Food Chemistry 203 (2016) 95–103

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

The effect of frying on glicydyl esters content in palm oil

Magda Aniołowska *, Agnieszka Kita

Department of Food Storage and Technology, Faculty of Food Science, Wrocław University of Environmental and Life Sciences, Chełmońskiego 37 Str., 51-630 Wrocław, Poland

ARTICLE INFO

Article history:
Received 10 January 2015
Received in revised form 25 December 2015
Accepted 2 February 2016
Available online 3 February 2016

Keywords:
Glycidyl fatty acid esters
LC–MS
Palm oil
Frying temperature

ABSTRACT

The changes in palm oil, as affected by frying temperature, and content of the glycidyl esters (GEs) were studied. Potato chips were fried intermittently in palm oil, which was heated for 8 h daily over five consecutive days. Frying was conducted at three frying temperatures: 150, 165 and 180 °C. Thermo-oxidative alterations of the oil were measured by acid and anisidine values, changes in fatty acid composition, total polar components, polar fraction composition and colour components formation. Content of GE was measured by liquid chromatography–mass spectrometry. Results showed that amount of products of hydrolysis, oxidation and polymerization (excluding decrease of degree of unsaturation) increased significantly as a function of frying temperature and time. Between GEs of fatty acids the most abundant were esters of palmitic and oleic acids. With increasing temperature and frying time, the content of GE decreased. The extent of GE decrease was correlated with degree of oil degradation.

1. Introduction

For several years, research has been done to try to characterise and describe physicochemical properties and methods for the determination of two types of compounds: 3-monochloropropane-1,2-diol fatty acids esters (3-MCPD esters) and glycidyl fatty acids esters (GE), which were new contaminants in food products, including foods that contained vegetable fats (Bakhiya, Abraham, Gürtler, Appel, & Lampen, 2011). Their structures were already known, in addition to possible mechanism for reactions occurring during the refining of edible oils. It was suggested that these compounds were formed from diacylglycerols (Fig. 1) under the influence of high temperatures (Destaillats, Craft, Dubois, & Nagy, 2012). The emphasis was put on the toxicity of the product of their deesterification – glycidol (BfR, 2009).

Glycidol is genotoxic and has an effect on gene mutations and unscheduled DNA synthesis (IARC, 2000; Bakhiya et al., 2011). Among refined vegetable oils, the largest quantities of GE were found in palm, corn and coconut oils (Weiβhaar & Perz, 2010; Blumhorst et al., 2013). We know direct and indirect methods for their determination in oils new research has described successive improvements of existing methods for the determination of GE in edible oils (MacMahon, Mazzol, Begley, & Diachenko, 2013).

For several years, researchers from around the world focused on GE and 3-MCPD esters as new contaminants in food, including in edible oils. Despite continued work to expand the knowledge about their formation mechanisms, there are still many issues that require further study. The results of their further transformation during popular processes used in food production, such as frying, will be interesting to study. This would provide answers to questions regarding ways to reduce the occurrence of GE and 3-MCPD esters, as well as their hydrolysis products, in edible oils.

Deep-frying is one of the most popular food processing methods. It is a fast and convenient technique for the production of foods with unique sensory properties that are highly appreciated by consumers, such as flavour, colour, palatability and texture (Brühl, 2014). During the frying of foods, fat is subjected to high temperatures in the presence of water and air, which results in the formation of a high number of new compounds through hydrolytic, thermal and oxidative reactions. Products of oil degradation, including diacylglycerols, could react and form GE at high temperatures that are typical in frying process (Fig. 1). Then, the GE could decompose to glycidol (BfR, 2009). The analysis of different physical factors, such as frying time, temperature and degree of degradation (mostly by hydrolysis) of the frying medium, could determine which parameters influence the amount of GE in frying oils, as well as in fried food. Following this, it would be possible to propose ways to decrease the amount of these components in fried products. In addition to being used as a frying medium, palm oils are predominant in the manufacturing of different type of foods on an industrial scale, as well as in fast food restaurants. This makes palm oil a model fat in frying experiments. Therefore, the objective of this research was to determine the effects of frying temperature and time on oil degradation and the content of GE.

---

* Corresponding author.
E-mail address: magda.aniolowska@wnoz.up.wroc.pl (M. Aniołowska).

http://dx.doi.org/10.1016/j.foodchem.2016.02.028
0308-8146/

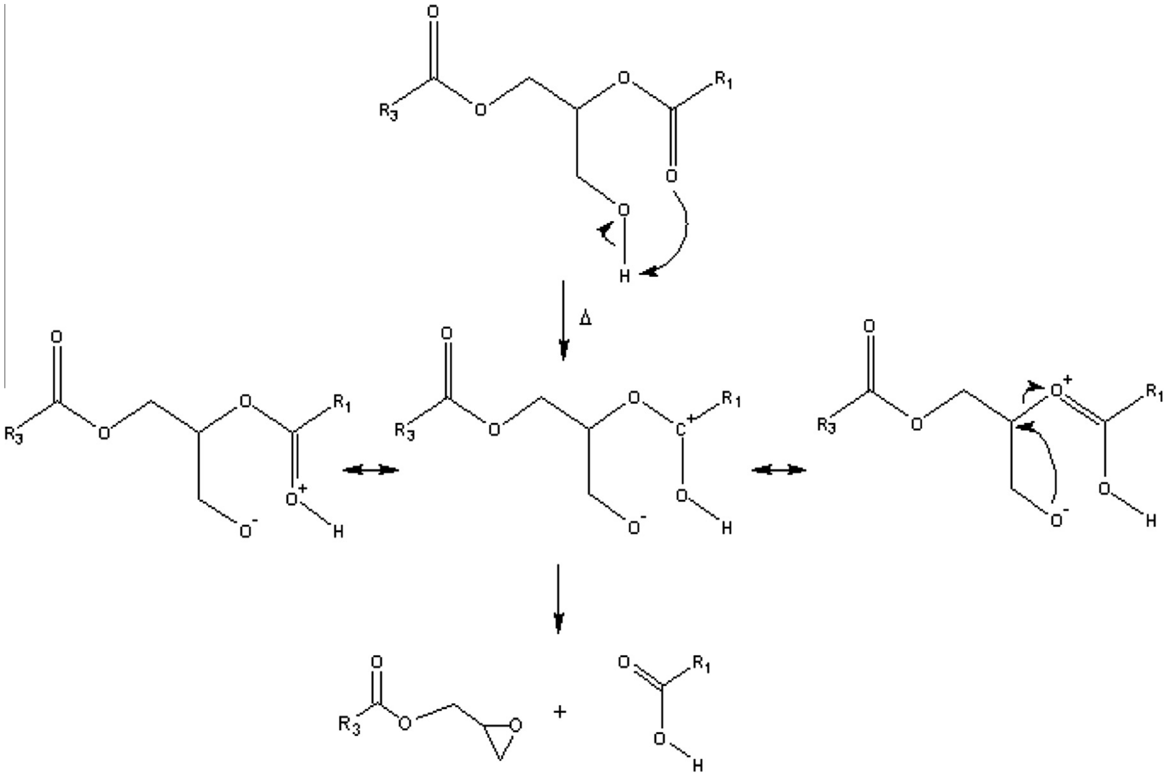

Fig. 1. Proposed mechanism for the formation of glycidyl ester from diacylglycerol at high temperatures (Destaillats et al., 2012).

2. Materials and methods

2.1. Materials

2.1.1. Oil and potatoes

A potato snack producer in Lower Silesia, Poland provided commercially refined, bleached and deodorised palm oil, as well as cv. Lady Rosetta potatoes for use in this study.

2.1.2. Chemicals

For the purposes of this study, we purchased petroleum ether bp 40–60 °C, *iso*-octane, methanol, ethanol, chloroform, diethyl ether, glacial acetic acid and methyl pentane, concentrated hydrochloric acid of analytical grade from Sigma–Aldrich (St. Louis, MO, USA). Benzene, boron trifluoride in methanol, dichloromethane of high performance liquid chromatography (HPLC) grade, *p*-anisidine, potassium hydroxide, benzoic acid, potassium iodide, sodium thiosulphate, sodium tetraborate, potassium dichromate, sodium bicarbonate, and starch from Merck (Darmstadt, Germany). In addition, we purchased methanol, acetonitrile, isopropanol, chloroform, acetone, ethyl acetate, diethyl ether, formic acid, n-hexane of HPLC grade from Sigma–Aldrich (St. Louis, MO, USA). These chemicals were used to prepare the GE-rich extracts from the oil, as well as for the mobile phases in the LC–MS. Ultra-pure water was prepared using a Milli-Q purification system (Millipore, Bedford, MA, USA) and was used in all procedures. All of the solvents used in the LC–MS analysis were HPLC grade, except for the water, which was LC–MS grade. All other reagents were of analytical grade.

Glycidyl palmitate (C16:0-GE) 98%, glycidyl stearate (C18:0-GE) 98%, glycidyl oleate (C18:1-GE) 98%, glycidyl linoleate (C18:2-GE) 90% and glycidyl linolenate (C18:3-GE) 85% were purchased as liquid calibration solutions from Wako Chemicals GmbH (Neuss Germany). We also obtained reversed-phase SPE cartridges, Sep-Pak Vac C18 cartridge 500 mg of sorbent (55–105 μm particle size) and the volume of 10 mL and normal-phase Sep-Pak Vac Silica cartridges 500 mg of sorbent (55–105 μm particle size) and the volume of 10 mL from Waters (Milford, MA, USA). The method was tested using deuterated internal standards (glycidyl palmitate (C16:0-GE-d5) 96%, glycidyl stearate (C18:0-GE-d5) 98%, glycidyl oleate (C18:1-GE-d5) 98%, glycidyl linoleate (C18:2-GE-d5) 98% and glycidyl linolenate (C18:3-GE-d5) 90%, which were purchased from Toronto Research Chemicals, Inc. (Toronto, ON, Canada).

2.2. Frying procedure and oil sampling

The frying was simultaneously conducted in 5 L capacity restaurant style stainless steel deep fryers (Beckers, Italy). After washing, the potato tubers were cut into slices of 1.0 ± 0.1 mm thickness (Robot Coupe CL 50E, USA). They were then washed in cold water and superficially dried using paper towels. A batch of 100 g of potato slices was fried in palm oil heated to 150, 165 and 180 °C. The time of frying at each temperature was specially related to the moisture content of the finished product (below 2%). Frying was conducted in 30 min cycles for eight hours daily for five days. At the end of each day of frying, the fryers were shut off and the oils were filtered to remove solid debris. Then, the oils were left to cool overnight. The oil was replenished before the frying process, to complete losses caused by collection of samples and absorbing fat by potato chips, adding additional fresh oil which volume was less than 5% of the total oil volume. 100 mL samples of oil from each fryer were taken daily (after 8, 16, 24, 32 and 40 h) and were kept frozen at −20 °C until analysed. The fresh and degraded oils were analysed for acid and anisidine values, colour, refractive index, fatty acid composition by GC, content and composition of polar fraction by HPSEC and of GE by LC–MS.