



Mechanism of formation of 3-chloropropan-1,2-diol (3-MCPD) esters under conditions of the vegetable oil refining



Jan Šmidrkal*, Markéta Tesařová, Iveta Hrádková, Markéta Berčíková, Aneta Adamčíková, Vladimír Filip

Department of Dairy, Fat and Cosmetics, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague, Czech Republic

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ABSTRACT

3-MCPD esters are contaminants that can form during refining of vegetable oils in the deodorization step. It was experimentally shown that their content in the vegetable oil depends on the acid value of the vegetable oil and the chloride content. 3-MCPD esters form approximately 2–5 times faster from diacylglycerols than from monoacylglycerols. It has been proved that the higher fatty acids content in the oil caused higher 3-MCPD esters content in the deodorization step. Neutralization of free fatty acids in the vegetable oil before the deodorization step by alkaline carbonates or hydrogen carbonates can completely suppress the formation of 3-MCPD esters. Potassium salts are more effective than sodium salts.

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1. Introduction

Esters of higher fatty acids and 3-chloropropan-1,2-diol (3-MCPD) are contaminants, which form during refining of vegetable oil in the deodorization step (Franke, Strijowski, Fleck, & Pudel, 2009; Matthaues, Pudel, Fehling, Vosmann, & Freudenstein, 2011) and/or physical refining. Deodorization is water steam distillation of volatile substances, during which the superheated water steam at temperature 180–260 °C is introduced under lowered pressure (3–20 mbar) into vegetable oil at temperature 180–260 °C.

The International Agency for Research on Cancer (IARC) characterizes 3-MCPD as possibly carcinogenic to humans, based on cancer incidents caused by 3-MCPD in laboratory animals (renal tubular tumors, Leyding cell adenomas). 3-MCPD's metabolite, glycidol, is also characterized by IARC as possibly carcinogenic to humans (IARC Monographs, 2012). Research on 3-MCPD has been

intensive in the past 10 years, and many countries already have regulations on the levels of 3-MCPD allowed in food, yet foods with a high concentration of 3-MCPD are still widely available to consumers. Removal methods must be introduced to ensure that the concentration of 3-MCPD in foods are within the required levels (Lee & Khor, 2015).

Vegetable oil contains before deodorization triacylglycerols (TAG), diacylglycerols (DAG), monoacylglycerols (MAG), (free) fatty acids and chloride compounds (chlorides, hydrogen chloride), alternatively organic chloride compounds. Chlorides come from parts of plants (pulp in cases of palm and olive) from which the oil was pressed and extracted; the free hydrogen chloride come from bleaching earth, by which the oil was bleached (Collison, 2010).

The concentration of 3-MCPD esters in vegetable oil after deodorization depends on the composition of the vegetable oil. In rapeseed oil, which contains only 2% of diacylglycerols and 0.1% of (free) fatty acids, the content of 3-MCPD esters as free 3-MCPD increases from 0.4 to 1.0 ppm. On the contrary, in palm oil, which consists of 5% of diacylglycerols and 0.24% of (free) fatty acids, the content of 3-MCPD increases from 1.0–4.4 ppm (Franke et al., 2009).

Literature indicates that 3-MCPD esters form from DAG and TAG (Rahn & Yaylayan, 2013), from MAG and DAG (Freudenstein,

Abbreviations: DAG, diacylglycerol; DPG, 1,3-dipalmitoylglycerol, 1,3-dipalmitin; HOSO, high oleic sunflower oil; HPC, (totally) hydrogenated palmstearin; MAG, monoacylglycerol; MPG, 1-palmitoylglycerol, 1-monopalmitin; MESO, sunflower oil methyl esters; TAG, triacylglycerol; TBAC, tetrabutylammonium chloride; TPG, tripalmitoylglycerol, tripalmitin; 3-MCPD, 3-chloro-1,2-propanediol; 2-MCPD, 2-chloro-1,3-propanediol.

* Corresponding author.

E-mail address: jan.smidrkal@vscht.cz (J. Šmidrkal).

Weking, & Matthauss, 2013; Hamlet et al., 2011; Matthauss et al. 2011; Shimizu, Vosmann, & Matthauss, 2012; Shimizu, Weitkamp, Vosmann, & Matthauss, 2013; Smidrkal et al., 2011) or from TAG (Destailats, Craft, Sandoz, & Nagy, 2012). There is a disagreement on whether free fatty acids are (Smidrkal et al., 2011) or are not (Freudenstein et al., 2013) the direct precursors of 3-MCPD esters formation.

To find out from which acylglycerol type the 3-MCPD esters form and if fatty acids influence their formation, experiments in inert conditions were carried out. The mixture of sunflower oil methyl esters with high content of oil acid (MESO) was chosen as the inert medium. The sunflower oil methyl esters were prepared by transesterification of the sunflower oil. The tetrabutylammonium chloride (TBAC) was the source of the chlorine; palmitic acid was used as the fatty acid of choice. The following reference acylglycerols (1-monopalmitoylglycerol (MPG), 1,3-dipalmitoylglycerol (DPG) and 1,2,3-tripalmitoylglycerol) were synthesized as pure substances. The above mentioned compounds were subsequently heated (240 °C) in various combinations in a reactor. Samples were taken in regular time intervals. The content of free 3-MCPD formed during 3-MCPD ester hydrolysis was determined in the samples.

Fatty acids split off a proton more easily at higher temperatures (>150 °C) and their acidity increases to the level of strong acids; as a result, they are able to catalyze esterification (De, Bhattacharyya, & Bandyopadhyay, 2002; Thomas & Sudborough, 1912).

This paper attempts to explain the origin of hydrogen chloride. We hypothesize that during the deodorization the equilibrium between a fatty acid and sodium chloride is established and fatty acid salt with hydrogen chloride is formed. The hydrogen chloride subsequently reacts with acylglycerol (the fastest reaction is with diacylglycerol). The necessary prerequisite of the reaction is the presence of fatty acid (RCOOH) and ionic bound chlorine (e.g. NaCl, KCl, TBAC), or maybe the presence of free hydrogen chloride.

2. Materials and methods

2.1. Chemicals

The following chemicals used were all products of Sigma-Aldrich Co (Steinheim, Germany): palmitic acid (>99%), tetrabutylammonium chloride ($\geq 97\%$), Na_2CO_3 (>99.5%), NaHCO_3 (>99.5%), KHCO_3 (>99.5%), K_2CO_3 (>99%). Palmstearin used was the product of AarhusKarlshamm (Czech Republic). Sunflower oil with high content of oleic acid was the product of Palma Group (Bratislava, Slovakia).

2.1.1. Sunflower oil methyl esters with high content of oleic acid (MESO)

The mixture of sunflower oil (acid value $0.2 \text{ mg KOH g}^{-1}$, 0.05% H_2O , 1000 g, 1.2 mol), methanol (0.05% H_2O , 292 ml, 7.2 mol) and potassium hydroxide (12.2 g, 0.22 mol) was stirred for 2 h in nitrogen atmosphere. After separation of the bottom glycerol phase, the upper ester phase was washed with distilled water ($5 \times 200 \text{ ml}$) to neutral reaction. After drying with sodium sulphate, the product was distilled in vacuum and the fraction was collected at 166–170 °C/100 Pa (880 g). The analytical parameters of MESO are listed in the Tables S1 and S2.

2.1.2. Hydrogenated palmstearin (HPS)

Nickel catalyst (4 g) was added at the temperature of 150 °C to the molten palmstearin (acid value $0.6 \text{ mg KOH g}^{-1}$, 200 g) and bubbled through by hydrogen ($20 \text{ L}\cdot\text{h}^{-1}$). Subsequently, the temperature was increased to 180 °C and the flow of hydrogen was increased to $80 \text{ L}\cdot\text{h}^{-1}$. The hydrogenation process was monitored

refractometrically. The refractive index readings stabilized after 1 h. Hydrogenation continued for an additional 1 h; then the reaction mixture was cooled down to 70 °C and the catalyst was filtered off. The analytical parameters of HPS are listed in the Tables S1 and S2.

2.2. Model deodorization

2.2.1. Model reactor

The model reactor was a vertical glass tube (length: 220 mm, inner diameter: 20 mm) fitted at the bottom with an argon feeding tube and sintered glass, and at the top with a tapered ground joint and an outlet tube (see Supplementary material Fig. S1) placed in an air bath adapted from an old GLC.

Small amounts of reactants (<300 mg) were added together using a small weighing dish, as such small amounts could not be accurately weighed separately.

2.2.2. Model deodorization ((MESO + MAG + 0.1% TBAC – acid value $1.0 \text{ mg KOH}\cdot\text{g}^{-1}$)

The MESO (14.5 g) was introduced into the reactor heated to 140 °C with argon inlet, then MPG (0.46 g, 1.4 mmol) was added and the temperature was increased to 240 °C within 15 min. Subsequently, first TBAC (15 mg, 0.054 mmol) and – after 30 s – palmitic acid (48 mg, 0.19 mmol) were added. After 1 min the first sample (time 0) was taken and immediately cooled down to a room temperature. Subsequent samples were taken in given time intervals.

The amount of palmitic acid required to obtain acid values 0.3; 1.0; 2.0 and $4.0 \text{ mg KOH g}^{-1}$ was 0, 48, 117 and 254 mg, respectively.

For additional experiments, the amount of MESO and DPG was 14.2 and 0.80 g (1.4 mmol), in the case of MESO and HPS the amount was 13.8 and 1.18 g (0.14 mol).

The testing of acylglycerol suitability was performed under the same conditions (see Fig. 1).

2.2.3. Model deodorization (HOSO + 0.1%TBAC + KHCO_3)

The HOSO (15 g) was introduced into the reactor at room temperature and with an argon inlet and the temperature was increased to 240 °C. TBAC (15 mg, 0.054 mmol) and – after 30 s – KHCO_3 (3.8 mg, 0.038 mmol) were added. Sampling protocol was as described above.

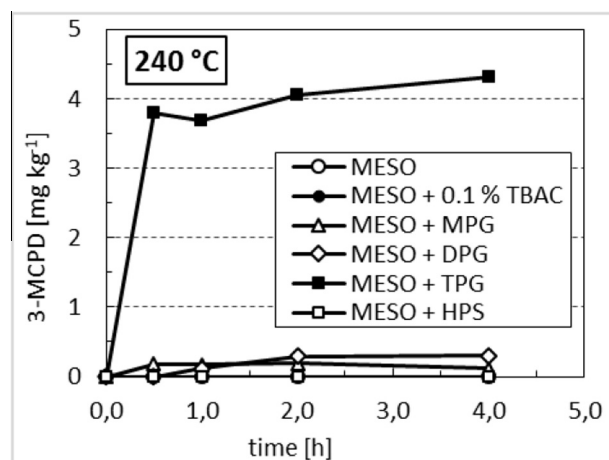


Fig. 1. Testing of used MESO and acylglycerols (blank experiment).

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