted in the presence of either glucose or 2-oxopropionic acid. Results of a second series of model experiments in which [$^{13}C_4{}^{15}N_2$]-asparagine ([$^{13}C_4{}^{15}N_2$]-Asn) and unlabeled 3-aminopropionamide were reacted together in the presence of glucose revealed a >12-fold higher efficacy of 3-aminopropionamide in acrylamide generation as compared to asparagine. Both [$^{13}C_3{}^{15}N_2$]-3-aminopropionamide and [$^{13}C_3{}^{15}N_1$]-acrylamide were formed during [$^{13}C_4{}^{15}N_2$]-Asn degradation in a ratio of about 1:4, supporting the idea that 3-aminopropionamide is a transient intermediate in acrylamide formation. In this study, 3-aminopropionamide was identified and quantified for the first time in foods, namely, in Gouda cheese. Although the fresh cheese contained low amounts of 3-aminopropionamide, its concentrations were much increased to ≈1300 μg/kg after thermal processing. In isotope labeling studies, performed by administering to the cheese [$^{13}C_4{}^{15}N_2$]-Asn in a ratio of 1:2 as compared to the "natural" concentrations of asparagine, similar ratios of unlabeled/labeled 3-aminopropionamide and unlabeled/labeled acrylamide were determined. Thus, 3-aminopropionamide could be verified as a transient intermediate of acrylamide formation during food processing.

KEYWORDS: Labeling experiments; 3-aminopropionamide; acrylamide; asparagine; Strecker reaction; Gouda cheese

INTRODUCTION

Shortly after the discovery of acrylamide as a thermally generated constituent of many processed foods (*1*), two research groups (*2*, *3*) were able to identify the free amino acid asparagine as the key precursor of acrylamide, when reacted at elevated temperatures in the presence of reducing carbohydrates, or thermal degradation products thereof. Because acrylamide is a potential carcinogen, since then, numerous efforts have been undertaken to minimize acrylamide formation during thermal food processing. Besides the reduction of temperature and processing time, other proposals include the addition of calcium chloride (*4*), amino acids (*5*, *6*), or acids (*7*−*10*), the reduction of ammonium hydrogen carbonate in the recipe (*10*−*13*), or the pretreatment of potatoes with asparaginase prior to the thermal processing (*10*, *12*−*14*).

Because influencing the formation pathway based on detailed knowledge of the possible transient intermediates would be another option to minimize acrylamide formation, several studies have been undertaken to elucidate details of the formation mechanism generating the amide from asparagine. On the basis of results of a recent comprehensive study on this topic (*15*), the direct formation of acrylamide by a thermally induced C−N bond cleavage of a glycosylamine formed from asparagine and an α-hydroxycarbonyl compound was proposed as the most probable pathway, whereas a Strecker-type degradation of asparagine via 3-oxopropionamide, or the corresponding alcohol 3-hydroxypropionamide, was more or less excluded (*15*).

In a previous investigation (*16*) we showed that 3-aminopropionamide is a very effective precursor of acrylamide, because >60 mol % of acrylamide was formed simply by thermally degrading 3-aminopropionamide at elevated temperatures without the addition of reducing carbohydrates. Because the propionamide can be regarded as the "biogenic amine" of asparagine, we proposed that its biochemical formation followed by a thermal degradation might be an alternative pathway leading to acrylamide without the need of carbohydrates (*16*, *17*). For example, using raw potato mash, we could show that 3-aminopropionamide is enzymatically formed within hours, but the formation rate was only moderate.

In a very recent study (*18*) aimed at getting a more detailed insight into the Strecker reaction, we found that aldehydes as

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well as primary amines can be formed from parent amino acids, such as phenylalanine or leucine, as a result of the Strecker degradation. These data suggest that also 3-aminopropionamide might be formed from asparagine during thermal processing of foods and, thus, might be regarded as a transient intermediate in acrylamide formation. However, up to now, no data on the occurrence of this amine in foods are available. The aim of the present investigation was, therefore, first, to quantitatively monitor the generation of 3-aminopropionamide in several model mixtures and, second, to elucidate its role in acrylamide formation in foods using Gouda cheese administered stable isotope-labeled asparagine as an example.

MATERIALS AND METHODS

Chemicals. 3-Aminopropionamide (β-alaninamide) hydrochloride was obtained from Chemos (Regenstauf, Germany), [$^2H_3$]- (98%) and [$^{13}C_3$]-acrylamide (99%) were from CIL (Andover, MA); acrylamide (99.9%), asparagine monohydrate, and glucose were from VWR International (Darmstadt, Germany); and 5-(dimethylamino)-1-naphthalene sulfonyl chloride (dansyl chloride), glycinamide hydrochloride, 2-oxopropionaldehyde (methylglyoxal), 1-hydroxypropan-2-one (acetol), 2-oxopropionic acid (pyruvic acid), norleucine, and [$^{13}C_4{}^{15}N_2$]-asparagine monohydrate were from Aldrich (Sigma-Aldrich, Steinheim, Germany). All other reagents were of analytical grade.

CAUTION: Acrylamide, as well as [$^2H_3$]- and [$^{13}C_3$]-acrylamide and dansyl chloride, is hazardous and must be handled carefully.

Model Studies. *Model I.* Binary mixtures of asparagine and either glucose or 2-oxopropionic acid (100 μmol each) were singly homogenized with silica gel (3 g; KG 60, 0.063−0.200 mm; containing 10% of water) (VWR International) and heated at 170 °C in closed glass vessels for the reaction times shown in the respective tables. After cooling, the internal standards norleucine (300−1000 μg), glycinamide (20 μg), and [$^2H_3$]-acrylamide (10−30 μg) as well as water (20 mL) were added, and the mixture was stirred for 15 min. The exact amounts of the internal standards were adjusted on the basis of results of preliminary quantitations. After ultrasonification (4 min), the suspension was centrifuged (4000 rpm; 10 min at 10 °C). The supernatant was filtered, and the amounts of the unreacted asparagine as well as those of 3-aminopropionamide and acrylamide formed were determined in the filtrate as described below.

Model II. A mixture of [$^{13}C_4{}^{15}N_2$]-asparagine (20 μmol), unlabeled 3-aminopropionamide (2 μmol), and glucose (20 μmol) was homogenized with silica gel (3 g; KG 60, 0.063−0.200 mm; containing 10% of water) and heated at 170 °C in closed glass vessels. After cooling, the internal standards norleucine, glycinamide, and [$^2H_3$]-acrylamide as well as water (20 mL) were added (for details see above) and, after equilibration, the suspension was worked up as described below.

Quantitation of 3-Aminopropionamide and [$^{13}C_3{}^{15}N_2$]-3-Aminopropionamide. To aliquots of both reaction mixtures obtained above (4 mL each) were added sodium hydrogen carbonate (20 mL; 0.25 mol/L) and dansyl chloride (8.1 mg in 10 mL of acetone), and the solution was stirred for 3 h at room temperature in the dark. After extraction four times with dichloromethane (total volume = 100 mL), the organic phases were combined and centrifuged for 5 min at 4000 rpm (10 °C) to separate the water, and the sample was analyzed by LC-MS/MS as described recently (*16*). The fragments *m*/*z* 308→156 (glycinamide; internal standard), *m*/*z* 322→156 (3-aminopropionamide), and *m*/*z* 327→156 ([$^{13}C_3{}^{15}N_2$]-3-aminopropionamide) were used to differentiate between the dansylated internal standard and the dansylated target molecules.

Quantitation of Acrylamide and [$^{13}C_3{}^{15}N_1$]-Acrylamide. Aliquots of both reaction mixtures obtained above (10 mL each) were applied onto an Extrelut NT 20 column (VWR International) and, after equilibration for 15 min, the elution of both analytes as well as the internal standard [$^2H_3$]-acrylamide was performed using ethyl acetate (100 mL). The solution was dried over anhydrous sodium sulfate and concentrated to ≈2 mL at about 20 kPa and 40 °C. This extract was directly used for GC-MS analysis as recently described (*19*). The ions *m*/*z* 72 (acrylamide), *m*/*z* 75 ([$^2H_3$]-acrylamide; internal standard), and *m*/*z* 76 ([$^{13}C_3{}^{15}N_1$]-acrylamide) were used to differentiate between both target molecules and the internal standard.

Table 1. Time Course of the Formation of 3-Aminopropionamide (3-APA) and Acrylamide (AA) in a Binary Mixture of Glucose and Asparagine (Asn) (Model I)

	3-APA		AA		Asn reacted	
reaction time (min)	concn (mmol/mol of Asn)	RSD[a] (%)	concn (mmol/mol of Asn)	RSD (%)	%	RSD (%)
5	1.6	0.91	7.8	2.9	40.8	1.3
10	2.3	0.31	14.4	9.6	69.7	2.1
20	1.9	0.16	20.6	10.2	86.5	3.9
30	3.3	0.18	16.8	1.0	93.8	5.5

[a] Relative standard deviation. Data are mean values of triplicates.

Quantitation of Asparagine and [$^{13}C_4{}^{15}N_2$]-Asparagine. Aliquots of both reaction mixtures obtained above (0.5 mL each) were dissolved in aqueous buffer, and the solution was stirred for 10 min for equilibration and, finally, filtered (0.45 μm; Spartan 13/0.45RC) (Schleicher und Schuell, Dassel, Germany). The asparagine concentrations were determined as described recently (*18*).

Isotope Labeling Studies in Gouda Cheese. To an aliquot of Gouda cheese (5 g) powdered in liquid nitrogen by means of a blendor (Moulinex, Radolfzell, Germany) was added [$^{13}C_4{}^{15}N_2$]-asparagine monohydrate (4.3 mg dissolved in water). After vortexing (10 s) and equilibration (30 min), the cheese was heated for 30 min at 180 °C. After the addition of tap water (80 mL) and the internal standards glycinamide (5 μg) and [$^{13}C_3$]-acrylamide (1.2 μg), the sample was stirred for 60 s, homogenized using an Ultraturrax (Jahnke & Kunkel, IKA-Labortechnik, Staufen, Germany) for 90 s, and ultrasonified for another 2 min. The suspension was centrifuged (10000 rpm, 10 min at 10 °C) (Beckman J2-HS, München, Germany), and the supernatant was defatted with hexane (total volume = 15 mL) and divided into two parts. These were used for the quantitation of either 3-aminopropionamide and [$^{13}C_3{}^{15}N_2$]-3-aminopropionamide or acrylamide and [$^{13}C_3{}^{15}N_1$]-acrylamide, respectively.

A second cheese sample (25 g) was thermally processed under the same conditions but without the addition of isotopically labeled asparagine. This sample was analyzed for the amounts of 3-aminopropionamide, acrylamide, and asparagine.

The quantitation of [$^{13}C_3{}^{15}N_2$]-3-aminopropionamide, 3-aminopropionamide, and asparagine was performed using the methods previously described (*18*). The quantitation of acrylamide and [$^{13}C_3{}^{15}N_1$]-acrylamide in the cheese samples was performed after derivatization with 2-mercaptobenzoic acid (*19*) to avoid peak overlapping caused by the cheese matrix.

RESULTS AND DISCUSSION

Model Experiments. At present, quantitative data neither on the amounts of 3-aminopropionamide formed from asparagine in model reactions nor in foods are available. Therefore, following the idea that 3-aminopropionamide is a transient intermediate in acrylamide formation in a Maillard-type reaction of a reducing sugar and asparagine, first, glucose and the amino acid were reacted in a model system with a low water content. The amounts of 3-aminopropionamide and acrylamide generated over time were monitored until the available asparagine was completely degraded (after 30 min). The results indicated (**Table 1**) that already after 5 min significant amounts of acrylamide as well as of 3-aminopropionamide were generated. 3-Aminopropionamide was measured with the highest amount in the sample reacted for 30 min; the acrylamide concentration was highest after 20 min. Although the amounts of 3-aminopropionamide were always lower as compared to acrylamide, in particular, the quite high concentrations of up to 0.3 mol % present after 30 min suggested that the propionamide might be a transient intermediate in acrylamide formation.

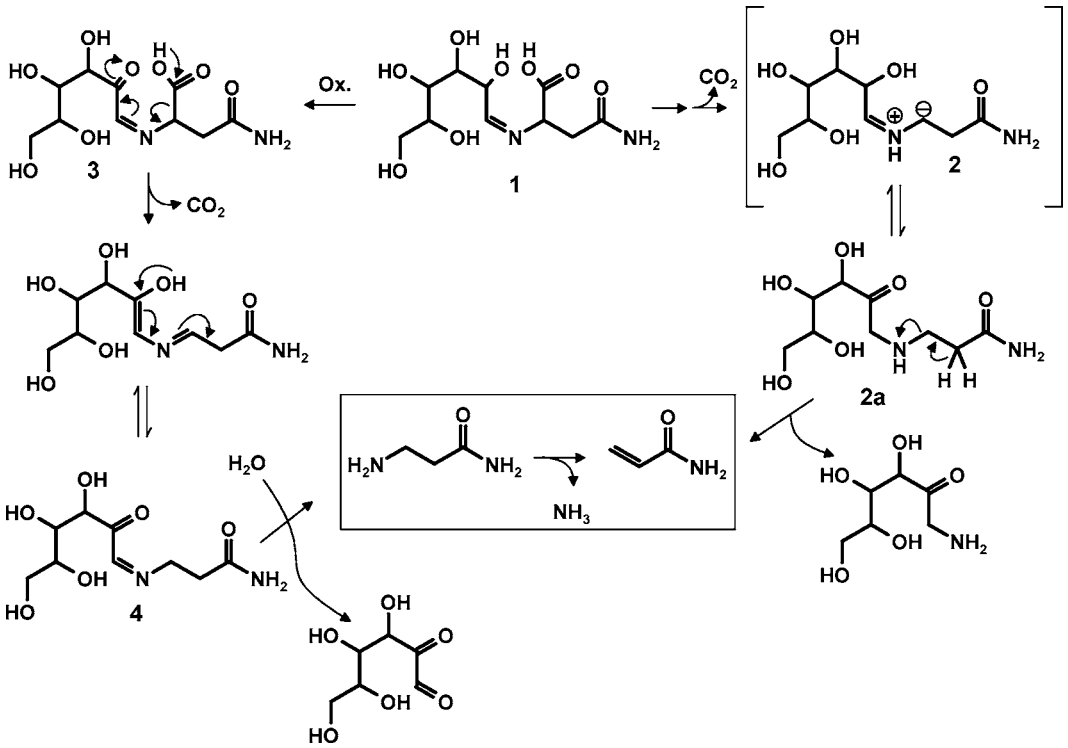

Figure 1. Possible degradation pathway of a glycosylamine of asparagine either leading directly to acrylamide via intermediates **2**/**2a** (based on a hypothesis given in ref *15*) or generating 3-aminopropionamide as a transient intermediate via intermediates **3** and **4**.

Table 2. Generation of 3-Aminopropionamide (3-APA) and Acrylamide (AA) in a Binary Mixture of Asparagine (Asn) and 2-Oxopropionic Acid (Model I)

	3-APA		AA	
reaction time (min)	concn (mmol/ mol of Asn)	RSD[a] (%)	concn (mmol/ mol of Asn)	RSD (%)
5	3.0	0.9	0.08	18.1
10	2.1	1.1	0.3	12.5
20	2.8	0.8	1.6	11.9
30	4.3	0.5	1.0	8.8

[a] Relative standard deviation. Data are mean values of triplicates.

Table 3. Time Course of the Degradation of Labeled Asparagine ($[^{13}C_4{}^{15}N_2]$-Asn) and Unlabeled 3-Aminopropionamide (3-APA) When Heated Together in the Presence of Glucose (Model II)

	$[^{13}C_4{}^{15}N_2]$-Asn		3-APA	
reaction time (min)	amount reacted (%)	RSD[a] (%)	amount reacted (%)	RSD (%)
2.5	16.5	5.4	26.3	5.8
5	31.8	9.8	56.9	8.3
10	72.0	0.1	79.7	3.4
20	95.3	1.2	92.5	5.2

[a] Relative standard deviation. Data are mean values of quadruplicates.

When the same experiment was performed, but with glucose replaced by 2-oxopropionic acid (**Table 2**), the time courses of 3-aminopropionamide and acrylamide formation differed from those obtained in the glucose/asparagine mixture. The reaction with 2-oxopropionic acid generated quite high amounts of 3-aminopropionamide already after a short heating period of 5 min, whereas the acrylamide generation was delayed. Because, as compared to the glucose reaction, lower amounts of acrylamide were formed, the data suggest the occurrence of different pathways in acrylamide formation from asparagine depending on the available "catalyst" initiating the decarboxylation/deamination of asparagine. However, on the other hand, the results clearly showed that 3-aminopropionamide is not only a minor degradation product of asparagine when reacted in the presence of glucose or α-oxocarbonyls.

On the basis of literature results (*15*), it can be suggested that 3-aminopropionamide and acrylamide are formed from glycosylated asparagine as shown on the right side of **Figure 1**. In a first step, the glycosylamine formed from asparagine and, for example, a hydroxycarbonyl compound (**1**; **Figure 1**) should undergo a decarboxylation leading to an ylide (**2**; **Figure 1**), which, after a rearrangement into **2a**, should directly generate acrylamide by cleavage of the C−N bond. This pathway would, however, not easily generate 3-aminopropionamide. Therefore, it can also be assumed that the glycosylamine is first oxidized into an oxo-imine (**3**; **Figure 1**). Such oxidation reactions are well-known to occur in the presence of, for example, trace amounts of metal ions and have previously been proven for the oxidation of Amadori compounds (*20*). Compound **3** would then easily undergo a decarboxylation leading to the oxo-imine **4**, which is finally hydrolyzed into 3-aminopropionamide (left side of **Figure 1**). Although such hydrolytic reactions might not be favored under the conditions used in this study, we could previously show that water is clearly an important reactant needed to form acrylamide (*17*). Intermediates structurally related to compound **4** can also directly be formed from asparagine and α-dicarbonyl compounds, such as deoxyosones or 2-oxopropionaldehyde, in a Strecker-type reaction.

Assuming that 3-aminopropionamide is a transient intermediate in acrylamide formation, its degradation rate must, at least, be of the same order of magnitude as that of asparagine, when reacted in the presence of glucose. Because in such experiments the degradation of the 3-aminopropionamide used as educt and the 3-aminopropionamide formed by asparagine degradation must be differentiated, a mixture of isotopically labeled asparagine and unlabeled 3-aminopropionamide was reacted with

Table 4. Time Course of the Formation of Labeled 3-Aminopropionamide ([$^{13}C_3{}^{15}N_2$]-3-APA) and Labeled Acrylamide ([$^{13}C_3{}^{15}N_1$]-AA) from Labeled Asparagine ([$^{13}C_4{}^{15}N_2$]-Asn) in Comparison to Unlabeled Acrylamide (AA) Formed from Unlabeled 3-Aminopropionamide (3-APA) When Reacted in the Presence or Absence of Glucose (Model II)

	[$^{13}C_3{}^{15}N_1$]-AA		[$^{13}C_3{}^{15}N_2$]–3-APA		AA	
reaction time (min)	concn (mmol/mol of [$^{13}C_4{}^{15}N_2$]-Asn)	RSD[a] (%)	concn (mmol/mol of [$^{13}C_4{}^{15}N_2$]-Asn)	RSD (%)	concn (mmol/ mol of 3-APA)	RSD (%)
2.5	2.7	12.9	0.6	11.1	31.4	9.1
5	5.5	16.0	1.4	10.8	72.8	10.2
10	11.8	1.0	3.9	8.9	158.1	2.4
20	12.5	7.0	2.6	5.1	180.6	5.3
2.5[b]	0.01	12.1	0.5	11.5	14.9	18.1
5[b]	0.01	14.2	0.7	14.2	43.4	8.4
10[b]	0.04	11.6	1.1	3.8	113.4	0.5
20[b]	0.12	15.2	1.0	9.9	285.2	5.2

[a] Relative standard deviation. Data are mean values of quadruplicates. [b] Reaction was performed in the absence of glucose.

glucose. The results of the quantitations (**Table 3**) indicated a much more rapid degradation of the (unlabeled) 3-aminopropionamide as compared to asparagine, in particular, after 150 or 300 s, respectively. Thus, it can be concluded that a reaction cascade leading to acrylamide from asparagine via 3-aminopropionamide is very probable (left side in **Figure 1**). Interestingly, after 10 and 20 min, respectively, the degradation rates of asparagine and 3-aminopropionamide were nearly identical.

Following the two pathways indicated in **Figure 1**, either predominantly labeled acrylamide (right side in **Figure 1**) or a mixture of labeled 3-aminopropionamide and labeled acrylamide (left side in **Figure 1**) should be generated from labeled asparagine in the model system. In addition, from the unlabeled 3-aminopropionamide, unlabeled acrylamide should be generated. Quantitation of the respective target molecules (**Table 4**) revealed the generation of significant amounts of [$^{13}C_3{}^{15}N_1$]-acrylamide from labeled asparagine and glucose (**Table 4**). The generation of [$^{13}C_3{}^{15}N_1$]-acrylamide and [$^{13}C_3{}^{15}N_2$]-3-aminopropionamide followed a time course similar to that found for the degradation of unlabeled asparagine (**Table 1**). From the unlabeled 3-aminopropionamide, which was reacted in parallel with labeled asparagine, high amounts of unlabeled acrylamide were formed (**Table 4**) and the yields were always >12-fold higher than those from labeled asparagine/glucose. These data clearly indicate that 3-aminopropionamide is a very potent precursor of acrylamide, and its degradation is obviously not much affected, for example, by a reaction with degradation products of glucose, which are, certainly, formed in the reaction system. The results also suggest that, once the 3-aminopropionamide is formed during asparagine degradation, acrylamide will very effectively be generated.

Another interesting result was obtained when the same mixture was reacted in the absence of glucose: As expected, the amounts of labeled 3-aminopropionamide and labeled acrylamide formed from [$^{13}C_4{}^{15}N_2$]-asparagine were much reduced as compared to the reaction in the presence of glucose (**Table 4**), but both degradation products were formed. These data indicate for the first time that asparagine does not necessarily need a reducing sugar to form acrylamide. Obviously at higher temperatures a direct decarboxylation/deamination of asparagine can also occur (**Figure 2**). This result would explain that acrylamide has been detected in nearly all processed foods, because low amounts of free asparagine are certainly present

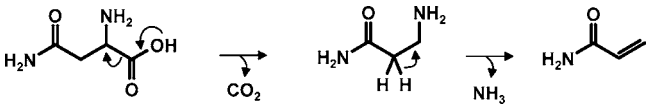

Figure 2. Possible generation of acrylamide by a direct decarboxylation/deamination of asparagine.

Table 5. Concentrations of Asparagine (Asn), 3-Aminopropionamide (3-APA), and Acrylamide (AA) in Gouda Cheese before and after Thermal Treatment

	Asn		3-APA		AA	
sample	concn (mg/kg)	RSD[a] (%)	concn (μg/kg)	RSD (%)	concn (μg/kg)	RSD (%)
unprocessed	1790	5.2	4.4	3.6	nd[b]	
processed	861	6.1	1324	2.7	189	8.9

[a] Relative standard deviation. Data are mean values of triplicates. [b] Not detectable (<10 μg/kg).

Table 6. Comparison of the Concentrations of Labeled 3-Aminopropionamide ([$^{13}C_3{}^{15}N_2$]-3-APA) and Labeled Acrylamide ([$^{13}C_3{}^{15}N_1$]-AA) with the Respective Unlabeled Compounds in a Thermally Treated Gouda Cheese Administered [$^{13}C_4{}^{15}N_2$]-Asparagine (860 mg/kg)

reaction product	concn[a] (μg/kg)	concn (mmol/mol of Asn or [$^{13}C_4{}^{15}N_2$]-Asn)	RSD[b] (%)
[$^{13}C_3{}^{15}N_2$]-3-APA	2106	4.12	3.6
[$^{13}C_3{}^{15}N_1$]-AA	90	0.22	12.4
3-APA	7165	6.0	2.0
AA	420	0.44	12.2

[a] Calculated on the basis of fresh weight. [b] Relative standard deviation. Data are mean values of triplicates.

in any food. The formation of acrylamide can also be assumed, for example, by a decarboxylation of fumaramic acid, which was earlier identified as a degradation product of asparagine (*21*).

As found in our previous study (*16*), the absence of glucose did, however, not much affect the formation of unlabeled acrylamide from unlabeled 3-aminopropionamide (**Table 4**). The concentrations of unlabeled acrylamide were even higher at 20 min of heating time as compared to the model system containing glucose, thereby corroborating that the generation of acrylamide is very effective if 3-aminopropionamide has been generated in a previous reaction step.

Gouda Cheese. To date, 3-aminopropionamide has never been reported as a food constituent. Because cheeses are known to contain a series of biogenic amines, it might be possible that 3-aminopropionamide is a natural constituent of such fermented dairy products. Therefore, 3-aminopropionamide and, in addition, acrylamide were quantified in a commercial Gouda cheese. The quantitative data indicated quite low amounts of 3-aminopropionamide (**Table 5**), showing that a biogenic formation of 3-aminopropionamide is not very probable. However, after thermal processing of the cheese in a baking oven for 30 min at 180 °C (cheese was brown, but still palatable), a tremendous increase of 3-aminopropionamide as well as of acrylamide was measured. The formation of both compounds was accompanied by a significant degradation of the free asparagine present in the cheese (**Table 5**).

To elucidate whether 3-aminopropionamide can also be regarded as a transient intermediate in acrylamide formation in processed cheese, the following experiment was performed: The cheese material was finely ground, and [$^{13}C_4{}^{15}N_2$]-asparagine

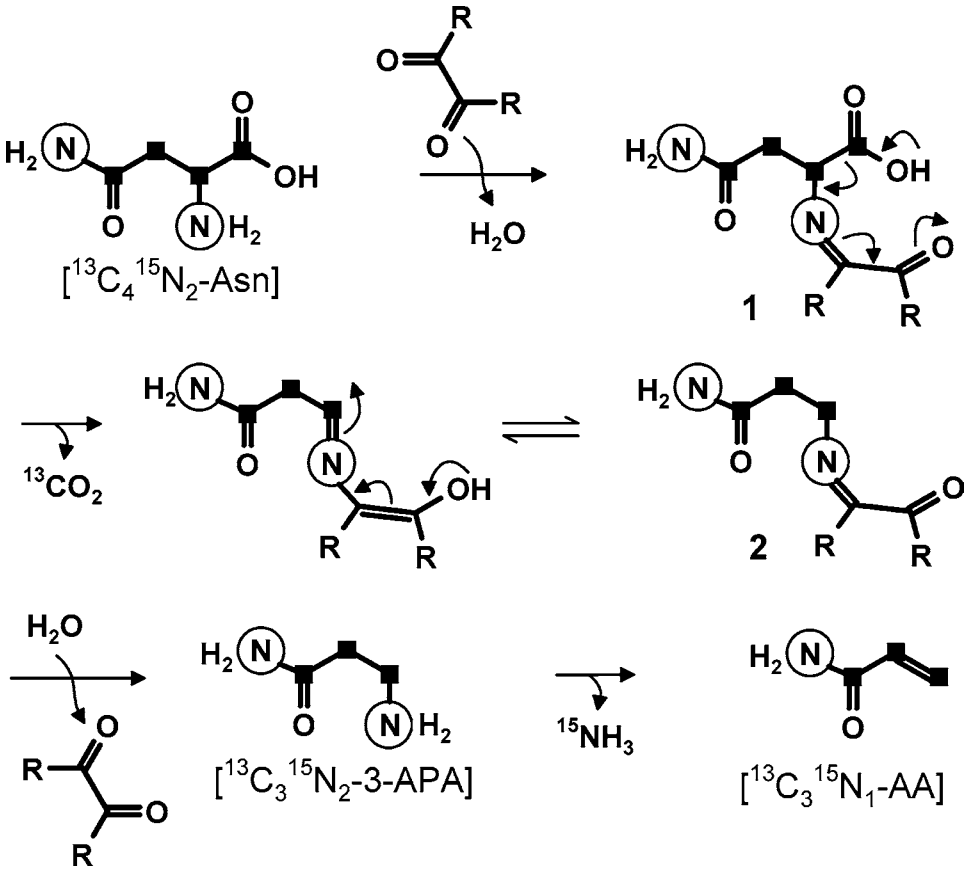

Figure 3. Reaction pathway suggesting 3-aminopropionamide as a transient intermediate in acrylamide formation in foods via a Strecker-type degradation: hypothesis based on the stable isotope labeling study in cheese (■, carbon-13 label; Ⓝ, nitrogen-15 label).

was added in a ratio of 1:2 as compared to the amount of free asparagine already present in the cheese. After thermal processing, the amounts of four target compounds, namely, 3-aminopropionamide, [$^{13}C_3{}^{15}N_2$]-3-aminopropionamide, acrylamide, and [$^{13}C_3{}^{15}N_1$]-acrylamide, were quantified. If the formation of acrylamide from asparagine proceeds via 3-aminopropionamide as intermediate, at least the quantitative ratios of both products should be similar. The results obtained (**Table 6**) indicated that high amounts of labeled as well as unlabeled 3-aminopropionamide were formed, both showing molar yields in the same area of magnitude (4.12 and 6.0 mmol, respectively) as compared to the amounts of the precursors asparagine and [$^{13}C_4{}^{15}N_2$]-Asn. Also, the molar yields of labeled and unlabeled acrylamide (0.22 and 0.44 mmol, respectively) were well correlated with the amounts of the labeled and unlabeled asparagine as well as the labeled and unlabeled 3-aminopropionamide, respectively.

In the experiment with labeled asparagine (**Table 6**), for cost reasons, a lower amount of cheese was used. This obviously caused the formation of different concentrations for 3-aminopropionamide and acrylamide, respectively, as compared to the data given in **Table 5**.

In summary, the data allow the conclusion that different pathways may lead from asparagine to acrylamide. However, the Strecker degradation should not be excluded in this process, because the structure of an aza-vinylogous β-keto acid (**1** in **Figure 3**), which can also be formed from asparagine and a hydroxycarbonyl compound (**3** in **Figure 1**), should facilitate asparagine decarboxylation. Once intermediate **2** (**Figure 3**) is formed, its hydrolysis yields 3-aminopropionamide, which in turn generates acrylamide upon heating.

However, it must be considered that it is not the Strecker aldehyde which can be regarded as the key intermediate, but 3-aminopropionamide, the Strecker amine of asparagine as detailed in ref *17*. Therefore, any parameter forcing the Strecker reaction to form the aldehyde, but not the amine, would avoid acrylamide formation.

Further investigations on the occurrence of 3-aminopropionamide in foods are underway.

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