

## ACRYLAMIDE AND QUINAZOLINDION: INDUSTRIAL APPLICATION

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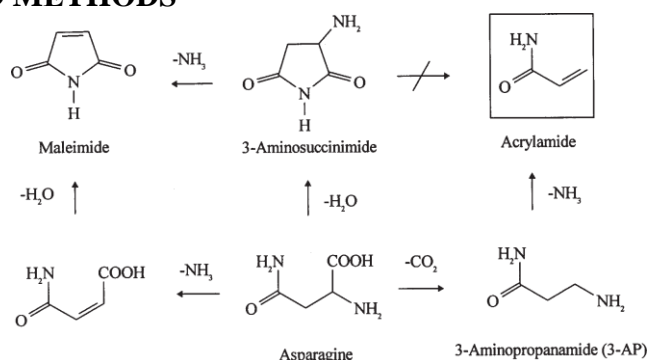
**Annotation:** Earliest reports on the origin of acrylamide in food have confirmed asparagine as the main amino acid responsible for its formation. Available evidence suggests that sugars and other carbonyl compounds play a specific role in the decarboxylation process of asparagine, a necessary step in the generation of acrylamide. It has been proposed that Schiff base intermediate formed between asparagine and the sugar provides a low energy alternative to the decarboxylation from the intact Amadori product through generation and decomposition of oxazolidin-5-one intermediate, leading to the formation of a relatively stable azomethine ylide.

**Keywords:** acrylamine, product, decarboxylation, industry, method.

### INTRODUCTION

This paper describes the progress made to date in understanding the fundamental mechanistic aspects of the formation of acrylamide. Essentially all experiments were conducted in a laboratory environment, and their validity in food remains to be assessed.

### MATERIALS AND METHODS



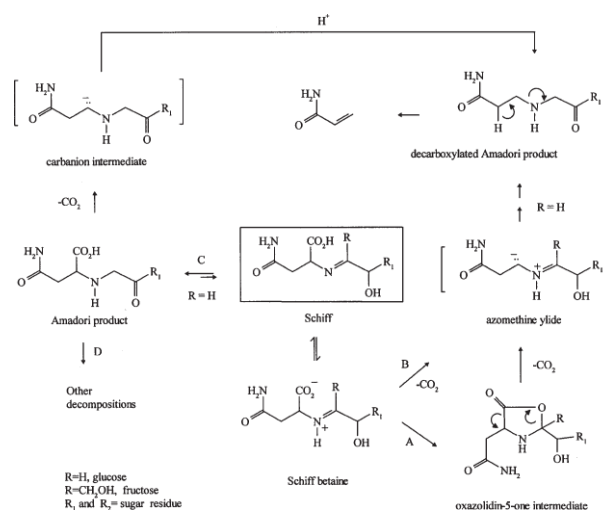
**Figure 1. Thermal degradation of asparagine.**

Initial investigations that followed the discovery of acrylamide in cooked food have led not only to the unambiguous identification of asparagine as the main amino acid precursor of acrylamide, but has also confirmed that the 3 carbon backbone of acrylamide and the amide nitrogen originate from corresponding locations in asparagine in model system studies using N and C-labeled precursors. Although thermally allowed decarboxylation and deamination reactions of asparagine alone, in principle, can produce acrylamide (Figure 1), the presence of sugars was necessary to effect the conversion of asparagine into acrylamide. Subsequent studies have indicated that any carbonyl-containing moiety can perform a similar transformation and that asparagine alone prefers to undergo intramolecular cyclization and form an imide (Figure 1) rather than decarboxylate and form acrylamide.

### RESULTS AND DISCUSSION

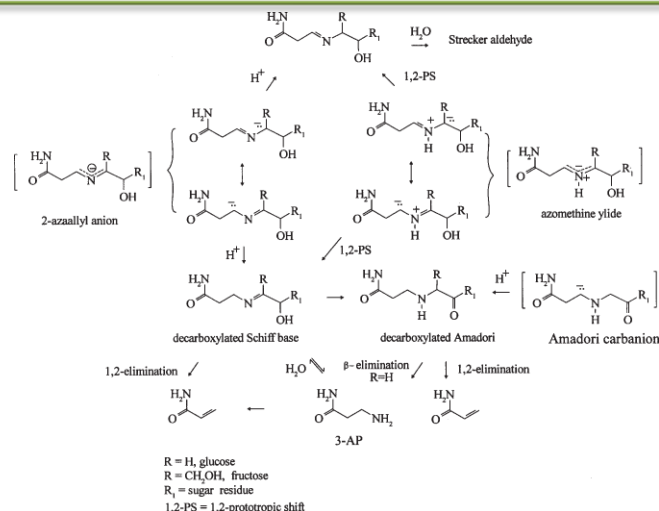
The first 2 reports (1, 2) published on the origin of acrylamide in food had entirely different perspectives on the mode of sugar-assisted decarboxylation of asparagine. Mottram et al. (1) proposed a known oxidative decarboxylation process known as Strecker degradation (7), which is a well established process in thermally generated aroma formation in food (1); however, this process will not

only decarboxylate asparagine but also at the same time oxidize it into Strecker aldehyde that needs further reduction and dehydration steps to be converted into acrylamide. On the other hand, Stadler et al. (2) reported the unexpected discovery of asparagine *N*-glycoside or Schiff base (Figure 2), the initial interaction product between glucose and asparagine, as the direct precursor of acrylamide, producing higher yields than any of the corresponding more stable Amadori product (Figure 2) or the sugar and asparagine mixtures. This critical finding provided the initial clues for the first detailed mechanism that linked decarboxylation to the presence of open form of asparagine *N*-glycoside (Schiff base) as proposed by Yaylayan et al. (Figure 2).



**Figure 2. Proposed mechanisms of formation of acrylamide by Yaylayan et al. (pathway A) and by Zyzaket al. (pathway B).**

The proposed mechanism was based on the known ability of imines (or Schiff betaines) formed between amino acids and aldehydes to undergo intramolecular cyclization (Figure 2, pathway A) initiated by the carboxylate anion and formation of oxazolidin-5-one intermediate (Figure 2). Manini et al. observed the formation of such an intermediate and its facile decarboxylation at room temperature in D-glucose/L-DOPA model system. However, literature evidence indicates that amino acids in the presence of carbonyl compounds such as aromatic aldehydes or ninhydrin undergo decarboxylation through the formation of oxazolidin-5-one intermediate. On the other hand, if the asparagine *N*-glycoside (Schiff base) is allowed to undergo Amadori rearrangement without decarboxylation, it can still undergo this step, but at much higher temperatures because the developing negative charge on the Amadori carbanion intermediate (Figures 2 and 3) is not stabilized similar to azomethine ylide. However, at this high temperature, competition with intramolecular cyclization to form *N*-substituted succinimide Amadori product might hinder acrylamide formation even further. According to Figure 3, both decarboxylated species, the Schiff base and Amadori products, are capable of generating acrylamide either directly or indirectly through release of 3-aminopropanamide (3-AP).



**Figure 3. Proposed role of reactive intermediates 2-azaallyl anion, azomethine ylide, and Amadori carbanion in the generation of acrylamide.**

## CONCLUSION

Thus, the food matrix adds to the complexity of elucidating reaction pathways in food, and confirms earlier observations that each food category needs careful and individual study. Furthermore, and owing to the importance of the Maillard reaction to the overall quality of manufactured foods, the process of decoupling aromagenesis from reactions leading to the formation of undesirable chemicals, therefore, becomes one of the main challenges that we face today.

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