A review on ten years 3-MCPD esters and Glycidyl esters in fats and oils

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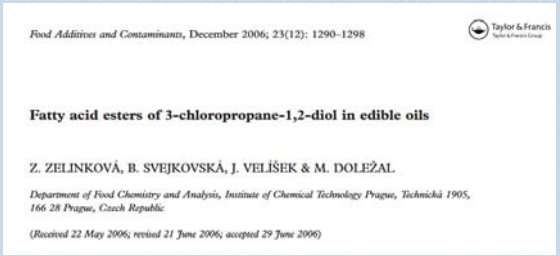
Beginning of the 3-MCPD ester story on fats and oils

October 2006: First scientific publication on esters of 3-chloropropane-1,2-diol (MCPD) in edible oils



Food Additives and Contaminants, December 2006; 23(12): 1290–1298

Taylor & Francis

Fatty acid esters of 3-chloropropane-1,2-diol in edible oils

Z. ZELINKOVÁ, B. SVEJKOVSKÁ, J. VELÍŠEK & M. DOLEŽAL

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(Received 22 May 2006; revised 21 June 2006; accepted 29 June 2006)

November 2007: Statement of the CVUA Stuttgart and the Max Rubner-Institut, Detmold

Formation of 3-MCPD and glycidyl esters during refining and modification of fats and oils: 1 – 15 **mg/kg**

Statement No. 047/2007 of the German Institute for Risk assessment, 11.12.2007

Toxicological importance of 3-MCPD ester was not clear, but BfR assumed a 100% degradation of the esters to free 3-MCPD

Toxicological assessment of free 3-MCPD

- Carcinogenic at animal tests with rats in high dosages
- SCF assumes no genotoxicity
- IARC classifies 3-MCPD as possibly carcinogenic to humans (2B)
- IARC classifies glycidol as probably carcinogenic to humans (2A)
- Limit: 20 µg/kg soy sauces and hydrolyzed plant protein (VO (EG) 1881/2006)
- TDI: 2 µg/kg BW (JECFA, EU, SCF)

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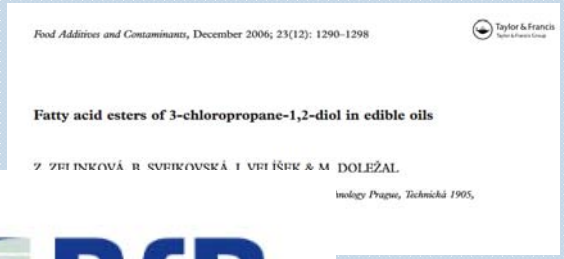
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- ...
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- TDI: 2 µg/kg BW (JECFA, EU, SCF)

BfR
Risiken erkennen – Gesundheit schützen

Säuglingsanfangs- und Folgenahrung kann gesundheitlich bedenkliche 3-MCPD-Fettsäureester enthalten

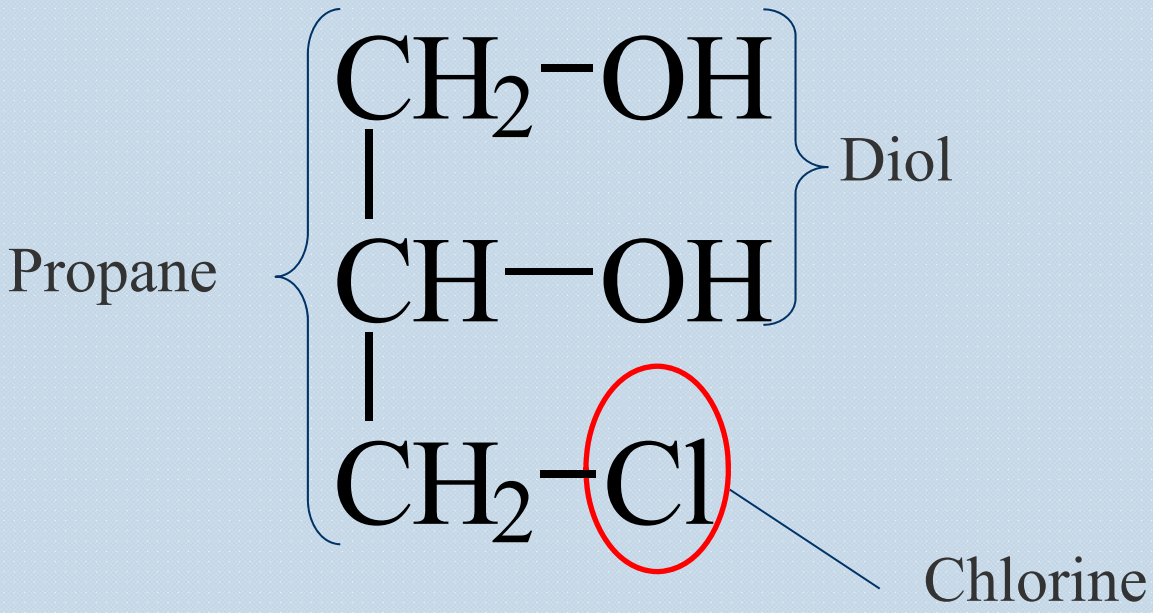
Stellungnahme Nr. 047/2007 des BfR vom 11. Dezember 2007

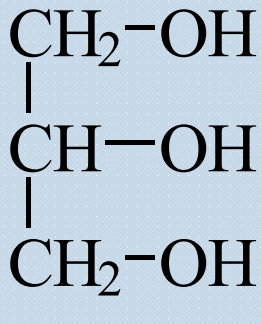
4·Framework·for·action/measures·¶

Das·CVUA·Stuttgart·hat·in·Kooperation·mit·der·Bundesforschungsanstalt·für·Ernährung·und·Lebensmittel,·Institut·für·Lipidforschung,·mögliche·Ursachen·für·die·Bildung·von·3-MCPD-Estern·untersucht.·Nahezu·die·Gesamtmenge·an·3-MCPD-Estern·wird·bei·der·Desodorierung·von·Speisefetten·und·Speiseölen·gebildet.·**From·the·perspective·of·the·risk·assessment·there·is·an·immediate·need·for·action·for·further·investigation·of·the·causes·and·a·search·for·alternative·techniques·for·the·production·of·refined·fats·with·the·aim·to·reduce·3-MCPD·esters·in·infant·milk**,·da·es·für·Säuglinge,·die·nicht·gestillt·werden·können,·außer·Humanmilch,·die·von·anderen·Müttern·stammt,·keine·Alternative·gibt.·¶

Occurrence and formation of 3-MCPD

Chloropropanols were first identified in 1978 by **Jan Velisek** in acid-hydrolysed plant proteins



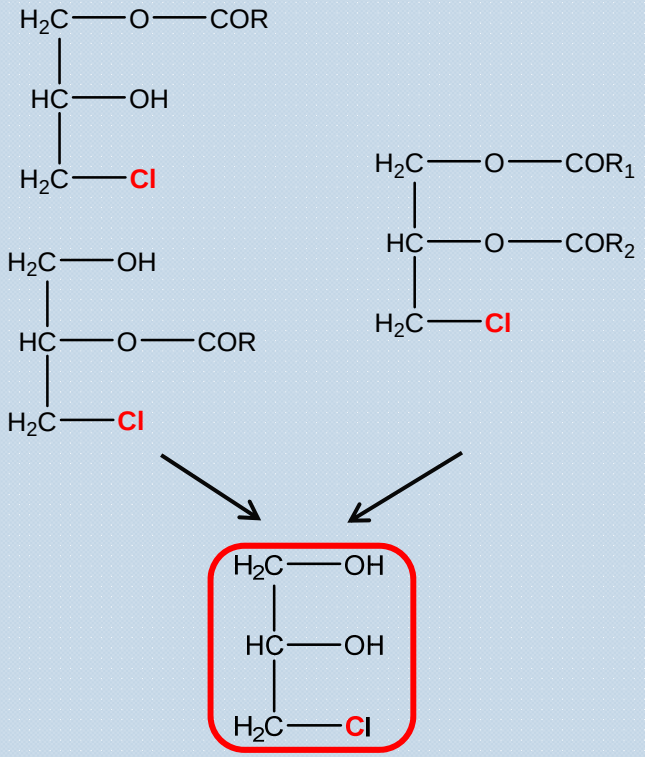


Formation during food processing

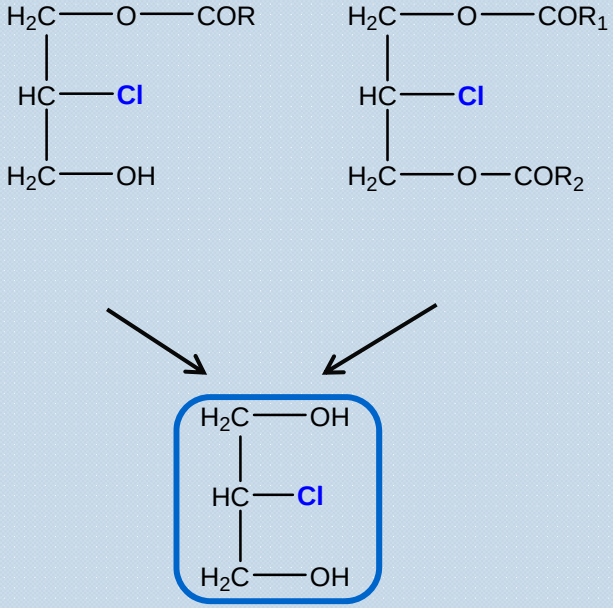
- **Processing of soy sauces**: Residues of lipids in the raw material are hydrolyzed by hydrochloric acid and glycerol reacts with chlorine
- **Baking, toasting**: Cracking of triacylglycerides at high temperature and reaction of the free glycerol with chlorine
- **Roasting**: coffee

MCPD and glycidyl esters

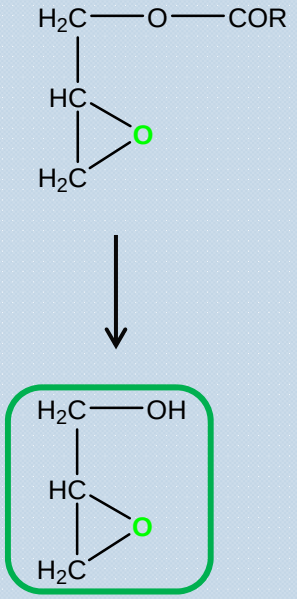
3-MCPD-FE



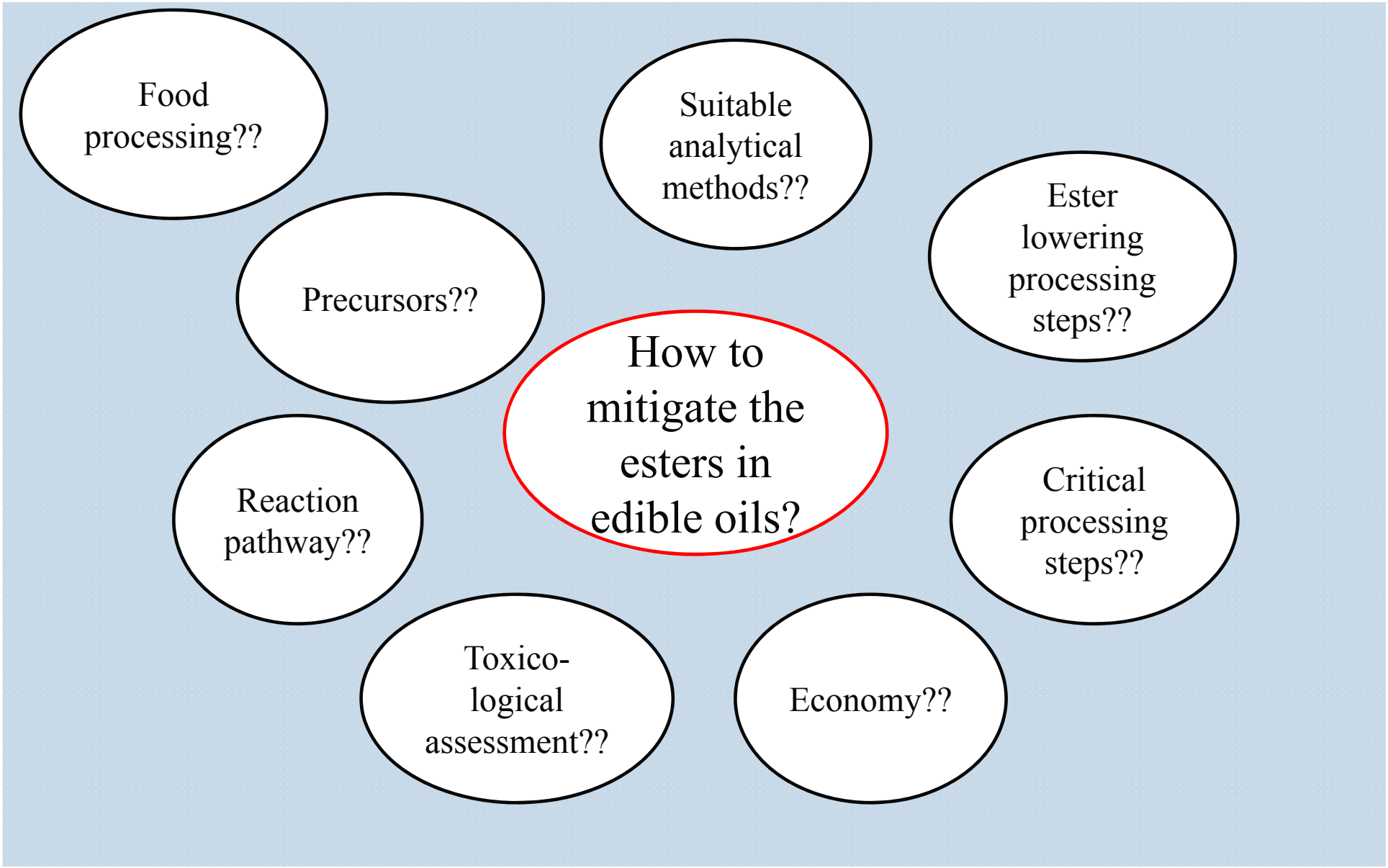
2-MCPD-FE



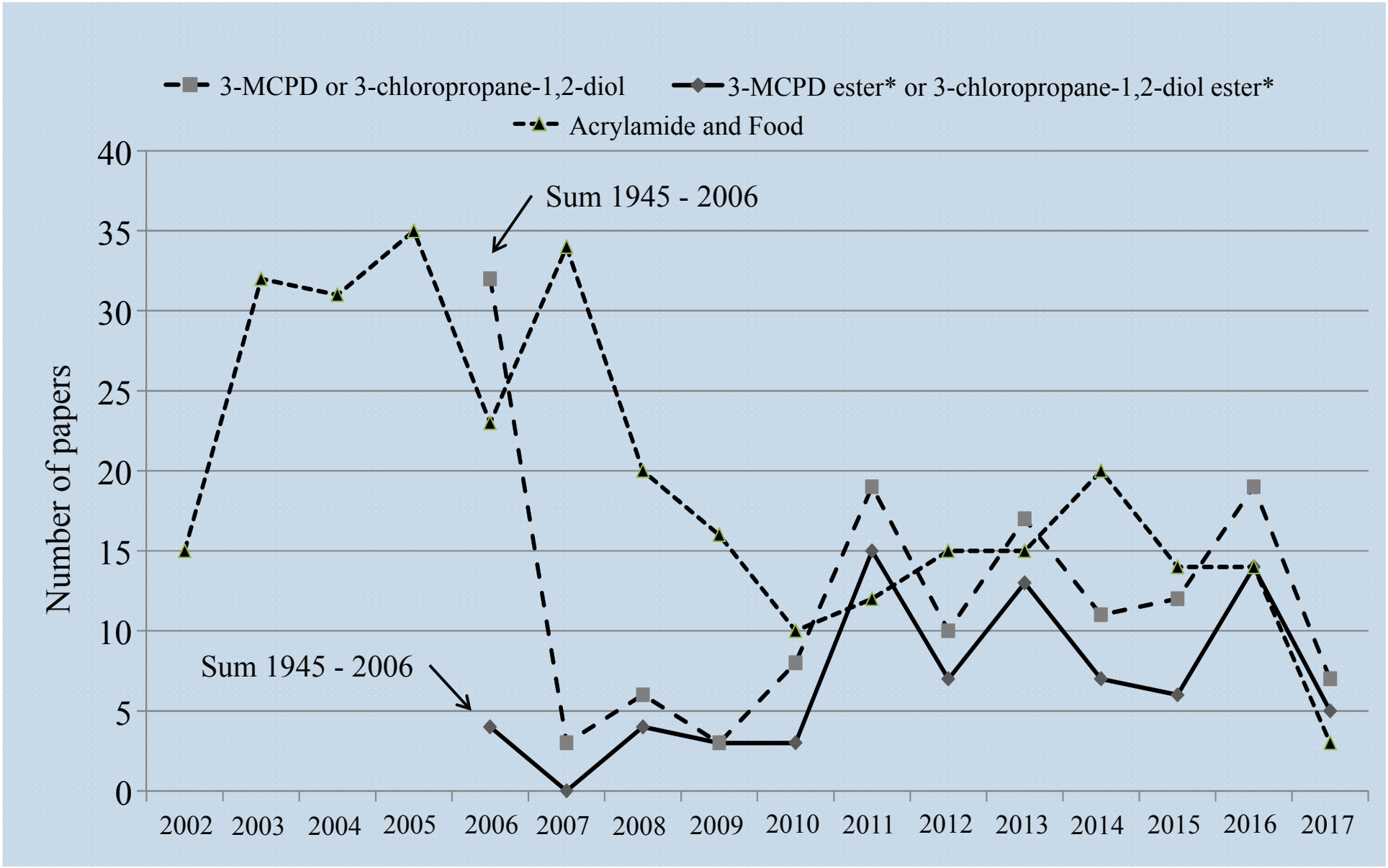
G-FE



Open questions at the beginning



Number of papers on 3-MCPD esters



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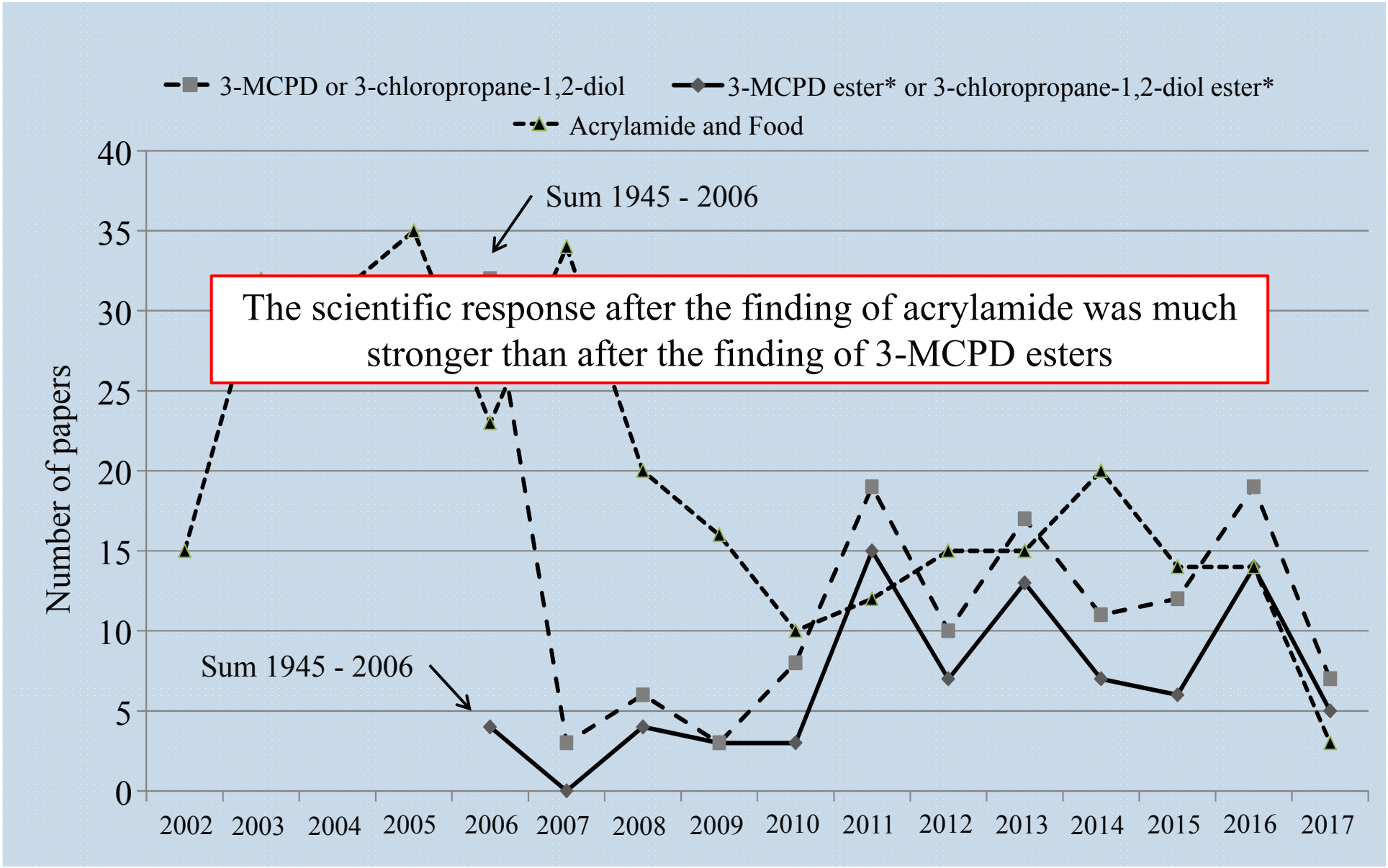


What do we know about the toxicological assessment of 3-MCPD and glycidyl ester today?

- Relative bioavailability of the esters and the free compounds is comparable → Esters have to assessed as the free compounds.
- It is unclear whether the results of animal experiments can be transferred to humans.
- No data regarding exposition to humans is available.
- Only less information regarding the uptake via different food is available.
- The average exposition of most population groups is below 1 µg/kg BW and day (EFSA).
- Recommendation 2014/661/EU: Content of bound and free 3-MCPD, 2-MCPD and glycidol in different food should be determined.
- TDI of 2µg/kg BW and day for 3-MCPD has been confirmed in newer assessments

But

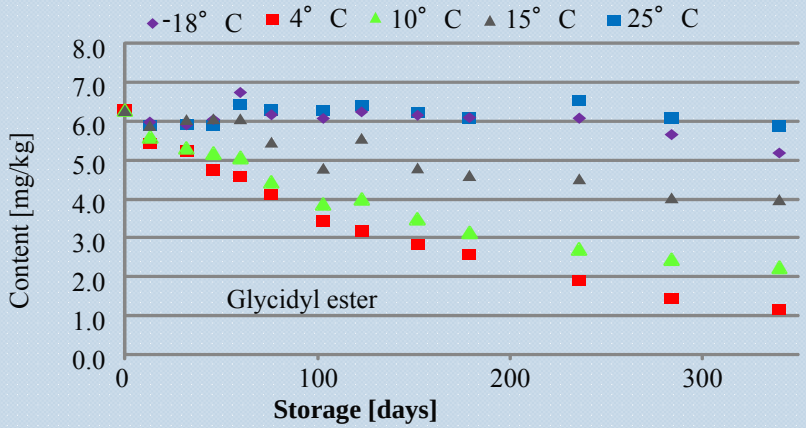
- The CONTAM Panel established in May 2016 a tolerable daily intake (TDI) of 0.8 µg/kg bw per day for 3-MCPD
- **Scientific opinion of the EFSA Panel on Contaminants in the Food Chain (CONTAM):**

  Glycerol-based process contaminants found in palm oil, but also in other vegetable oils, margarines and some processed foods, **raise potential health concerns** for average consumers of these foods in all young age groups, and for high consumers in all age group

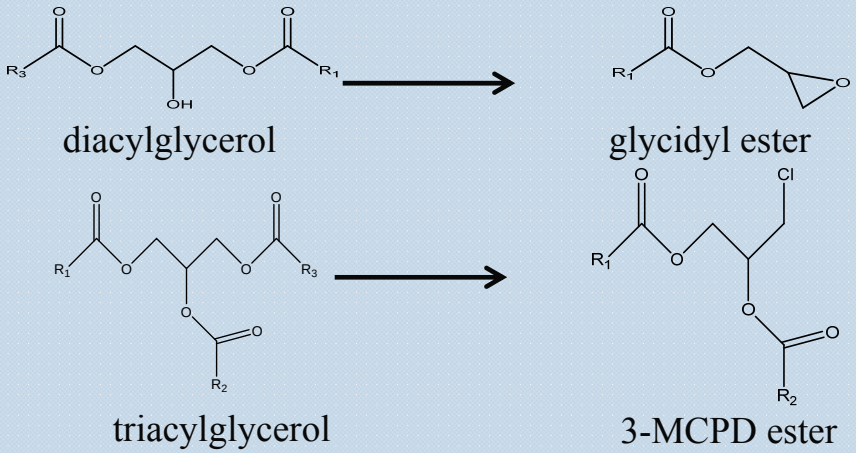
Where we are today with the analytical methods?

- **Three validated methods for fats and oils are available (DGF-C-VI 18 (10); AOCS Cdabc-13).**
- Several other direct and indirect methods are available.
- Validate, indirect methods give comparable results while results of direct methods are less comparable.
- Direct methods are only partly suitable for the determination of individual esters, but the determination of the total amount is good.
- A lot of different approaches for the determination of the esters in food are under discussion but only one validated method for complex food (margarine, spreads) is available → **more validated methods are necessary**.
- Joint Research Centre Institute for Reference Materials and Measurements (IRMM) published on March 17th, 2015 a report on the development and validation of analytical methods for the determination of 3-MCPD and glycidyl ester in food (in house validation).
- The automation of the determination 3-MCPD and glycidyl ester is feasible.
- Decomposition of glycidyl esters in the fridge.

For further analysis of glycidyl esters
storage of oil samples in the fridge is not recommended



What is the formation pathway for MCPD and glycidyl esters?



Requirements for the formation of 3-MCPD and glycidyl esters:

- chlorine containing compounds
- triacylglycerols
- mono- and diacylglycerols
- phospholipids
- glycerol
- temperature
- time

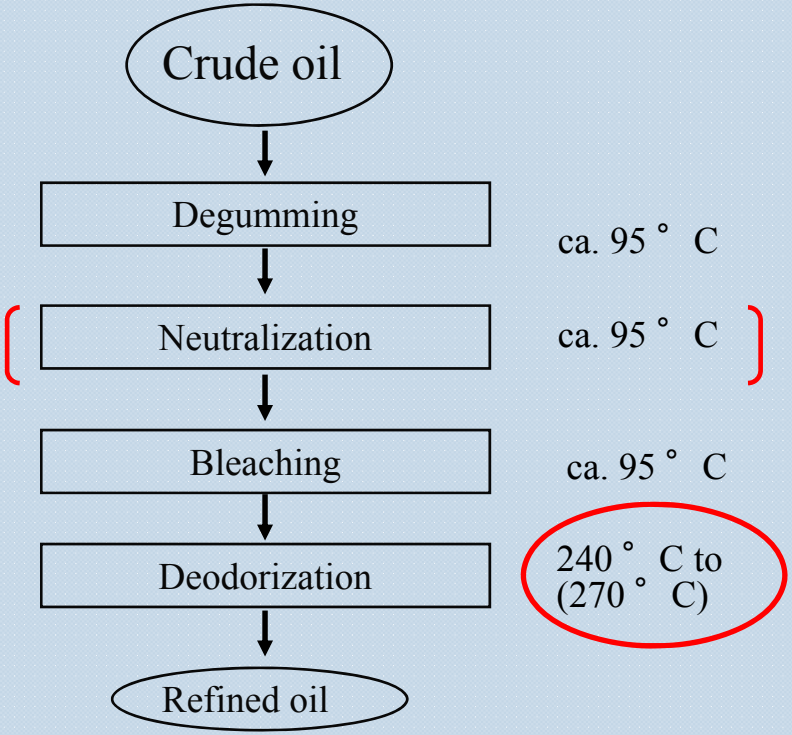
Formation of 3-MCPD and glycidyl ester is a heat induced reaction that is influenced by the availability of reaction partners and reaction conditions

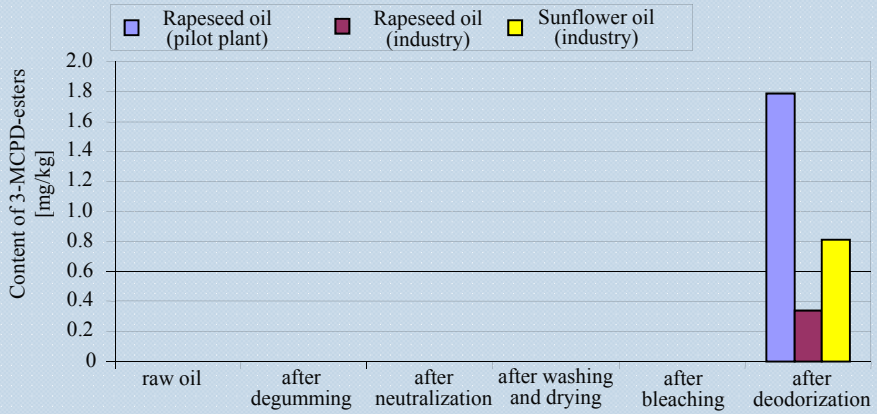
SN_2 nucleophilic attack by chloride ions or formation of reactive intermediates such as acyloxonium ion or an epoxide ring (Eur. J. Lipid Sci. Technol. 2011, 113, 323-329)

Free radicals mediated the formation of 3-monochloropropanediol (3-MCPD) fatty acid diesters from diacylglycerols at high temperature under a low-moisture condition (J. Agric. Food Chem. 2013, 61, 2548-2555)

One publication suggested that some antioxidants, such as TBHQ, PG, and AP, could be potential inhibitors of 3-MCPD esters in practice (J. Agric. Food Chem 2015, 63, 9850-9854)

Refining process



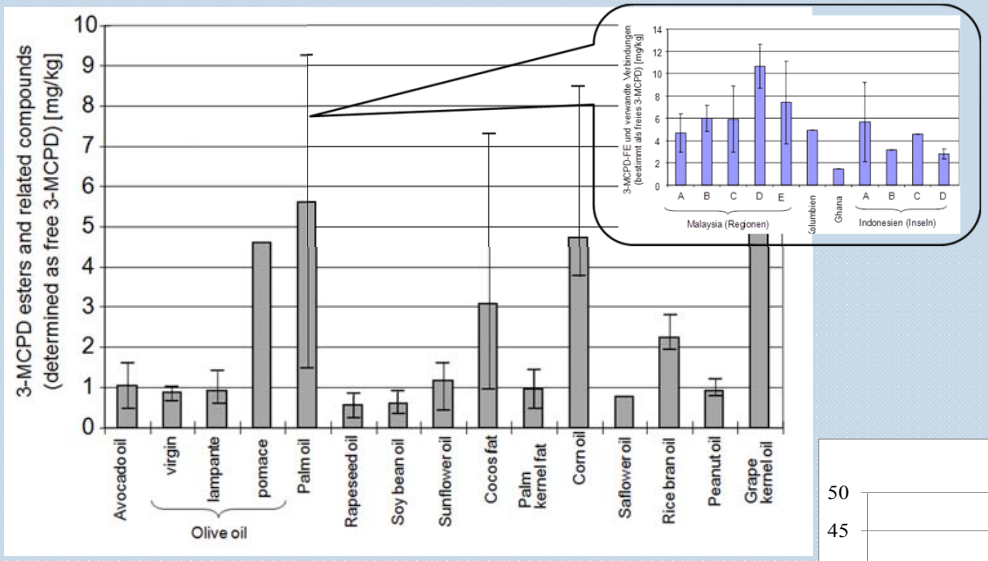


	Hydro-carbons < 20	PAH	Pesticides	Aflatoxin B1	Zeara-lenone
Crude oil					
Degumming					
Neutralization					93 %
Bleaching					77 %
Deodoriziation					

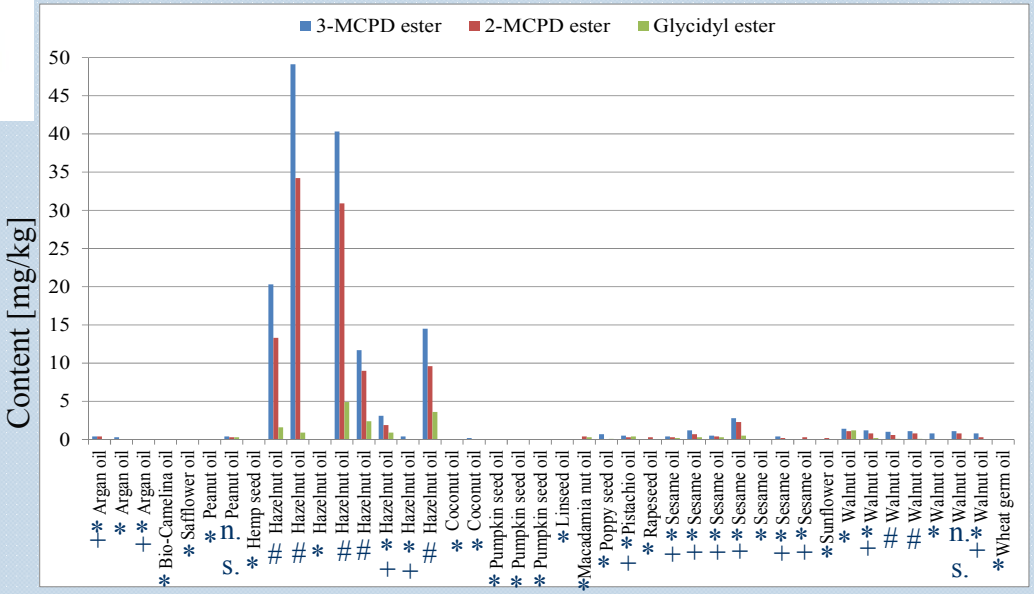
chemical refining
physical refining
Both chemical refining

Source: Dr. van Duijn, Fediol

Potential of different types of oil to form 3-MCPD and glycidyl ester



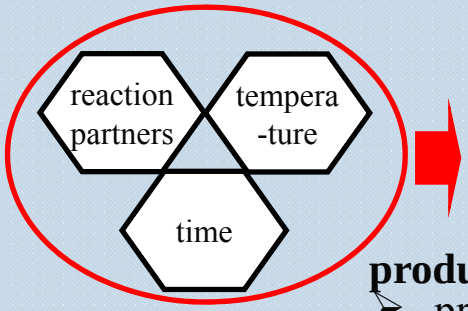
*cold pressed +roasted #refined



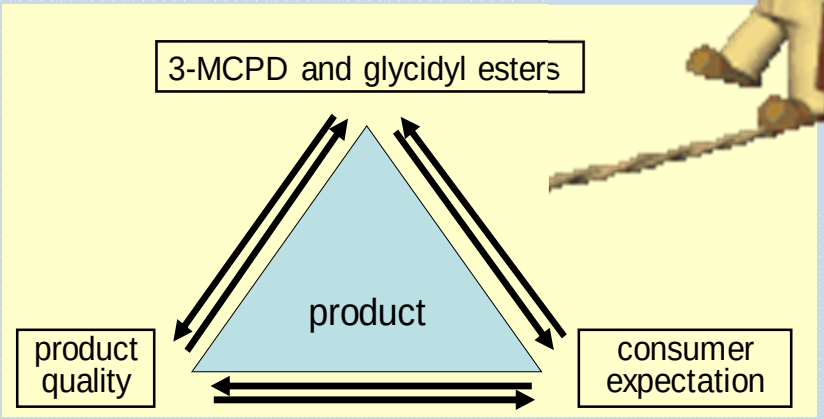
3-MCPD and glycidyl ester not only a problem for palm oil

Difficulties to reduce 3-MCPD and glycidyl ester in fats and oils

Reducing the content of esters in fats and oils



product quality
- properties
- smell and taste
- stability
- safety (contaminants)



Legitimate consumer expectation regarding food quality

Aim: Reduction of the content of 3-MCPD and glycidyl ester with simultaneous maintenance of the product quality

Options for the mitigation of 3-MCPD and glyidyl esters

With the available means it is possible to reduce the content of 3-MCPD and glycidyl esters significantly in fats and oils, especially for risk products, **but it costs money.**

Research projects on 3-MCPD esters in Germany

Investigations on the formation of 3-monochloropropane-1,2-diol fatty acid esters (3-MCPD esters) in vegetable oils and development of minimization strategies (2009 – 2011) (AiF 16004 BG)

Fundamentals for a large scale application of processes for the production for edible oils and fats with reduced content of 3-MCPD fatty acid esters and related compounds (2011 – 2014) (AiF 17059 BG)

Max Rubner-Institut, Detmold (MRI)

Pilot Pflanzenöl-technologie Magdeburg e.V. (PPM)

Deutsche Forschungsanstalt für Lebensmittelchemie (DFA)

Deutsches Institut für Lebensmitteltechnik

Results

- Harvest and oil processing strongly influence potential for the formation of the esters
- Suggestion of minimization strategies for the refining process
- Suggestion of alternative approaches for refining (two-step deodorization, short-path distillation)
- Post-treatment of fully refined oil by adsorbents
- Development of an direct analytical method for 3-MCPD and glycidyl esters

Prediction of the potential of raw material for the formation of 3-MCPD and glycidyl ester?

Sime Darby: Marker molecule (MEMM) for 3-MCPD ester formation identified (Euro Fed Lipid Congress 2015, Florence)

- New precursor molecule identified that correlates well with 3-MCPD ester levels in refined oils
- Tested in various types and qualities of crude palm oil

Knowledge about MEMM levels in crude oils allows optimization of the refining process with respect to the predicted potential of 3-MCPD ester formation

→ lower levels of the esters in the refined oil are possible

But: The name of the marker molecule(s) (MEMM) is still not published

Legal assessment of the ester?

- Risk management is defined in EU regulation 178/2002, Article 3 with different possibilities
  - → injurious to health??
  - → unfit for consumption??
  - → probable cumulative toxic effects
  - → probable immediate and/or short-term and/or long-term effects of that food on the health??
- No clear regulation for the legal assessment of the esters is available.
- 315/1993 (technical avoidance) and/or 178/2002 (unsafe food), but health risk is not clear.
- Only few activities of official laboratories due to missing regulations.
- Discussion about limits.

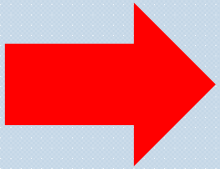
Food	**3-MCPD ester**	**Glycidyl ester**
Fats and oils	2.0	1.0
infant formula and follow-on formula (pulver)	0.125	0.075
infant formula and follow-on formula (liquid)	0.015	0.010

What are the measures of the industry?

- A toolbox for the mitigation as been prepared under the leadership of BLL
- Numerous measures for the avoidance and mitigation of the esters have been developed
- Reformulation of products reduces the content of 3-MCPD and glycidyl esters in fatty food
- Replacement of highly contaminated fats and oil during processing
- Use of low contaminated batches for special products
- Content in baby food has been reduced significantly
- Commodities of palm oil is partially still too high in the content of the esters
- Implementation of the measures costs money

Summary

- The toxicological assessment of 3-MCPD and glycidyl ester has to be similar to the free compounds.
- Several standardized indirect methods are available and in use in practice, the application of direct methods is seldom.
- A lot of tools for the mitigation of 3-MCPD and glycidyl esters are developed and recommended in the last ten year but the introduction into industry is slow.
- Products with lower amounts of esters are more expensive.
- The definition of a limit for 3-MCPD and glycidyl esters is under discussion



After ten years of research a lot of progress has been achieved, but some questions are still open

Thank you for your attention

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