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Investigation and kinetic evaluation of furan formation in tomato paste and pulp during heating

H. Gül Akıllıoğlu [a], K. Savaş Bahçeci [b], Vural Gökmen [a,*]

[a] Department of Food Engineering, Hacettepe University, Beytepe, Ankara, Turkey
[b] Department of Food Engineering, Hitit University, Çorum, Turkey

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ABSTRACT

Due to its high ascorbic acid content and acidic environment, tomato is susceptible for furan formation during heat treatment. In this study, kinetics of furan formation was analyzed in order to have an understanding of the reactions taking place in tomato pulp during heating. Also several tomato paste samples were investigated in terms of their furan and hydroxymethylfurfural (HMF) concentrations, and the possible furan precursors. Paste samples were found to contain 3.3–13 ng/g furan and 0.9–39.4 μg/g HMF (dry weight basis). Freshly prepared tomato pulps were heated at 70, 80, and 90 °C for different times, and analyzed for ascorbic acid, dehydroascorbic acid, and furan concentrations. The formation rates of furan in the very first 5 min of heating at 70, 80, and 90 °C were 0.0071, 0.0130, and 0.0168 nmol/g·min, respectively. Rate constants related to reactions taking place during furan formation were estimated by multi-response kinetic modeling. The results revealed that ascorbic acid oxidation is the critical step in furan formation reaction mechanism during heating of tomato pulp, and prevention of oxidation during processing might help to limit furan formation.
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1. Introduction

Tomato is an important crop grown in different parts of the world. Its total production has continuously got an increase in the world, and reached to a total of around 164 million tones by the year 2013 according to FAOSTAT database (2015). It is widely consumed as either fresh or as a processed food product, such as tomato juice, tomato puree, tomato sauce, ketchup, and tomato paste. There is an increasing demand of tomato products consumption due to the beneficial health effects. Tomato consumption is correlated with reduced risk of coronary heart disease, certain cancer types, hypertension, and reduced serum lipid levels (Agarwal, Shen, Agarwal, & Rao, 2001; Ordonez-Santos, Vazquez-Oderiz, Arbones-Macineira, & Romero-Rodriguez, 2009; Perveen et al., 2015; Rao & Agarwal, 1999; Walfisch et al., 2007; Willcox, Catignani, & Lazarus, 2003). These beneficial effects are attributed to its high concentrations of vitamin C, carotenoids, especially lycopene and β-carotene, and phenolic compounds (Abushita, Daood, & Biacs, 2000; Akanbi & Oludemi, 2004; Capanoglu, Beekwilder, Boyacioglu, Hall, & De Vos, 2008; Sanchez-Moreno, Plaza, de Ancos, & Cano, 2006). In the common production technique of tomato paste, the juice obtained from the fruit moves through a series of evaporators to remove the water at elevated temperatures. Although the evaporator systems have been modernized so far, due to the heat treatment applied in evaporation and pasteurization steps, some sensorial and nutritional consequences are unavoidable. Concentrations of carotenoids, phenolic compounds, and vitamins decrease, and antioxidant activity of the product is reduced correspondingly (Cosmai, Summo, Caponio, Paradiso, & Gomes, 2013; Gahler, Otto, & Bohm, 2003; Koh, Charoenprasert, & Mitchell, 2012; Mahieddine et al., 2011; Patras, Brunton, Da Pieve, Butler, & Downey, 2009; Perez-Conesa et al., 2009; Podsedek, Sosnowska, & Anders, 2003). Moreover, heat treatment is responsible for the formation of some mutagenic and carcinogenic compounds such as furan and hydroxymethylfurfural (HMF) (Anese, Manzocco, Calligaris, & Nicoli, 2013). Previous studies have shown that HMF might also induce genotoxic and mutagenic effects in bacterial and human cells and promote colon and liver cancers in rats and mice (Anese & Suman, 2013). Furan is listed as 'possibly carcinogenic to humans' (Group 2B) by the International Agency for Research on Cancer (IARC, 1995). Moro et al. (2012) reported that furan was a potent hepatotoxin and hepatocarcinogen in rodents.

Formation of HMF is considered to be an indicator of the intensity of heat treatment, and levels of HMF has been used for the evaluation of harmful effects of heat treatment in several foods including tomato paste (Giovanelli & Lavelli, 2002; Hidalgo & Pompei, 2000; Hidalgo, Pompei, & Zambuto, 1998; Rajchl, Cizkova, Voldrich, Jiruskova, & Sevcik, 2009; Rufian-Henares, Garcia-Villanova, & Guerra-Hernandez, 2008). HMF can be formed in two mechanisms; through Maillard reaction taking place between amino acids and sugars and also through sugar dehydration in acidic conditions during heat treatment of foods.

* Corresponding author at: Department of Food Engineering, Hacettepe University, Beytepe Campus, 06800 Ankara, Turkey.
E-mail address: vgokmen@hacettepe.edu.tr (V. Gökmen).

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It is also known that unlike other process contaminants, the levels of HMF in processed foods can increase during storage, especially in acidic foods like tomato products. Another process contaminant found in tomato paste is furan. According to the report of European Food Safety Authority, furan levels higher than 100 μg/kg could be found in tomato soup (EFSA, European Food Safety Authority, 2010). Also amounts changing from 4 to 39 ppb were reported in tomato sauces (Zoller, Sager, & Reinhard, 2004).

Furan forms in food during heat treatment as a result of ascorbic acid, polyunsaturated fatty acid and Maillard reaction pathways. Sugars, ascorbic acid, unsaturated fatty acids, amino acids, and carotenoids are the precursors of furan (Locas & Yaylayan, 2004; Mariotti et al., 2012). Ascorbic acid (AA) and its oxidized form dehydroascorbic acid (DHAA) were reported to be the most susceptible precursors of furan among all (Fig. 1) (Locas & Yaylayan, 2004). Acidic condition of food product was found to promote furan formation (Fan, Huang, & Sokorai, 2008; Limacher, Kerler, Conde-Petit, & Blank, 2007; Nie et al., 2013).

High ascorbic acid concentration, acidic environment, and long storage time constitutes together favorable conditions for furan formation in tomato paste. In this study, tomato pulp obtained in the laboratory was heat-treated in order to investigate in depth the effects of heat treatment on furan and HMF. Kinetics of furan formation was analyzed in order to have a better understanding of the reactions taking place in real food matrix. Model system studies are appreciated since they give mechanistic insight into reactions. However it is important to understand how the components in a real food matrix react during food processing. Also several tomato paste samples were analyzed in terms of their HMF and furan concentrations, and the possible furan precursors, besides their some physicochemical properties.

2. Materials and methods

2.1. Chemicals and consumables

Formic acid, potassium hexacyanoferrate (Carrez I), zinc sulfate (Carrez II), and sodium hydroxide were of analytical grade and obtained from Merck (Darmstadt, Germany). Methanol (≥99.9%), acetonitrile (≥99.9%) and water (ChromasolV grade) were purchased from Sigma-Aldrich (Steinheim, Germany). L-(+)-Ascorbic acid (min. >99.7%), L-(+)dehydroascorbic acid, furan (99.9%), were obtained from Merck (Darmstadt, Germany). d4-Furan (for NMR 99% atom) was purchased from Acros Organics (New Jersey). Syringe filters (nylon, 0.45 μm) were supplied by Waters (Milford, MA, USA).

2.2. Preparation and heat treatment of tomato pulp

Mature tomatoes used for the production of pulp were purchased from a local market in Ankara. Tomatoes were washed with tap water to remove residues and extraneous matter adhering to the fruit and cut in quarters. A kitchen blender was used for smashing fresh tomatoes and the mashed tomato pulp was separated from skins and seeds by sieving. 5 g of freshly prepared tomato pulp was weighed into 20 mL headspace vial at 4 °C and screw-capped immediately. The vials were placed in water baths maintained at 70, 80, and 90 °C, and heated for different times up to 30 min. After heat treatment, the contents of glass vials were cooled immediately by immersing the vials in cold water. Fresh and heated samples were analyzed for AA, DHAA, furan and HMF.

Number of tomato paste samples (n = 14) obtained from local markets in Çorum and Ankara were also analyzed for furan, HMF, furan precursors (AA and DHAA), as well as for some other quality characteristics.

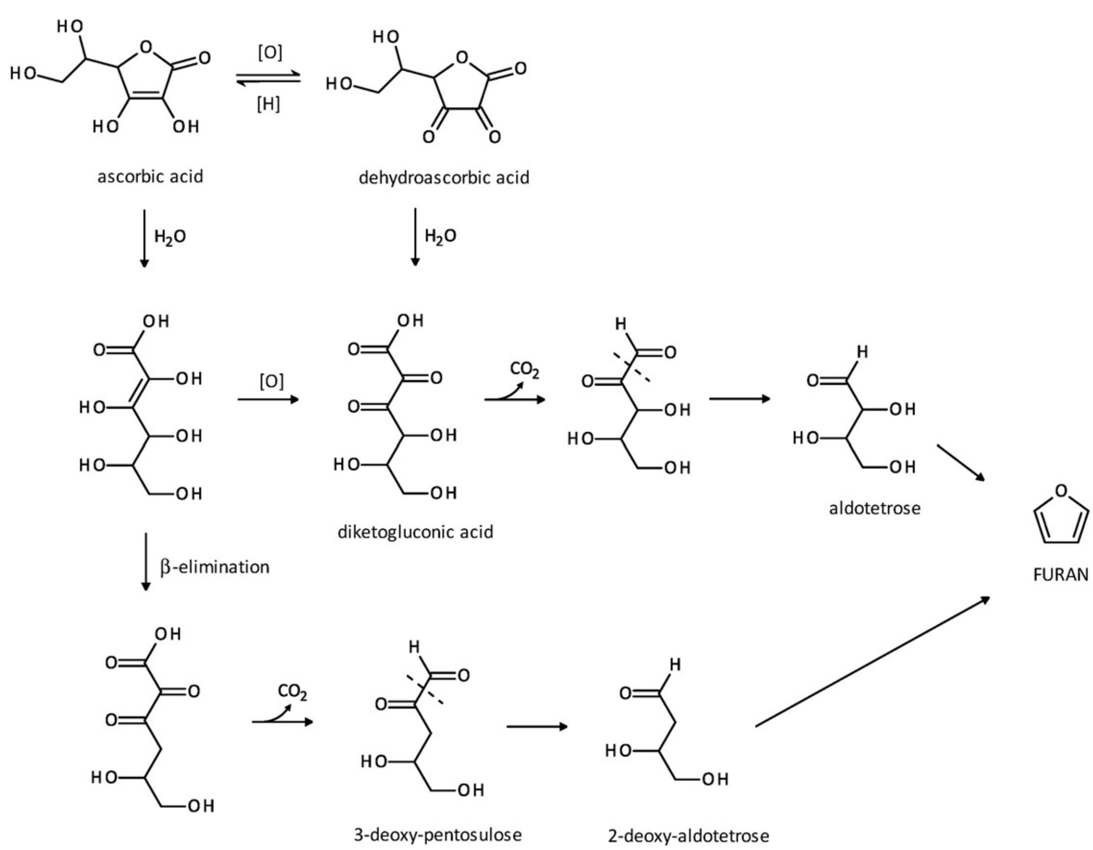

Fig. 1. Furan formation from ascorbic acid.
Adapted from Locas & Yaylayan, 2004.

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