

## 3-Chloropropane-1,2-diol in Models Simulating Processed Foods: Precursors and Agents Causing its Decomposition

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### Abstract

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Formation of 3-chloropropane-1,2-diol (3-MCPD) was studied in model mixtures consisting of sodium chloride and either glycerol or various lipids (phospholipids, monoacylglycerols, diacylglycerols, triacylglycerols) derived mainly from palmitic and oleic acids. The average amount of 3-MCPD formed from these precursors after 30 min of heating at 200°C was from 9.7 (lecithin), to 5.1 (diacylglycerols), 4.7 (glycerol), 3.1 (triacylglycerols), and 2.9 (monoacylglycerols) µmol/mol, respectively. The formation of 3-MCPD from glycerol (one of the major precursors) was also studied in the presence of glutathione, cysteine, disodium carbonate and sodium bicarbonate, i.e. compounds having the potential to decompose 3-MCPD or to prevent its formation. The compound the most active in preventing the formation of 3-MCPD was sodium bicarbonate followed by disodium carbonate, cysteine and glutathione. The addition of glutathione lowered the level of 3-MCPD produced from glycerol and NaCl to approximately 80%, of cysteine to 42%, of disodium carbonate to 14%, and of sodium bicarbonate to as little as 8% in comparison to samples with no additive.

**Keywords:** chloropropanediols; 3-chloropropane-1,2-diol; 3-monochloropropane-1,2-diol; 3-MCPD; acylglycerols; phospholipids; glycerol; glutathione; cysteine; carbonates

Acid-hydrolysed vegetable protein (acid-HVP) commonly manufactured by hydrolysis of protein-rich vegetable materials with hydrochloric acid was introduced in 1886 and since then has been regularly used as a food seasoning and ingredient of savoury foods such as soups, sauces, gravy mixes, bouillon cubes, soya sauce, etc. Since 1978, several chlorine-containing C3 alcohols (commonly called chloropropanols) have been found as contaminants of acid-HVP (VELÍŠEK *et al.* 1978). The principal chloropropanol found in the traditionally processed acid-HVP is 3-MCPD (3-chloropropane-1,2-diol), first identified in model experiments with lipids hydrolysed by hydrochloric

acid in 1979 (VELÍŠEK *et al.* 1979; DAVÍDEK *et al.* 1980) and then in acid-HVP in 1981 (DAVÍDEK *et al.* 1982). Its enantiomers, i.e. (*R*)-3-MCPD and (*S*)-3-MCPD, have been found in the acid-HVP as a racemic mixture quite recently (VELÍŠEK *et al.* 2002). As a consequence, manufacturers have been modifying their production processes to reduce the levels of 3-MCPD in acid-HVP.

Based on the findings of numerous toxicological studies, the European Commission Scientific Committee for Food concluded in 1995 that 3-MCPD should be regarded as a genotoxic carcinogen (EC Scientific Committee for Food 1995). Because of the potential hazards to human health, the limit of 1 mg/kg 3-MCPD

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in HVP (on dry basis) was established by the Food Chemical Codex in December 1997 (CODEX 2001). Commission Regulation 466/2001 which came into effect as from 5<sup>th</sup> April 2002 set a maximum level of 0.02 mg/kg for 3-MCPD in soy sauce and acid-HVP within the European Community.

It has been established that hydrochloric acid and lipids occurring in the raw materials used for the acid-HVP production are precursors of chloropropanols (VELÍŠEK *et al.* 1978). Model experiments with glycerol (VELÍŠEK *et al.* 1979; COLLIER *et al.* 1991), triacylglycerols (VELÍŠEK *et al.* 1979; DAVÍDEK *et al.* 1982; COLLIER *et al.* 1991), phospholipids (VELÍŠEK *et al.* 1982; COLLIER *et al.* 1991), and lipids isolated from raw materials (VELÍŠEK *et al.* 1982) have clearly shown that 3-MCPD is predominantly formed by the reaction of hydrochloric acid with residual lipids associated with the proteinaceous material used in the production of HVP. It has been shown that the most important precursors of chloropropanols are triacylglycerols and, to a smaller extent, phospholipids and glycerol in decreasing order. Corresponding reaction mechanisms have been presented (COLLIER *et al.* 1991).

Recent studies (CREWS *et al.* 2002; HAMLET *et al.* 2002) have demonstrated in a range of foods and food ingredients the presence of 3-MCPD levels of 10–30 µg/kg as a consequence of the processing and storage conditions. These studies have been mainly focused on three sectors of the food industry, i.e. on meat products (salami, beefburgers), dairy products (processed cheese, cheese alternatives), and cereal products (malt, malt extract), respectively. Domestic cooking of foods has been also shown to result in elevated levels of 3-MCPD in, e.g., toasted biscuits and breads, doughnuts, grilled cheeses and fried batters (CREWS *et al.* 2001).

It has been shown (CALTA *et al.* 2003) in models simulating processed foods that 3-MCPD evidently arises at elevated temperatures from lipids and sodium chloride naturally present or intentionally added. The level of 3-MCPD strongly depends on the concentration of sodium chloride and reaches the maximum value at about 4–7% of NaCl and in media containing approximately 13–17% water. Evidently, further studies are needed to investigate

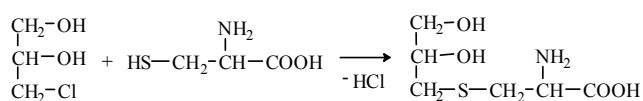
the formation of 3-MCPD from lipids and sodium chloride under conditions more typical for baking, roasting and toasting processes. The aim of this research was to study the formation of 3-MCPD in models using systems with low water activity that simulate surface layers of foods so to compare the potential of various classes of lipids as the precursors of 3-MCPD.

Another aim of this work was to evaluate the potential of various additives to lower the level of 3-MCPD formed. Glutathione and cysteine were selected as the representatives of sulfur-containing organic compounds, disodium carbonate and sodium bicarbonate were the representatives of inorganic compounds. These substrates were chosen as the representative reagents since they either occur naturally in foods or have been commonly used as food additives (e.g. dough improvers, dough raising agents etc.).

Glutathione occurs in animal cells in relatively large amounts (300–1500 mg/kg) while in higher plants and microorganisms lower levels of glutathione have been found. For example, wheat flour contains 10–15 mg/kg glutathione (VELÍŠEK 2002). Most proteins contain 1–2% cysteine, its level in wheat is about 2.5% (g/16 g N). Wheat contains glutathione and cysteine in the free state as thiol compounds (GSH, CSH), in the oxidised form (GSSG, CSSC) and in the protein-bound forms (GSSP, CSSP) (BELITZ & GROSCH 1999).

Glutathione and cysteine, in their thiol forms, significantly influence the rheological properties of wheat flour dough through thiol-disulfide interchange with wheat gluten. These thiols decrease the dough strength and stability as the viscosity of the dough drops. Cysteine hydrochloride added to doughs used for some pasta products and biscuits at about 0.01% lowers the required kneading time by 15–20%. It also inhibits the formation of the Maillard reaction products, melanoidins. For breadmaking, where flours with a high gluten content are used, the optimised levels of cysteine increase the loaf volume.

Sodium bicarbonate and disodium carbonate have been used as food additives (E 500), either as chemical individuals or in mixtures, e.g. in the



3-chloropropane-1,2-diol

cysteine

S-(2,3-dihydroxypropyl)cysteine

Figure 1. Reaction of 3-MCPD with cysteine

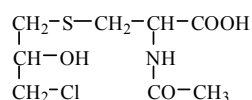


Figure 2. Structure of 3-chloro-2-hydroxypropylmercapturic acid

production of cocoa and cocoa products, for the adjustment of pH in certain foods and as raising agents for bakery products.

The reaction of 3-MCPD with cysteine in neutral media leads predominantly to the formation of *S*-(2,3-dihydroxypropyl)cysteine (Figure 1). *N*-(2,3-dihydroxypropyl)amino acids are the major products in alkaline media (VELÍŠEK *et al.* 1991). Analogous reactions can be expected with reduced glutathione. The thiol group of either cysteine or glutathione can open the ring of epoxides. For instance, 3-chloro-2-hydroxypropylmercapturic acid (Figure 2) has been identified (together with free 3-MCPD) in urine of rats dosed intraperitoneally with epichlorohydrin (DE ROOIJ *et al.* 1996). This acid arose as a detoxification product by the reaction of epichlorohydrin with glutathione and by hydrolysis of the adduct. Reactions of 3-MCPD with cysteine and other thiols may, at least partly, explain the absence of 3-MCPD in, e.g., roasted coffee. It is well known that green coffee beans contain higher levels of cysteine than, e.g., barley during roasting of which 3-MCPD forms. During roasting of coffee, several volatile thiols are formed such as 2-furfurylthiol, 3-methylbut-2-en-1-thiol and other compounds (BELITZ & GROSCH 1999).

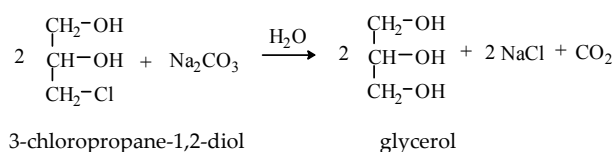


Figure 3. Reaction of 3-MCPD with disodium carbonate

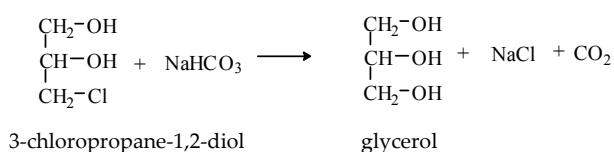


Figure 4. Reaction of 3-MCPD with sodium bicarbonate

The reaction of 3-MCPD with either disodium carbonate (Figure 3) or sodium bicarbonate (Figure 4) gives glycerol as the final degradation product.

## MATERIALS AND METHODS

**Chemicals.** 3-Chloropropane-1,2-diol (98%, 3-MCPD) was obtained from Merck (Germany), phenylboronic acid, palmitoylchloride (95%), DL- $\alpha$ -monopalmitin (98%), 1,3-dipalmitoylglycerol (99%), tripalmitin (99%), triolein (99%), isopropylidene glycerol were from Fluka Chemie (Switzerland), 1-monooleoyl-*rac*-glycerol (99%), 1,3-diolein (99%) and 2-methoxyethanol from Sigma (St Luis, USA), propane-1,2-diol from Aldrich Chemie (Germany), glycerol, Tween 80, reduced glutathione, cysteine, sodium chloride (NaCl), disodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) from Lachema (Czech Republic). Crude soy lecithin was supplied by Setuza a.s. (Czech Republic), and purified according to MARMER (1985) by extraction with acetone (purity 93.6%). Methyl laurate, methyl myristate, methyl palmitate and methyl stearate were synthesised.

**Synthesis of monoacylglycerols.** Monoacylglycerols were synthesised at the Department of Dairy and Fat Technology, ICT Prague, according to the method of CHANDRAN and BHATNAGAR (1968) with slight modification. Sodium (0.0145 mol) and methanol (1 ml) were added to isopropylidene glycerol (0.4 mol) heated to 50°C. Methyl ester of fatty acid (0.2 mol) was added and the mixture was heated to 170°C, stirred for 3 hours and then cooled to room temperature. The mixture dissolved in 300 ml of diethyl ether was extracted with water (three 150 ml portions), dried over anhydrous disodium sulfate, and the solvent was removed. The scission of the resulting 1-acylisopropylidene glycerol (0.138 mol) was achieved by dissolving the ester in 220 ml of 2-methoxyethanol and 82.5 g of boric acid and refluxing over a steam bath for 3 hours. The cooled mixture was mixed with diethyl ether (500 ml), washed with water (four 300 ml portions), dried over anhydrous disodium sulfate, and the solvent was evaporated. The crude *sn*-1-monacylglycerol was recrystallised from diethyl ether. The purity of the synthesised *sn*-1-monacylglycerols (determined by GLC/FID) was as follows: laurate 97.2%, myristate 92.5%, palmitate 91.4%, stearate 97.5%.

**Reaction of 3-MCPD precursors with sodium chloride.** The respective 3-MCPD precursor, i.e. glycerol, acylglycerols, lecithin (200 mg each), NaCl

(10 mg, i.e. 3.47% w/w, i.e. 5% w/w with respect to the respective 3-MCPD precursor), and an inert emulsifier (Tween 80, 30 mg) were placed in a 5 ml glass tube, 48  $\mu$ l water was added (its content was 16.67% w/w, i.e. 20% w/w of the dry matter), the tube was sealed and heated in an oven at 200°C for 30 min and then cooled to room temperature. The cold tube was opened, 0.2 ml of the internal standard (propane-1,2-diol, 200  $\mu$ g) in water was added. The tube content was transferred to a separating funnel and the tube was rinsed with three portions of hexane (one 4 ml portion and two 3 ml portions) and the individual washings were transferred to the separating funnel. The tube was then rinsed with 2 ml of water, this washing was added to the separating funnel and the content was shaken. The aqueous extract was collected in a 25 ml distillation flask. The washing and extraction were repeated with three additional 2 ml portions of water. The final aqueous extract was evaporated to dryness. The residue was dissolved in 2 ml of 20% sodium chloride solution and used for the determination of 3-MCPD by gas-liquid chromatography.

**Reaction of glycerol with glutathione, cysteine, disodium carbonate and sodium bicarbonate.** Glycerol (200 mg), NaCl (10 mg, 3.47% w/w), emulsifier Tween 80 (30 mg) and reduced glutathione ( $\gamma$ -L-glutamyl-L-cysteinylglycine)/cysteine/disodium carbonate/sodium bicarbonate (0.0 mg, 0.2 mg, 0.5 mg, 1 mg) were placed in a 5 ml glass tube, water was added to make its content 16.67% w/w (i.e. 20% w/w when expressed as % of the sum glycerol/NaCl/emulsifier/additive), the tube was sealed and heated in an oven at 200°C for 30 min. The procedures for the extraction were as described for above the reaction with sodium chloride.

The formation of 3-MCPD as influenced by the time of heating at 200°C was determined in the same models with glycerol as the precursor of 3-MCPD. Reaction mixtures containing 0.2 mg of glutathione/cysteine/disodium carbonate/sodium bicarbonate were heated in an oven for 0, 5, 10, 15, 20, 25, 30 min. A model containing glycerol only was analysed for comparison as blank. The procedures for the extraction were the same as described for the reaction with sodium chloride.

**Determination of 3-chloropropane-1,2-diol by GLC/FID.** The method of PLANTINGA *et al.* (1991) was used with slight modifications. The residue was dissolved in 2 ml of 20% NaCl solution in a 25 ml flask and heated with 0.2 ml phenylboronic acid in acetone (250 mg/ml) for 20 min at 90°C.

The flask was cooled and its content was extracted with 2 ml hexane. One  $\mu$ l of the hexane layer was analysed by gas-liquid chromatography at a split rate of 2:1 using an SPB-I fused silica capillary column (30 m  $\times$  0.20 mm i.d., 0.80  $\mu$ m film thickness, Supelco, USA) fitted to a Hewlett-Packard 6890 gas chromatograph equipped with a flame ionisation detector. The oven temperature was initially set to 80°C, raised to 300°C at a rate of 5°C/min, and kept at 300°C for 16 min. The injector and detector port temperatures were set to 250°C and 300°C, respectively. The helium carrier gas flow was 0.5 ml/min. Two parallel determinations of each sample were made. The results were expressed either in mg of 3-MCPD per 1 kg of the respective precursor or in  $\mu$ mol of 3-MCPD per 1 mol of the substrate.

**Determination of 3-chloropropane-1,2-diol by GLC/MS.** The analysis was carried out using an Agilent Technologies 6890N gas chromatograph equipped with a Series 5973 mass selective detector and a data processing system (MSD ChemStation, G1701CA version C.00.00). The separation of 3-MCPD boronate was performed on a DB-1HT capillary column (15 m  $\times$  0.25  $\mu$ m i.d., 0.1  $\mu$ m film thickness; Agilent Technologies, USA). The helium carrier gas was supplied at a constant flow rate of 0.8 ml/min. The sample was injected into the split injection port (split ratio 2:1) at 260°C, with a solvent delay of 2 min. The oven temperature was initially set to 80°C, then programmed to rise at a rate of 4°C/min to 110°C and then at a rate of 20°C/min to 300°C, and kept at this temperature for 10 min.

Target analytes were ionised by electron impact (EI) at 70 eV. Quantitative analysis was performed in the multiple ion detection (MID) mode using ions  $m/z$  91 and 147 of propane-1,2-diol phenylboronate, used as the internal standard, and ions at  $m/z$  91, 147 and 196 of 3-MCPD phenylboronate. The method was used for the determination of 3-MCPD formed from glycerol and 1-monoacylglycerols, FID was used as the detector in all other instances.

## RESULTS AND DISCUSSION

### Formation of 3-chloropropane-1,2-diol from selected precursors

Pure commercially available and synthesised 1-monoacylglycerols (a homologous series of compounds derived from lauric, myristic, palmitic,

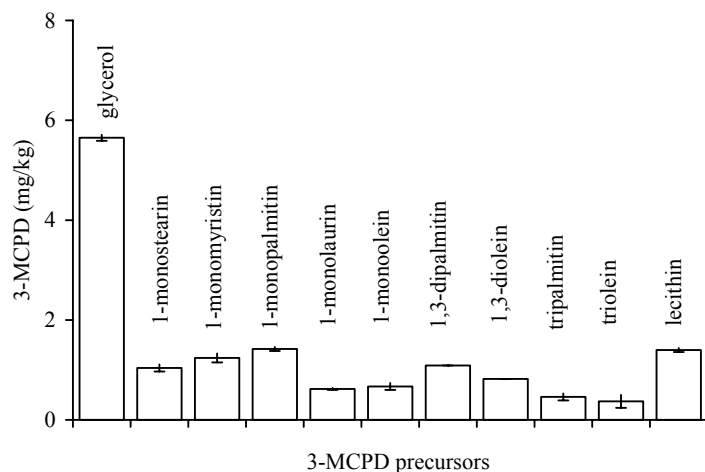


Figure 5. Formation of 3-MCPD (mg/kg precursor) from pure selected precursors

stearic, and oleic acids), 1,3-diacylglycerols and triacylglycerols derived from either palmitic or oleic acid were studied for their ability of producing 3-MCPD on heating with sodium chloride. Glycerol and lecithin were analysed for comparison. The amounts of 3-MCPD formed from the individual chemicals are presented in Figure 5 in common units (mg/kg precursor) to show the amount of the respective precursor formed and its impact on the final level of 3-MCPD. Figure 6 shows the amounts of 3-MCPD formed as expressed in  $\mu\text{mol/mol}$  precursor to enable the assessment of the respective precursor ability to form 3-MCPD, and to explain its reactivity related to its structure.

It seems (Figure 6) that the most potent precursor of 3-MCPD was lecithin, followed by diacylglycerols, glycerol, and other acylglycerols. Glycerol can be expected to be the major precursor of 3-MCPD in, e.g., fermented foods including certain types of cheeses, bread and malt while in other

instances acylglycerols can be expected to be the major precursors. Phospholipids do not seem to be an important source of 3-MCPD as they generally occur in foods in low amounts. For example, the content of phospholipids is 0.01–0.1% in pork lard, 0.02 in refined vegetable oils, and 0.5–1.5% in wheat lipids, respectively (VELÍŠEK 2002).

3-MCPD can form from phospholipids and acylglycerols by direct nucleophilic substitution of the acyl group by chloride ion but these primary products have to be finally hydrolysed to free 3-MCPD. Another possibility is the prior hydrolysis of the fatty acid (phosphoric acid) moiety in the respective precursor leading to glycerol where the direct nucleophilic substitution of the hydroxyl group follows. Figure 6, a plot of 3-MCPD concentrations v.s. the individual precursors where the values are expressed in  $\mu\text{mol/mol}$  precursor, shows that the individual precursors of 3-MCPD hardly differ in their ability to produce 3-MCPD. This means that, if enough water is present in the

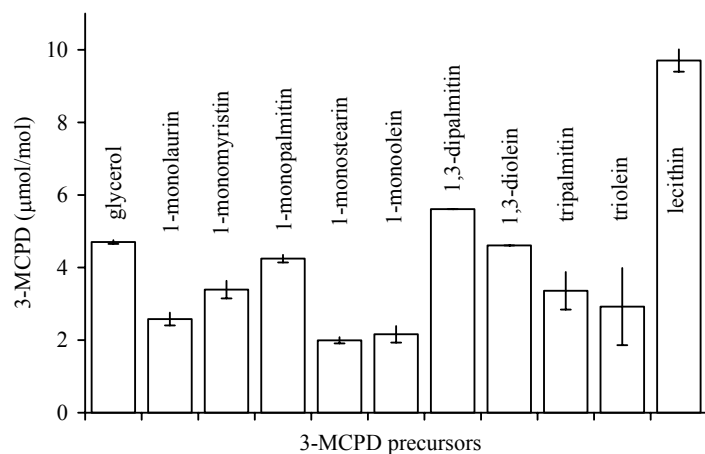


Figure 6. Formation of 3-MCPD ( $\mu\text{mol/mol}$  precursor) from pure selected precursors (lecithin was expressed as *sn*-1,2-dioleoyl-3-phosphocholine)

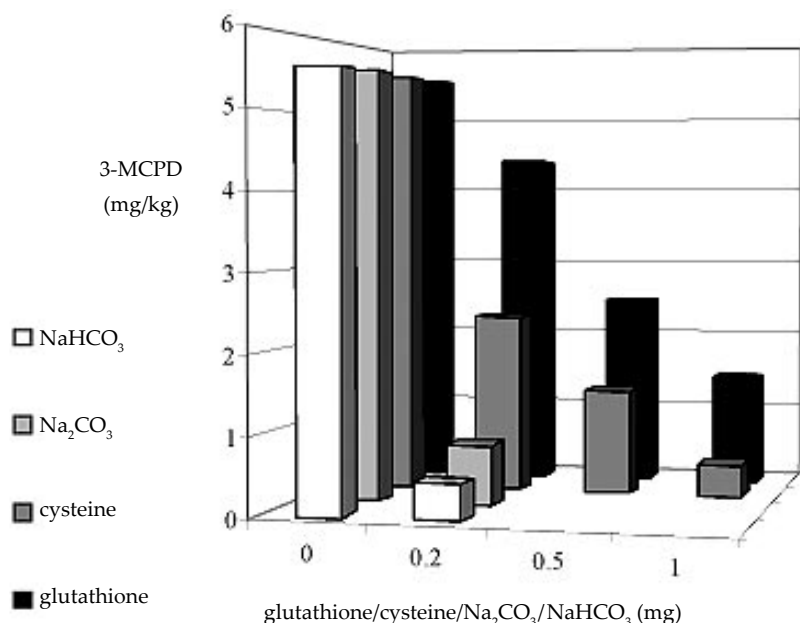


Figure 7. Formation of 3-MCPD (in mg/kg precursor) from glycerol and NaCl in the presence of glutathione/cysteine/NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub>

system, both pathways discussed above proceed with comparable reaction rates.

#### Formation of 3-chloropropane-1,2-diol affected by selected additives

Formation of 3-MCPD from glycerol and NaCl in the presence of all the four reagents (glutathione, cysteine, disodium carbonate, sodium bicarbonate) is summarised in mg per kg of precursor in Figure 7, and in  $\mu\text{mol}$  per mol of precursor in Figure 8.

It can be seen that the amount of 3-MCPD generated from glycerol and NaCl was inversely proportional to the amount of glutathione added to the model mixture. The highest level of 3-MCPD was found in models without glutathione while the lowest amount of 3-MCPD (about ten times lower than in those without glutathione) was formed in models containing 1 mg of glutathione. Analogous results were obtained using model mixtures with cysteine, this compound, however, was even more active in the decomposition of 3-MCPD than glutathione.

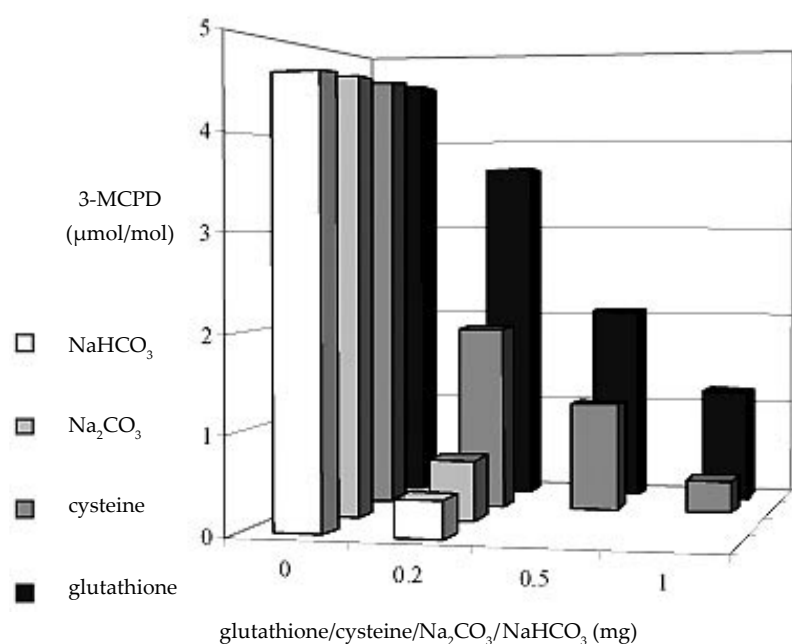


Figure 8. Formation of 3-MCPD (in  $\mu\text{mol/mol}$  precursor) from glycerol and NaCl in the presence of glutathione/cysteine/NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub>

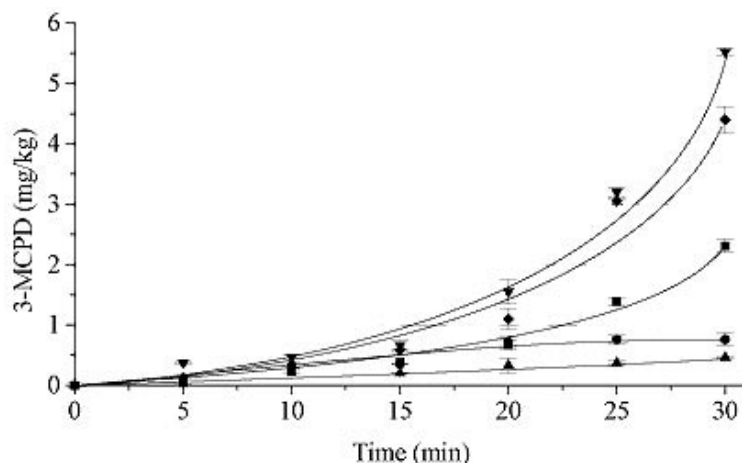


Figure 9. Formation of 3-MCPD (mg/kg glycerol) as a function of time

▼ = glycerol, ◆ = glycerol/glutathione,  
■ = glycerol/cysteine, ● = glycerol/Na<sub>2</sub>CO<sub>3</sub>,  
▲ = glycerol/NaHCO<sub>3</sub>

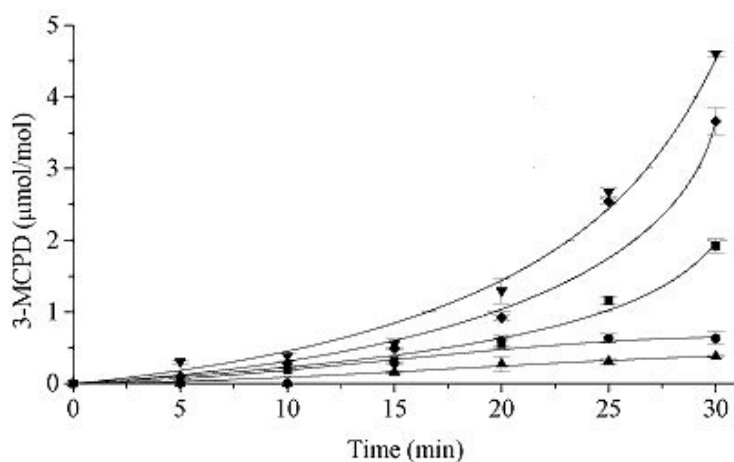


Figure 10. Formation of 3-MCPD (μmol/mol glycerol) as a function of time

▼ = glycerol, ◆ = glycerol/glutathione,  
■ = glycerol/cysteine, ● = glycerol/Na<sub>2</sub>CO<sub>3</sub>,  
▲ = glycerol/NaHCO<sub>3</sub>

The differences in the reactivity of these two thiols can be explained by their different mobility and/or solubility in the reaction mixture (emulsion).

Similar results were obtained using either disodium carbonate or sodium bicarbonate instead of glutathione or cysteine. Both reagents act in a similar way, i.e. by increasing the pH of the reaction mixture but it seems that their different reactivities do not simply reflect their different dissociation constants ( $4.31 \times 10^{-7}$  mol/l and  $5.61 \times 10^{-11}$  mol/l for bicarbonate and carbonate, respectively) as in this case disodium carbonate would be more active than sodium bicarbonate. The only explanation of this phenomenon is that sodium carbonate needs water (one mol per one mol) to be able to react with 3-MCPD, and water is a limiting factor in our emulsions. When 0.2 mg of the carbonates were added, the amount of the 3-MCPD formed was reduced. Disodium carbonate reduced the 3-MCPD level to only 0.76 mg/kg, while the

corresponding value found for cysteine was 2.31 mg/kg. Sodium bicarbonate was even more effective as the amount of 3-MCPD formed was only 0.46 mg/kg. When the level of either carbonate was increased to 0.5 mg or 1.0 mg, no 3-MCPD formation could be detected.

The amounts of 3-MCPD formed in the mixtures containing 0.2 mg glutathione/cysteine/NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> during 30 min of the reaction are plotted against the reaction time in Figure 9 (in mg/kg) and Figure 10 (in μmol/mol). As it can be seen, the most active additive compound was sodium bicarbonate followed by disodium carbonate, cysteine, and glutathione. The addition of 0.2 mg of the respective additive represents only 0.083% of the total weight of the reaction mixture but it results in a substantial reduction of the level of 3-MCPD formed. The addition of glutathione reduced the level of 3-MCPD produced from glycerol and NaCl to approximately 80%, of cysteine to 42%, of disodium carbonate to

14%, and of sodium bicarbonate to as little as 8% in comparison to the blank.

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## Souhrn

VELÍŠEK J., CALTA P., CREWS C., HASNIP S., DOLEŽAL M. (2003): **3-Chloropropan-1,2-diol v modelových systémech simulujících zpracování potravin: prekurzory a činidla způsobující jeho rozklad.** Czech J. Food Sci., 21: 153–161.

Byl studován vznik 3-chloropropan-1,2-diolu v modelových směsích obsahujících chlorid sodný a glycerol nebo různé lipidy převážně odvozené od palmitové a olejové kyseliny (fosfolipidy, monoacylglyceroly, diacylglyceroly, triacylglyceroly). Průměrné množství 3-chloropropan-1,2-diolu vzniklé z uvedených prekurzorů po 30 minutách zahřevu na 200 °C se poněkud lišilo. Z lecithinu vzniklo 9,7, z diacylglycerolů 5,1, z glycerolu 4,7, z triacylglycerolů 3,1 a z monoacylglycerolů 2,9  $\mu$ molu 3-chloropropan-1,2-diolu z 1 molu prekurzoru. Vznik 3-chloropropan-1,2-diolu z jednoho z hlavních prekurzorů, tj. glycerolu, byl dále studován v přítomnosti glutathionu, cysteinu, uhličitanu sodného a hydrogenuhličitanu sodného, tzn. sloučenin schopných reagovat s 3-chloropropan-1,2-diolem a předcházet tak jeho vzniku nebo jej rozkládat. Nejaktivnější sloučeninou byl hydrogenuhličitan sodný, dále následoval uhličitan sodný, cystein a glutathion. Přídavek glutathionu snížil množství vzniklého 3-chloropropan-1,2-diolu na zhruba 80 %, cysteinu na 42 %, uhličitanu sodného na 14 % a hydrogenuhličitanu sodného dokonce na 8 % v porovnání s modelem, který tyto látky neobsahoval.

**Klíčová slova:** chlorpropandioly; 3-chloropropan-1,2-diol; 3-monochloropropan-1,2-diol; 3-MCPD; acylglyceroly; fosfolipidy; glycerol; glutathion; cystein; uhličitan

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