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Research Article

Chlorogenic acid increased acrylamide formation through promotion of HMF formation and 3-aminopropionamide deamination

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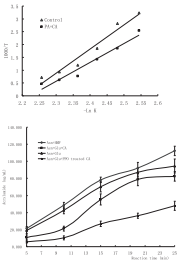
HIGHLIGHTS

- Chlorogenic acid increased the formation of acrylamide while its quinone one inhibited.
- Chlorogenic acid increased acrylamide formation by enhancing HMF production.
- It decreased the activation energy for conversion of 3-APA to acrylamide.
- It kept high redox potential that may inhibited acrylamide elimination.

GRAPHICAL ABSTRACT



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ABSTRACT

This research was aimed to investigate why chlorogenic acid, presents at high concentrations in some food raw material, influences acrylamide formation. In the asparagine/glucose Maillard reaction system (pH = 6.8), addition of chlorogenic acid significantly increased acrylamide formation and inhibited its elimination. In contrast, the quinone derivative of chlorogenic acid decreased acrylamide formation. Three mechanisms may be involved for increasing acrylamide formation by chlorogenic acid. Firstly, it increased the formation of HMF, which acts as a more efficient precursor than glucose to form acrylamide. Secondly, it decreased activation energy for conversion of 3-aminopropionamide (3-APA) to acrylamide (from 173.2 to 136.6 kJ/mol), and enhances deamination from 3-APA. And thirdly, it prevented attack of the produced acrylamide from free radicals by keeping high redox potential during the Maillard reaction.

1. Introduction

Acrylamide is a food contaminant formed mainly through Maillard reaction during high-temperature processing. It has neurotoxic and genotoxic properties, and is known to act as a carcinogen in rodents [1]. The contents of acrylamide vary among different types of food. Fried potato chips, coffee and toasted chicory contain much higher levels of acrylamide than other high temperature-processed foods [1,2], with the highest reported concentrations of 12,000, 539, and 4015 μg/kg, respectively [3–5].

Food ingredients play an important role in acrylamide formation. A considerable number of antioxidants, including vitamin C, vitamin E, ferulic acid, tert-butylhydroquinone, butylated hydroxyanisole, butylated hydroxytoluene, epigallocatechin gallate, sodium erythorbate, antioxidants from bamboo leaves, tea polyphenols, and spice extracts have all been reported to influence acrylamide formation [6–11]. However, reports on relationships

Abbreviations: 3-APA, 3-aminopropionamide; Asn, asparagine; CA, chlorogenic acid; Ea, activation energy; Glu, glucose; HMF, hydroxymethylfurfural; ORP, oxidation–reduction potential; PBS, phosphate buffer solution; PPO, polyphenol oxidase.

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between antioxidants and acrylamide contents in food have been controversial [11].

Coffee beans and potato tubers contain high concentrations of chlorogenic acid (41,640 and 1481 mg/kg, respectively) [12,13], which can be oxidized to quinone by polyphenol oxidase during processing steps such as peeling and cutting [14]. It was reported that addition of chlorogenic acid at low level (30 μmol/100 g) or at very high level (1 mmol/ml) decreased acrylamide formation both in biscuits and and asparagine/glucose reaction model [15,16]. However, the mechanisms underlying this effect remain to be investigated. In the present study, we investigated the effects of chlorogenic acid at moderate concentration (50 μmol/ml) and its quinone derivative (prepared using polyphenol oxidase instead of hydrogen peroxide as we previously reported) [17], on the formation of acrylamide during high-temperature processing, focusing on the mechanism by which it promotes deamination of 3-APA and HMF formation.

2. Experimental

2.1. Chemicals

Chlorogenic acid, HMF, asparagine, and glucose were purchased from Aladdin Reagents Database Inc. (Shanghai, China). Acrylamide standard (>99.8%) and $^{13}C_3$-labeled acrylamide (99%) were obtained from Sigma-Aldrich Company (St. Louis, MO, USA) and Merck-Schuchardt (Hohenbrunn, Germany), respectively. 3-Aminopropionamide hydrochloride (β-alaninamide hydrochloride, 3-APA) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). High-performance liquid chromatography (HPLC)-grade methanol and polyphenol oxidase (845 U/mg) were obtained from J. T. Baker (USA) and Worthington Biochemical Corporation (Lakewood, NJ, USA), respectively.

2.2. Effects of chlorogenic acid and its quinone derivative on acrylamide formation

An equimolar asparagine/glucose Maillard reaction system was used to investigate the effects of chlorogenic acid on acrylamide formation. Each 20-ml stainless-steel test tube contained 4 ml of 0.1 M phosphate buffer solution (PBS, pH = 6.8) with different concentrations of chlorogenic acid (both phenol and quinone type, at addition levels of 0.002, 0.02, and 0.2 mmol, respectively), 1 mmol asparagine and 1 mmol glucose. The test tubes were capped with Teflon pad-filled stainless steel cap and the mixtures were heated at 160 °C in an oil bath installed with a magnetic stirrer for 20 min. After cooling, the reaction mixtures were decanted into 14-ml centrifuge tubes and deionized water was added to make a total volume of 10 ml in each tube. The mixtures were then centrifuged at 4000 rpm for 20 min on an Allegra 21 R centrifuge (Beckman, USA). Concentrations of acrylamide and HMF in the supernatant were then determined.

The quinone derivative of chlorogenic acid was prepared using polyphenol oxidase. Chlorogenic acid (5 mmol) and 100 mg of polyphenol oxidase were successively dissolved in 100 ml of 0.1 M PBS (pH = 6.8), and the reaction mixture was then placed in a 250-ml Erlenmeyer flask and incubated at 25 °C for 60 min with shaking at 150 rpm. After the reaction was completed, polyphenol oxidase was removed using a Pellicon® XL 50 cassette and a Labscale TFF system. HPLC analysis showed that all chlorogenic acid was transformed to its quinone derivative.

2.3. Effect of chlorogenic acid or its quinone derivative on acrylamide formation during Maillard reaction

A total of 4 ml of chlorogenic acid or its quinone derivative (50 μmol/ml, dissolved in 0.1 M PBS, pH = 6.8) were mixed with 1 mmol of asparagine and 1 mmol of glucose in a 20-ml stainless-steel test tube. The mixtures were heated at 160 °C for 5, 10, 15, or 20 min. The amount of acrylamide formed under these conditions was then determined. Two reaction models, 1 mmol of asparagine reacted with 1 mmol of glucose or HMF without addition of chlorogenic acid in 4 ml PBS, were as the controls.

2.4. Effect of chlorogenic acid acrylamide elimination

An equimolar asparagine/glucose (1 mmol) model reaction system containing 200 μg of $^{13}C_3$-labeled acrylamide and 0.2 mmol of chlorogenic acid or its quinone derivative in 0.1 M PBS (pH = 6.8) was used to assess the effect of chlorogenic acid on the elimination of acrylamide during the reaction process. The same system containing no chlorogenic acid or its quinone derivative was used as control.

2.5. Effect of chlorogenic acid on oxidation–reduction potential in the Maillard reaction system

Oxidation–reduction potential of the supernatant of the Maillard reaction system described above was determined in the presence or absence of 0.2 mmol of chlorogenic acid at different reaction times using an ORP-422 model oxidation–reduction potential detector (Beijing Zhongxi Yuanda Scientific Instrument Co., Ltd., Beijing, China).

2.6. Effect of chlorogenic acid on acrylamide formation from 3-aminopropionamide (3-APA)

pH value of 2.5 mM 3-APA solution was adjusted to 3.0, 4.0, 5.0, 6.0, or 7.0 using 0.1 M NaOH. Each solution (4 ml) was placed in a stainless-steel test tube and heated in an oil bath at 160 °C for 15 min. The amounts of acrylamide produced under these conditions were then determined. Based on results obtained from the effect of pH, 2 ml of 5.0 mM 3-APA (dissolved in 0.1 M PBS, pH = 6.8) and 2 ml of chlorogenic acid or its quinone derivative (0.1 mmol/ml dissolved in 2 ml of 0.1 M PBS, pH = 6.8) were mixed, placed in a stainless-steel test tube and heated in an oil bath at 160 °C for 5, 10, 15, and 20 min. The amounts of acrylamide produced were then determined.

2.7. Activation energies for the formation of acrylamide from 3-APA

A solution (4 ml) containing 10 μmol of 3-APA and 0.2 mmol of chlorogenic acid (in 0.1 M PBS buffer, pH = 6.8) was heated in an oil bath at 120, 130, 140, 150, 160, and 170 °C for 5, 10, and 15 min, respectively. Activation energy for the conversion of 3-APA to acrylamide under each specific condition was determined as follows.

Rate constant at a specific reaction temperature was obtained from the slope of a linear plot of the amount of acrylamide produced against reaction time. The effect of temperature on reaction rate constant k was expressed by the Arrhenius equation [18,19]:

$$\ln k = \ln A - \frac{E_a}{RT}$$

where R is universal gas constant (8.314 J/K mol), T is temperature, k is reaction rate constant, E_a is activation energy, and A is frequency factor.

A plot of $(-\ln K)$ versus $1/T$ yields a straight line with a slope of E_a/R.