3-Chloropropane-1,2-diol Fatty Acid Esters in Potato Products

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Abstract: The occurrence of 3-chloropropane-1,2-diol fatty acid esters (bound 3-MCPD) in French fries and potato chips is reported. These products belong to the group of foodstuffs with high amount of 3-MCPD esters. Bound 3-MCPD was determined in all analysed samples in following concentrations: pre-frying French fries 27–64 μg/kg, French fries (final product) 100–258 μg/kg and potato chips 229–1008 μg/kg. Palm oil used for frying potato chips was analysed as well and the bound 3-MCPD levels ranged from 654 to 1920 μg/kg. 3-MCPD esters are formed in these products as a consequence of the processing technique. Especially frying oil represents the main source of these contaminants in frying potato products.

Keywords: 3-chloropropane-1,2-diol; 3-MCPD; bound 3-MCP; potato products

INTRODUCTION

3-MCPD and its fatty acid esters are contaminants that are formed during processing and manufacture of certain foods and food ingredients. Chloropropanols were identified in acid hydrolysed vegetable proteins that are produced by acid hydrolysis of plant protein materials (Davídek *et al*. 1982). 3-MCPD might be also formed in the food as a result of a reaction between a chlorine source and a lipid source. This reaction is accelerated during the heat processing of foods (Hamlet *et al*. 2002). The Commission of the European Communitites established a maximum level of 20 μg/kg, based on a 40% dry matter content, for 3-MCPD in hydrolysed vegetable protein and soy sauce (EC 2001).

Fatty acid esters of 3-MCPD are stable intermediates or by-products on the pathway leading from fats to 3-MCPD. It was demonstrated that 3-MCPD monoesters and 3-MCPD diesters are accepted by intestinal lipase as substrates *in vitro* (Seefelder *et al*. 2008). Recent studies showed that esters of 3-MCPD were found in various foodstuffs such as pickled olives, coffee, crisp bread, salty crackers, potato crisps and French fries, salami, certain types of ham, as well as some cheeses (Svejkovská *et al*. 2004). Generally, the amount of 3-MCPD in any food or food ingredient released from 3-MCPD esters by hydrolysis (bound 3-MCPD) largely exceeds that of free 3-MCPD. Relatively high levels of bound 3-MCPD contain edible oils, notably the refined palm and olive oils (Zelinková *et al*. 2006; Karšulínová *et al*. 2007). 3-MCPD fatty acid esters were also determined in breast milk and infant and baby foods (Zelinková *et al*. 2008, 2009).

The aim of this work was to determine 3-MCPD fatty acid esters in potato products such as potato chips and French fries. The amount of bound 3-MCPD in potato chips was correlated to the amount of bound 3-MCPD in palm oils used to frying potato chips.

MATERIALS AND METHODS

Chemicals. 3-Chloropropane-1,2-diol (3-MCPD, > 98%) was purchased from E. Merck (Germany), 3-MCPD-d_5 (99.4%) from Dr. Ehrenstorfer GmbH (Germany), phenylboronic acid (PBA, ≥ 97%)

and sulphuric acid (> 95%) from Fluka Chemie (Switzerland). Ester of 3-MCPD with palmitic acid and deuterium labelled ester of 3-MCPD-d_5 with palmitic acid were synthesised according to Kraft *et al*. (1979) an purified on a silica gel column using light petroleum ether/diethyl ether mixtures. All other reagents and solvents were of analytical grade.

Analysed samples. It was analysed 32 samples of French fries (16 samples – pre-frying and 16 samples – final product). French fries were produced with the same technology from two cultivars of potatoes grown in two localities (Table 1). Palm oil Master Frit (Italy) was used as frying oil. The pre-frying was carried out at temperature 158°C for 2 min and the samples were deep-frozen to temperature –18°C. The finally frying was carried out at 180°C for 3 minutes. Furthermore 16 samples of potato chips (Table 2) were analysed. Potatoes were grown in locality Valečov and after harvest were fried at temperature 170°C for 2 minutes. Two series (A and B) of the samples were obtained during two frying days. Palm oil used for frying potato chips were analysed for 3-MCPD content as well.

Isolation of lipids. The lipids were extracted by the Soxhlet method (Standard Methods 1964).

Determination of free and bound 3-MCPD. Free and bound 3-MCPD was analysed according the method of Divinová *et al*. (2004). Three parallel examinations of each sample were made.

GC/MS analysis. Capillary GC/MS analysis of bound 3-MCPD was carried out on an Agilent Technologies 6890N gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a quadrupole mass selective detector Agilent 5975 MSD (70 eV). Gas chromatography was performed on a capillary column Equity-1 (30 m × 0.25 mm × 1 µm, Supelco, Bellefonte, PA, USA). The injector was held at 250°C (splittles), the column temperature was programmed from 80°C (1 min) to 170°C at a rate of 10°C/min, then to 200°C at a rate of 3°C/min and then to 300°C (15 min) at a rate 10°C/min. Helium was used as the carrier gas (flow rate 0.8 ml/min), 1 µl sample was injected. For quantification purposes, single-ion monitoring was used to monitor ions at *m/z* 147 (3-MCPD) and at *m/z* 150 (3-MCPD-d_5).

RESULTS AND DISCUSSION

Model experiments simulating processed foods showed that 3-MCPD esters arise from either acylglycerols or glycerol in a reaction with naturally present or intentionally added sodium chloride. The formation of 3-MCPD is a multivariate problem, which depends not only on fat, salt and water contents, but also on processing temperature and time. This work is focused on the occurrence of bound 3-MCPD in French fries (pre-frying and final fried) and potato chips.

The French fries samples produced from two potato cultivars grown in two localities were analysed for fat and 3-MCPD content. The content of lipids in the pre-frying samples were much lower (2.7–4.3%) in comparison with final product

Table 1. Analysed samples of pre-frying French fries and final frying French fries

Sample	Cultivar/locality	Fat content (%)		Sample	Cultivar/locality	Fat content (%)	
		pre-frying	frying			pre-frying	frying
1K1	Karin/Velhartice	2.7	10.5	1G1	Granola/Velhartice	3.6	10.3
1K2	Karin/Velhartice	2.9	10.2	1G2	Granola/Velhartice	3.5	9.6
1K3	Karin/Velhartice	3.3	9.6	1G3	Granola/Velhartice	3.1	10.1
1K4	Karin/Velhartice	4.3	10.7	1G4	Granola/Velhartice	3.2	9.6
2K1	Karin/Valečov	4.1	8.8	2G1	Granola/Valečov	3.5	10.3
2K2	Karin/Valečov	4.0	9.4	2G2	Granola/Valečov	3.3	10.9
2K3	Karin/Valečov	3.0	8.7	2G3	Granola/Valečov	2.7	9.3
2K4	Karin/Valečov	3.0	9.3	2G4	Granola/Valečov	3.2	10.0
Average Karin		3.4	9.7	Average Granola		*3.3*	10.0
Average Valečov		3.4	9.6	Average Velhartice		*3.3*	10.1

Table 2. Analysed samples of potato chips

Sample	Cultivar	Fat content (%)	Sample	Cultivar	Fat content (%)
A-1	Pirol	37.1	B-1	Lady Clare	41.4
A-2	Pirol	39.9	B-2	Lady Clare	40.7
A-3	Crispy	44.2	B-3	Lady Clare	42.3
A-4	Crispy	41.9	B-4	Lady Clare	42.3
A-5	Crispy	44.0	B-5	Lady Clare	42.9
A-6	Crispy	42.8	B-6	Lady Clare	40.2
A-7	Crispy	43.3	B-7	Saturna	41.8
A-8	Saturna	40.0			
A-9	Saturna	41.1			

(8.7–10.9%). The free form of 3-MCPD was not detected or was under the limit of quantification (< 9 μg/kg) in all samples, although each sample contained relatively high amount of bound 3-MCPD. Also in this case were measured much lower concentrations of 3-MCPD esters in pre-frying French fries (27–64 μg/kg), than in final French fries (100–258 μg/kg), as shown Figure 1. The average levels of bound 3-MCPD were following: cultivar Karin 44 μg/kg, cultivar Granola 40 μg/kg, locality Velhartice 45 μg/kg and locality Valečov 39 μg/kg. No significant differences were observed in regard to the potato cultivar or growing locality. It is evident that the amount of 3-MCPD fatty acid esters is connected with the content of lipids in these products. It was proven that potato chips fat is predominantly consisted of oil used for frying chips (more than 99%). Bound 3-MCPD in fresh potatoes was determined to be very low (2.2 μg/kg), higher amount was measured in potato flakes (17.9 μg/kg) (Doležal et al. 2008). It was also shown, that bound 3-MCPD is contained in refined edible oils, especially in refined palm oil (average 2821 μg/kg) (Karšulínová *et al*. 2007). Oils using for frying could be therefore the main source of these contaminants occurring in final fried products.

Based on the latest knowledge, the analysis of potato chips and oils used for their frying were made. The fat content in potato chips ranged from 39.9 to 44.2%. As was expected, bound 3-MCPD in frying oils was significantly higher (654–1920 μg/kg) than in potato chips (229–1008 μg/kg). The results of analysis is summarised in Figure 2. Bound 3-MCPD in frying oil samples was in average 2.4 times higher than in potato chips. Similarly were compared bound 3-MCPD in frying oil with bound 3-MCPD in fat of potato chips. The value 0.99 was calculated as the average ratio, which also demonstrated that 3-MCPD esters in potato products originated predominantly from the frying oil.

CONCLUSIONS

Edible oils (especially refined oils) represent the main source of these contaminants in frying foods. Further studies should be therefore focused on the strategies to reduce these compounds in edible oils or preferentially used oils with low levels of these contaminants.

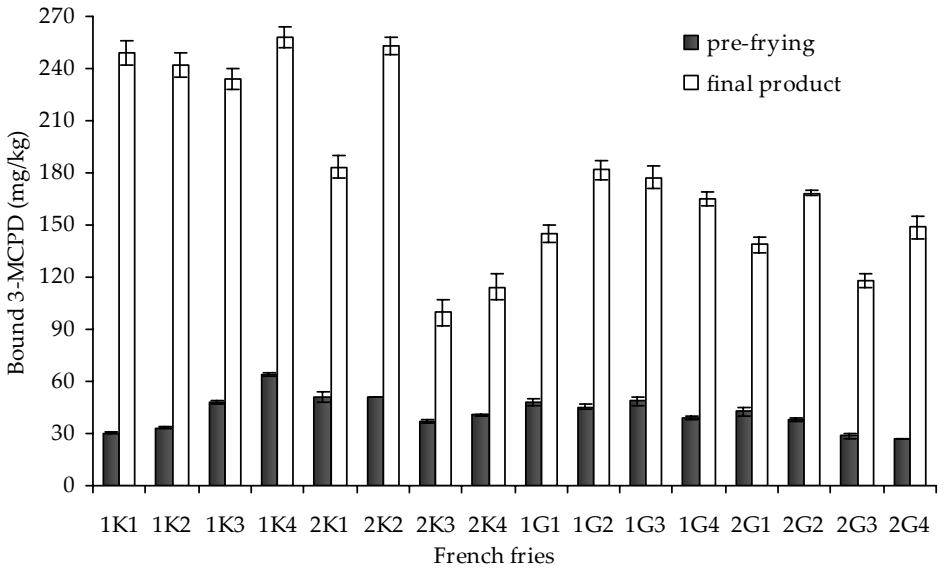

Figure 1. Bound 3-MCPD in French fries

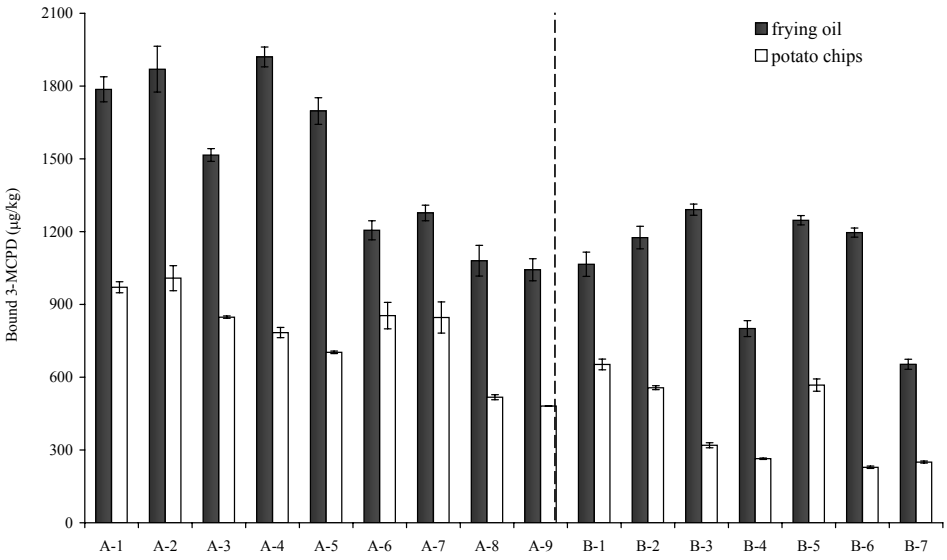

Figure 2. Bound 3-MCPD in frying oils and potato chips

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