Analysis of Bread Lipids for 3-MCPD Esters

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Abstract: Objective of this work was determination of processing contaminant known as 3-MCPD (3-chloropropane-1,2-diol) in its free and bound form in breads with defined parameters of processing. Selected and analysed were 24 samples, which represented two sets of breads produced in bakeries equipped with a continual line. In all cases determinations were carried out for breadcrumb and crust separately. The first set of samples were wheat-rye breads produced chronologically in ten days in the bakery Michelská pekárna, slightly different in temperatures and times of baking. The second set contained 14 samples of wheat-rye breads with a content of rye flour less than 40% differing in the yeast type and acidity. These breads were produced in the bakery Kontinua. The fat content was determined in all samples by Soxhlet extraction. Free and bound 3-MCPD was determined by gas chromatography–mass spectrometry method. Concentration of free 3-MCPD in samples was at interval < 9–54.5 μg/kg. Concentration of bound 3-MCPD was at interval 1.56–23.60 mg/kg of fat (i.e. 5.7–84.9 μg/kg of sample).

Keywords: bread; 3-chloropropane-1,2-diol; 3-MCPD; 3-MCPD esters; contaminants

INTRODUCTION

Esters of 3-chloropropane-1,2-diol (3-MCPD) with fatty acids were first identified in hydrolysed vegetable proteins in 1980 and later in aniline denaturated rapeseed oil decontaminated using hydrochloric acid and in the neutral lipid fraction of goat milk. Recently bound forms of 3-MCPD were found in a number of foods. The 3-MCPD esters represent a new class of processing food contaminants derived from lipids. In general, it appears that the formation of 3-MCPD esters in edible oils is linked with a preliminary heat treatment of oilseeds and oil refining (Zelinková *et al*. 2006). Our recent findings indicate that the formation of 3-MCPD esters (monoesters and diesters with higher fatty acids) is characteristic of a variety of processed foods. 3-MCPD esters represent the bound form of 3-MCPD, from which free 3-MCPD can be released by a lipase-catalysed hydrolysis. In the majority of cases, the amount of bound 3-MCPD exceeds that of free 3-MCPD (Doležal *et al*. 2005; Divinová *et al*. 2007; Karšulínová *et al*. 2007; Zelinková *et al*. 2008, 2009).

MATERIAL AND METHODS

Chemicals. 3-Chloropropane-1,2-diol (98%), hexane for organic trace analysis and tetrahydrofurane p.a. (99.5%) were obtained from Merck (Darmstadt, Germany), phenylboronic acid and sulphuric acid for organic trace analysis (> 95%) were from Fluka Chemie (Buchs, Switzerland), 3-chloropropane-1,2-diol-d_5 (99.4%) was from Dr. Ehrenstorfer (Augsburg, Germany), acetone p.a. (99.5%) and methanol p.a. were products of Lach-Ner (Neratovice, Czech Republic), diethyl ether p.a. (99.7%), petroleum ether p.a. (b.p. 40–60°C), sodium bicarbonate (99.5%) and sodium chloride p.a. (99.9%) were products of Penta (Chrudim, Czech Republic).

Materials. The first set of 10 samples were wheat-rye breads produced chronologically in ten days in the bakery Michelská pekárna, slightly different in temperatures and times of baking (Table 1). The second set contained 14 samples of wheat-rye breads with a content of rye flour less than 40% differing in the yeast type and acidity of the starter dough (Table 2). These breads were produced in the bakery Kontinua.

Table 1. Temperatures and time of baking for 10 samples from the bakery Michelská pekárna

Sample No.	Temperatures in the segments of oven (°C)									Time (min)
	1	2	3	4	5	6	7	8	9	
16	300	300	220	235	265	230	200	200	180	44
17	295	290	225	230	265	230	200	205	185	44
18	–	295	230	235	–	245	200	200	185	44
19	–	305	225	225	270	230	200	195	180	48
20	305	300	230	230	265	230	200	200	195	46
21	305	305	235	250	265	235	205	205	175	46
22	300	300	235	225	265	230	200	200	180	45
23	305	305	235	230	270	235	205	205	190	44
24	305	305	235	235	265	235	205	205	185	46
25	315	310	255	240	280	240	210	210	190	42

Methods. Free 3-MCPD and its esters were determined according to the modified GC/MS procedure of Divinová *et al*. (2004) described in detail by Divinová *et al*. (2007). Three parallel determinations of each sample were made.

RESULTS AND DISCUSSION

Determination of 3-MCPD (3-chloropropane-1,2-diol) in its free and bound form in white wheat breads showed that the highest levels of both free and bound 3-MCPD were found in the hottest region of loaf, i.e. the crust. Effect of temperature on the production of 3-MCPD was observed also after toasting of sliced breads (Hamlet & Sadd 2004).

The first set of 10 samples were wheat-rye breads produced with defined parameters of processing on a continual line chronologically in ten days in the bakery Michelská pekárna, slightly different in temperatures in individual parts of oven and time of baking (Table 1). Concentration of free 3-MCPD in samples of the first set was at interval < 9–33.0 μg/kg with no significant differences between breadcrumb and crust (Figure 1). Concentration of bound 3-MCPD (Figure 2) was at interval 1.56–21.13 mg/kg of fat (i.e. 5.7–71.9 μg/kg of sample). Dissimilarity of baking conditions were not so sufficient to make differences in production of 3-MCPD excluding samples No. 24 and 25, where higher temperatures lead to two times higher level of free and bound 3-MCPD.

Acidity of reaction medium has evident straight impact on 3-MCPD production as was shown recently on model systems and also influences enzymic activity in doughs. The second set contained 14 samples of wheat-rye breads with a content of rye flour less than 40% differing in the yeast type and acidity. These breads were produced in the bakery Kontinua. Concentration of free

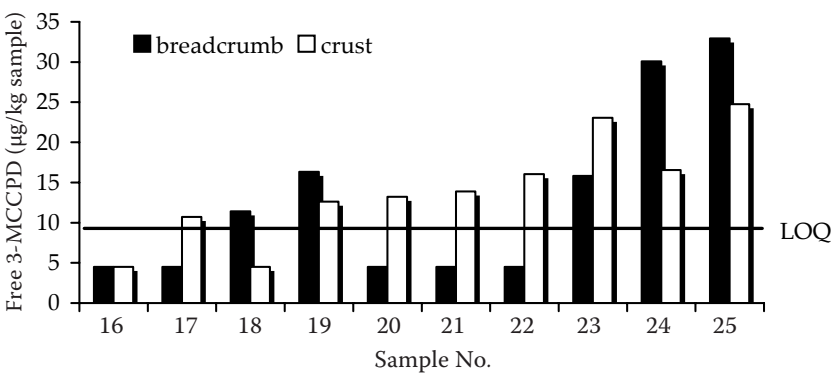

Figure 1. Concentration of free 3-MCPD in bread after slightly different baking conditions

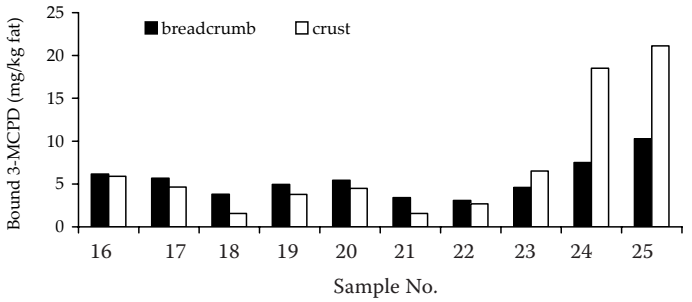

Figure 2. Concentration of bound 3-MCPD in bread after slightly different baking conditions

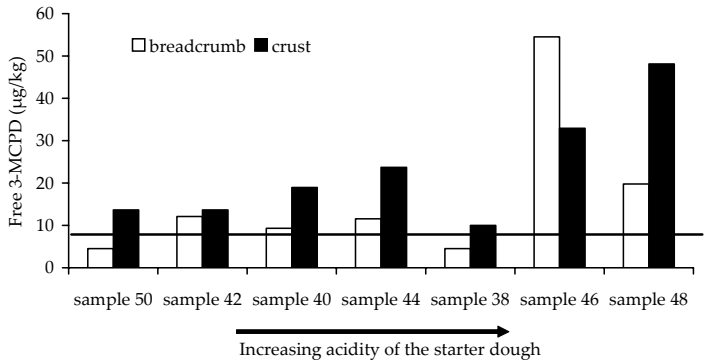

Figure 3. Concentration of bound 3-MCPD in bread according to increasing acidity of the starter dough

3-MCPD in samples of the second set was at interval < 9–54.5 µg/kg. Concentration of bound 3-MCPD was at interval 2.18–23.60 mg/kg of fat (i.e. 19.7–84.9 µg/kg of sample). The trend of arising level of free 3-MCPD was obvious at arrangement of samples with stabilised yeast according to increasing acidity of the starter dough (Figure 3), but no straight dependence on concentration of bound 3-MCPD was observed.

Table 2. Acidity of starter dough and breadcrumb in 14 samples from the bakery Kontinua

Sample No.	Acidity of starter dough	Acidity of breadcrumb
37	22.7	7.1
38	27.2	7.8
39	23.2	7.2
40	23.8	7.8
41	23.2	7.2
42	23.0	7.8
43	22.3	7.1
44	26.8	7.8
45	24.8	6.9
46	28.2	7.5
47	26.0	7.5
48	29.1	6.9
49	27.7	7.6
50	19.8	6.5

Acidity = ml NaOH (c = 0.1 mol/l)

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