Formation Pathways for 3-MCPD di-Esters and Glycidyl Esters under Thermal Conditions

Amaury Patin, Brian Craft, Kornèl Nagy and Frédéric Destaillats

Symposium on MCPD Esters and Glycidyl Esters Analytics, Toxicology, Risk Assessment, Mitigation. Where we are today?

Berlin June 2017

Outline

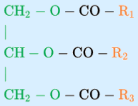
1. Scope of the presentation
2. Formation of MCPD di-Esters under thermal conditions
3. Formation of Glycidyl Esters under thermal conditions
4. Perspectives for future research

Investigating the formation pathways is a pre-requisite to design efficient strategies to minimize the occurrence of MCPD di-esters and Glycidyl esters in food products

Source of reactive chloride

- What are the sources of chloride in fats and oils?
- How can Cl be activated to react with acylglycerols?

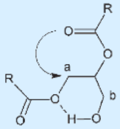
Reactivity of acylglycerols



$$\begin{array}{l} CH_2-O-CO-R_1 \\ | \\ CH-O-CO-R_2 \\ | \\ CH_2-O-CO-R_3 \end{array}$$

- What is the reactivity of the different acylglycerols?
- What are their potency to be converted into MCPD di-esters and Glycidyl esters?

Mechanism of formation



- What are the mechanisms involved?
- What is the limiting step?

Influence of processing conditions

- What are the key processing parameters influencing the formation of MCPD di-esters and Glycidyl esters during fats and oils refining?

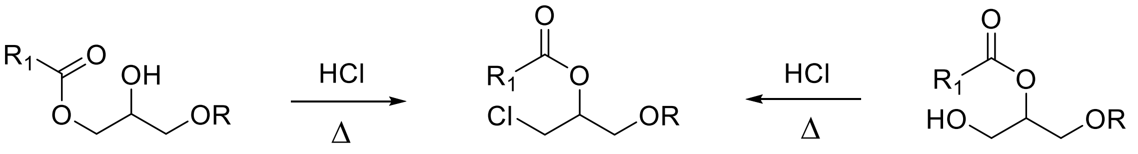
To optimize/adapt processing conditions and minimize formation during refining

Outline

1. Scope of the presentation
2. Formation of MCPD di-Esters under thermal conditions
3. Formation of Glycidyl Esters under thermal conditions
4. Perspectives for future research

It is well established that TAG and DAG are the two acylglycerols species that can lead to the formation of MCPD di-esters

- From DAG (also possible with MAG)

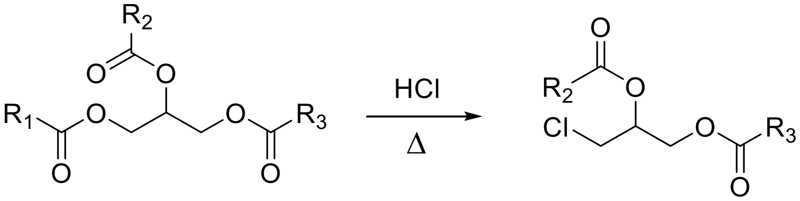


1,3-DAG or 1-MAG

1,2-DAG or 2-MAG

R_1CO_2H = Fatty acid
MAG: R = H
DAG: ROH = Fatty Acid

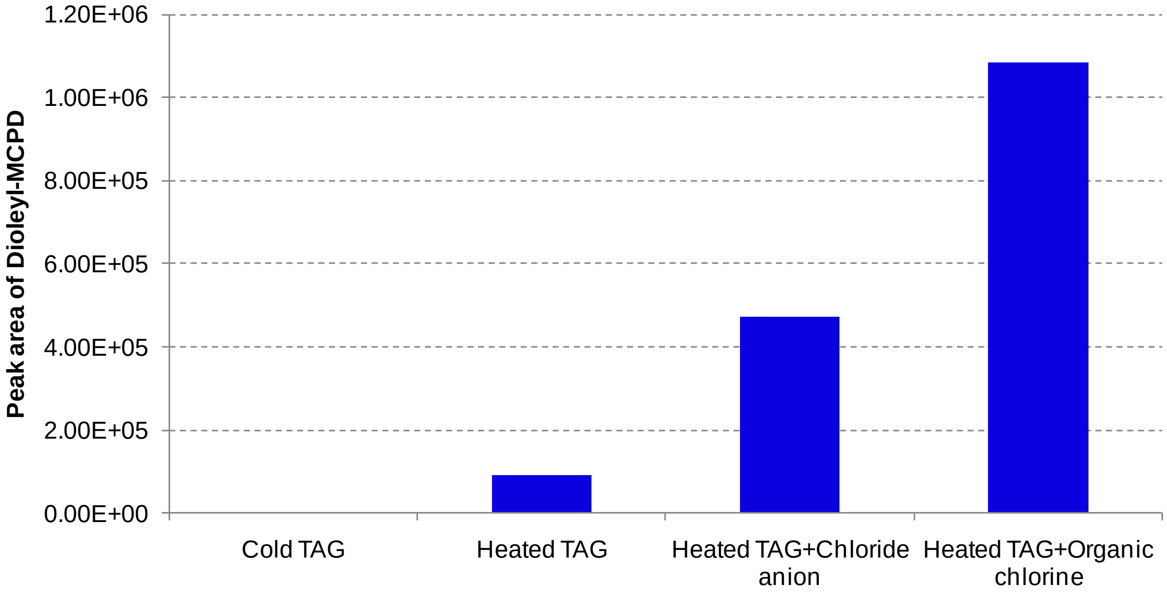
- From TAG



R_1CO_2H, R_2CO_2H acid &
R_3CO_2H = Fatty acid

Sources: Šmidrkal et al., Food Chemistry 2016, 211 124–129; Destaillats et al. Food Add. Cont. 29 (2012) 29–37; Rahn et al., Eur. J. Lipid Sci. Technol. 2011, 113, 323–329; Zhang *et al.*, J. Agric. Food Chem. 2013, 61, 2548−2555

The reaction starts with the formation of hydrogen chloride at high temperature (>150°C) from organochlorines or chloride salts

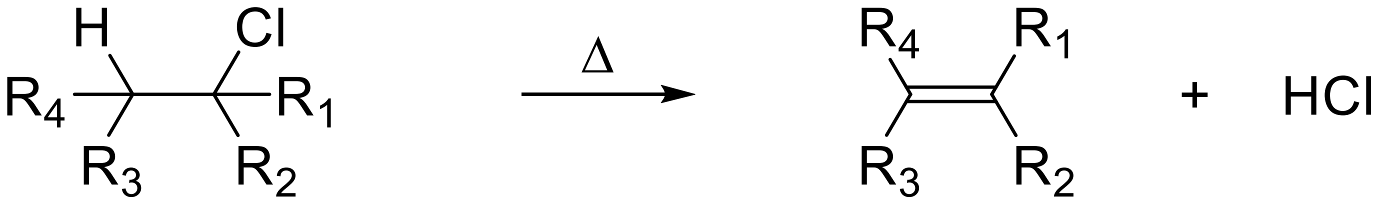


Abundance of MCPD dioleate in cold triolein or after heating at 235°C in presence of a source of ionic chloride and organochlorine.

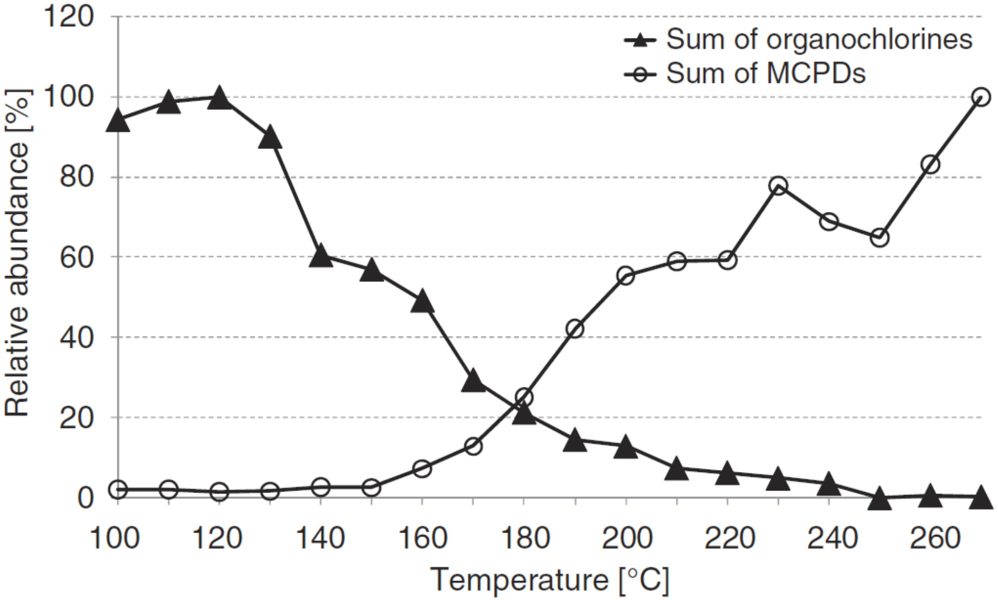
Sources: F. Destaillats, B. Craft and K. Nagy, 2011 (unpublished data)

Hydrogen chloride can be formed by dehydrochlorination of organochlorines at high temperature

- From organochlorines



Dehydrochlorination of organochlorines in palm oil is leading to the formation of MCPD di-esters at temperature >150°C)

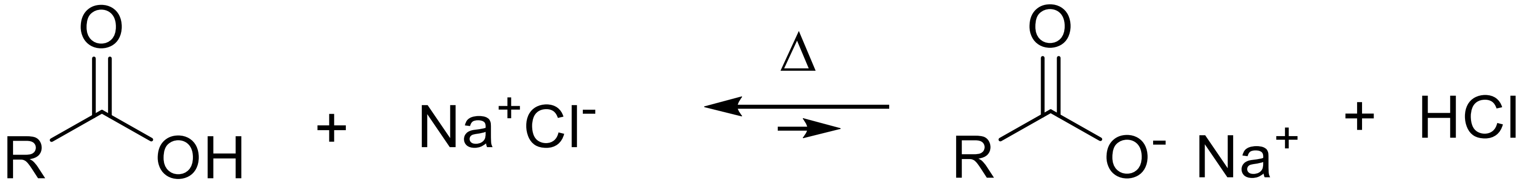


- **Relative abundance of selected organochlorines and levels of MCPD di-esters formed during the in-vitro heat treatment of crude palm oil**
- **The progressive decomposition of these chlorinated substances along with the appearance of MCPD esters implies that they may indeed serve as a source of chlorine for the formation of MCPD esters.**

Sources: Nagy *et al.*, Food Additives & Contaminants: Part A, 2011, 28:11, 1492-1500

Hydrogen chloride can also be formed by reaction of chloride salts such as NaCl with free fatty acids at high temperature (>150°C)

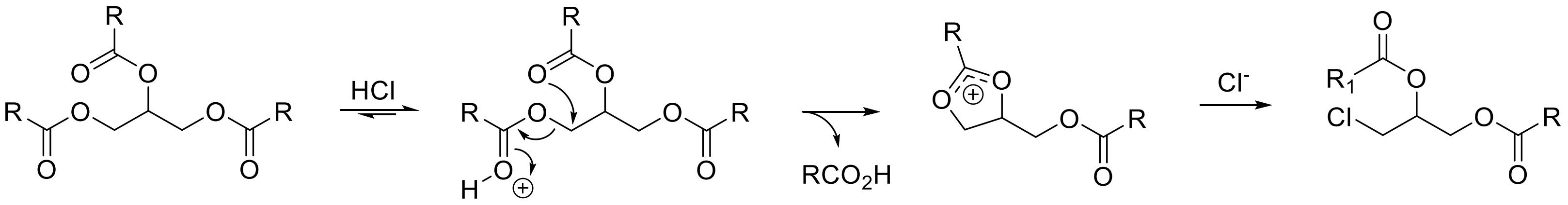
- From free fatty acids (FFA) and chloride salts such as NaCl



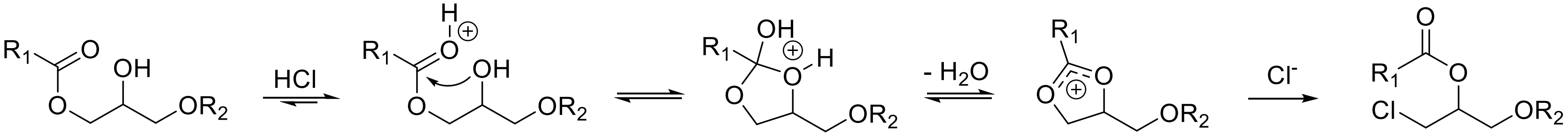
Sources: Šmidrkal et al., Food Chemistry 2016, 211 124–129

HCl can induce the protonation of the oxo- group of TAG and DAG leading to the formation of a cyclic-acyloxonium ion intermediates

- From TAG

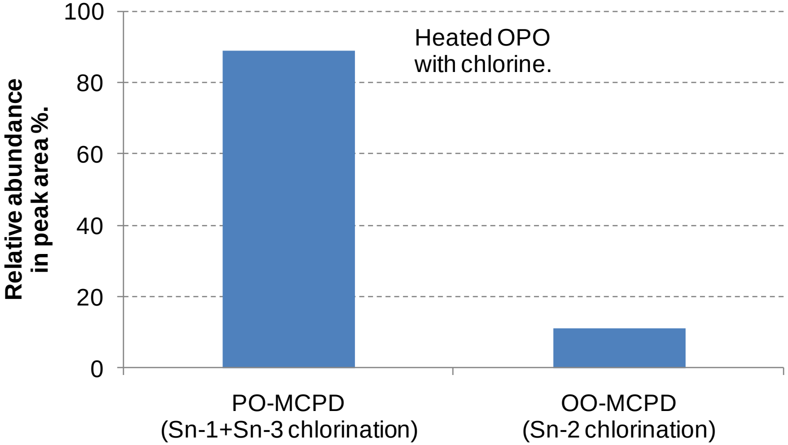


- From DAG (also possible from MAG giving rise to the formation of MCPD mono-esters)



R_2 = H or FA

Model experiments confirmed that both DAG and TAG are involved in the formation of MCPD di-esters and that 1(3)-chloro isomers are favored

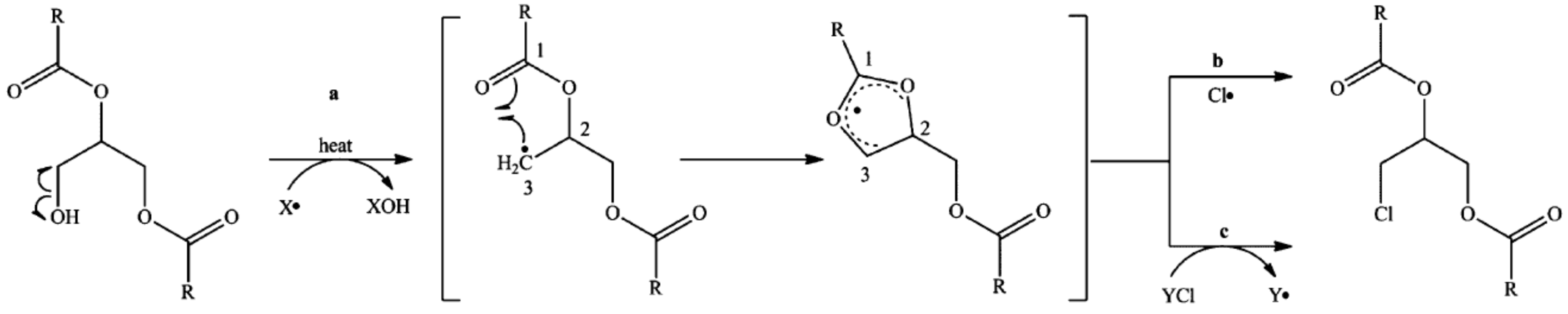


Proportion of MCPD di-esters formed by chlorination of OPO at different positions on the glycerol backbone

Experiments with MOB, SPO, and OPO gave similar results and on average the overall data resulted in the calculation of a 5:1 ratio between 1(3)- to 2-MCPD di-esters formed

Sources: Destaillats *et al.*,Food Additives & Contaminants: Part A, 29 (2012) 29–37.

A radical mechanism involving the formation of a cyclic-acyloxonium radical has been as well suggested and supported by electron-spin resonance data



DAG I II 3-MCPD diester

X = L, LO

Y = H, Cl, $C_6H_6Cl_5$, Na, K, FeCl, $FeCl_2$, CuCl, ZnCl

Source: Zhang *et al.*, J. Agric. Food Chem. 2013, 61, 2548−2555

Experimental data suggests that occurrence of MCPD di-esters in deodorized fats and oils can be controlled

Quality of the crude oil

- The formation of MCPD di-esters is greatly influence by the quality of the crude oil and particularly the content of FFA, DAG and Cl source (both organic and inorganic)

FFA removal before deodorization

- In chemical refining, neutralization of the oil has been shown to be effective to prevent the formation of HCl by reaction of free fatty acids and chloride salts (i.e. NaCl)

Alternative processing

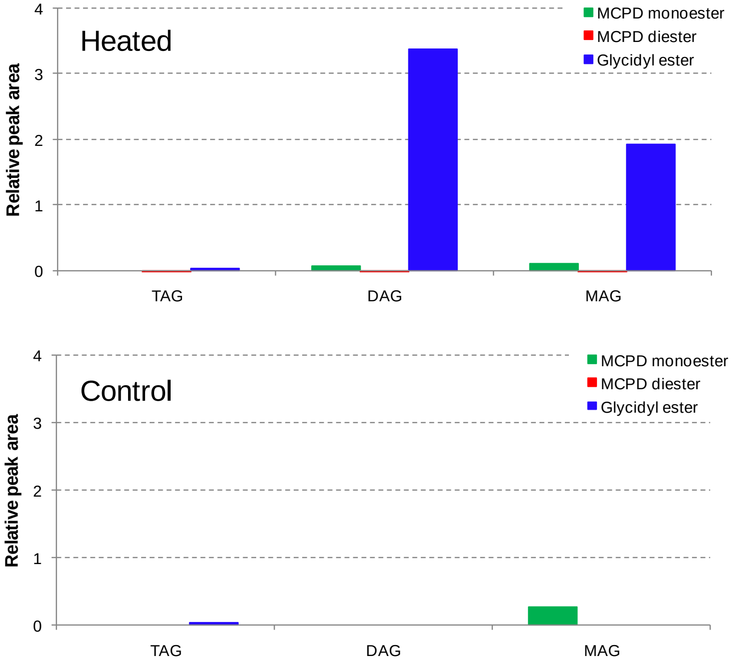
- Short path distillation in combination with mild deodorization is a promising avenue to minimize the formation of HCl and reaction with acylglycerols

Sources: Pudel *et al.,* Eur. J. Lipid Sci. Technol. 2016, 118, 396–405; Šmidrkal *et al.*, Czech J. Food Sci., 2011 29: 448–456; Šmidrkal *et al.*, Food Chemistry 211 (2016) 124–129; Matthäus and Pudel, Lipid Technology 2013 25:151–155; Craft *et al.*, Food Additives and Contaminants 2012, 29: 354–361

Outline

1. Scope of the presentation
2. Formation of MCPD di-Esters under thermal conditions
3. Formation of Glycidyl Esters under thermal conditions
4. Perspectives for future research

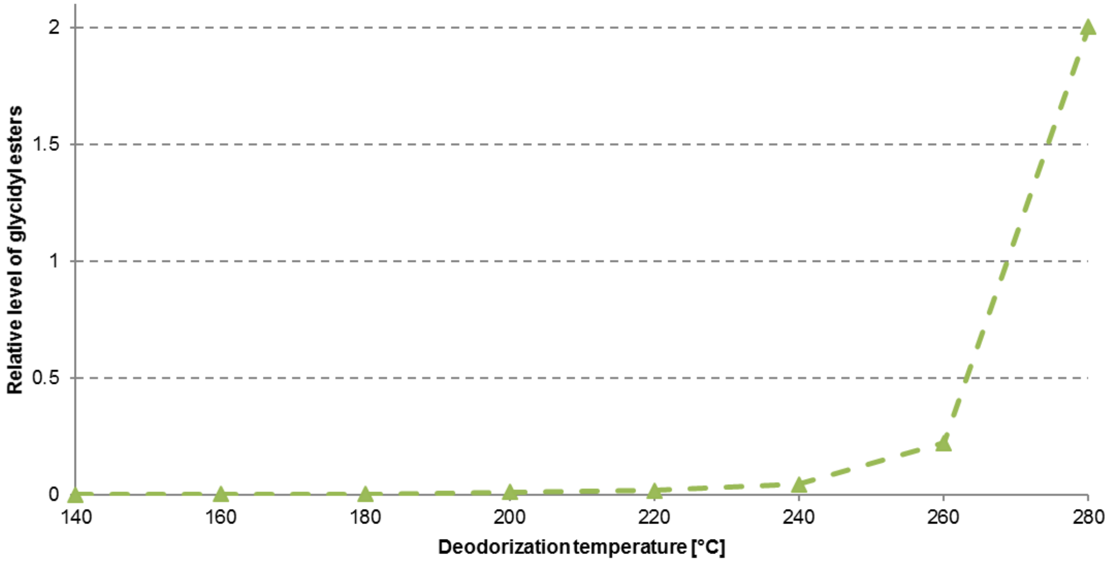
It is well established that DAG and MAG are the two acylglycerols species that can lead to the formation of Glycidyl Esters



- Formation of Glycidyl-heptadecanoate from TAG (triheptadecanoin), DAG (diheptadecanoin) and MAG (monoheptadecanoin) upon heat treatment at 235°C for 3h.

Sources: F. Destaillats *et al.*, Food Chemistry 131 (2012) 1391–1398

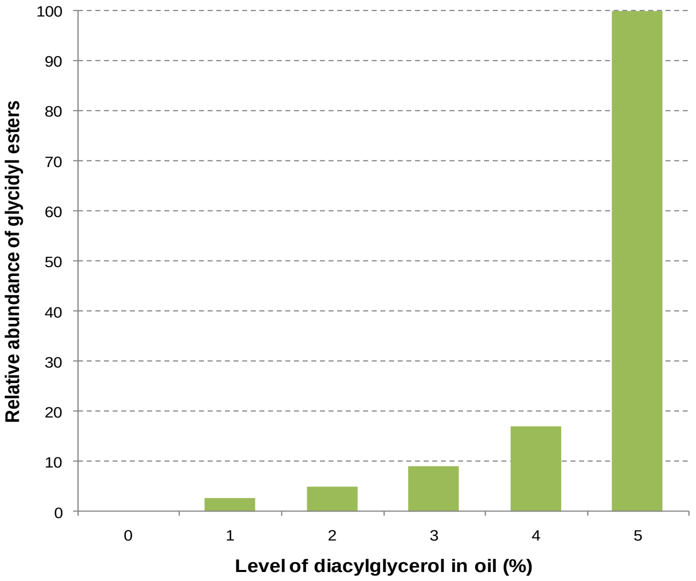
The formation of GE from DAG is temperature dependent and accelerate above 200°C



- Time course of the formation of glycidyl vaccenate from divaccenin heated under nitrogen for 1 h at temperatures ranging from 100 to 280°C.
- The results supports This reaction is detectable above 200°C and yields greater GE abundance with increased temperature

Sources: F. Destaillats, B. Craft and K. Nagy, 2011 (unpublished data)

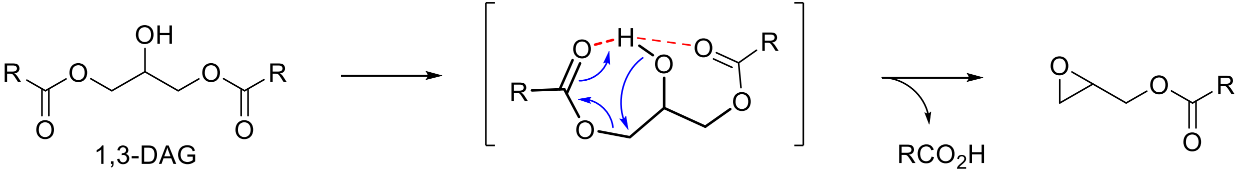
DAG is the main acylglycerol species present in Refined and Bleached (RB) oils and which explain why high GE levels can be observed in oils containing high DAG (*i.e.* palm)



- Influence of the concentration of DAG on the formation of glycidyl esters (upon heat treatment at 235°C for 3h
- The results were normalized to the level GEs found in the sample with 5% DAG

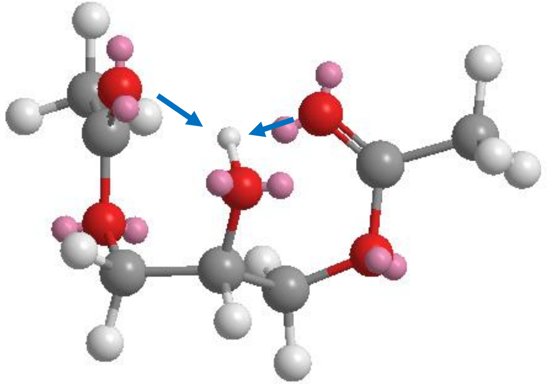
Sources: Craft *et al.*, Food Chemistry 132 (2012) 73–79

The formation of GE from DAG involves the loss of a free fatty acid residue by intramolecular nucleophilic substitution

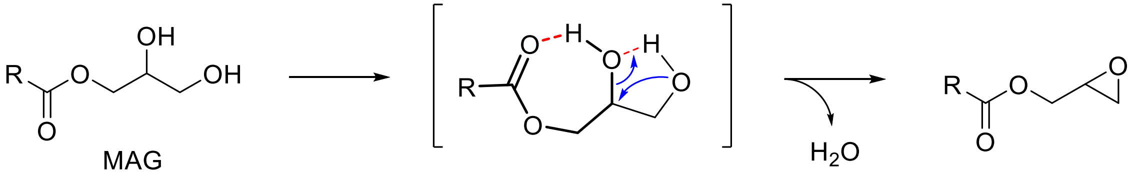


- Intramolecular nucleophilic substitution is favored by intramolecular hydrogen bonds which stabilize the intermediate and increase the nucleophilicity of the oxygen on the hydroxyl group

- During the nucleophilic substitution, the proton on the hydroxyl group will also activate the leaving of the fatty acid

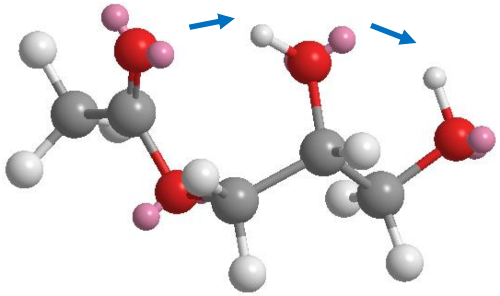


The formation of GE from MAG involves the loss of water involving intra-molecular hydrogen bonds

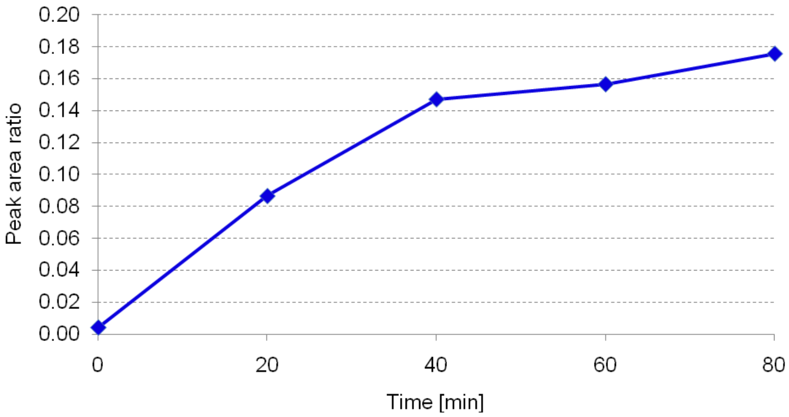


- For MAG, different H bonds are involved. In particular, the nucleophilicity of the oxygen in position 2 will be decreased by its participation in the H bonding with the hydroxyl in position 3

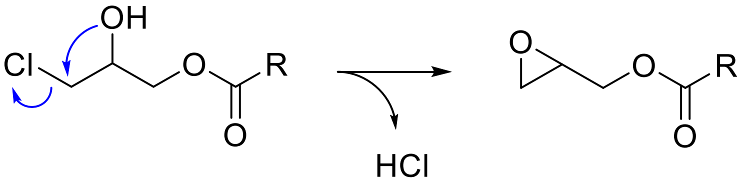
- This time, it is the oxygen in position 3 that will substitute the OH (HO^- is the less good leaving group than $RCOO^-$)



The formation of GE from MCPD mono-ester has also been demonstrated but is expected to be marginal due to the low content of MCPD mono-ester formed during deodorization



- Time course of the formation of glycidyl-palmitate from MCPD mono-palmitate heated at 235°C in hexadecane under nitrogen.
- The mechanism of formation involves the loss of a molecule of HCl by dehydrochlorination



Sources: F. Destaillats, B. Craft and K. Nagy, 2011 (unpublished data)

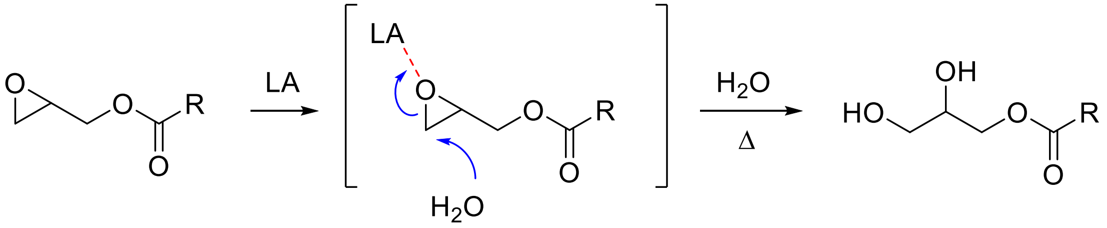
Experimental data suggests that occurrence of Glycidyl Esters in deodorized fats and oils can be avoided

Control of the formation

- The formation of Glycidyl Esters during fats and oils refining can be minimized by maintaining deodorization temperature below 200-220°C

Post deodorization treatment

- Glycidyl Esters formed during deodorization can be adsorbed or converted into MAG by ring opening



LA = Lewis acid

Sources: Craft *et al.*, Food Chemistry 2012, 132, 73–79, Strijowski et al., Eur. J. Lipid Sci. Technol. 2011, 113, 387–392; Shimidzu et al., Journal of Oleo Science 2012, 61, 23-28

Research

Outline

1. Scope of the presentation
2. Formation of MCPD di-Esters under thermal conditions
3. Formation of Glycidyl Esters under thermal conditions
4. Perspectives for future research

Perspective for future research

- Systematic screening of the solution and conditions to efficiently and economically convert Glycidyl Esters into monoacylglycerol post-deodorization

- Investigate the use of (large scale) short path distillation in combination (or not) with mild deodorization as a cost efficient alternative to deodorization of oils (*incl.* vegetable oils) to limit exposure of fats and oils to excessive temperature