Effect of Antioxidants on Acrylamide Content in Model Systems

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INTRODUCTION to ACRYLAMIDE

- Acrylamide (AA) is a chemical toxicant and is estimated to be present in foods that make up 40% of daily calorie consumption
- The European Commission set benchmark levels for AA content in standard food products in 2018, and these limits are being lowered this year (2023)[1]
- Classified as a Class 2A carcinogen by the International Agency for Research on Cancer
- Maillard reaction by-product
  - Especially prevalent in carbohydrate-rich foods cooked at high temperatures (>120˚C)
  - Produced simultaneously with desirable colour and flavour compounds
- Formed via the reaction between asparagine and a carbonyl source. The latter is commonly a reducing sugar, but lipid oxidation products can also play a role[2]
- Can be degraded into break-down products with continued heating
- Antioxidants have been investigated as additives to reduce AA levels, although their structure and concentration drastically affect their efficacy[3]

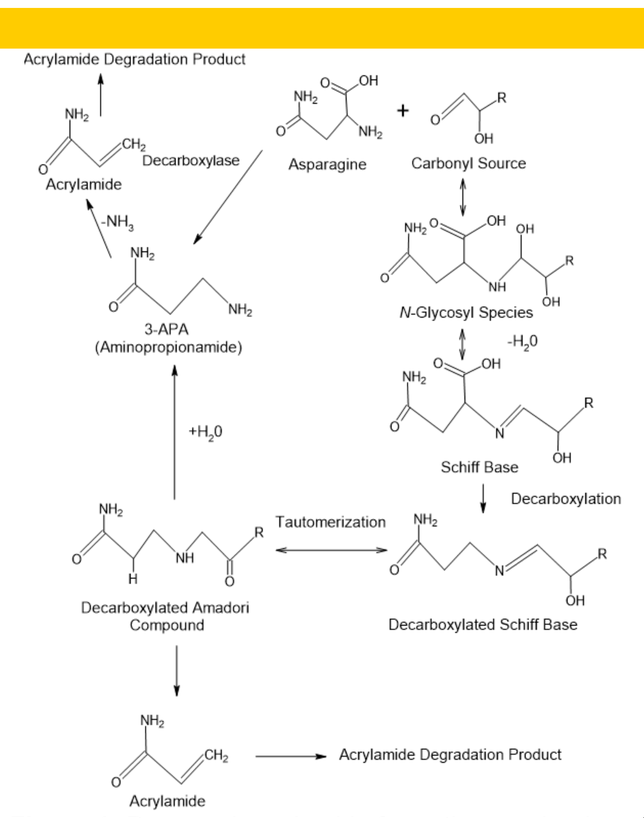

Figure 1: Proposed acrylamide formation mechanisms[4]

MATERIALS and METHODS

- Equimolar (25 mM) model systems were prepared using asparagine and glucose in 0.1 M phosphate buffer system (pH=6.80)
- 0-12.5 mM of antioxidants (ferulic acid, gallic acid, or glutathione) were added
- Model systems were heated in sealed reaction tubes in a circulating oil bath at 150 ˚C for 30 minutes, after which they were immediately cooled in an ice bath
- The AA content was quantified using reversed-phase HPLC equipped with a UV/diode array detector, and AA was detected at 200 nm and quantified using an external standard, with a calibration line prepared with AA concentrations from 0.01 to 10 µg/mL (r^2=0.9993)

ANTIOXIDANT MECHANISMS of ACTION

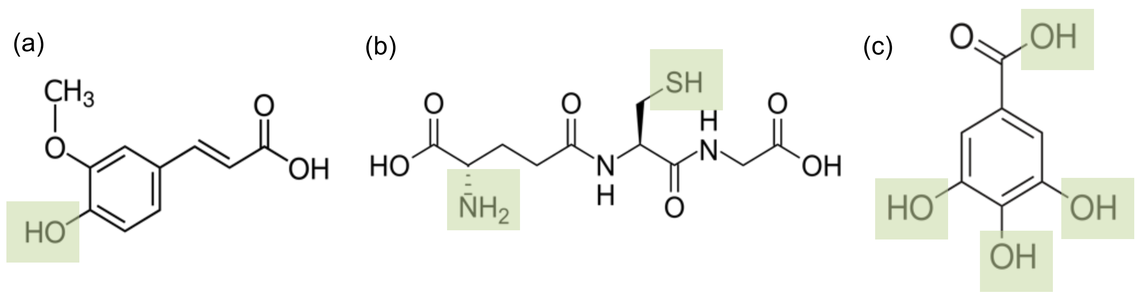

Figure 2: Structure of (a) ferulic acid, (b) glutathione, and (c) gallic acid, with relevant chemical groups highlighted.

- Ferulic acid scavenges free radicals with a phenolic hydroxyl group, preventing a decrease in AA content by preventing free-radical induced elimination[5]
  - > Oxidized ferulic acid increases free-radical induced elimination and significantly decreases AA[6]
- Glutathione competes with asparagine for glucose in the AA formation reaction, and can also form a Michael adduct with AA via the thiol group (an amino group in close proximity accelerates this reaction)
  - > The Michael addition however can re-form 3-aminopropionamide which can then increase the AA content
- Gallic acid has multiple phenolic hydroxyl groups that act as hydrogen donors in a quinone-amine interaction between flavonoids and 3-aminopropionamide, blocking the formation of AA

ACRYLAMIDE MITIGATION in MODEL SYSTEMS

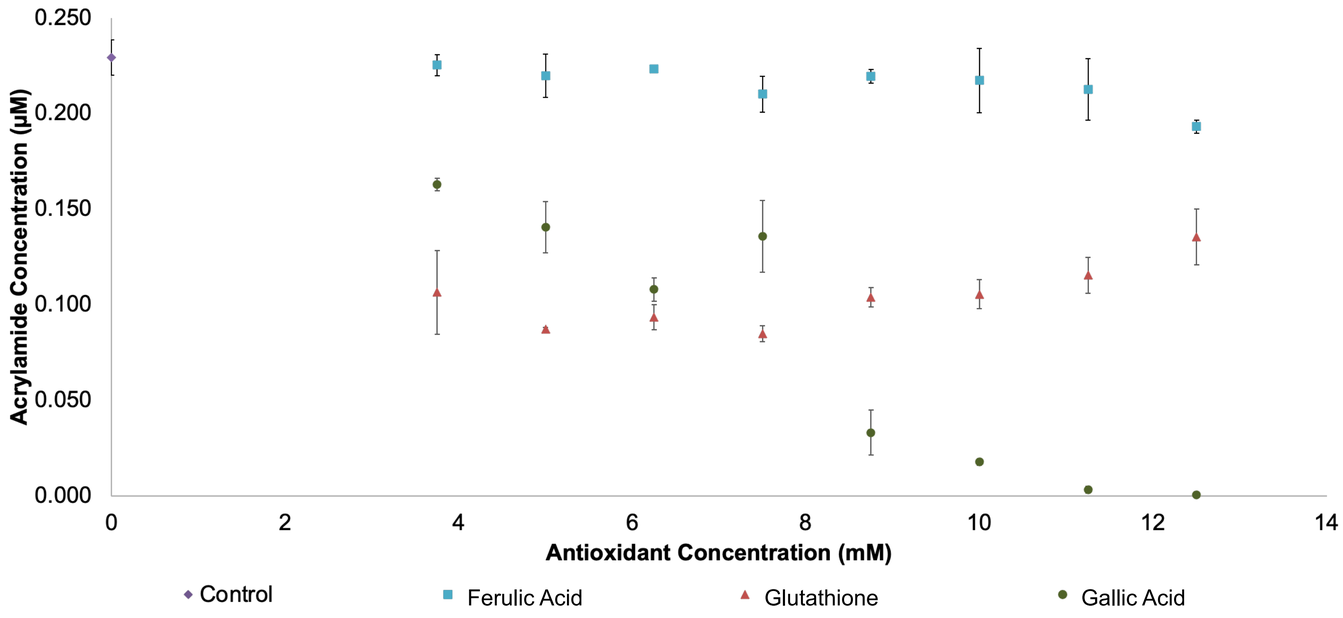

Figure 3: AA concentration (µg/mL) after heating (30 min, 150 ˚C) in equimolar (25 mM) asparagine-glucose model systems, with 0-12.5 mM of antioxidant added

- Ferulic acid
  - The addition of ferulic acid at any studied level had no significant effect on the final AA content
  - In previous work, ferulic acid had an AA promoting effect while oxidized ferulic acid caused a significant decrease in AA[5,6]
- Glutathione
  - Glutathione has an optimal addition level between 5 and 7.5 mM, however all concentrations of glutathione decrease acrylamide content compared to the control
  - Glutathione has been shown to decrease AA in both model systems and baked cookies[7]
- Gallic acid
  - Acrylamide content decreases with increasing gallic acid concentration (with an outlier at the 7.5 mM addition level)
  - In previous works, gallic acid had no effect on acrylamide contents in an aqueous system, but significantly reduced AA in emulsion based models[8,9]

CONCLUSIONS

- Final AA content was reduced by the addition of gallic acid and glutathione
- The structure and mechanism of the chosen antioxidant has a large impact on the efficacy of that antioxidant in the selected matrix
- Insight in the structure and mechanism of antioxidants should guide the selection of antioxidants in order to most effectively decrease AA content

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