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# Formation of 3-chloropropane-1,2-diol esters in model systems simulating thermal processing of edible oil

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ABSTRACT

3-chloropropane-1, 2-diol (3-MCPD) esters are a kind of food processing contaminants that especially occur in edible oil. This study investigated the impact of various factors on the formation of 3-MCPD esters in edible oil models with sodium chloride as chlorine donator during heat processing. The amount of 3-MCPD esters generated in the models were positively correlated with the concentration of sodium chloride. $Fe^{3+}$ could significantly promote the formation of 3-MCPD esters. The formation of 3-MCPD esters also depended on pH value of oil, heating temperature and time. The highest level of 3-MCPD esters were obtained at pH 4.0 (2925.3 μg/kg), at 220 °C (9509.8 μg/kg) and for 8 h (4852.4 μg/kg), respectively. 3-MCPD esters were generated much more in the continuous heating model than in the intermittent one. The results are valuable to better understand the formation of 3-MCPD esters and also can provide references for reduction of 3-MCPD esters during edible oil processing and household cooking.



## 1. Introduction

3-chloropropane-1,2-diol (3-MCPD), as a heat-produced food contaminant, was concerned by the public in past decades. 3-MCPD was detected in acid-hydrolyzed vegetable proteins (acid-HVP) (Davidek, Velíšek, Kubelka, Janíček, & Šimicová, 1980; Velíšek et al., 1978, 1980) and various processed foods, including meat (Crews et al., 2002; Kuntzer & Weisshaar, 2006), smoked foods (Kuntzer & Weisshaar, 2006), cereal-derived foods (Hamlet, Jayaratne, & Matthews, 2002), etc. 3-MCPD was also detected in our daily foods such as bread (Breitling-Utzmann, Köbler, Herbolzheimer, & Maier, 2003), coffee (Doležal, Chaloupská, Divinová, Svejkovská, & Velišek, 2005). 3-MCPD was classified as possibly carcinogenic to humans (Group 2B) by International Agency for Research on Cancer (IARC) (IARC., 2012).

A wide range of concentrations of 3-MCPD esters had been detected in a variety of food products (Crews, 2012; Svejkovska et al., 2004).

In edible oils, 3-MCPD esters were higher than free 3-MCPD in the contents (Craft, Chiodini, Garst, & Granvogl, 2013; Zelinková, Svejkovská, Velíšek, & Doležal, 2006). 3-MCPD esters could be hydrolyzed by lipase to release free 3-MCPD (Hamlet & Sadd, 2004; Seefelder et al., 2008). In addition, the related studies showed that 3-MCPD esters had toxic effects on experimental animals (Bakhiya, Abraham, Gürtler, Appel, & Lampen, 2011; Barocelli, Corradi, Mutti, & Petronini, 2011; Liu et al., 2012). Therefore, 3-MCPD esters have been received much attention in recent years.

The studies aimed at effects of oil refining on the formation of 3-MCPD esters had been carried out (Franke, Strijowski, Fleck, & Pudel, 2009; Ramli et al., 2011; Sampaio et al., 2013; Zulkurnain et al., 2012). According to those studies, the formation of 3-MCPD esters was found to be associated with high temperature. The formation of 3-MCPD esters had also been studied by simulating oil processing under deodorizing temperature (Ermacora & Hrncirik, 2014a; Freudenstein, Weking, & Matthäus, 2013; Svejkovska, Dolezal, & Velisek, 2006, which suggested that acylglycerols (mono-, di- and tri-) were the precursors of 3-MCPD esters. The decrease of 3-MCPD esters was also observed in model system over the range of 100–230 °C (Svejkovskă et al., 2006). The degradation pathway was found involving isomerisation, dechlorination and

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deacylation reactions (Ermacora & Hrncirik, 2014b). In despite of the large number of investigations on 3-MCPD esters in edible oils, the formation mechanism of 3-MCPD esters in edible oil is still unclear so far. Moreover, those studies almost concentrated on palm oil, rather than other cooking oil. Recently, study suggested that iron ions catalyzed the formation of 3-MCPD esters (Zhang et al., 2015). However, there are no any reports on the effects of other metal ions on the formation of 3-MCPD esters. Furthermore, establishing models is a common method used for study of food derived contaminants. In addition, in order to find out effective mitigation methods for oil manufacturing or family cooking, all possible influential factors associated with the formation of 3-MCPD esters should be investigated.

In the present study, the impacts of selected factors on the formation of 3-MCPD esters were systemically studied in model systems. The selected influential factors included oil type, concentration and proportion of NaCl solution, heating temperature and time, pH value, and different heating style, as well as metal ions. In order to find out that whether the oil type affects the formation of 3-MCPD esters, both crude oil and refined oil were introduced as reactant in the models made in the present study. The models reaction conditions, namely temperature (70–250 °C) and time (0.25–24 h) and their impacts on the formation of 3-MCPD esters were also studied. In addition, the impacts of the concentration and proportion of NaCl, pH value of oil, heating style and metal ions were also studied and discussed. The results of this study are significant to discover the formation mechanism of 3-MCPD esters in edible oil. Also the results are valuable for looking for reduction measures.

## 2. Materials and methods

### 2.1. Materials

$D_5$-3-MCPD-1,2-bis-palmitoyl ester and 3-MCPD-1,2-bis-palmitoyl ester were purchased from Sigma–Aldrich (St Louis, USA) and CDN isotopes (Quebec, Canada), respectively. Phenylboronic acid (PBA, 97%) was bought from Aladdin Reagent (Shanghai China). Other chemicals and reagents were obtained from Damao Chemical Reagent (Tianjin. China).

Refined edible oils (rapeseed oil, sunflower oil, peanut oil, sesame oil, soybean oil, palm oil, camellia oil, perilla oil and corn oil) were purchased from local supermarkets (Nanchang, China). Rapeseeds, sunflower seeds and peanut seeds were also purchased from local supermarkets (Nanchang, China), crude oils were produced from oil seeds with or without roasting process in laboratory.

Silicone oil was purchased from Bald Silicone Technology Company (Hangzhou, China).

### 2.2. Methods

#### 2.2.1. The influence of selected factors on formation of 3-MCPD esters in model system

*2.2.1.1. Oil types.* Ten mL oil (crude or refined) and 1 mL NaCl solution (216 g/L) were mixed in a 20 mL glass tube with a magnetic stir bar. The well-blended mixtures were heated at 160 °C for 1 h in silicone oil bath. The mixtures then were cooled to room temperature and stored at 4 °C prior to the determination of 3-MCPD esters.

*2.2.1.2. NaCl.* One mL of NaCl solution with different concentration (0, 72,144, 216, 288, and 360 g/L) were respectively mixed with 10 mL of crude rapeseed oil in a 20 mL glass tube with a magnetic stir bar. After being heated at 160 °C for 1 h, mixture were cooled to room temperature and stored at 4 °C prior to the determination of 3-MCPD esters.

Ten mL oil was mixed with different proportion of NaCl solution (0, 10, 20, 40, 60 and 80 g/100 g), respectively. After being heated at 160 °C for 1 h, mixtures were cooled to room temperature and stored at 4 °C prior to the determination of 3-MCPD esters.

*2.2.1.3. pH value.* Buffer solutions with different pH value (pH 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5 and 8.0) were prepared using dipotassium phosphate solution and potassium dihydrogen phosphate solution. 0.5 mL of each buffer solution was added into the model system which consisted of 10 mL crude rapeseed oil and 0.5 mL NaCl solution (216 g/L). After being heated at 160 °C for 1 h, mixtures were cooled to room temperature and stored at 4 °C prior to the determination of 3-MCPD esters.

*2.2.1.4. Heating temperature.* Ten mL crude rapeseed oil and 1 mL NaCl solution (216 g/L) were mixed and then heated at different temperature (70, 100, 130, 160, 190, 220 and 250 °C, respectively) for 1 h. After heating, the mixtures were cooled to room temperature and stored at 4 °C prior to the determination of 3-MCPD esters.

*2.2.1.5. Heating time.* Ten mL crude rapeseed oil and 1 mL NaCl solution (216 g/L) were mixed and heated at 160 °C for different time (0.25, 0.5, 0.75, 1, 2, 4, 8, 12, 16, 20 and 24 h, respectively). After heating, the mixtures were cooled to room temperature and stored at 4 °C prior to the determination of 3-MCPD esters.

*2.2.1.6. Intermittent heating.* Ten mL crude rapeseed oil and 1 mL NaCl solution (216 g/L) underwent thermal treatment at 160 °C for one “8-h”, two “4-h”, four “2-h” and eight “1-h”, respectively. After heating, the mixtures were cooled to room temperature and stored at 4 °C prior to the determination of 3-MCPD esters.

*2.2.1.7. Metal ions.* Ten mL crude rapeseed oil and 0.5 mL 360 g/L NaCl solution were mixed. Different nitrate metal ($Zn^{2+}$, $Al^{3+}$, $Ca^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Mg^{2+}$) with concentration of 0.1 mol/L were added into the mixture respectively. Metal ions solution were substituted by water serving as control group. The mixtures were heated at 160 °C for 1 h. After heating, the mixtures were cooled to room temperature and stored at 4 °C prior to the determination of 3-MCPD esters.

#### 2.2.2. 3-MCPD esters analysis

From each sample 100 mg (±0.5 mg) aliquot was weighed into a 5.0 mL screw cap vial. Each aliquot was spiked with 100 μL of internal standard solution. And after addition of 100 μL tert-butyl methyl ether, the vials were shaken until the sample material was completely dissolved. Two hundred microlitres sodium methoxide solution was added to each vial, afterwards the vials were sealed and shaken shortly. The reaction time for ester cleavage was 4 min, then the reactions were stopped by addition of 600 μL of acidified sodium bromide solution. Afterwards 600 μL of iso-hexane was added, the vials were sealed and shaken vigorously. The mixtures were allowed to remain at room temperature for approximately 5 min, followed by quantitative separation and discarding of the organic phases using Pasteur pipettes. This step was repeated with another 600 μL of iso-hexane. Using new Pasteur pipettes, the aqueous phases resulted were extracted three times with each 600 μL of a mixture of diethyl ether and ethyl acetate (3:2,mL:mL). The organic extract without fraction of the aqueous phase was combined in a new screw cap vial containing a small amount of anhydrous sodium sulphate, followed by addition of 100 μL of the derivatizing reagent (PBA). The reaction was proceeded at 25 °C for 15 min. Each reaction mixture was evaporated