The origin of 3-MCPD esters and glycidyl esters in meat products

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Abstract

Undesirable compounds such as *trans*-unsaturated fatty acids, cyclic fatty acids and polymers of acylglycerols can be formed during the heat stress of lipids. It has recently been discovered that chlorination of acylglycerols also takes places with the formation of the processing contaminants, i.e. of chloropropanol esters. In 2001, the European Commission's Scientific Committee for Food established a Tolerable Daily Intake for 3-MCPD of 2 $\mu g.kg^{-1}$ of body weight. In 2002, a maximum permitted level of 0.02 $mg.kg^{-1}$ was then determined in the European Union in acid protein hydrolysates and soy sauce (for products with a dry matter content of 40%). This work focuses on the possible formation of these compounds in meat products during heat processing. The gas chromatography method with mass detection was used for the determination of the content of contaminants.

3-MCPD esters, glycidyl esters, GC/MS, bacon

Introduction

The 3-chloropropane-1,2-diol (3-MCPD) and its esters with fatty acids belong to the group of chemical substances known as chlorinated derivatives of glycerol and referred to as chloropropanols. In the food industry, they are considered processing contaminants of foodstuffs. They have been found in a wide range of foodstuffs and food ingredients (Svejkovská et al. 2004). Their elevated levels have even been found in baby food (Zelinková et al. 2009). In 2001, the European Commission's Scientific Committee for Food established a Tolerable Daily Intake (TDI) for 3-MCPD of 2 $\mu g.kg^{-1}$ of body weight. In 2002, a maximum permitted level of 0.02 $mg.kg^{-1}$ was then determined in the European Union in acid protein hydrolysates and soy sauce (for products with a dry matter content of 40%) in which 3-MCPD is formed in large quantities by the reaction of concentrated hydrochloric acid with residual lipids and glycerol, and must then be degraded in an alkaline environment before product finalisation.

Not merely free 3-MCPD, but also esters of it, are formed by the action of high temperatures in foodstuffs. Temperature and period of heating have the greatest influence on the formation of these contaminants. Their total amount depends, however, on the content of precursors, i.e. chloride anions and the pertinent organic compounds, particularly glycerol and its partial esters with fatty acids. Their formation is also influenced by the water activity in the food and its influence on the hydrolysis of triacylglycerols (Svejkovská et al. 2006). The toxicity of 3-MCPD esters is not yet fully known, though it is anticipated in view of the release of 3-MCPD by *in vivo* lipase-catalysed reactions.

The aim of this study was to compare various possibilities for the contamination of meat products by 3-MCPD esters.

Materials and Methods

The content of 3-MCPD and 2-chloropropane-1,3-diol (2-MCPD) esters and glycidyl esters in samples of streaky bacon and refined sunflower oil purchased on the retail market in the Czech Republic was determined in the study.

Some of the samples of streaky bacon were dry-fried in a pan at 180 °C for 1 minute and 30 seconds on each side. The remaining samples were shallow-fried in 100 ml of refined sunflower oil at 158 °C for 1 minute and 30 seconds on each side. Immediately after shallow-frying, the fat from the surface of the sample was extracted with

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diethyl ether and analysed separately. The samples were then homogenised in diethyl ether, filtered and washed with water in a divider. The diethyl ether fraction was evaporated until dry.

A total of 100 mg of the lipid fraction obtained in this way was subsequently transferred to a pear-shaped flask and a solution of NaBr in sulphuric acid added (Ermacora et al. 2012). The sample was kept at 50 °C for 15 minutes and then neutralised by the addition of a solution of $NaHCO_3$. Hexane, into which the analytes were extracted, was added to the sample. Methanol with sulphuric acid was added to the evaporation residue of the hexane phase and the sample left in a thermostat warmed to 40 °C for interesterification for 16 hours. After reaction, the sample was neutralised by the addition of a solution of $NaHCO_3$. The organic phase was evaporated from the sample. A solution of Na_2SO_4 was added to the evaporation residue and esters of fatty acids removed by double extraction with hexane. Derivatising agent in the amout of 250 µl (a solution of phenylboronic acid in acetone) was then added to the aqueous phase, and the sample sonificated for 5 minutes. The derivatised analytes were extracted into hexane and subsequently analysed by the GC/MS method (Divinová et al. 2004). The analyses were performed in three parallel assays.

Results and Discussion

The content of 3-MCPD in meat products is generally low, ranging from an undetectable quantity to 0.081 $mg.kg^{-1}$ (Crew et al. 2002; Chung et al. 2008). A content of 3-MCPD esters of less than 3.3 $mg.kg^{-1}$ of fat has been determined in meat products (Svejkovská et al. 2004).

The content of bound 3-MCPD in streaky bacon was 0.15 $mg.kg^{-1}$ and the content of glycidyl esters 0.3 $mg.kg^{-1}$ of fat. The content of 2-MCPD esters was beneath the limit of detection (lower than 0.04 $mg.kg^{-1}$). After the bacon was dry-fried in a pan for 3 minutes, the content of 3-MCPD esters rose to 0.32 $mg.kg^{-1}$ and the content of glycidyl esters increased to 0.42 $mg.kg^{-1}$. The increase in the content of 3-MCPD was made possible by the presence of precursors – both chlorides (the content of NaCl was 3.0% weight) and partial glycerol esters.

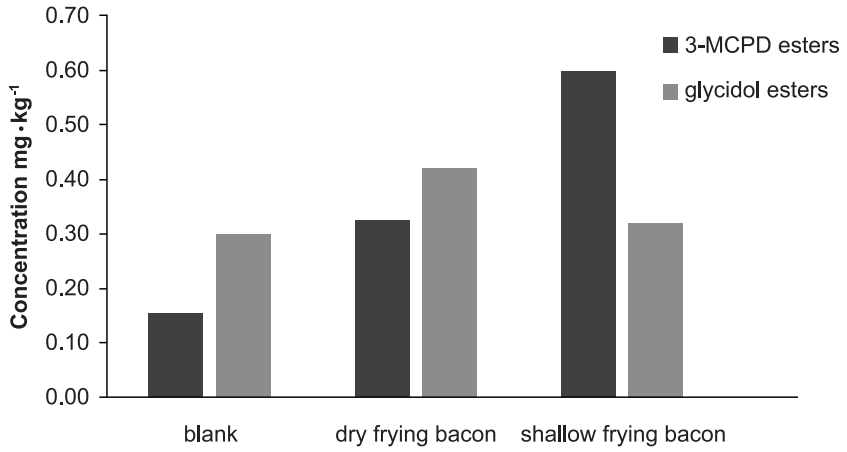

Fig. 1. The content of 3-MCPD esters and glycidyl esters in bacon before and after heat processing

In the second experiment, bacon was shallow-fried in ordinary refined sunflower oil. Refined fats are known to contain significant quantities of these contaminants, which are formed primarily during the deodorisation step of the refining process. The unused oil was found to contain 2.52 $mg.kg^{-1}$ of 3-MCPD esters, 1.54 $mg.kg^{-1}$ of 2-MCPD esters and

0.53 mg.kg^{-1} of glycidyl esters. The fat on the surface of the shallow-fried bacon contained 2.02 mg.kg^{-1} of 3-MCPD esters, 0.92 mg.kg^{-1} of 2-MCPD esters and 0.47 mg.kg^{-1} of glycidyl esters. The shallow-fried bacon itself contained 0.6 mg.kg^{-1} of 3-MCPD esters, 0.37 mg.kg^{-1} of 2-MCPD esters and 0.32 mg.kg^{-1} of glycidyl esters. There was, therefore, also an increase in the content of contaminants inside the matrix in this sample.

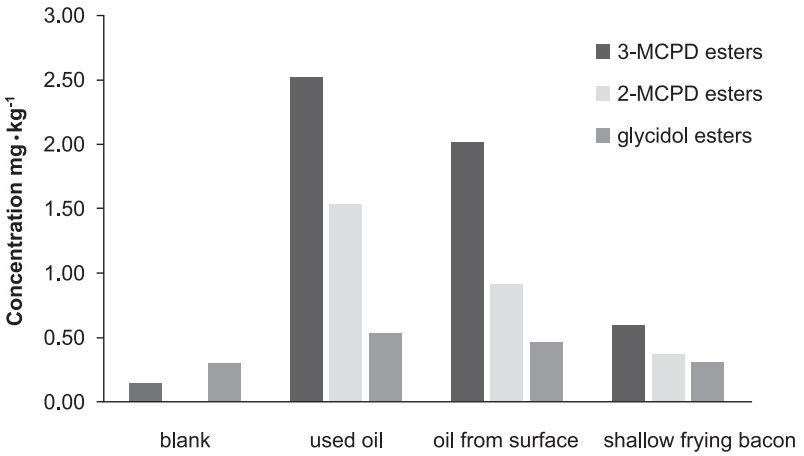

Fig. 2. The content of chloropropanediol esters and glycidyl esters in oil and bacon before and after heat processing

Conclusions

Streaky bacon contains a relatively small amount of the processing contaminants chloropropanediol esters and glycidyl esters, though there is considerable potential for their increase even after a short period of dry frying due to the presence of chloride ions (from added sodium chloride) and partial glycerol esters. The experiment demonstrated an increase of 113% in the content of 3-MCPD esters and an increase of 40% in the content of glycidyl esters in the lipid fraction. The content of these contaminants may, then, increase when bacon is shallow-fried. In this case, the quantity of contaminants transferred from the frying medium to the food being prepared may be significant. This may occur during the use of refined oil, in which the quantity of chloropropanol esters and glycidyl esters may be high – of the order of units of mg.kg^{-1} (Zelinková et al. 2006). The high ratio between the surface area and the weight of the slices leads to a considerable proportion of frying fat remaining on the food prepared and represents the principal cause of the increased content of these contaminants in the final food.

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