3-MCPD & Co – Further Update

2- and 3-monochloropropandiols (2-MCPD and 3-MCPD) belong to the chloropropanol class of compounds and can occur in foods as a result of acid treatment or intense heating processes.

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What are 3-MCPD & Co?

In addition to the free compound forms, chloropropanols also occur in bound form. 3-MCPD, 2-MCPD-, and glycidyl fatty acid esters (3-MCPDE, 2-MCPDE, and GE; cf. diagram 1) can form during the refining process of edible oils, especially in the deodorisation stage. These can be detected as undesirable process contaminants – so-called foodborne toxicants – in vegetable fats and oils and in foods produced thereof.

What is their toxicological classification?

From a toxicological point of view, the free substances are particularly noteworthy since during the digestion process in the gastrointestinal tract there is an almost complete deesterification, freeing up the free substances (2-MCPD, 3-MCPD, and Glycidol). In animal studies, free 3-MCPD were shown to have caused an increase in kidney cells. The International Agency for Research on Cancer (IARC) has classified free 3-MCPD as "possibly carcinogenic to humans" (group 2B). The data available for 2-MCPD is not yet sufficient to exclude a risk to public health. And yet because of its structural similarity to 3-MCPD, a similar toxicological relevance is assumed. Glycidol has mutagenic and carcinogenic properties and has been classified by the IARC as being "probably carcinogenic to humans" (group 2A).

What is new on the legal front?

No maximum levels have been set for 2-MCPDE and 3-MCPDE in foods. Only free 3-MCPD has been subject to a maximum level of 20 µg/kg in hydrolysed vegetable protein and soy sauces for several years now pursuant to Regulation (EC) No 1881/2006. The European Commission is due to set maximum levels for GE in vegetable fats and oils and in infant formula and follow-on formula. The draft provides for a maximum level of 1,000 µg/kg of GE in vegetable fats and oils. It is basically forbidden to market any foods that contain contaminants in amounts considered harmful to health.

How have analytical techniques developed?

In the meantime, a large number of methods for quantifying 3-MCPDE, 2-MCPDE, and GE have come into existence. In this regard, one can differentiate between direct and indirect methods. The direct methods determine each individual 2-MCPDE, 3-MCPDE, and GE congener

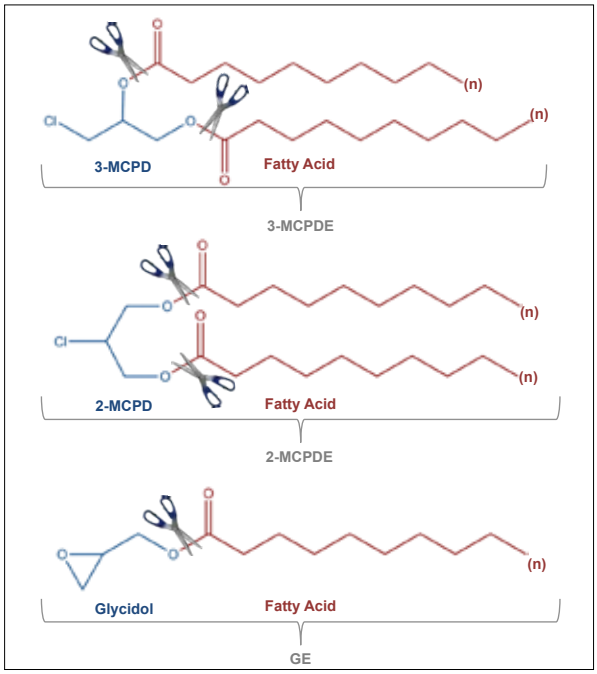

Figure 1: Overview of the structural formulas of 3 MCPD & Co

(cf. LCI-Focus issue 7/8 2008: Wie viele 3-MCPD Ester gibt es? Ein Rechenmodell / How many 3-MCPD esters are there? A Calculation Model) for example using LC-MS/MS (liquid chromatography-tandem mass spectrometry). However, analysis is made more difficult due to the need for a great number of isotope-marked standards for each individual substance. Hence routine analysis has widely adopted the indirect methods which determine the esters group-wise as a total amount. Fundamentally the indirect analysis methods are based upon splitting the esters into their free components, isolating them, and subsequently applying derivatisation. The subsequent detection process uses GC-MS (gas chromatography-mass spectrometry). The numerous methods differ mainly in terms of the type of ester hydrolysis (acidic, alkaline, or using enzymes) and the various derivatisation possibilities (PBA, phenylboronic acid; HFBA, heptafluorobutyric anhydride; HFBI, heptafluorobutyrylimidazole).

3-MCPDE and GE analysis began in 2007 with the original "Weißhaar method", which became known as the DGF C III 18 method. However, this indirect method was withdrawn by the German Society for Fat Science (DGF) and the revised version was published as the DGF Standard Method C VI 17. From 2009 to 2011 the Federal Institute for Risk Assessment (BfR) presented and optimised several indirect BfR methods (BfR 8-01, 9-01 and 10-01) which were respectively based on chloride-free approaches, various hydrolysis methods, and different derivatisation reagents. A series of indirect methods were also published by the American Oil Chemists' Society (AOCS) (AOCS Cd 29a 13/"Unilever", AOCS Cd 29b 13/"Kuhlmann 3 in 1", AOCS Cd 29c 13/"DGF", AOCS Cd 30 15). If deesterification is conducted under mild conditions (–22°C for 16 hours), simultaneous determination of 3-MCPDE, GE and also 2-MCPDE is possible. Going by the latest method developments, it is now possible to determine the bound forms and the free substances in one and the same procedure which is also known as the "Kuhlmann 5 in 2 method". In this context, the polar and nonpolar fractions are separated from each other and respectively subjected to further analysis. This enables the determination of the five process contaminants directly in the foods containing fat. SV