

## Optical Isomers of Chloropropanediols: Mechanisms of their Formation and Decomposition in Protein Hydrolysates

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### Abstract

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Protein hydrolysates produced by hydrochloric acid hydrolysis were analysed for 3-chloropropane-1,2-diol and its enantiomers. It was found that (*R*)-3-chloropropane-1,2-diol and (*S*)-3-chloropropane-1,2-diol were present in the hydrolysates in equimolar concentrations. Model experiments with glycerol, triolein and soy lecithin heated with hydrochloric acid in solution showed that these materials were precursors of 3-chloropropane-1,2-diol and 2-chloropropane-1,3-diol and, as expected, yielded racemic 3-chloropropane-1,2-diol. Yields of 3-chloropropane-1,2-diols decreased in the order triolein > lecithin > glycerol. The mechanisms of 3-chloropropane-1,2-diol enantiomers formation during the production of protein hydrolysates are presented and discussed as well as the reaction pathways of their decomposition in alkaline media *via* the corresponding intermediates, (*R*)- and (*S*)-glycidol, respectively. Both epoxides are hydrolysed to glycerol and form a variety of products with hydrolysate constituents.

**Keywords:** chloropropanediols; chloropropanols; 3-chloropropane-1,2-diol; 2-chloropropane-1,3-diol; glycidol; MCPD; enantiomers; protein hydrolysates

Chemical hydrolysates of proteins or hydrolysed vegetable proteins (HVP) are commonly produced by hydrolysis with hydrochloric acid (HCl) of various proteinaceous vegetable materials, for example oilseed meals and wheat gluten. They are widely used as seasonings and ingredients in processed savoury food products and pre-prepared foods. It has been established that HCl reacts with lipids present in the raw material used for the production of HVP yielding free fatty acids, partial acylglycerols, glycerol and other compounds (VELÍŠEK 1989). Glycerol chlorohydrins (including chloropropanediols) have been identified as minor products resulting from the reaction of HCl with acylglycerols, phospholipids and glycerol (VELÍŠEK *et al.* 1979, 1980; DAVÍDEK *et al.* 1980). Investigations focused on these glycerol monochlorohydrins have shown that the major chlorinated propanols in HVP are 3-chloropropane-1,2-diol (also known as 3-monochloropropane-1,2-diol, 3-MCPD) and 2-chloropropane-1,3-diol (2-MCPD), their relative proportions being approximately in the ratio of 10:1. For example, typical HVP

contained 100–800 mg/kg 3-MCPD and 10–90 mg/kg 2-MCPD (VELÍŠEK 1989; VELÍŠEK & LEDAHUDCOVÁ 1993). Recent surveys have reported high levels of 3-MCPD in some samples of soy sauce imported into the UK (MACARTHUR *et al.* 2000) and in soy sauces and similar products available in China (JIN *et al.* 2001). In addition, lower levels of 3-MCPD have been found in certain foods such as salami, beefburgers, biscuits, cream crackers, doughnuts (CREWS *et al.* 2002), and in ingredients such as dark speciality malts, modified starches and meat extracts (HAMLET *et al.* 2002). Domestic cooking of foods has also been shown to result in elevated levels of 3-MCPD in, e.g., toasted bread and grilled cheeses (CREWS *et al.* 2001).

The toxicological effects of glycerol chlorohydrins have been intensively studied. A recent review of the toxicological, metabolic and mechanistic data on 3-MCPD (LYNCH *et al.* 1998) showed its genotoxicity *in vitro*, but there was no evidence of genotoxicity *in vivo*. It was concluded that tumours reported in certain animals had de-

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veloped as a result of non-genotoxic mechanisms and were considered not to be relevant to humans exposed to trace amounts of 3-MCPD.

The (*S*)-enantiomer of 3-MCPD (*S*)-3-MCPD was found to possess antifertility activity but none of the detrimental effects on kidneys that could be associated with the (*R*)-isomer (*R*)-3-MCPD (PORTER & JONES 1982). The antifertility effect is based on the inhibition of the conversion of fructose to lactate catalysed by glyceraldehyde phosphate dehydrogenase (FORD & WAITES 1982; JONES & FORD 1984). In 2001, the EU Scientific Committee for Food (SCF) reviewed the toxicological data on 3-MCPD and set a Tolerable Daily Intake (TDI) for 3-MCPD to 2 µg/kg/bodyweight/day (SCF 2001).

Toxicological studies on 3-MCPD were considered by the UK Committee on the Mutagenicity of Chemicals in Food, Consumer Products and the Environment (COM) in October 2000. The committee concluded that 3-MCPD could be regarded as having no significant genotoxic potential *in vivo* (COM 2000). The UK Food Advisory Committee (FAC) has advised industry that they should “continue to take all steps necessary to reduce the concentrations of 3-MCPD in foods and food ingredients to the lowest technologically achievable” (FAC 2000). The European Commission has introduced legislation coming into effect in 2003 which sets a limit of 0.020 mg/kg 3-MCPD in HVP and soy sauce (European Commission 2001).

Heating HVP at a slightly alkaline pH has been used by several producers of HVP to decrease the level of chloropropanediols (VELÍŠEK 1989; DOLEŽAL 1997).

3-MCPD is a chiral compound derived from prochiral glycerol. Its enantiomers have been widely used as versatile chiral synthons in the synthesis of various chiral natural products and pharmaceuticals (KASAI *et al.* 1998). Despite years of study devoted to chloropropanols, there has been no previous focus on the occurrence of the individual optical isomers of 3-MCPD in HVP or in processed foods. The mechanisms of chloropropanol formation in HVP and in processed foods remain still not completely understood, and so do the factors influencing chloropropanol formation, stability, decomposition, and secondary reactions. As the proteinaceous vegetable material can also contain chiral nonracemic compounds, one cannot exclude *a priori* the chiral induction during their hydrolysis and, subsequently, the preferential formation of one enantiomer of 3-MCPD. The research described here was intended to identify the individual enantiomers of 3-MCPD in HVP which is a prerequisite for the understanding of the mechanisms of their formation and decomposition.

## MATERIALS AND METHODS

**Materials.** 3-MCPD was obtained from Merck (Germany), (*R*)-(-)-3-chloropropane-1,2-diol, (*S*)-(+)-3-chloropropane-1,2-diol and phenylboronic acid were obtained from

Fluka Chemie (Switzerland). Propane-1,3-diol was obtained from Aldrich Chemie (Germany), glycerol and Tween 80 from Lachema (Czech Republic) and triolein from Downs Development Chemicals Ltd. (UK). Crude soy lecithin (Setuza, Czech Republic) was purified by extraction with acetone. The purity of the product was estimated on the basis of its content of phosphorus determined by atomic absorption spectrometry. The content of phosphorus was 29.2 g/kg and thus the purity of lecithin was 93.6% according to MARMER (1985). HVP samples included crude soy sauce obtained from local producer and two commercial soy sauces.

**Instrumentation.** All protein hydrolysates and model samples were analysed by gas-liquid chromatography (GLC) using a Chiraldex G-TA fused silica capillary column (30 m × 0.25 mm i. d., 0.125 µm film thickness, Astec, USA) fitted to a Hewlett-Packard 6890 gas chromatograph equipped with a flame ionisation detector. The oven temperature was held at 130°C for 40 min. The detector and injection port temperatures were 180°C and the helium carrier gas flow was set to 1 ml/min. One microlitre of each sample was injected with a split ratio of 100:1.

For the analysis of the triolein and soy lecithin hydrolysis products, a DB-1HT fused silica capillary column (15 m × 0.25 mm i. d., 0.10 µm film thickness, J&W Scientific, USA) was used. The oven temperature was set initially to 100°C and then raised to 340°C at a rate of 10°C per min, and finally kept at 340°C for 20 min. The injector and detector port temperatures were set to 300°C and 340°C, respectively. The helium carrier gas flow was 2.0 ml per min. One ml of sample was injected at a split rate of 50:1.

To confirm the identity of the compounds, gas chromatography with full-scanning mass spectrometry was applied using a G1800A GCD gas chromatograph (Hewlett-Packard, Palo Alto, USA) with the same chiral column operating under the same conditions as above. Mass spectra were obtained by EI ionisation at 70 eV over the range of 10–425 mass units, with the ion source temperature of 230°C.

## Procedures

**Determination of 3-chloropropane-1,2-diol enantiomers.** The method of PLANTINGA *et al.* (1991) was employed with a slight modification. One ml of sample and 1 ml of internal standard solution (propane-1,3-diol, 1 mg per ml in 20% sodium chloride solution) were heated for 20 minutes at 90°C with 0.4 ml phenylboronic acid in acetone in a 5 ml flask. After derivatisation and extraction, 1 µl of the hexane layer was analysed by GLC.

**Reaction of glycerol, triolein, and lecithin with hydrochloric acid.** The reaction mixture consisted of 5 mmol glycerol (triolein, lecithin) and 0.5 mol hydrochloric acid (a solution containing 6 mol/l HCl was used). The mixture was refluxed for 16 hours, then cooled to room temperature and extracted five times with 20 ml of diethyl ether.

The aqueous phase was adjusted with sodium hydroxide to pH 6, filtered and made up to 100 ml with water. Samples (1 ml) were taken for the analysis of 3-MCPD enantiomers.

**Hydrolysis of 3-chloropropane-1,2-diol esters from humins.** Lipids (2 g) extracted from humins with diethyl ether were treated with 20 ml of 1M hydrogen chloride in anhydrous methanol. After 16 h at ambient temperature, the reaction mixture was neutralised with 1M methanolic sodium hydroxide and washed five times with 10 ml of diethyl ether. The methanol solution was filtered, evaporated to dryness and the residue was analysed for 3-MCPD enantiomers.

**Degradation of 3-chloropropane-1,2-diol in alkaline HVP.** A sample of a soybean meal hydrolysate (200 g) was adjusted to pH 8.5 with 40% aqueous sodium hydroxide, made up to 250 ml and heated to 90°C. Aliquots of about 10 ml were taken, cooled, weighed, adjusted to pH 6 with concentrated hydrochloric acid and made up to 20 ml. Samples (1 ml) were taken for the analysis of 3-MCPD enantiomers.

## RESULTS AND DISCUSSION

### Determination of 3-chloropropane-1,2-diol enantiomers

Three samples of HVP produced by the traditional technological process were analysed and found to contain 351, 337, and 20 mg/kg 3-MCPD, respectively. The individual optical isomers of 3-MCPD were separated in the form of their phenylboronates and found to occur in the ratio of 1:1 i.e. as a racemic mixture (Fig. 1). Retention indices of (*S*)-3-MCPD and (*R*)-3-MCPD phenylboronates were 1665 and 1667, respectively (the separation factor of 1.02). Structures of the individual enantiomers are shown in Fig. 2.

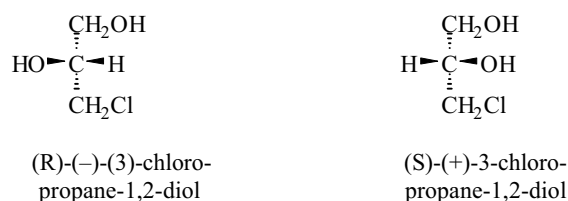


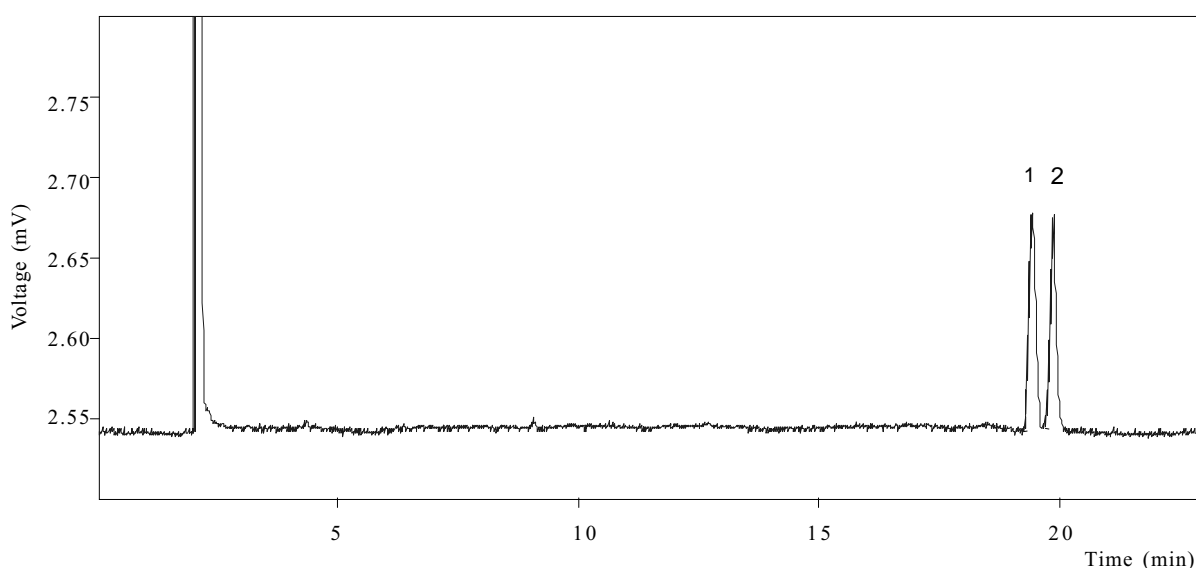
Fig. 2. Stereoformulae of optically active 3-chloropropane-1,2-diols

### Reaction of glycerol, triolein and lecithin with hydrochloric acid

Reaction of glycerol, triolein and lecithin with HCl under conditions typical for HVP manufacture (6 molar HCl, 1:100 molar ratio of substrate to HCl, heating for 16 h under reflux, i.e. at about 120°C) gave 3.3 to 13% of the theoretical yield of 3-MCPD (Table 1). Yields of 3-MCPD from triolein and lecithin were four and two times higher, respectively, than those from glycerol. Yields of 3-chloropropane-1,2-diol from triolein were about 10 times higher than the yields from lecithin, and about 100 times higher than from glycerol. COLLIER *et al.* (1991) obtained comparable results from the reaction of the same precursors heated with 5.5 molar HCl at 107°C for 16 h (2.2%, 5.7%, and 4.0% of the theoretical yield, respectively).

As expected for achiral or racemic substrate, it was further found that all the materials used gave approximately the same distribution of both 3-MCPD enantiomers, and in all these cases 3-MCPD was obtained as a racemate.

Triolein and lecithin were hydrolysed by HCl to a great extent. The major hydrolysis products of triolein were oleic acid (80%), dioleoylglycerols (8.1%) and monooleoyl-



1 = (*S*)-isomer (169 mg/kg), 2 = (*R*)-isomer (168 mg/kg), total amount = 337 mg/kg

Fig. 1. GC separation of 3-MCPD enantiomers in HVP as the corresponding phenylboronates

Table 1. Reaction of glycerol, triolein and lecithin with HCl

Reactants	Theoretical yield of 3-MCPD (%)			Yield relative to glycerol	<i>(R)</i> -isomer/ <i>(S)</i> -isomer ratio
	<i>(R)</i> -isomer	<i>(S)</i> -isomer	total		
Glycerol	1.6	1.7	3.3	1.0	0.9
Triolein	6.3	7.0	13	4.0	0.9
Lecithin	3.3	3.3	6.6	2.0	1.0

glycerols (10%), 1.9% of the starting material remained unhydrolysed. Lecithin yielded 85% free fatty acids, 0.2% diacylglycerols, 1% monoacylglycerols with 13% unchanged phospholipids.

It is well known that glycerol reacts with HCl giving rise to 3-MCPD and 2-MCPD. The distribution of both these isomers (present in the ratio of 2:1, approx.) is the result of the nucleophilic substitution of the hydroxyl groups by chloride anion, in accord with the statistical substitution of the two equivalent primary hydroxyls and one secondary hydroxyl group (COLLIER *et al.* 1991). Hydroxyl groups of glycerol are first protonated by HCl to alkyloxonium ions (conjugated acids). With the primary hydroxyls, the next stage is mainly the  $S_N2$  reaction in which the chloride ion displaces a molecule of water from the alkyloxonium cation. This pathway is stereospecific and proceeds with the inversion of configuration at the carbon that bears the leaving group (CAREY 2000). As both primary hydroxyl groups in glycerol are enantiotopic, their reactivities in substitution reaction with achiral chloride ion are equal and the substitution yields racemic 3-MCPD. However, chiral nonracemic compounds present in reaction media could, in theory, participate in the formation of transition states. Such process could result in a predominant formation of only one of the enantiomers of 3-MCPD. With the secondary hydroxyl group, this stage could in addition to

$S_N2$  also be, to some extent, the  $S_N1$  reaction in which the alkyloxonium ion dissociates to a carbenium cation (carbocation) and water. Following its formation, the carbenium cation is captured by chloride ion under the formation of 2-MCPD (Fig. 3).

According to COLLIER *et al.* (1991), triacylglycerols and phospholipids do not form chloropropanediols *via* prior hydrolysis to glycerol. The reaction of triacylglycerols with HCl proceeds principally *via* the partial diesters (1,3-diacylglycerols and 1,2-diacylglycerols) through the formation of a cyclic acyloxonium ion intermediate (Fig. 4).

The intermediate is opened by chloride ion yielding either diesters of 3-MCPD or diesters of 2-MCPD. To some extent, diesters of these chloropropanols can also arise from triacylglycerols (monoesters of chloropropanols arise from diacylglycerols) by direct nucleophilic substitution of the acyl group by chloride ion as found by MARCH (1992). Diesters of chloropropanols can be hydrolysed by HCl to the corresponding monoesters and subsequently to 3-MCPD and 2-MCPD. The ratio of the chloropropanediol isomers (3-MCPD to 2-MCPD, approximately ten to one) is controlled by the steric and electronic effects arising from the terminal ester group which directs the nucleophilic chloride anion to the  $CH_2$  carbon atom.

Diesters and monoesters of 3-MCPD have been already identified in HVP by VELÍŠEK *et al.* (1980). In this work,

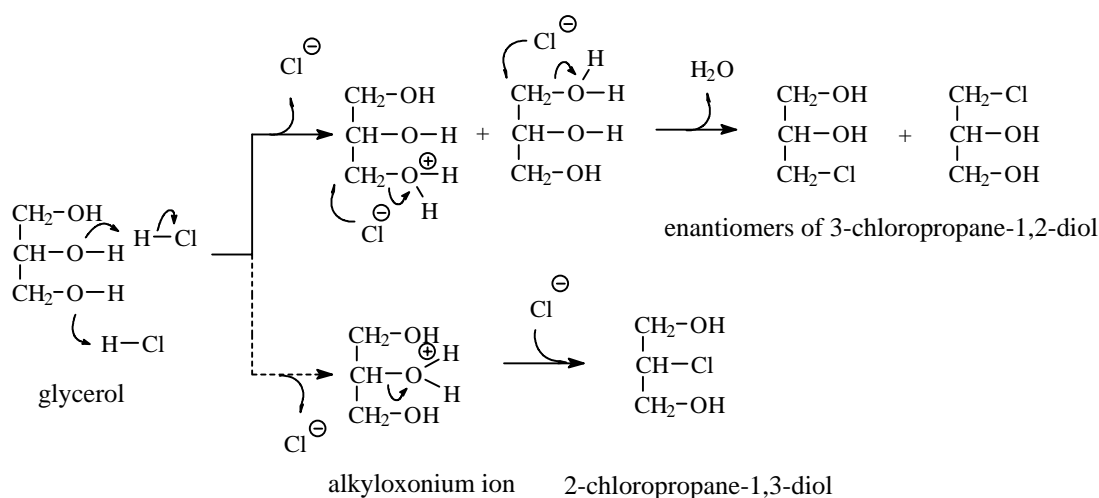


Fig. 3. Reaction of glycerol with HCl

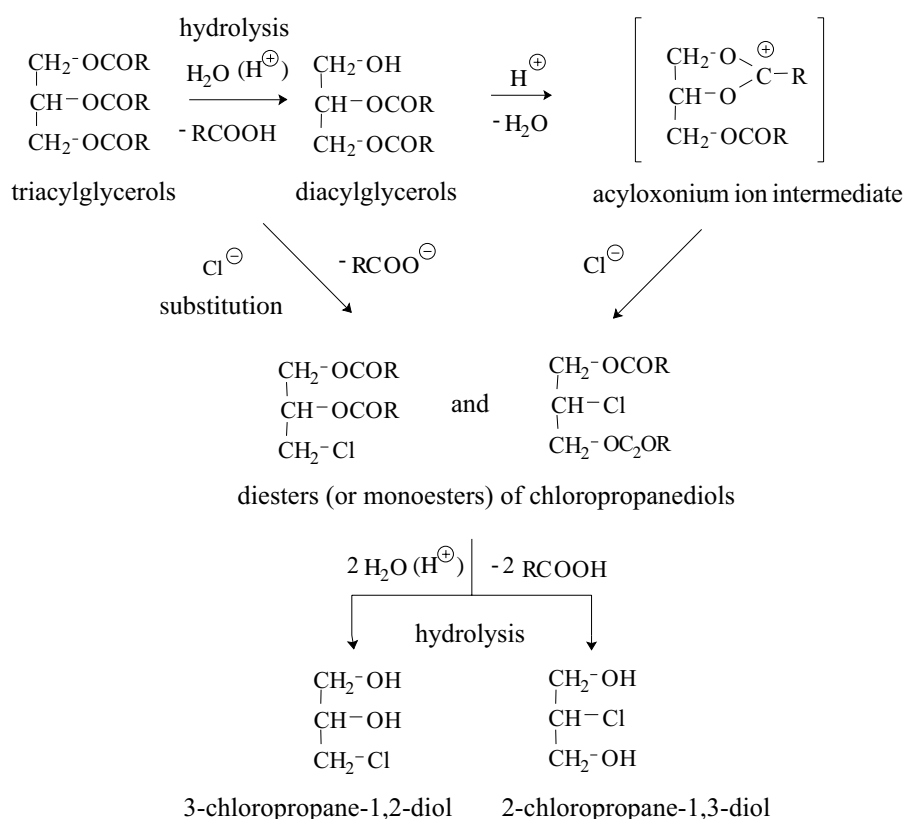
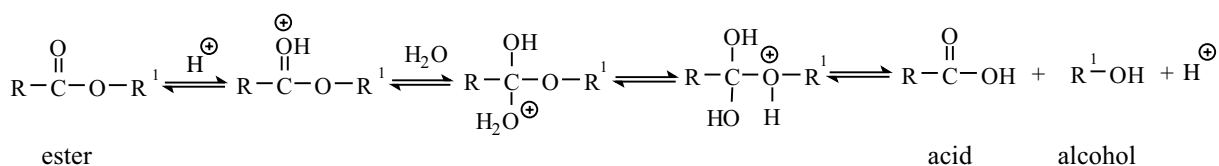


Fig. 4. Formation of chloropropanediols from acylglycerols

diesters and monoesters of 3-MCPD isolated from humins (the waste products of HVP manufacture) were hydrolysed by HCl and free 3-MCPD enantiomers were separated. It was found that the (*R*)- and (*S*)-enantiomers were again present in the ratio of 1:1. Based on these results, it can be concluded that diesters and monoesters of 3-MCPD are present in humins (and in trace amounts also in HVP) as racemic mixtures of the corresponding enantiomers. Stereospecific analysis of diesters of 3-MCPD found in goat's milk (MYHER *et al.* 1986) also showed that they were present as a racemate.

The acid-catalysed hydrolysis of triacylglycerols to diacylglycerols and of chloropropanediol esters to chloropropanediols is a reversible reaction (mechanistic designation  $A_{AC}2$ , where A denotes acid catalysis, AC indicates acyl-oxygen bond cleavage, digit 2 indicates bimolecular nature of the rate-determining step) (Fig. 5).

Our experiments with *sn*-1,2-diacylglycero-3-phosphatidylcholine showed that phospholipids were preferentially hydrolysed to totally deacylated derivatives, i.e. to a mixture of *sn*-glycero-3-phosphatidylcholine (and *sn*-glycero-2-phosphatidylcholine), or of *sn*-glycero-3-phosphatidic acid (and *sn*-glycero-2-phosphatidic acid) from which chloropropanediols arose by substitution reactions. Similarly to acylglycerols, chloropropanediols could also arise from the original phospholipids by the direct nucleophilic substitution of either the acyl group or the phosphate by chloride ion (Fig. 6). They generated a higher yield of chloropropanediols than glycerol but lower yields of chloropropanediols than triacylglycerols (COLLIER *et al.* 1991). Similarly to glycerol, phospholipids exercised little regioselectivity due to facile intramolecular isomerisation of *sn*-glycero-3-phosphatidylcholine to *sn*-glycero-2-phosphatidylcholine or *sn*-glyce-

Fig. 5. Hydrolysis of fatty acid esters in acid media by  $A_{AC}2$  mechanism



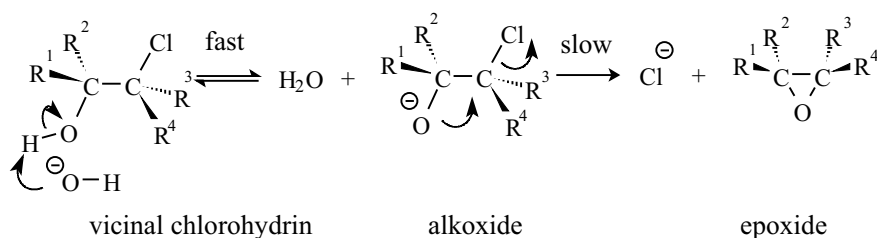


Fig. 8. Mechanism of dehydrochlorination of vicinal chlorohydrins in alkaline medium

one can accept the formation of two diastereoisomers in the reaction (Fig. 7).

In alkaline media, the decomposition of chloropropanediols is very rapid. The reaction with hydroxyl ions brings the alcohol function of the chlorohydrin to equilibrium with its corresponding alkoxide (alcoholate). The alkoxide oxygen attacks the carbon that bears the leaving chloride atom to give the epoxide. This step determines the reaction rate of dehydrochlorination. As in other nucleophilic substitution reactions, the nucleophile approaches the carbon from the side opposite the bond to the leaving chloride so that the intramolecular  $S_N$  reaction takes place with the conversion of configuration at the carbon that bears the chloride leaving group. The reaction is diastereoselective and its mechanism is outlined in Fig. 8.

Analogously to other vicinal chlorohydrins, (*R*)-3-chloropropane-1,2-diol ( $R^1 = H$ ,  $R^2 = CH_2OH$ ,  $R^3 = R^4 = H$ ) gives (*R*)-glycidol, (hydroxymethyl)oxirane, by base-promoted ring closure while (*S*)-3-chloropropane-1,2-diol ( $R^1 = CH_2OH$ ,  $R^2 = R^3 = R^4 = H$ ) yields enantiomeric (*S*)-glycidol (Fig. 9). Thus, the racemic mixture of both isomers of glycidol is obtained by the treatment of HVP with alkali. For example, optically active (*S*)-glycidol was prepared from (*S*)-3-chloropropane-1,2-diol by the action of potassium carbonate (MIYATA *et al.* 1997). Stereoformulae of the chiral glycidols (also known as oxiranemethanols or oxiranylmethanols) are given in Fig. 10.

The glycidol isomers produced are not stable but the rate of 3-MCPD decomposition is higher than that of the decomposition of glycidols. As a result, glycidols accumulate in some HVP treated with alkali (DOLEŽAL 1997). The concentration of glycidol depends on the temperature and the pH of the hydrolysate. For example, at 65°C (pH 9) the maximum concentration of glycidol, equal to about one third of the quantity of the original 3-MCPD, is reached within five minutes.

Accordingly, symmetric cyclisation of the prochiral 2-MCPD (the elimination of proton occurs from either C-1 or C-3 hydroxyl group, followed by ring closure, Fig. 8) in achiral media always leads to a mixture of both optically active glycidols.

Epoxides are very reactive compounds in which the epoxide ring can be opened by a variety of nucleophiles

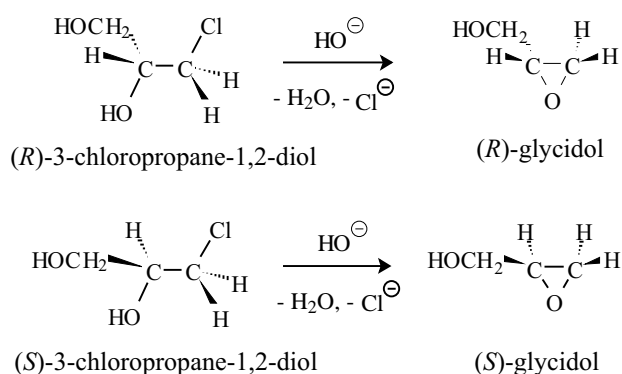


Fig. 9. Dehydrochlorination of 3-chloropropane-1,2-diol to glycidol

(water, alcohols, thiols, amines, acids etc.). Nucleophilic ring opening of epoxides has many of the features of the  $S_N2$  reaction (inversion of configuration is observed at the carbon at which substitution occurs, Fig. 11). Asymmetrical epoxides are attacked at the less substituted, less sterically hindered carbon of the ring from the side opposite to the carbon-oxygen bond (CAREY 2000).

The decomposition of chloropropanediols in alkaline medium is currently employed by some producers for the decontamination of HVP which is achieved by heating raw hydrolysates at a pH greater than seven. In our experiments, a HVP sample which contained 337 mg/kg 3-MCPD was adjusted to pH 8.5 and heated to 90°C for 30 min to simulate the decontamination process. Aliquots of the alkaline hydrolysate were taken at six minute intervals and analysed for 3-MCPD enantiomers. The final concentration of 3-MCPD after heating for 30 min was 33.9 mg/kg. The rate constants of decomposition of the individual enanti-



Fig. 10. Stereoformulae of optically active glycidols

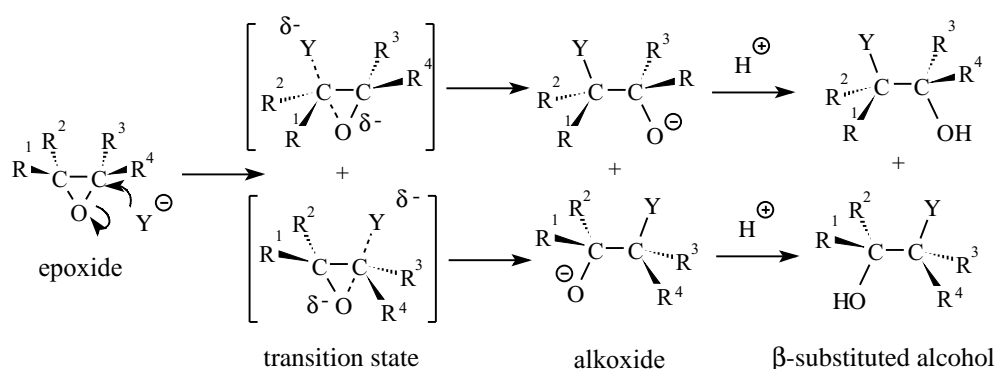


Fig. 11. Nucleophilic ring opening of epoxides

omers were calculated (first order reaction) to be  $1.9 \pm 0.3 \times 10^{-3}$ /s for both enantiomers. In other words, both enantiomers of 3-MCPD decomposed at the same rate in alkaline media and we did not observe any possible chiral influence of chiral nonracemic compounds in raw hydrolysates on the decomposition of 3-MCPD.

In HVP, the oxirane rings of both optically active glycidols are opened mostly by the action of water with the formation of glycerol (DOLEŽAL 1997). Other nucleophiles present in HVP such as HCl, chlorides, ammonia, amino acids and alcohols open the oxirane rings of glycidols to some extent. For example, the reaction of (*R*)-glycidol with HCl gives rise to (*R*)-chloropropane-1,2-diols. The major reaction product with ammonia was (*S*)-3-aminopropane-1,2-diol while (*R*)-3-aminopropane-1,2-diol arose from (*S*)-glycidol. Their racemic mixture was found in HVP (VELÍŠEK *et al.* 1992). Reactions of glycidols with amino group of amino acids led to chiral *N*-(2,3-dihydroxypropyl)amino acids (VELÍŠEK *et al.* 1991), the reaction of glycidols with glycerol yielded polyglycols (DOLEŽAL 1997). Reactions of chiral hydroxymethyloxiranes with nucleophiles were used for the synthesis of optically active natural compounds (KHAN *et al.* 1999; KITAORI *et al.* 1999; NAZIH *et al.* 2000).

This work has demonstrated that (*R*)-3-MCPD and (*S*)-3-MCPD are present in equimolar concentrations in acid hydrolysates of vegetable proteins used as food ingredients, and that they decompose at the same rate in alkaline media. It has been confirmed through model system experiments that glycerol, triolein, and soy lecithin are precursors of 3-MCPD and in accordance with the theoretical assumptions yield racemic mixtures of its enantiomers.

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## Souhrn

VELÍŠEK J., DOLEŽAL M., CREWS C., DVOŘÁK T. (2002): **Optické izomery chloropropanediolů: mechanismus jejich vzniku a rozkladu v hydrolyzátech bílkovin**. *Czech J. Food Sci.*, **20**: 161–170.

Potravinářské hydrolyzáty bílkovin získané hydrolyzou kyselinou chlorovodíkovou byly analyzovány na obsah 3-chloropropan-1,2-diolu a jeho enantiomerů. Bylo zjištěno, že (*R*)-3-chloropropan-1,2-diol a (*S*)-3-chloropropan-1,2-diol byly v hydrolyzátech přítomny v ekvimolárních koncentracích. V modelových experimentech s glycerolem, trioleinem a sójovým lecithinem zahříváných s kyselinou chlorovodíkovou se prokázalo, že tyto sloučeniny jsou prekurzory 3-chloropropan-1,2-diolu a 2-chloropropan-1,3-diolu a že poskytují racemickou směs enantiomerů 3-chloropropan-1,2-diolu. Množství vzniklého 3-chloropropan-1,2-diolu klesalo v pořadí triolein > lecithin > glycerol. Práce uvádí a diskutuje mechanismy vzniku 3-chloropropan-1,2-diolu a jeho enantiomerů

a 2-chlorpropan-1,3-diolu během výroby bílkovinných hydrolyzátů. Uvedeny jsou rovněž mechanismy rozkladu enantiomerů 3-chlorpropan-1,2-diolu v alkalickém prostředí, kdy jako meziprodukty vznikají (*R*)- a (*S*)-glycidol. Ten se dále hydrolyzuje na glycerol a se složkami hydrolyzátu poskytuje řadu dalších produktů.

**Klíčová slova:** chlorpropandioly; chlorpropanoly; 3-chlorpropan-1,2-diol; 2-chlorpropan-1,3-diol; glycidol; MCPD; enantiomery; bílkovinné hydrolyzáty

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