FOOD CHEMISTRY

Chapter 3 : Lipids

3.1 DEFINITIONS AND CLASSIFICATION

What are the lipids ?

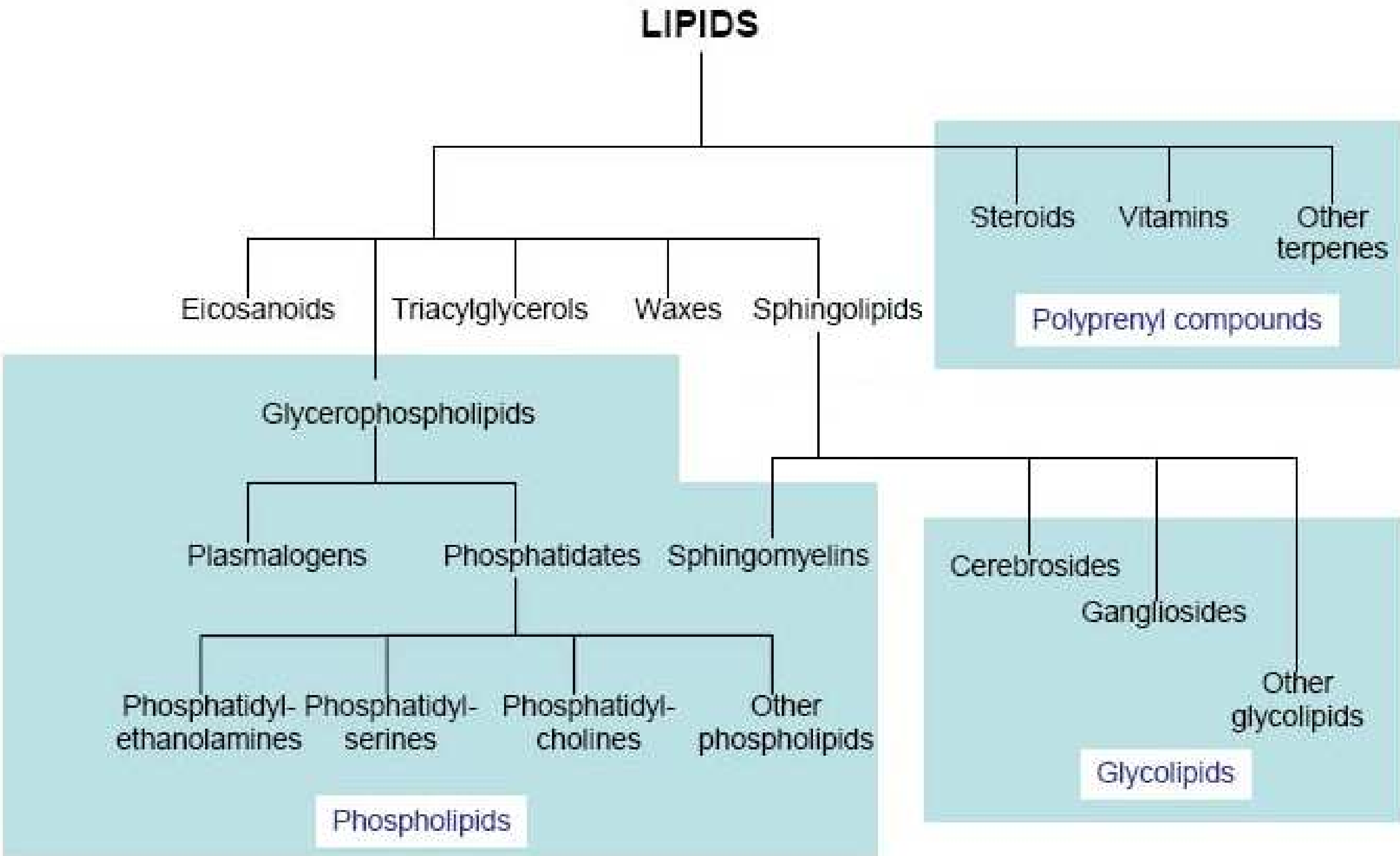
There is no widely-accepted definition

→ Naturally occurring compounds, which have in common a ready solubility in organic solvents such as hydrocarbons, chloroform, benzene, ethers and alcohols.

→ Fatty acids and their derivatives, and substances related biosynthetically or functionally to these compounds.

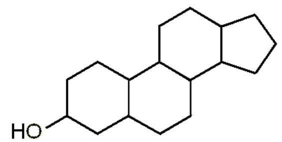
3.1 DEFINITIONS AND CLASSIFICATION

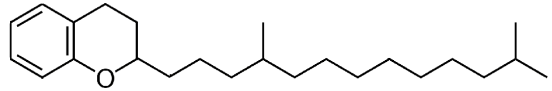
The lipid families



3.1 DEFINITIONS AND CLASSIFICATION
A recent lipid classification

Fatty acids	Carboxylic acids with aliphatic chains
Acyl glycerol lipids	Glycerol esterified with one to three fatty acids
Glycolipids	Carbohydrate associated to acylglycerols or fatty acids
Phospholipids	Acylglycerol esterified with one or two phosphate moieties
Sphingosides	Long-chain bases linked to a fatty acid
Sterols	Substituted hydroxy-sterane
Tocols	Substituted long chain benzopyrane
Waxes	Long chain esters of fatty acids





E. Fahy & al., J. Lipid Res., 46, 839-861 (2005)

3.2 SOURCES

Occurrence of lipids in food and seeds

FOOD	***% lipids***
Butter	83
Potato chips	40
Milk chocolate	32
Egg	11
Chicken meat	6
Milk	4
Cod	1

SEEDS	***% lipids***
Cocoa	55
Peanuts	45
Canola	40
Palm	40
Sunflower	40
Olive	30
Soybean	20

3.3 FATTY ACIDS

Fatty acids	Carboxylic acids with aliphatic chains
Acyl glycerol lipids	Glycerol esterified with one to three fatty acids
Glycerophospholipids	Acylglycerol esterified with one or two phosphate moieties
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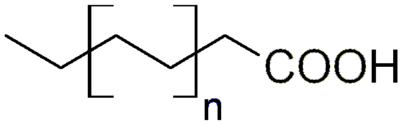
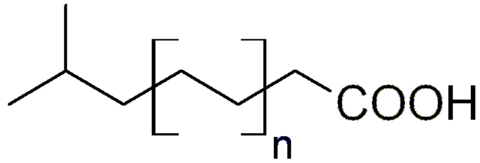
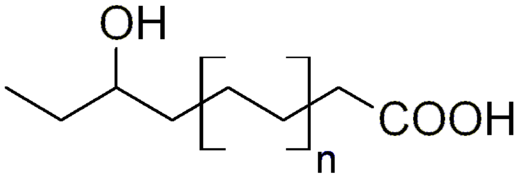
3.3 FATTY ACIDS
Types of fatty acids



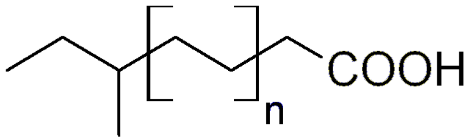
Saturated FA



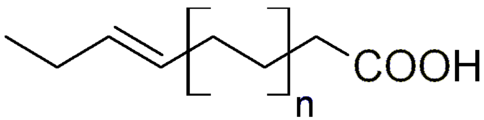
Iso branched FA



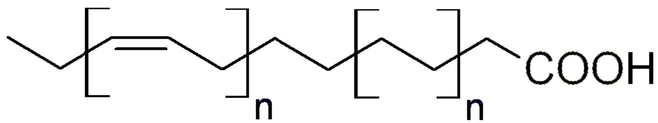
Hydroxylated FA



Ante-iso branched FA



Trans mono-unsaturated FA

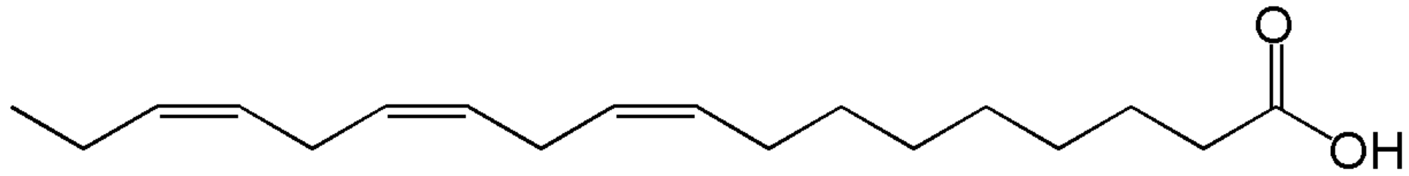


All-cis poly-unsaturated FA

3.3 FATTY ACIDS
Nomenclature

Shorthand description 18 : 3 (n-3) or 18 : 3 ω3

Number of carbon atoms — Number of double bonds — Position of the first double bond (starting from the methyl end of the chain)



► Assumes that double bonds are all *cis.*

► Assumes that double bonds are separated by a methylene group.

3.3 FATTY ACIDS

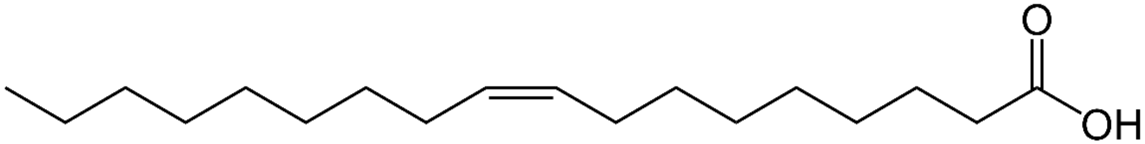
Trivial names of some fatty acids

16:0	Palmitic acid	18:3(n-3)	α-linolenic acid
18:0	Stearic acid	18:3(n-6)	γ-linolenic acid
18:1(n-9)	Oleic acid	20:0	Arachidic acid
18:2(n-6)	Linoleic acid	22:1(n-9)	Erucic acid

3.3 FATTY ACIDS

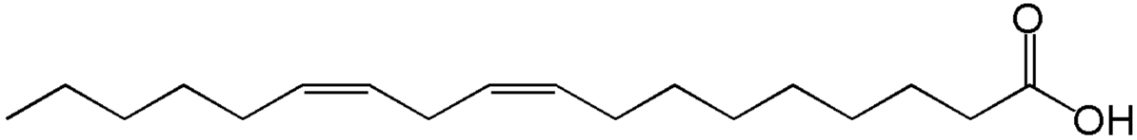
Some unsaturated fatty acids

oleic acid



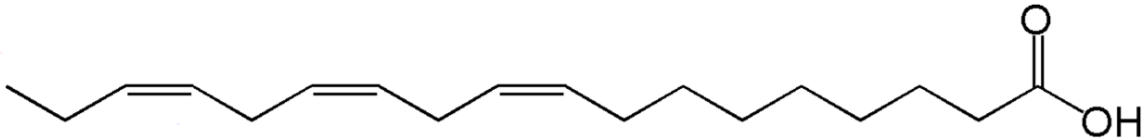
18:1 (n-9)

α-linoleic acid



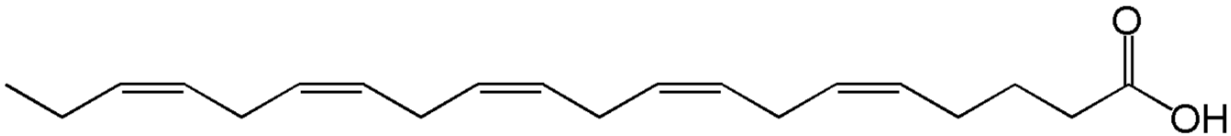
18:2 (n-6)

α-linolenic acid



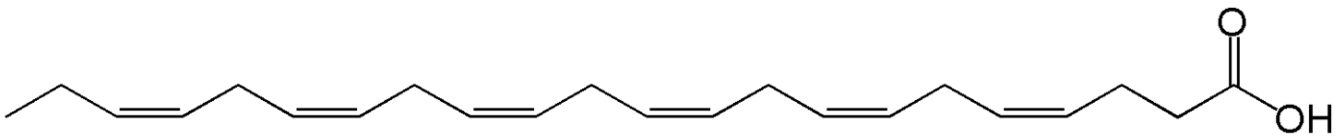
18:3 (n-3)

EPA



20:5 (n-3)

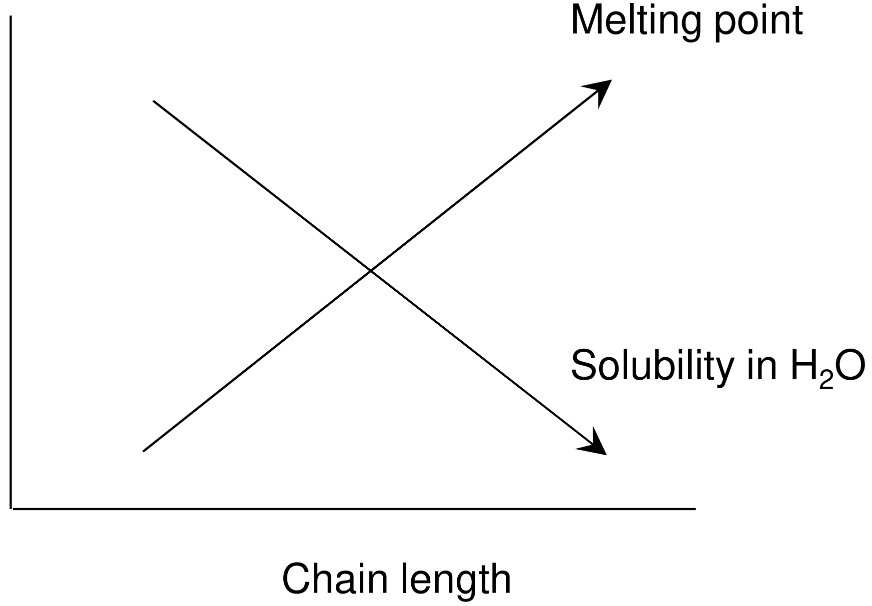
DHA



22:6 (n-3)

3.3 FATTY ACIDS

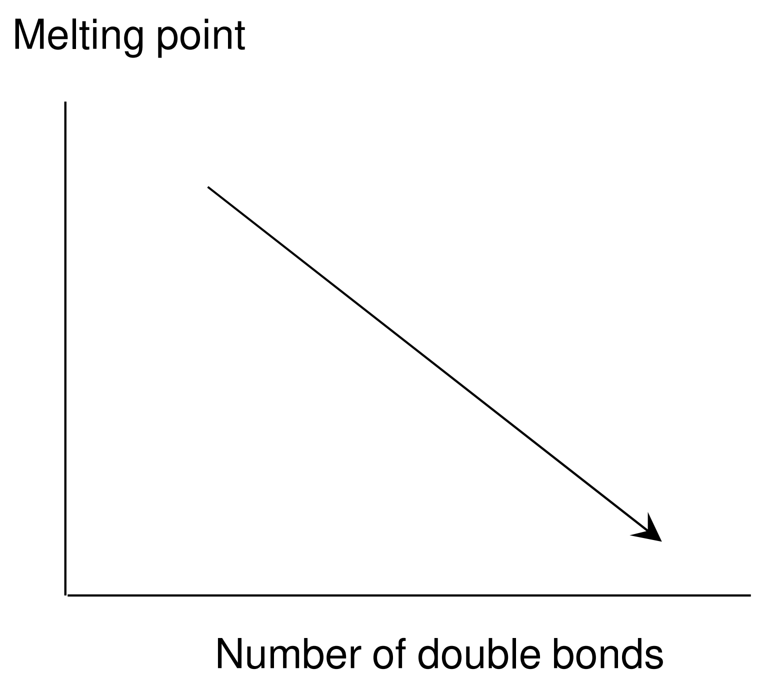
Effect of chain length on solubility and melting points



Fatty acid	*MP (°C)*	*Sol in H_2O (mg/l)*
C4	- 8	
C6	- 4	9700
C8	16	750
C10	31	60
C12	44	5.5
C14	54	1.8
C16	63	0.8
C18	70	0.4

3.3 FATTY ACIDS

Effect of double bonds on melting points



Fatty acid	*MP (°C)*
C16:0	60
C16:1	1
C18:0	63
C18:1	16
C18:2	-5
C18:3	-11
C20:0	75
C20:4	-50

3.3 FATTY ACIDS

Melting points and composition of oils

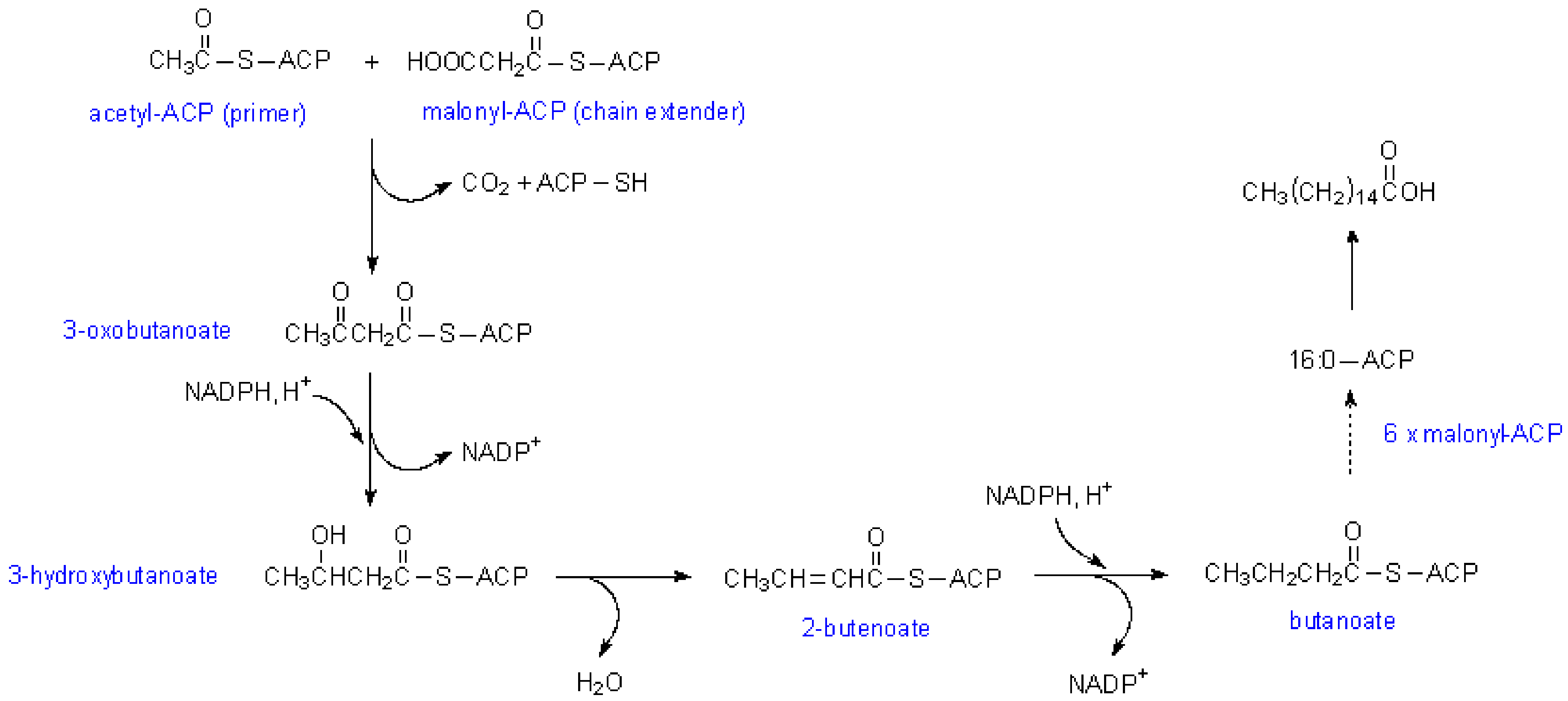
	Sunflower oil	*Soya oil*	*Peanut oil*	*Palm oil*	*Coconut oil*
Melting point range (°C)	-18 to -20	-8 to -18	-2 to -3	23 to 30	20 to 28
% of saturated fatty acids	12	14	18	84	87





3.3 FATTY ACIDS

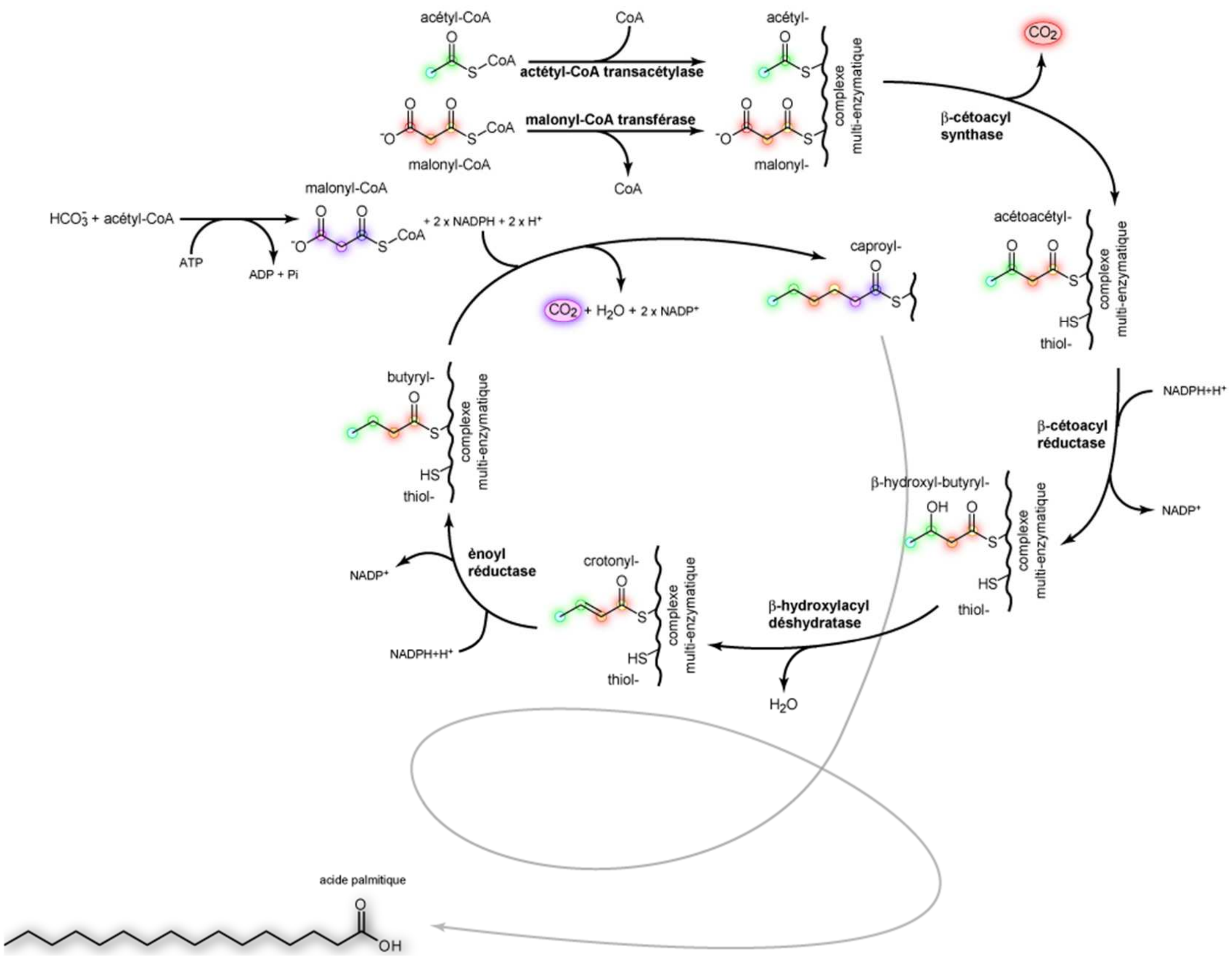
Even numbers of carbon atoms : biosynthesis of palmitic acid



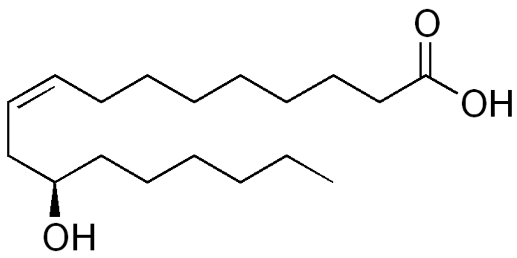
ACP : Acyl carrier protein

3.3 FATTY ACIDS

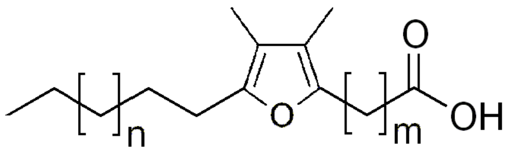
Lipogenesis: biosynthesis of palmitic acid



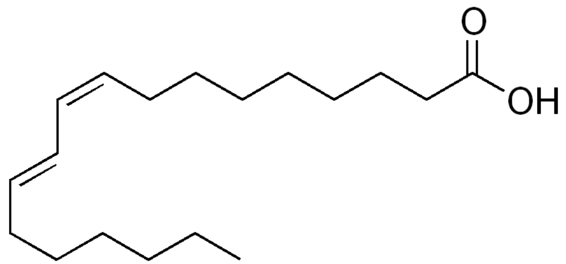
3.3 FATTY ACIDS
Uncommon fatty acids



Ricinoleic acid (90% of castor bean oil) E1503



Furanoïd fatty acids (up to 6% of fish liver oil)



Rumenic acid (a conjugated linoleic acid – CLA – found in milk)

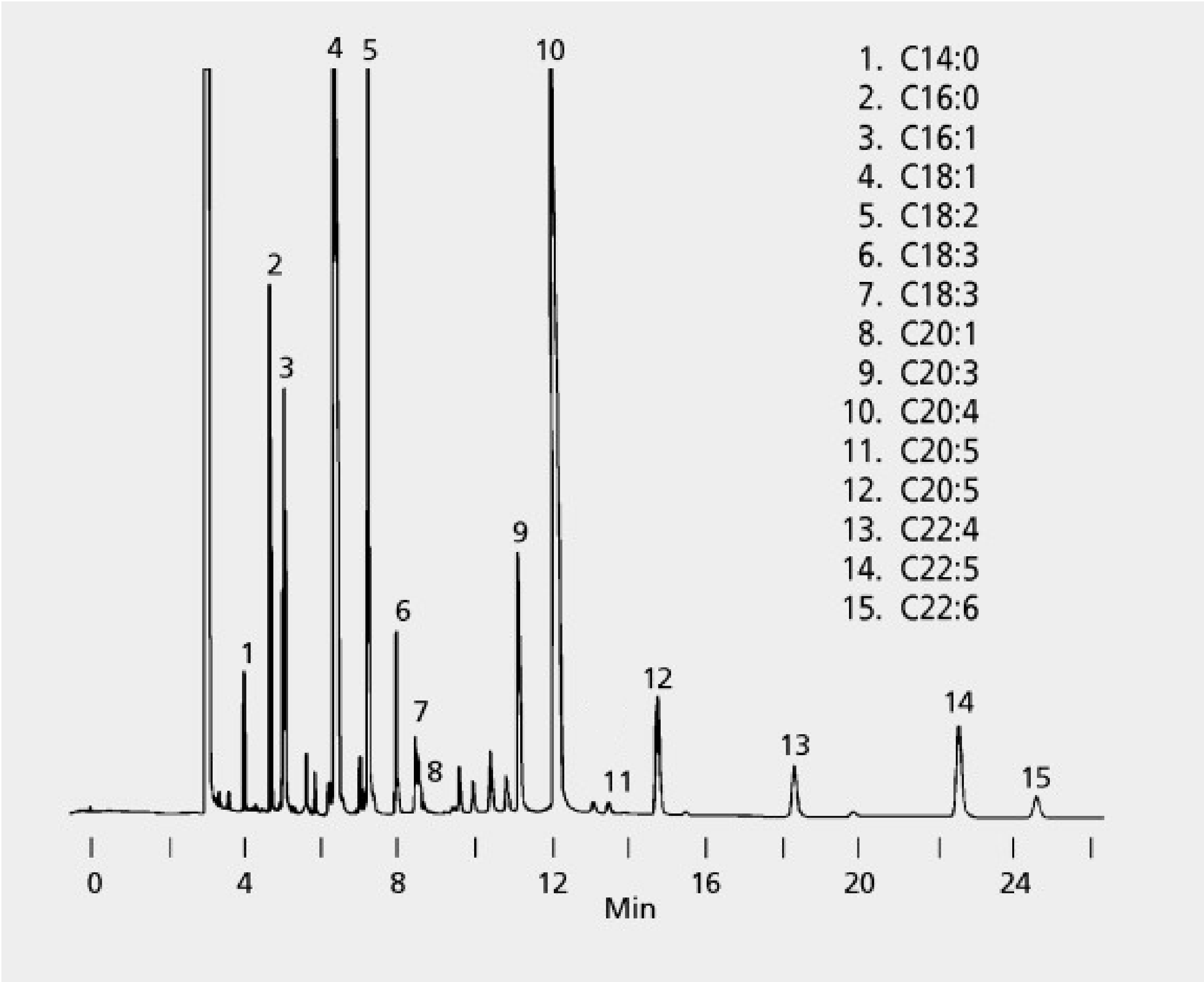
3.3 FATTY ACIDS

Distribution in some oils and fats (in percents)

Fatty acid	Peanut	Rapeseed	Olive	Sunflower	Palm	Butter	Lard	Fish oil
6:0						2		
8:0						1		
10:0						2		
12:0						3		
14:0					1	9	2	7
16:0	10	5	13	6	44	24	26	16
16:1 (n-7)			2			1	3	9
18:0	2	2	3	4	4	8	14	3
18:1 (n-9)	43	15	71	25	40	17	44	11
18:2 (n-6)	36	77	11	64	10	1	10	4
20:0	1							
20:1 (n-9)	2							
20:4 (n-4)	3							
20:5 (n-3)								18
22:6 (n-3)								12

3.3 FATTY ACIDS

Gas chromatography of fatty acids methyl esthers



3.4 ACYL GLYCEROLS

Fatty acids	Carboxylic acids with aliphatic chains
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Glycolipids	Carbohydrate associated to acylglycerols or fatty acids
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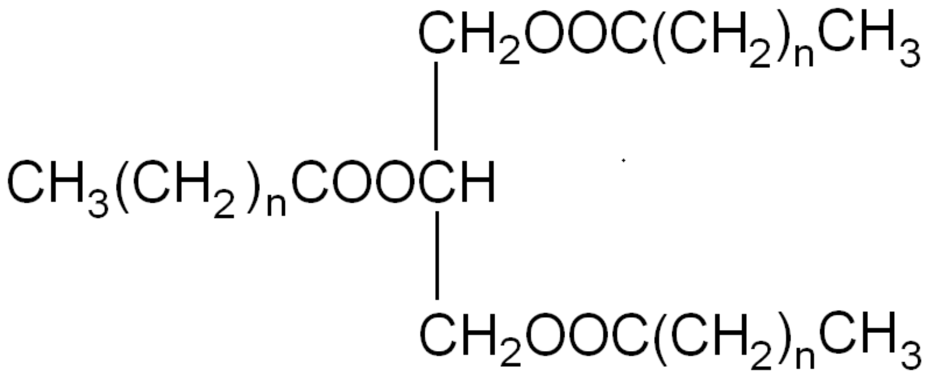
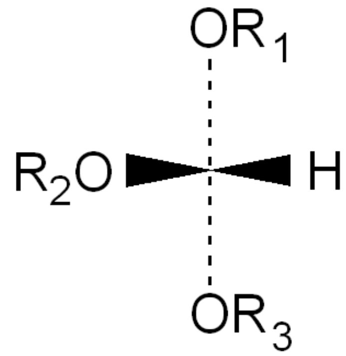
3.4 ACYL GLYCEROLS

The Hirschmann numbering system





sn-1

sn-2

sn-3

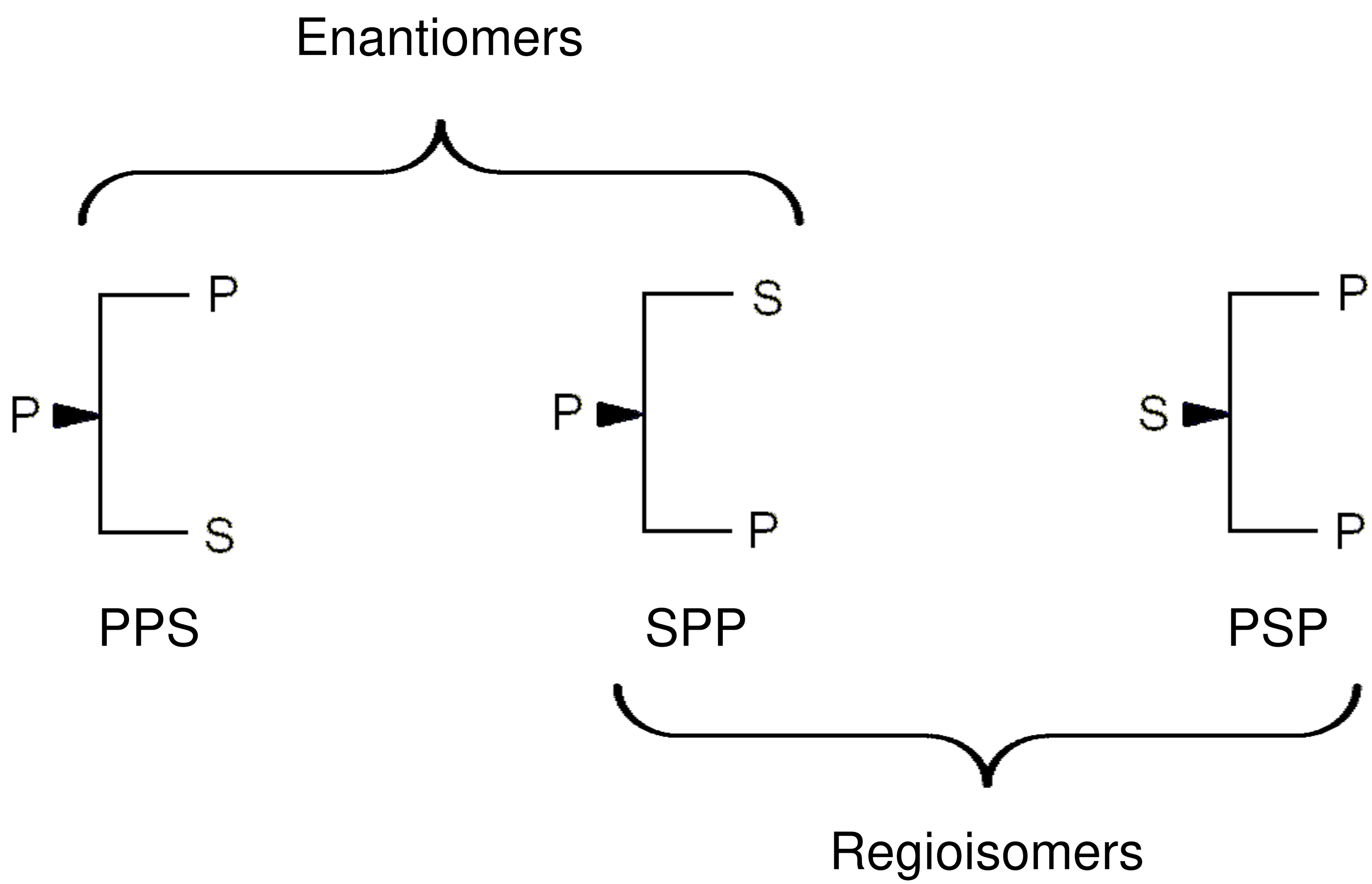
stereospecific numbering

OPL means Oleic (18:1) in pos. sn-1, Palmitic (16:0) in sn-2 and Linoleic (18:2) in sn-3

H. Hirschmann, J. Biol. Chem. <u>235</u>, 2762-2767 (1960)

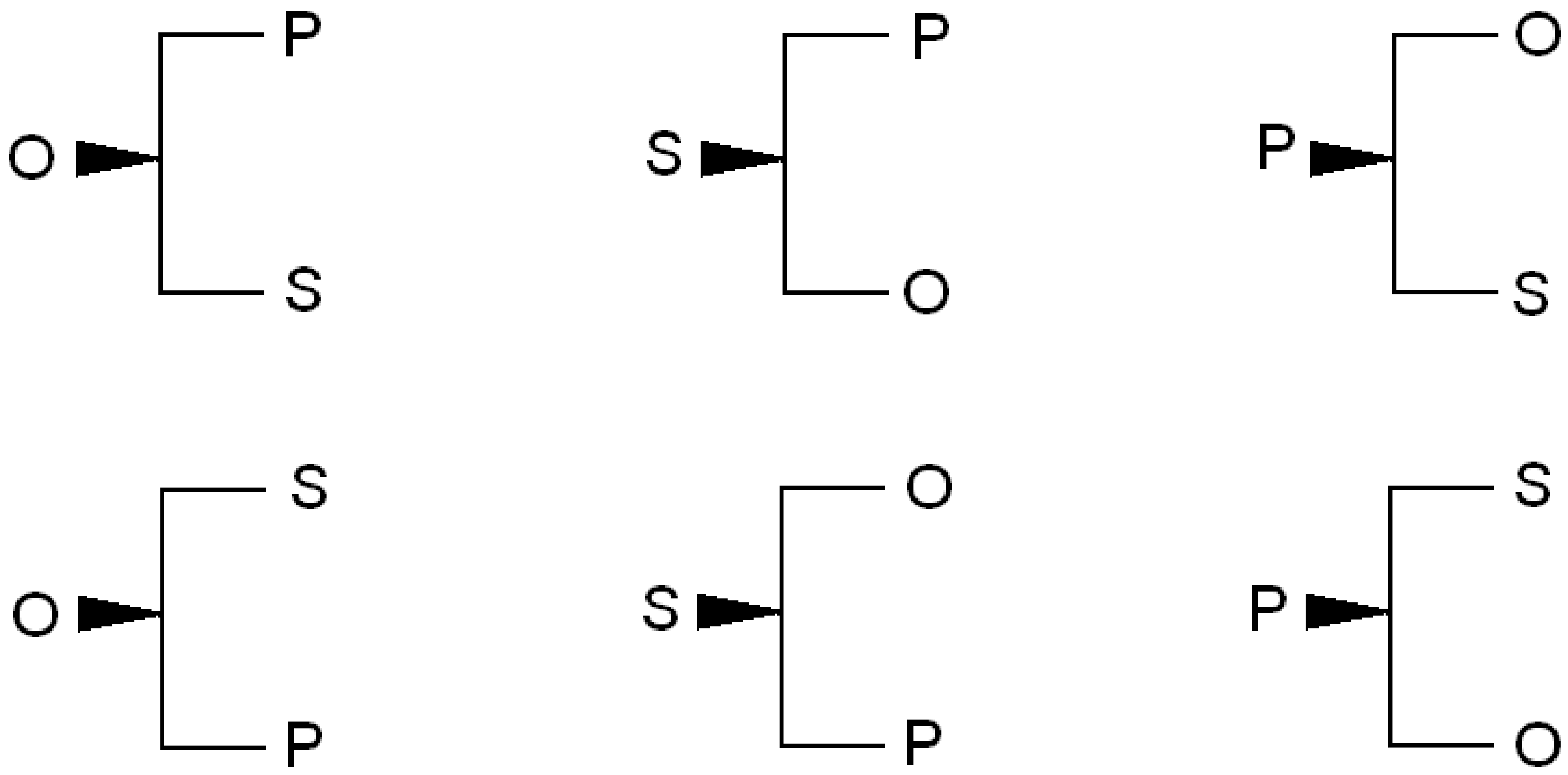
3.4 ACYL GLYCEROLS

Stereoisomers of dipalmitoylstearyl-glycerol



3.4 ACYL GLYCEROLS

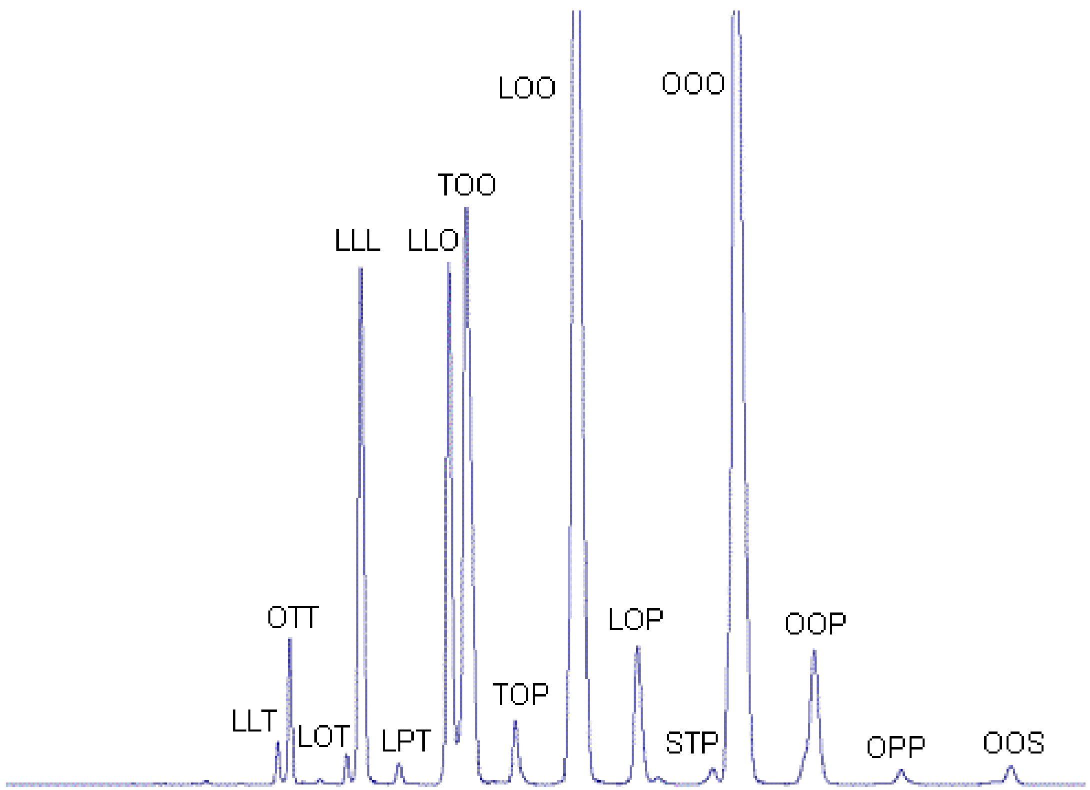
Stereoisomers of palmitoylstearyloleyl-glycerol



3 regioisomers, each having 2 enantiomers

3.4 ACYL GLYCEROLS

HPLC of triacylglycerols from low-erucic rapeseed oil



P = palmitate, S = stearate, O = oleate, L = linoleate, T = linolenate

3.5 FUNCTIONALIZED LIPIDS

Fatty acids	Carboxylic acids with aliphatic chains
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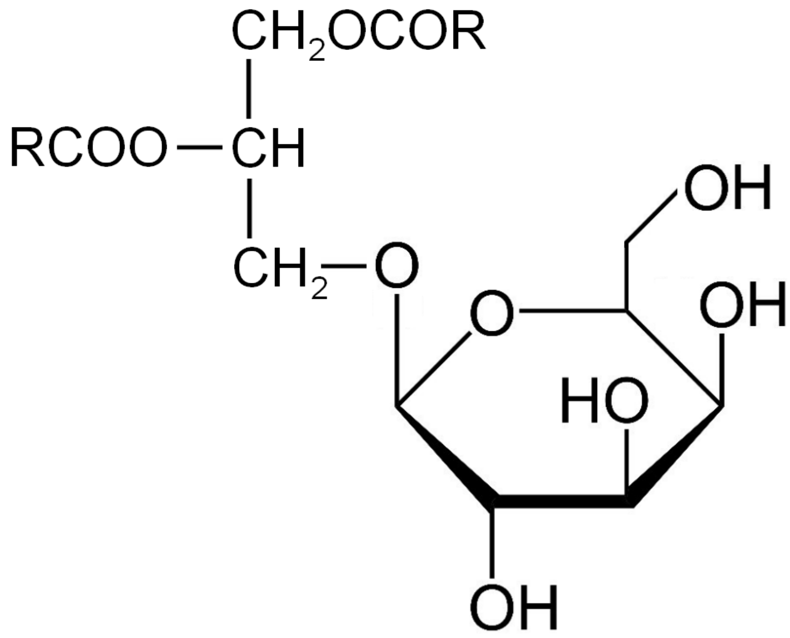
3.5 FUNCTIONALIZED LIPIDS

Structure of glycolipids



Galactosyldiacyl-glycerol

Abundant in chloroplast membranes

(up to 25% in spinach)

3.5 FUNCTIONALIZED LIPIDS

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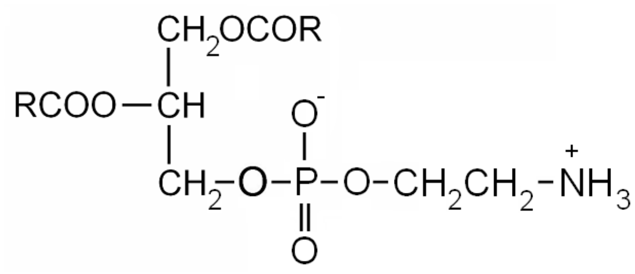
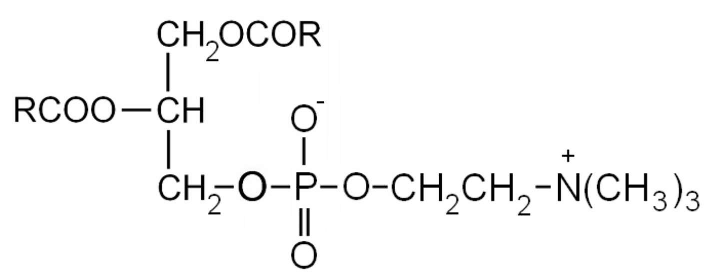
3.5 FUNCTIONALIZED LIPIDS

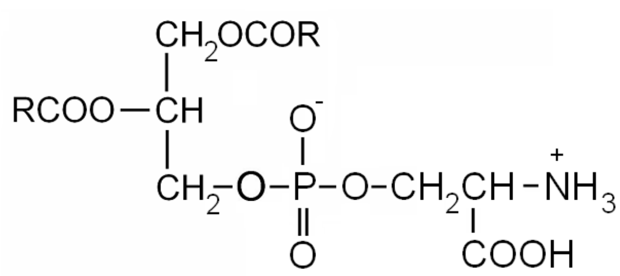
Some phospholipids



Phosphatidyl-ethanolamine



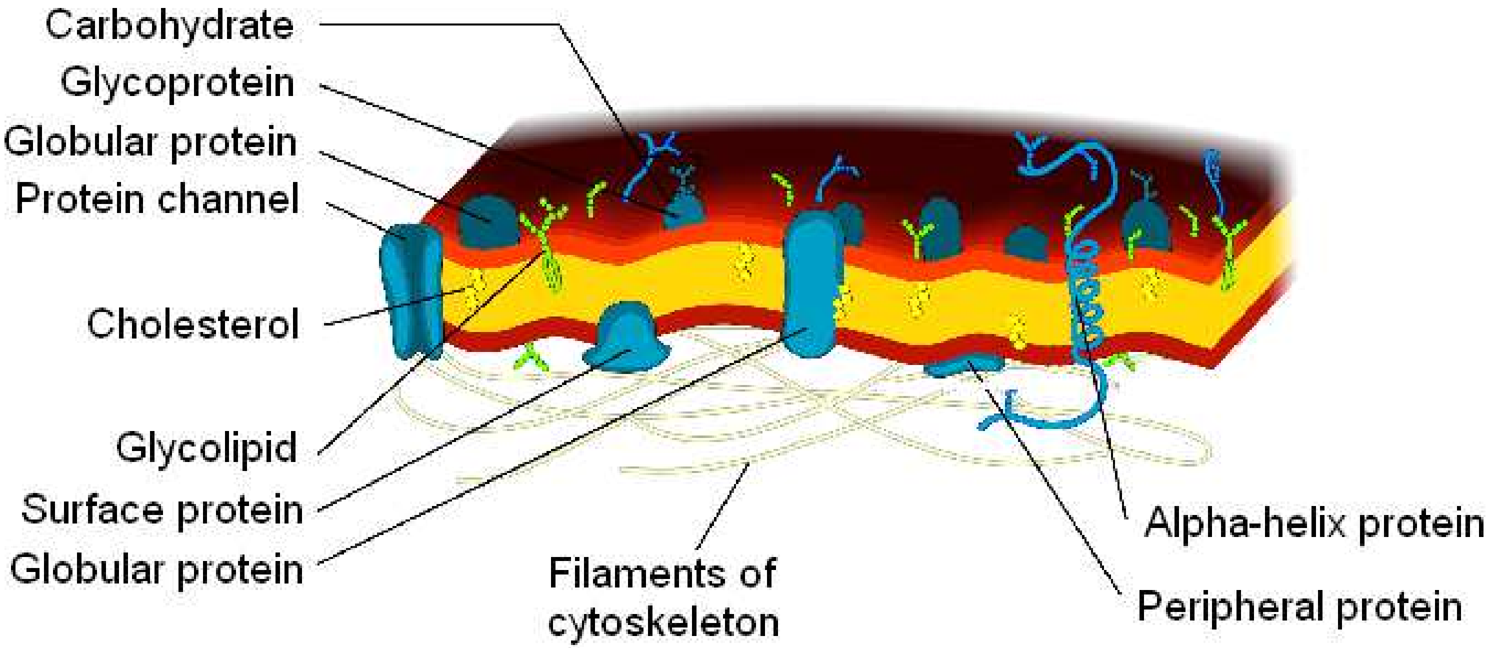
Phosphatidyl-choline
(lecithin)



Phosphatidyl-serine

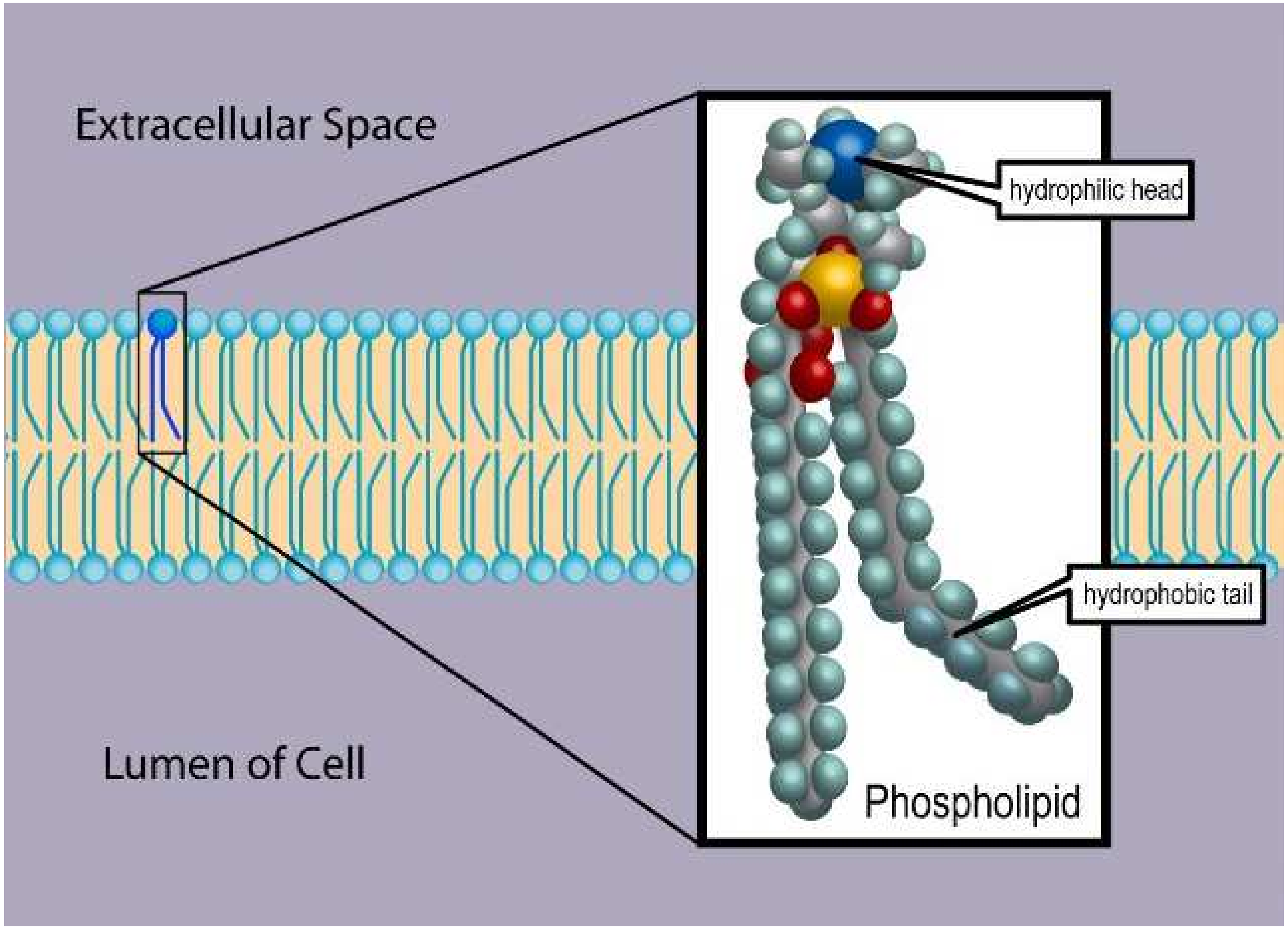
3.5 FUNCTIONALIZED LIPIDS

Cell membrane diagram



3.5 FUNCTIONALIZED LIPIDS

Lipid bilayer of cell membranes



3.6 STEROLS AND TOCOLS

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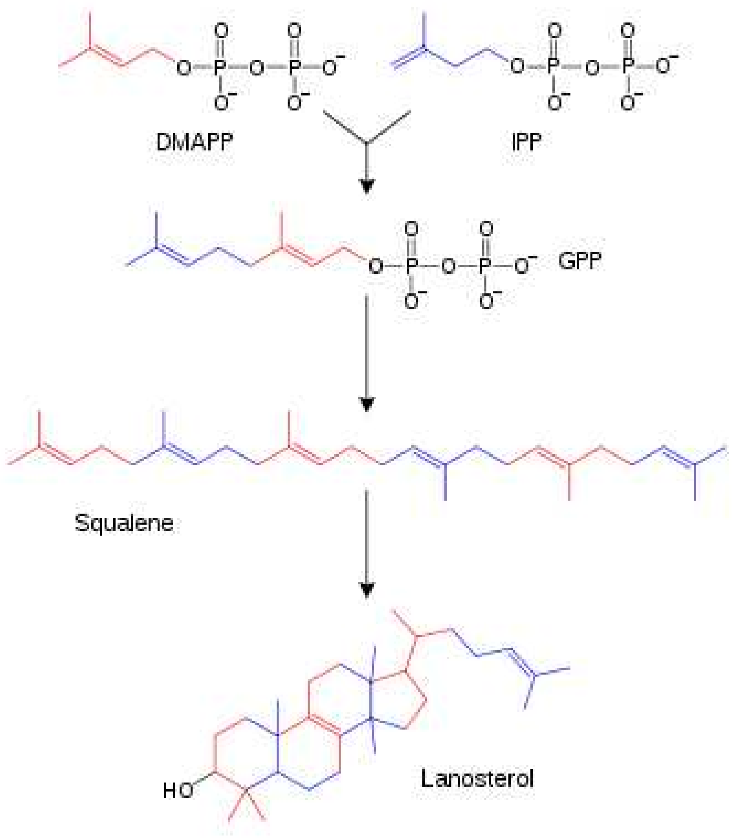
3.6 STEROLS AND TOCOLS

Biosynthesis of isoprenoïd compounds



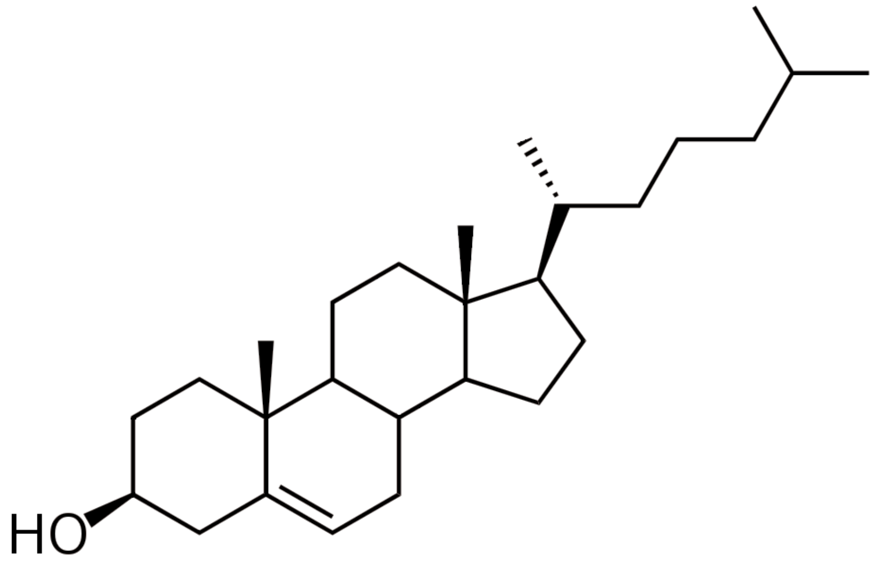
DMAPP Dimethylallyl pyrophosphate

IPP Isopentenyl pyrophosphate

GPP Geranyl pyrophosphate

3.6 STEROLS AND TOCOLS

Cholesterol occurence

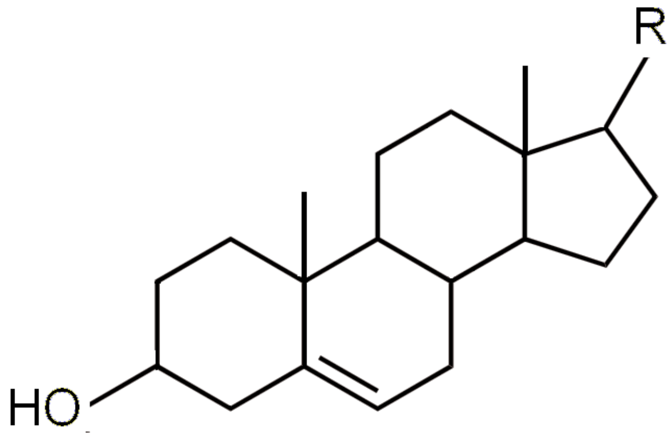


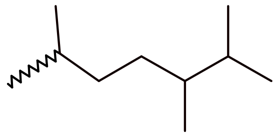
C27 - sterol

Food	*Amount (mg/100g)*
Calf brain	2’000
Egg yolk	1’000
Pork kidney	410
Pork liver	340
Butter	240
Pork meat	70
Beef meat	60
Halibut	50

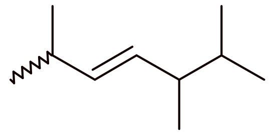
3.6 STEROLS AND TOCOLS

Some phytosterols

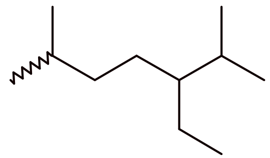




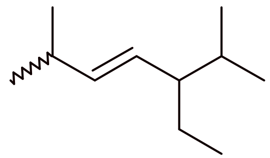
Campesterol C28



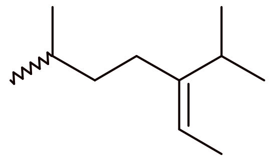
Brassicasterol C28



Sitosterol C29



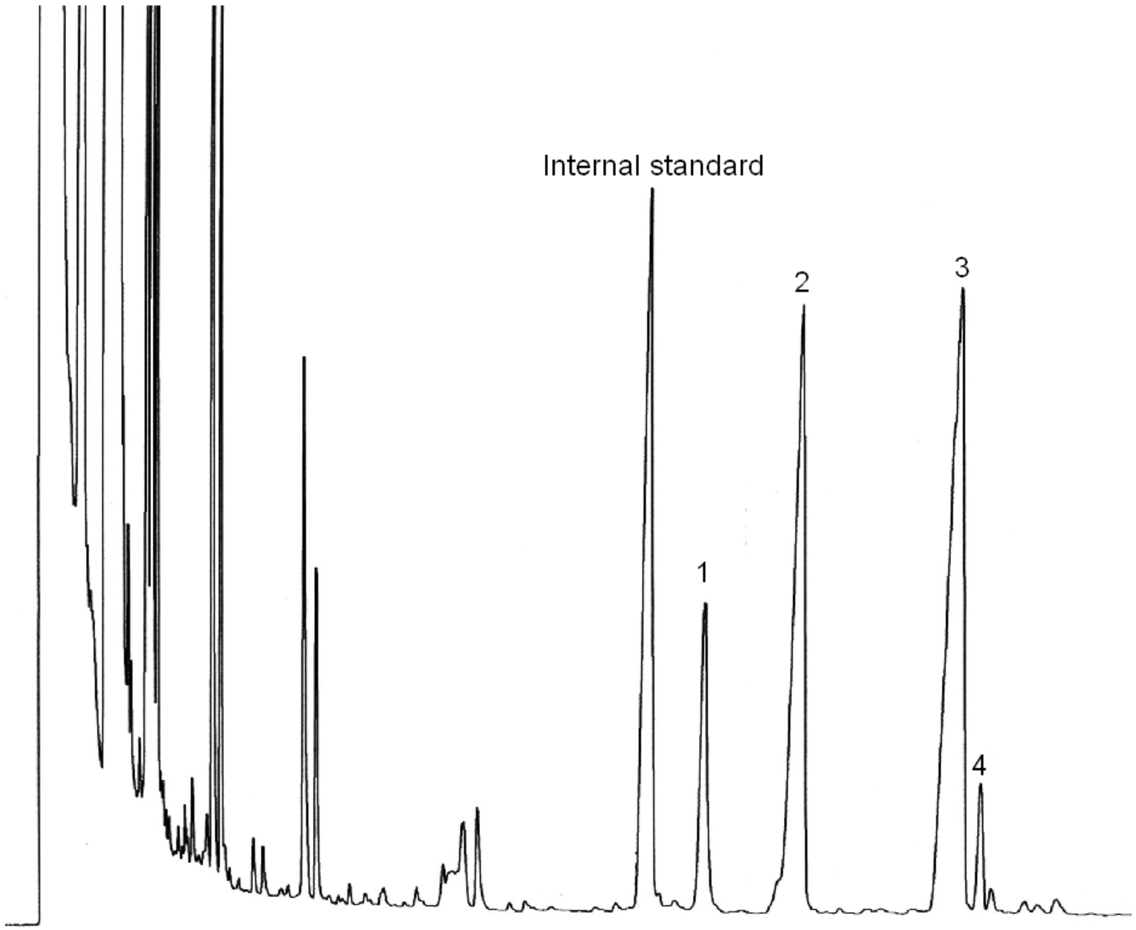
Stigmasterol C29



Avenasterol C29

3.6 STEROLS AND TOCOLS

Phytosterol analysis of rapeseed oil by gas chromatography



1 Brassicasterol

2 Campesterol

3 Sitosterol

4 Avenasterol

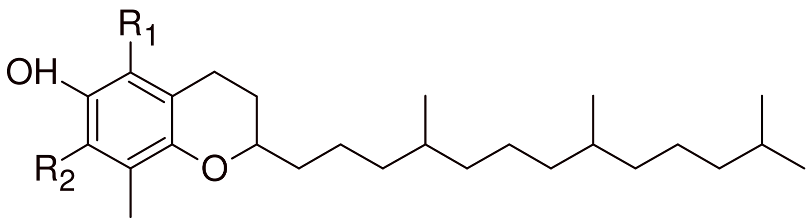
3.6 STEROLS AND TOCOLS

Phytosterol contents of some oils (in %)

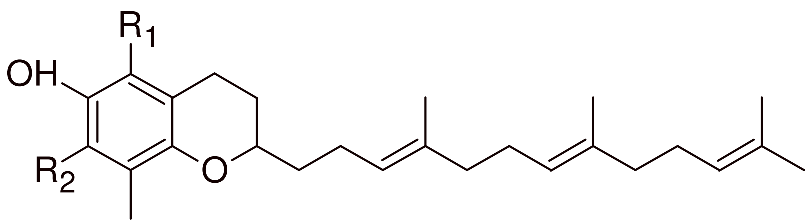
Oil	***Total PS (%)***	***Campesterol***	***Stigmasterol***	***Sitosterol***	***Avenasterol***
Peanut	0.25	13	11	75	-
Corn	0.90	22	7	62	4
Rapeseed	0.84	29	-	55	6
Olive	0.16	4	2	85	9
Soya	0.37	22	19	54	2
Cocoa	0.25	9	28	63	-

3.6 STEROLS AND TOCOLS

Structures of tocols



Tocopherols (T)



Tocotrienols (TT)

T / TT	R_1	R_2
α	CH_3	CH_3
β	CH_3	H
γ	H	CH_3
δ	H	H

3.6 STEROLS AND TOCOLS

Occurrence of tocols (in ppm)

Oil	*α -T*	*β -T*	*γ -T*	*δ -T*	*α -TT*	*β -TT*	*γ -TT*	*δ -TT*
Palm	170	-	30	-	200	2	340	65
Soja	100	8	1150	440	-	-	-	-
Sunflower	760	25	15	-	-	-	-	-
Corn	280	55	1050	55	50	8	160	5
Rapeseed	210	60	550	15	-	-	-	-

3.7 CHEESE – Imitation - *composition*

Lasagne al Forno-assiette de pâtes avec de la viande hachée. Conditionnée sous atmosphère protectrice. Ingrédients : tomates, viande porc, lait entier, semoule de blé dur, eau, fromage**, huile végétale**, amidon de maïs modifié, protéine de lait, œufs entiers, farine de blé, sel de cuisine, sucre, épices, herbes aromatiques, céleri, levure, farine de graine de caroube, citrate de sodium. Sans exhausteurs de goût. Sans addition de conservateurs. Sans addition de colorants.

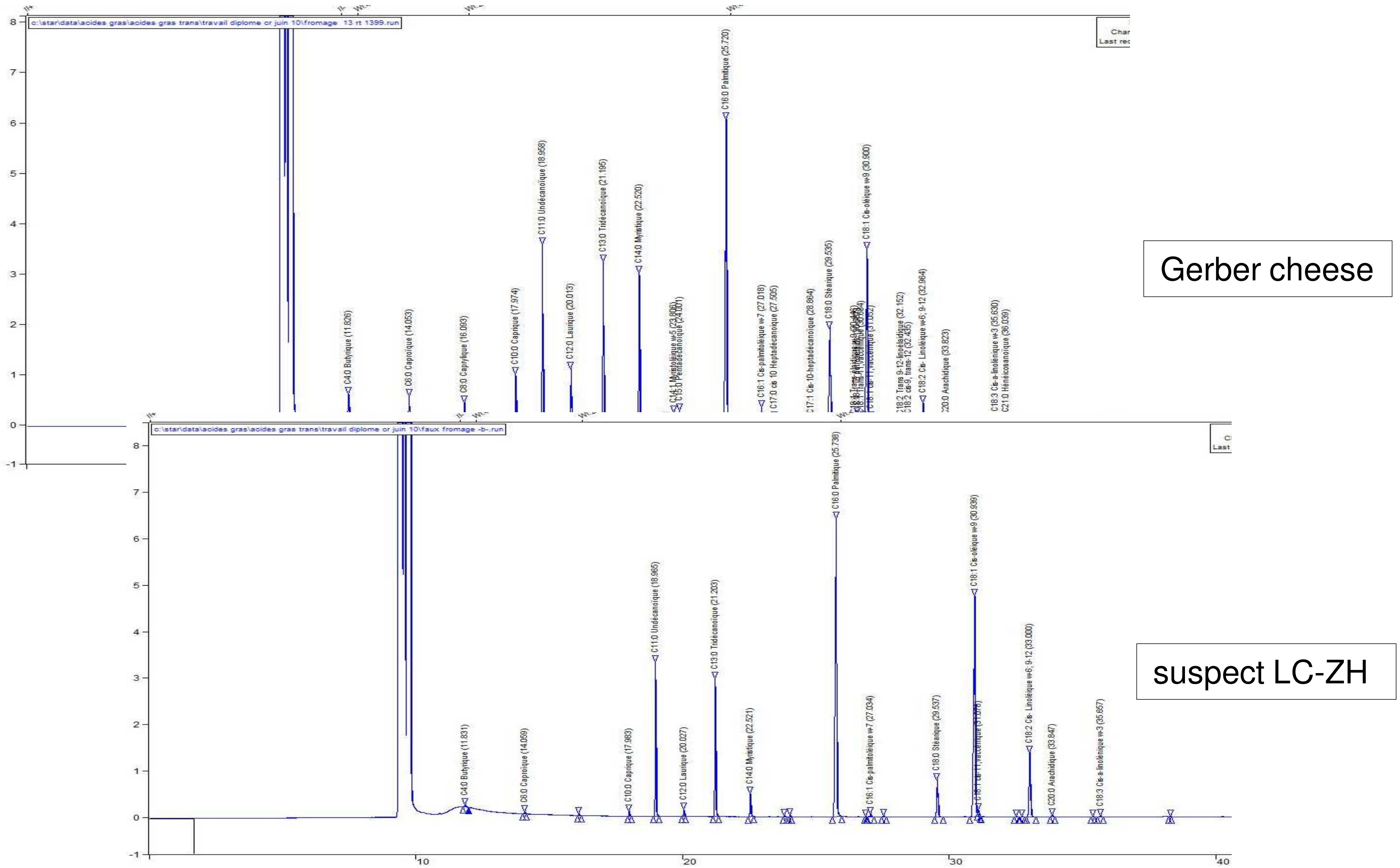
Ingredients: tomatoes, meat pork, whole milk, wheat, water, cheese, vegetable oil, starch of modified corn, protein of milk, eggs , wheat flour, common salt, sugar, spices, aromatic herbs, celery, yeast, flour of seed of carob, citrate of sodium. Without flavor enhancers. Without conservatives' Without addition of colouring agents

Recipe (cheese ?): Vegetable fat, some protein of milk, add some starch, some salt, a pinch of colouring agents, aromas and flavor enhancers

3.7 CHEESE – Imitation - *analytical strategy*

- the distribution in fatty acids
- the presence of phytostérols
- the content in cholesterol
- the presence of plant or animal DNA

3.7 CHEESE – Imitation - distribution in fatty acids

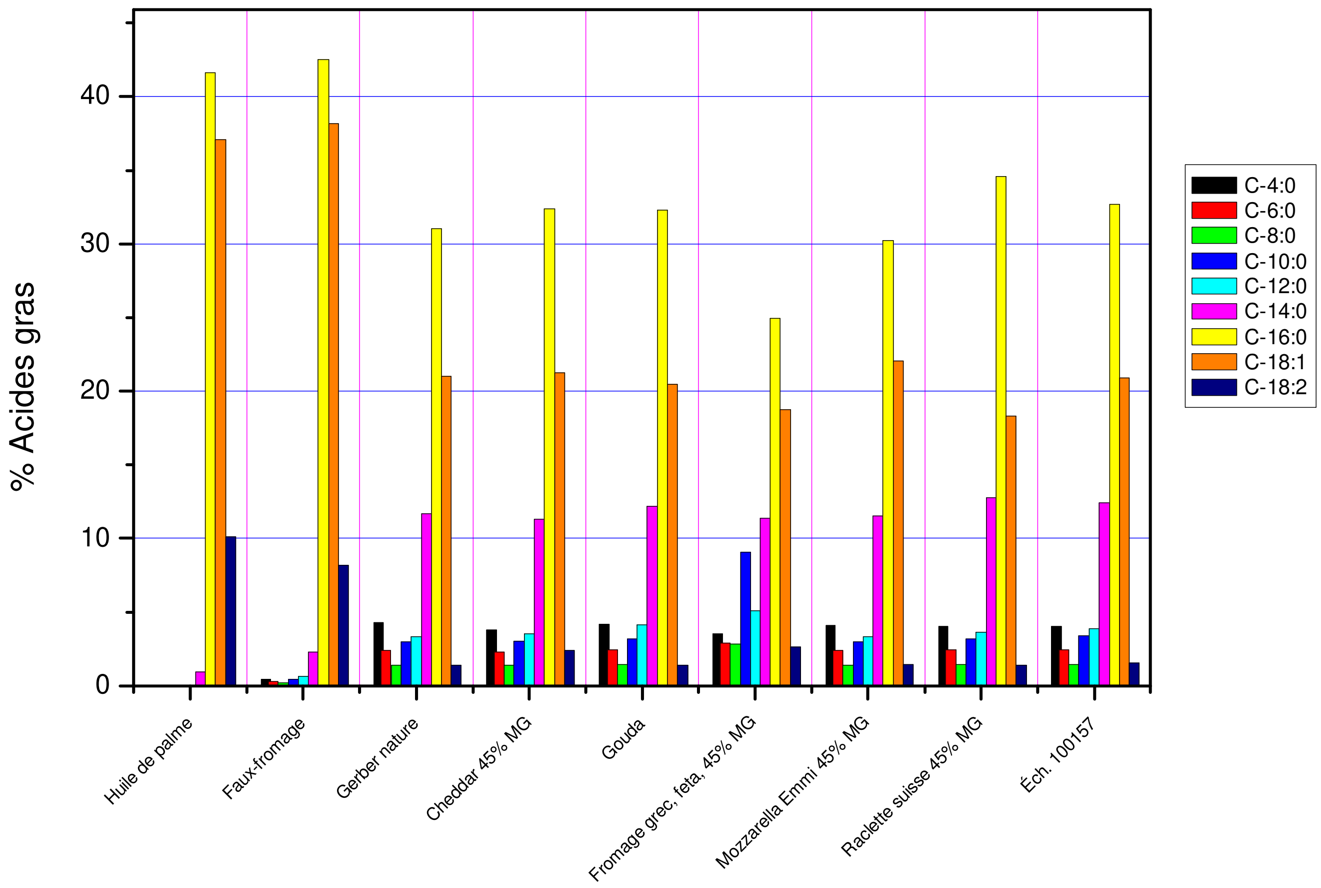


3.7 CHEESE – Imitation - distribution in fatty acids

Échantillons	Acides gras								
	C-4:0 Butyrique	C-6:0 Caproïque	C-8:0 Caprylique	C-10:0 Caprique	C-12:0 Laurique	C-14:0 Myristique	C-16:0 Palmitique	C-18:1 Oléique	C-18:2 linoléique
Gerber bonjour 45% MG	4.21	2.40	1.41	3.15	3.60	12.07	32.08	20.16	1.4
Gerber fromage fondu ¼ gras	4.32	2.57	1.49	3.27	3.73	12.55	33.83	19.41	0.0
Lait condensé	4.55	2.5	1.51	3.52	3.94	12.42	30.84	20.22	1.62
Lait de soja	0.0	0.0	0.0	0.0	0.0	0.0	10.78	18.44	57.16
Gouda	4.17	2.46	1.41	3.15	4.14	12.19	32.26	20.47	1.36
Fromage grec, feta, 45% MG	3.56	2.88	2.80	9.04	5.10	11.35	24.96	18.78	2.64
Mozzarella Emmi 45% MG	4.07	2.36	1.36	2.98	3.3	11.53	30.22	22.07	1.44
Raclette suisse 45% MG	4.05	2.43	1.44	3.16	3.64	12.75	34.61	18.32	1.36
Éch. 100157	4.05	2.44	1.45	3.4	3.86	12.39	32.71	20.9	1.54
Éch. 100158	3.76	2.36	1.48	3.47	4.34	12.62	33.19	19.51	1.4
Huile de palme	0.0	0.0	0.0	0.0	0.0	0.96	41.6	37.1	10.1
Faux-fromage	0.43	0.26	0.18	0.40	0.61	2.3	42.5	38.14	8.19

FA composition

3.7 CHEESE – Imitation - distribution in fatty acids



3.7 CHEESE – Imitation - presence of phytostérols

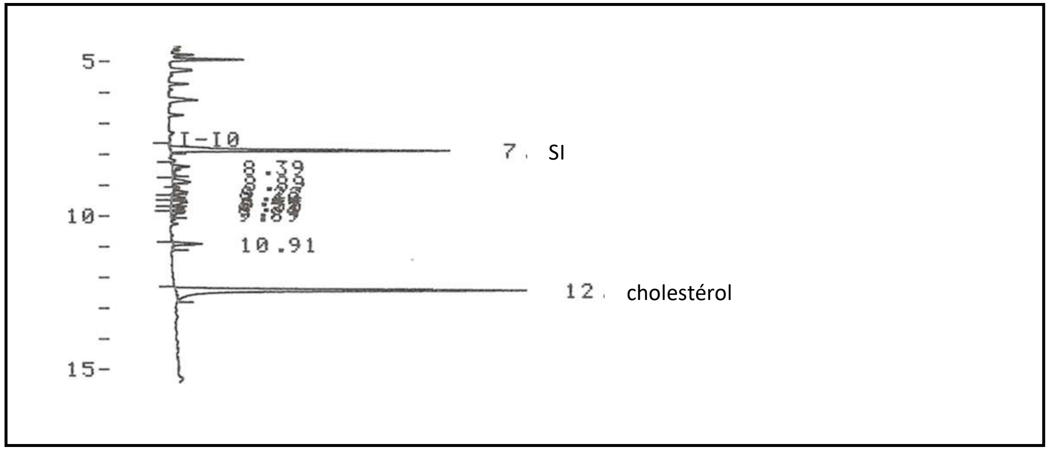
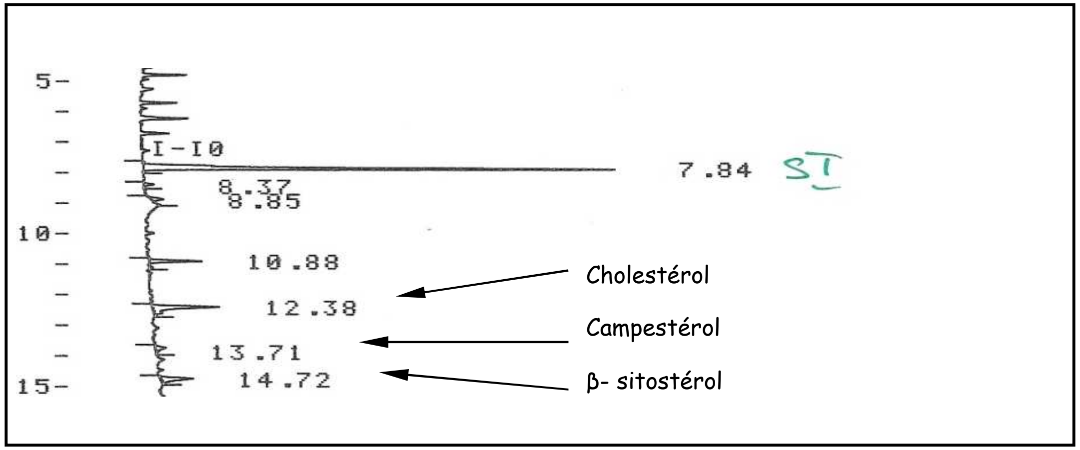


Fig.3.11. Composition en stérols de l’échantillon fromage fondu Gerber

Fig.3.12. Composition en stérols de l’échantillon fromage suspect LC-ZH

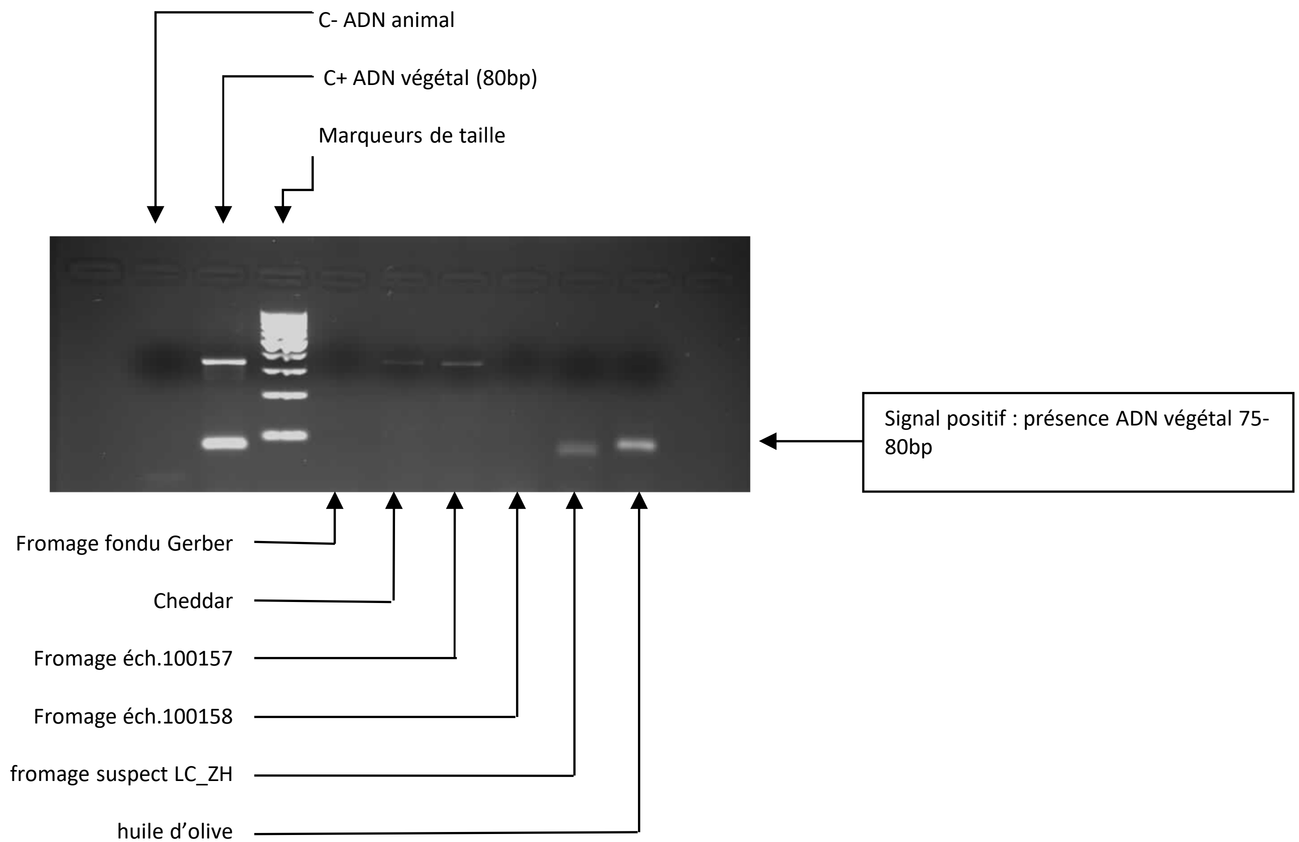


3.7 CHEESE – Imitation - content in cholesterol

Gerber cheese	: 1437 mg/kg de MS
Cheddar	: 1295 mg/kg de MS
Cheese N° 100157	: 1300 mg/kg de MS
Cheese N° 100158	: 1380 mg/kg de MS
suspect cheese LC-ZH	: 184 mg/kg de MS

MS : dry matter

3.7 CHEESE – Imitation - presence of plant or animal DNA



3.7 WAXES

Fatty acids	Carboxylic acids with aliphatic chains
Acyl glycerol lipids	Glycerol esterified with one to three fatty acids
Glycolipids	Carbohydrate associated to acylglycerols or fatty acids
Phospholipids	Acylglycerol esterified with one or two phosphate moieties
Sphingosides	Long-chain bases linked to a fatty acid
Sterols	Substituted hydroxy-sterane
Tocols	Substituted long chain benzopyrane
Waxes	Long chain esters of fatty acids

3.7 WAXES
Composition and properties

Waxes : mixtures of
- long chain esters of fatty acids
- fatty alcools
- long chain hydrocarbons

Present on the surface cells to prevent dehydration or infection of microorganisms

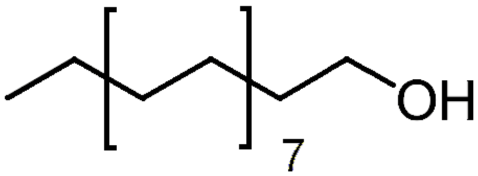
Present in fish oils, epidermal cells and animal products (e.g.bees wax)

Waxes are oil-soluble and crystallize at room temperature

➡ Waxes are removed during the edible oil refining process

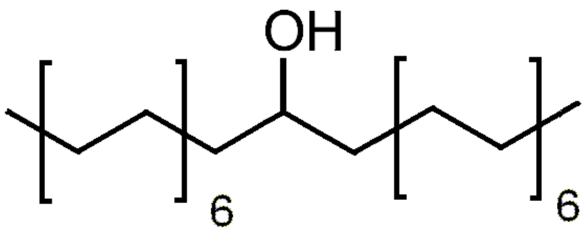
3.7 WAXES

Some natural fatty alcools and ketones



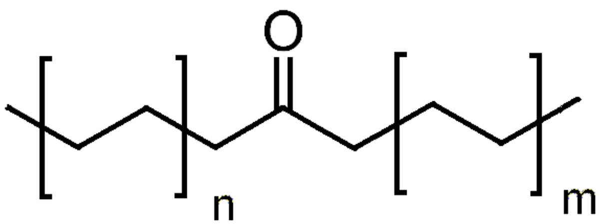
Stearoyl alcool $C_{18}H_{37}OH$

Abundant in fish oil



Nonacosane-15-ol $(C_{14}H_{29})_2CHOH$

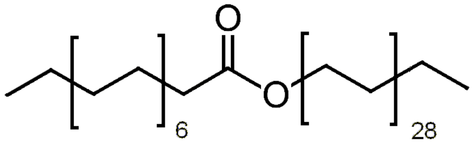
Present in cabbage leaf wax



N-alcanones C23 to C33 (odd numbers !)

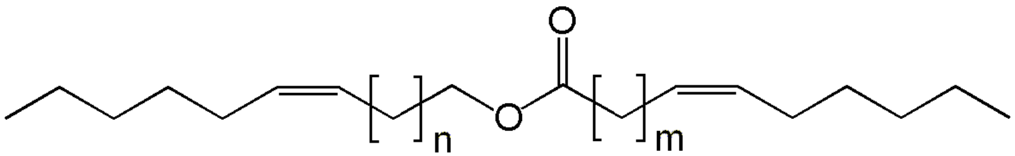
Present on the surface of apple skin

3.7 WAXES
Some natural fatty esters and alcenes



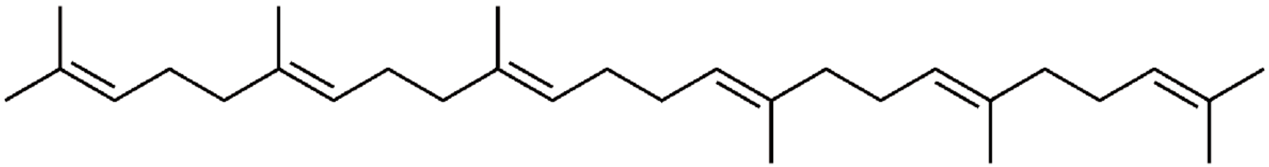
Triacontanylpalmitate $C_{15}H_{31}COOC_{30}H_{61}$

Principal component of beeswax



18:1, 20:1 and 22:1 fatty acids linked to 20:1, 22:1 and 24:1 fatty alcohols

Present in jojoba oil (Simmondsia chinensis)



Squalene

Shark liver oil, rice bran, wheat germ and olives

3.8 NUTRITIONAL ASPECTS

Association between lipids and cardiovascular risks

Trans fatty acids

Saturated fatty acids

Cholesterol

EPA and DHA

Phytosterols

α-linolenic acid

Linoleic acid

3.8 NUTRITIONAL ASPECTS
Dietary recommendations

Values for a 2'000 kcal diet	Lowest physiological need (g)	Recommended daily allowance
Total fatty acids (FA)	30	35 - 40
C18:2 (n-6) Linoleic acid	2	4
C18:3 (n-3) α-linolenic acid	0.8	1
C22:6 (n-3) DHA	0.25	0.25
C20:5 (n-3) EPA	-	0.25
Saturated FA	-	< 12
Trans - FA	-	< 1.5

The ratio ω-6 / ω-3 should be lower than 5

In many western diets, it lies between 10 and 25 !

3.8 NUTRITIONAL ASPECTS

Occurrence of the $\omega - 3$ family

18:3 (n-3)	CH_3-CH_2-(CH=CH-CH_2)$_3$-(CH_2)$_6$-COOH	α-linolenic acid (ALA)
20:5 (n-3)	CH_3-CH_2-(CH=CH-CH_2)$_5$-(CH_2)$_3$-COOH	Eicosapentaenoïc acid (EPA)
22:6 (n-3)	CH_3-CH_2-(CH=CH-CH_2)$_6$-CH_2-COOH	Docosahexaenoïc acid (DHA)

FISH	Name	% *EPA/DHA*
Tuna	*Thunnus spp.*	0.3 – 1.3
Salmon	*Salmo salar*	1.3 – 2.2
Halibut	*Hypoglossus spp.*	0.7 – 1.3
Swordfish	*Xiphias gladius*	0.9 – 1.2

SEED	Name	% ALA
Flaxseed	*Linum usitatissimum*	18.1
Hempseed	*Cannabis sativa*	8.7
Walnut	*Juglans regia*	6.3
Pecan nut	*Carya illinoiensis*	0.6

3.8 NUTRITIONAL ASPECTS

Occurrence of the $\omega-6$ family

18:2 (n-6) CH_3-$(CH_2)_4$-$(CH=CH-CH_2)_2$-$(CH_2)_6$-COOH Linoleic acid (LA)

18:3 (n-6) CH_3-$(CH_2)_4$-$(CH=CH-CH_2)_3$-$(CH_2)_3$-COOH γ-linolenic acid (GLA)

20:4 (n-6) CH_3- $(CH_2)_4$-$(CH=CH-CH_2)_4$-CH_2-COOH Arachidonic acid (ARA)

Product	*% LA*
Safflower oil	78
Sunflower oil	68
Peanut oil	32
Egg yolk	16
Olive oil	10
Butter	2

Product	*% GLA*
Borage oil	22
Blackcurrant oil	17
Hemp oil	5

Product	*% ARA*
Veal liver	1.0
Mutton meat	0.3
Whole egg	0.9

3.8 NUTRITIONAL ASPECTS

Effect of fat type on nutrients absorption

Meal triacylglycerol profile modulates postprandial absorption of carotenoids :

Experiment : Salads rich in carotenoïds (lutein, lycopene, beta-carotene and zeaxanthin) topped with 3 different fats

	Saturated	Mono-unsaturated	Poly-unsaturated
	Butter oil	Canola oil	Soybean oil

3 grams

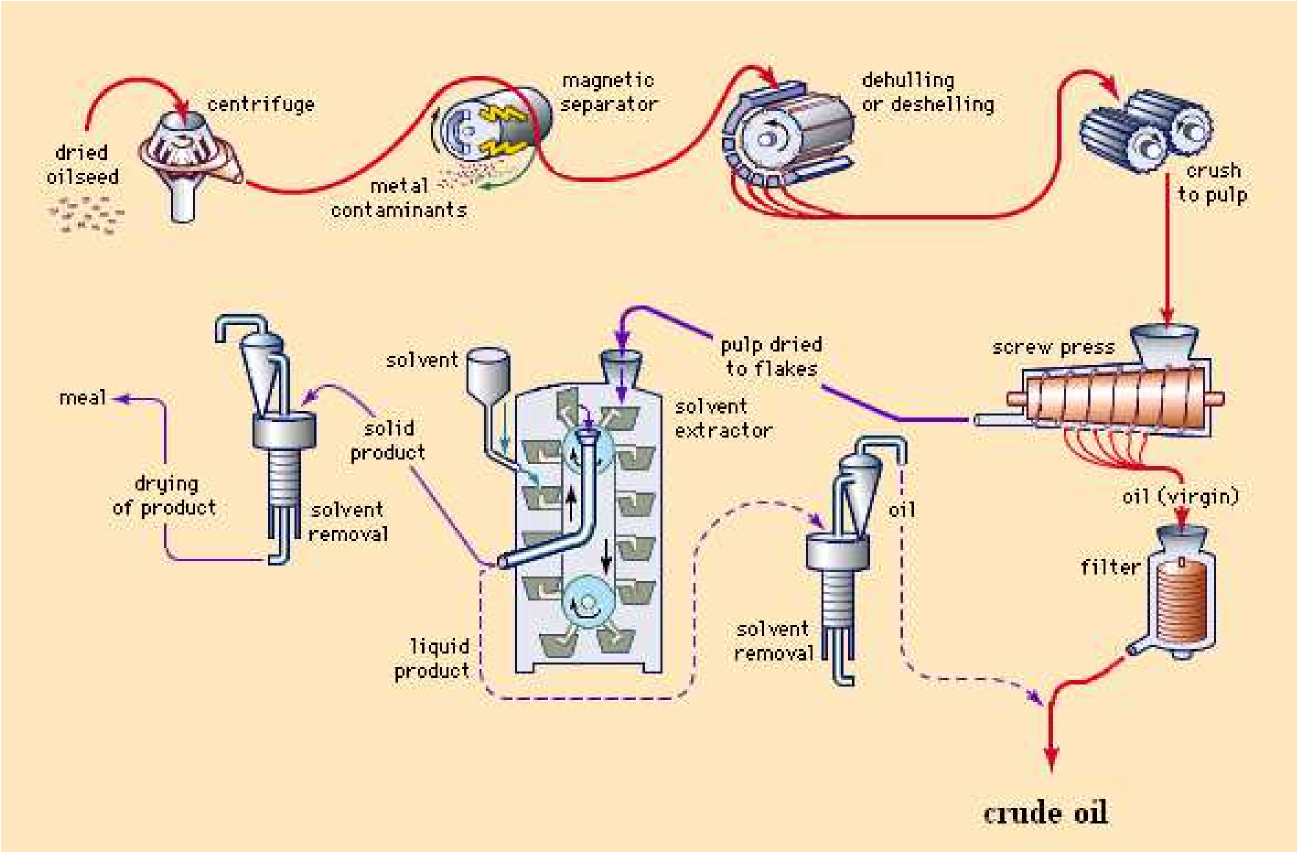
8 grams

20 grams

S. R. Goltz & al. Mol. Nutr. & Food Res., 56 866 - 877 (2012)

3.9 FATS AND OILS PRODUCTION

Oil extraction from oilseeds



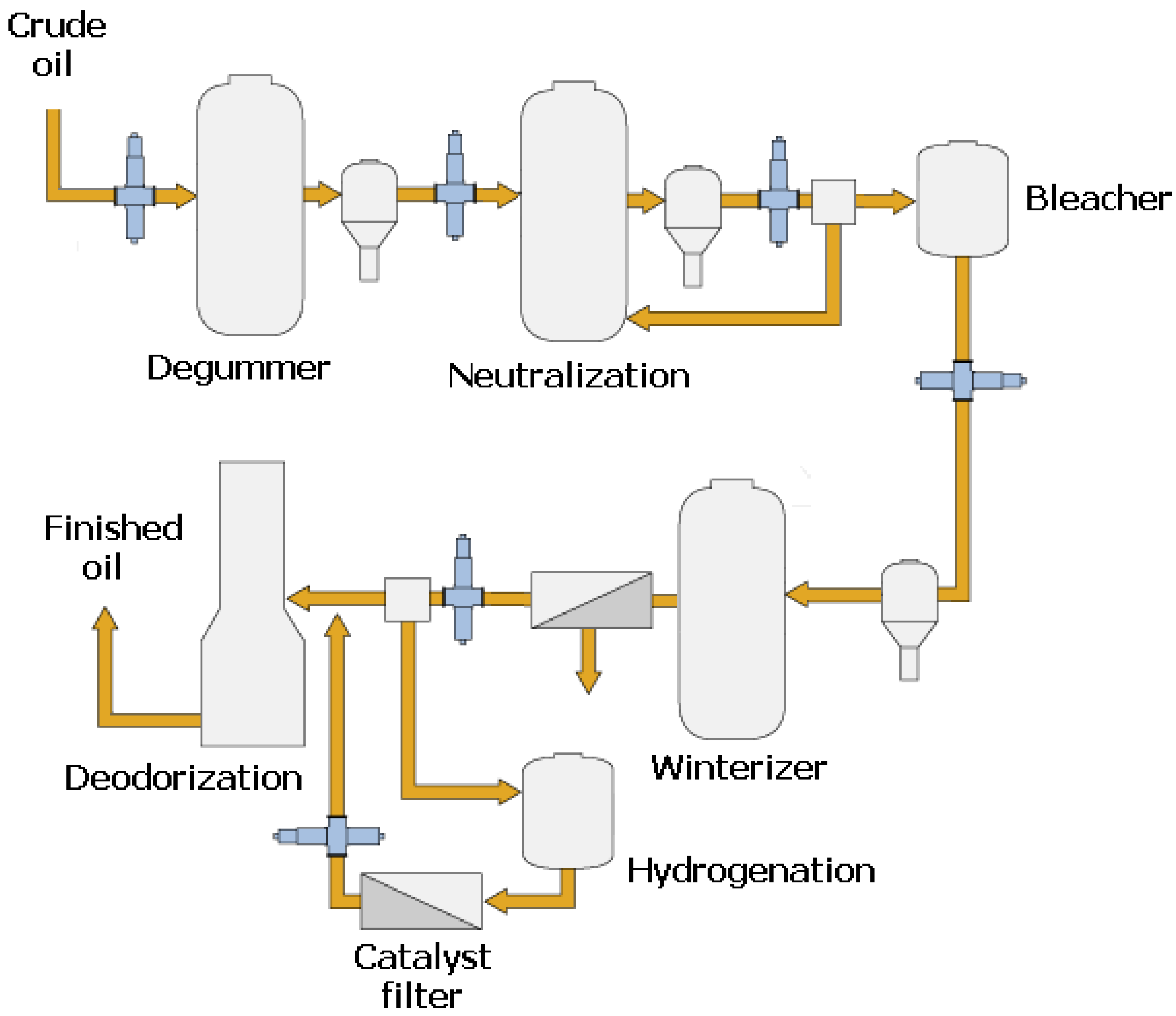
3.9 FATS AND OILS PRODUCTION

Oil refining steps

Elementary step	*Additive*	*Removed compounds*
Degumming	Water / H_3PO_4	Phospholipids (gums)
Neutralization	Water / NaOH	Free FA's Soaps
Bleaching	Adsorbent (eg. bentonite)	Pigments
Winterization	Cooling	Waxes
Deodorization	Steam	Volatile compounds

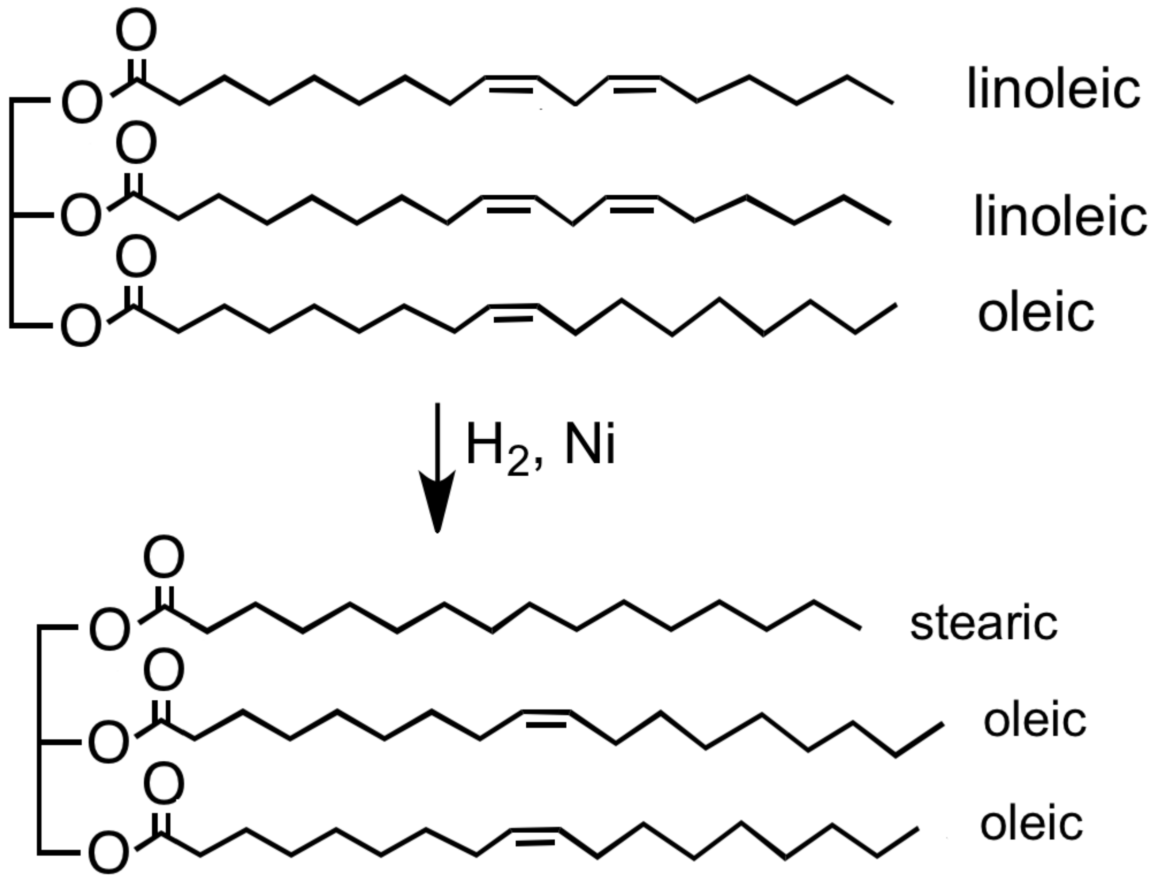
3.9 FATS AND OILS PRODUCTION

Oil refining scheme



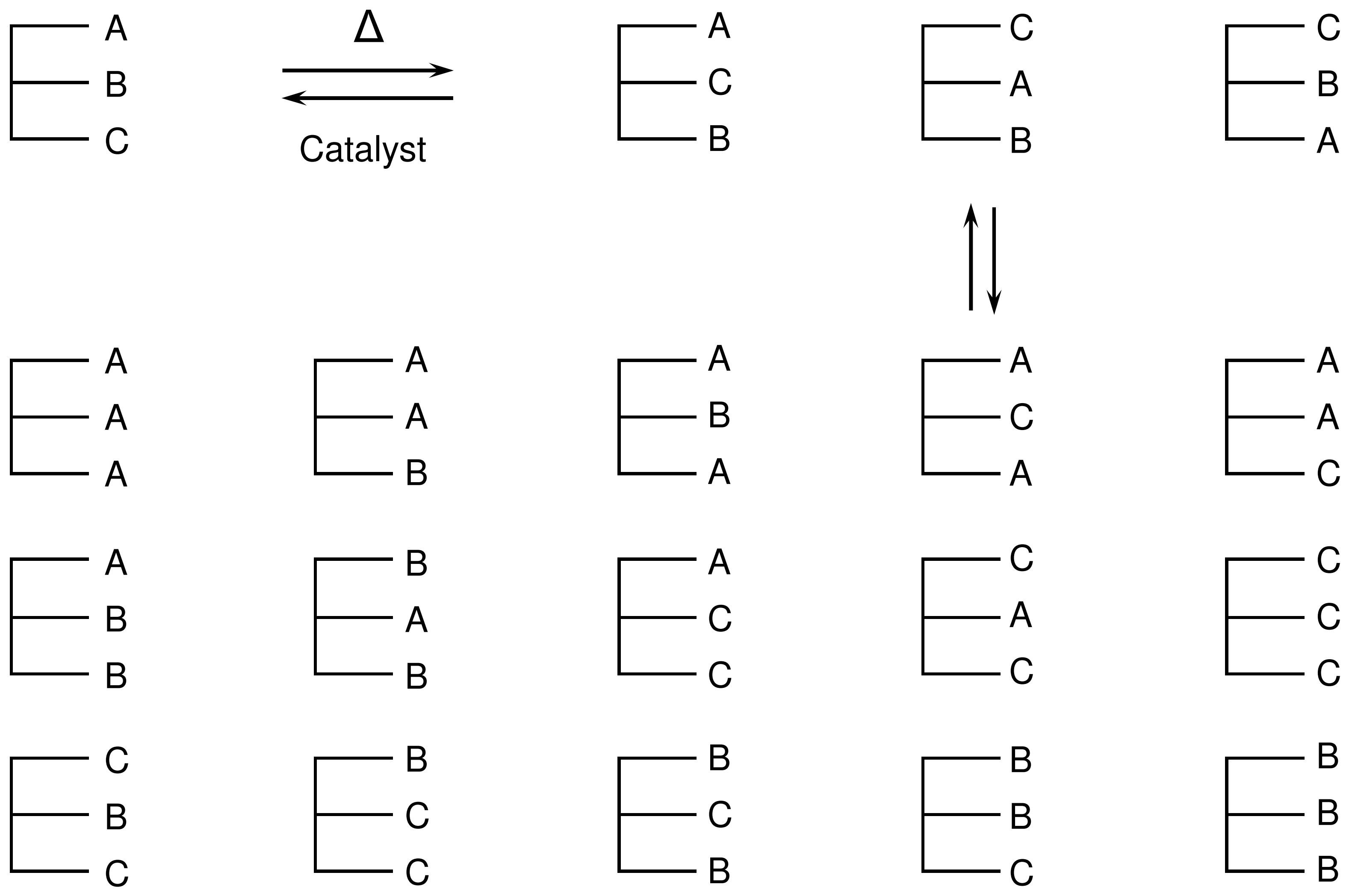
3.9 FATS AND OILS PRODUCTION

Partial hydrogenation



3.9 FATS AND OILS PRODUCTION

Inter- and intra-esterification



3.9 FATS AND OILS PRODUCTION

The origin of margarine

Emperor Louis Napoleon III of France offered a prize to anyone who could make a satisfactory substitute for butter, suitable for use by the armed forces and the lower classes

3.9 FATS AND OILS PRODUCTION
The inventor of margarine

Hippolyte Mège-Mouriès

During the 1860s, the pharmacist Mège-Mouriès studied the chemistry of fats, and his research culminated in 1869 with the filing of a patent for margarine. He won the prize established by Napoléon III, with a butter substitute obtained from beef tallow and skim milk.

In 1871, he sold his patent to the dutch entrepreneur Antonius Johannes Jurgens, whose company Margarine Unie would later become Unilever.

3.9 FATS AND OILS PRODUCTION

The current production of margarine

Margarine is a water-in-oil emulsion (80% fat) obtained in essentially four steps :

- Preparation of the oil phase by hydrogenation and/or interesterification
- Emulsification of water or skim milk with the oil phase
- Cooling and mechanical handling of the emulsion
- Freezing and crystallization

Margarin contains many additives : emulsifiers, organic acids, aromas, food colours, preservatives, vitamins

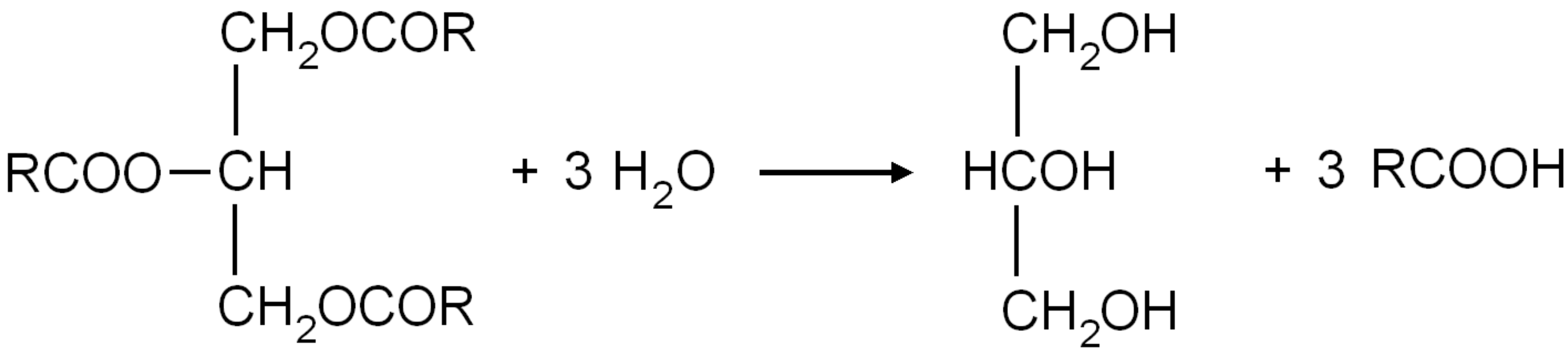
3.10 DEGRADATIONS

Types of reactions

	CAUSATIVE AGENT	MAIN PRODUCTS
Hydrolysis	Water	Free fatty acids Mono- and diacylglycerols
Oxidations	Oxygen	Oxidized acylglycerols Aldehydes Ketones Alcools
Thermal reactions	Heat	Cyclized acylglycerols Di- and oligomeric acylglycerols
Photochemical reactions	Light	Isomers
Enzymatic degradations	Enzymes	Free fatty acids Methylketones

3.10 DEGRADATIONS

Hydrolysis



Produces free fatty acids, glycerol, mono- and diglycerides

Catalysed by H^+ or OH^- ions

Can occur enzymatically due to *lipases*

- ► Cause of rancidity defect in raw milk
- ► Useful in certain types of cheese (eg. *Penicillium roqueforti*)

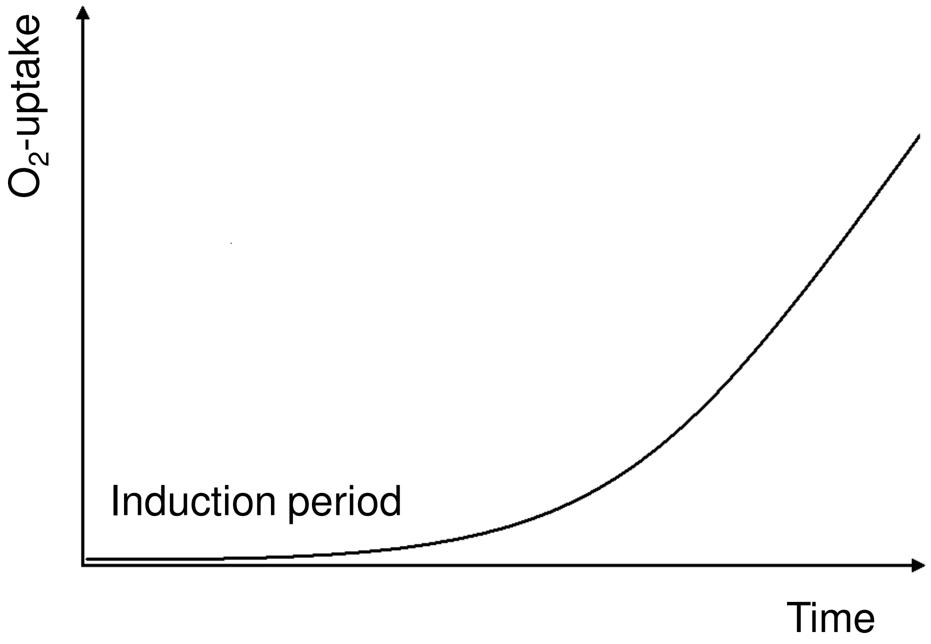
3.10 DEGRADATIONS
Enzymatic lipid hydrolysis

Vegetables → Release of enzymes due to mechanical disturbances

	Acyl lipids (µmol/g)	Free fatty acids (µmol/g)
Fresh potato homogenate	2.04	1.40
Potato homogenate after 10 minutes at 0°C	1.71	1.75
Potato homogenate after 10 minutes at 25°C	0.54	2.90

Pancreatic lipases → Important for the intestinal absorption of FA's

3.10 DEGRADATIONS
Kinetics of autoxidation



Rate of oxidation is influenced by :

- ► Fatty acids composition
- ► Presence of anti-oxidants
- ► Oxygen concentration
- ► Water contents
- ► Temperature
- ► Light

3.10 DEGRADATIONS

Elementary steps of autoxidation

Chain initiation — Formation of $R^\bullet$ (alkyl), $RO^\bullet$ (alkoxyl) or $ROO^\bullet$ (peroxyl) radicals

Chain propagation

$$R^\bullet + O_2 \rightarrow ROO^\bullet$$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet$$

$$RH + {}^\bullet OH \rightarrow R^\bullet + H_2O$$

Chain amplification

$$ROOH \rightarrow RO^\bullet + {}^\bullet OH + ROO^\bullet$$

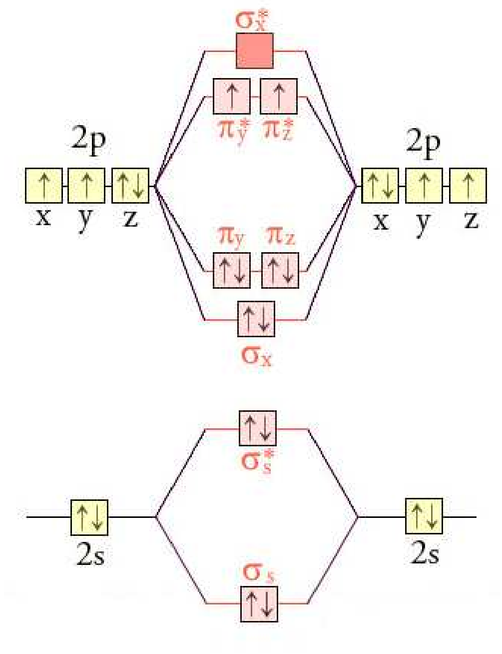
Chain termination

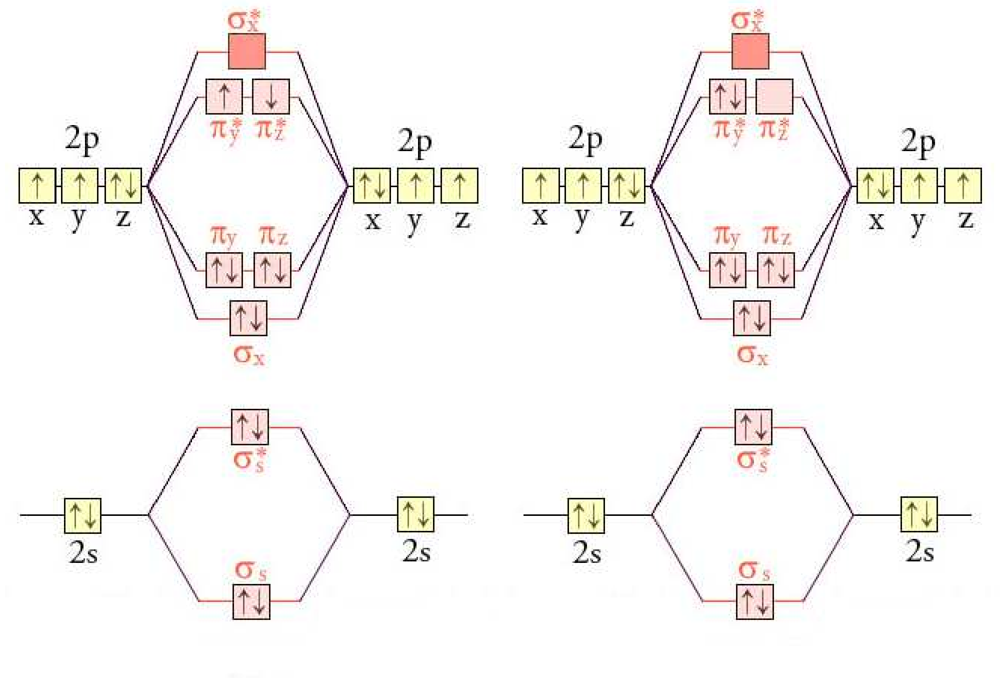
$$2\,R^\bullet \rightarrow R\text{-}R$$

$$ROO^\bullet + R^\bullet \rightarrow ROOR$$

3.10 DEGRADATIONS

Chain initiation by reaction with singlet oxygen





Triplet state (total spin S=1)

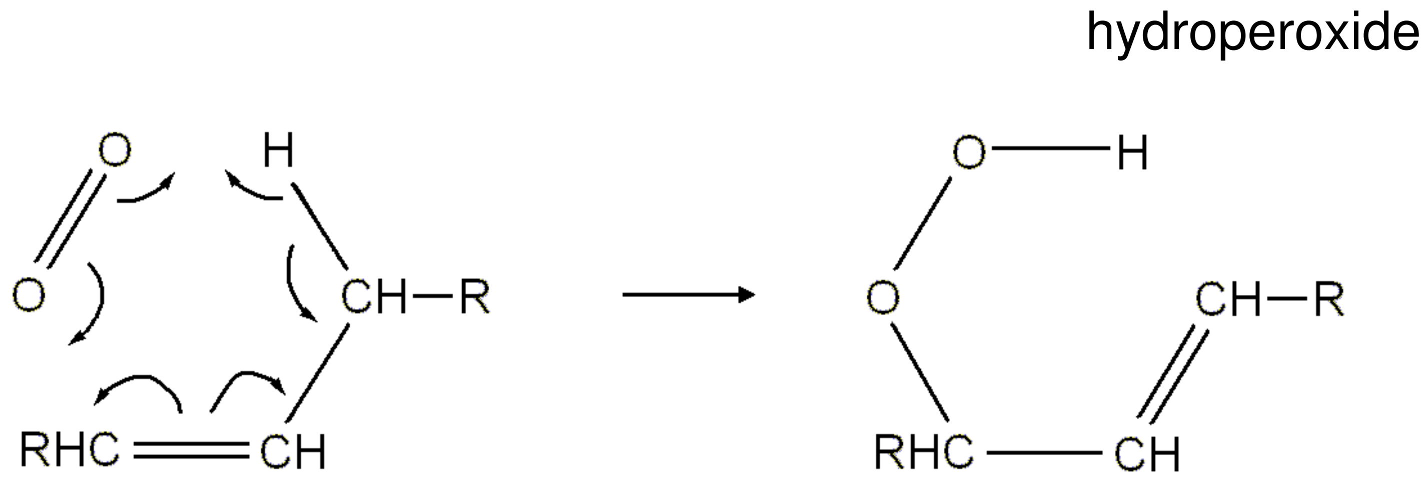
Multiplicity 2S + 1 = 3

Singlet state (total spin S=0)

Multiplicity 2S + 1 = 1

Highly reactive species

3.10 DEGRADATIONS
Cycloaddition of singlet oxygen



Singlet oxygen is a very electrophilic ethylenic type of bond

3.10 DEGRADATIONS

Metal-induced radical reactions

Mediated by Fe, Cu, Co, Mn

Example : $2\ \text{Heme-Fe}^{2+} + O_2 + 2\ H^+ \rightarrow 2\ \text{Heme-Fe}^{3+} + H_2O_2$

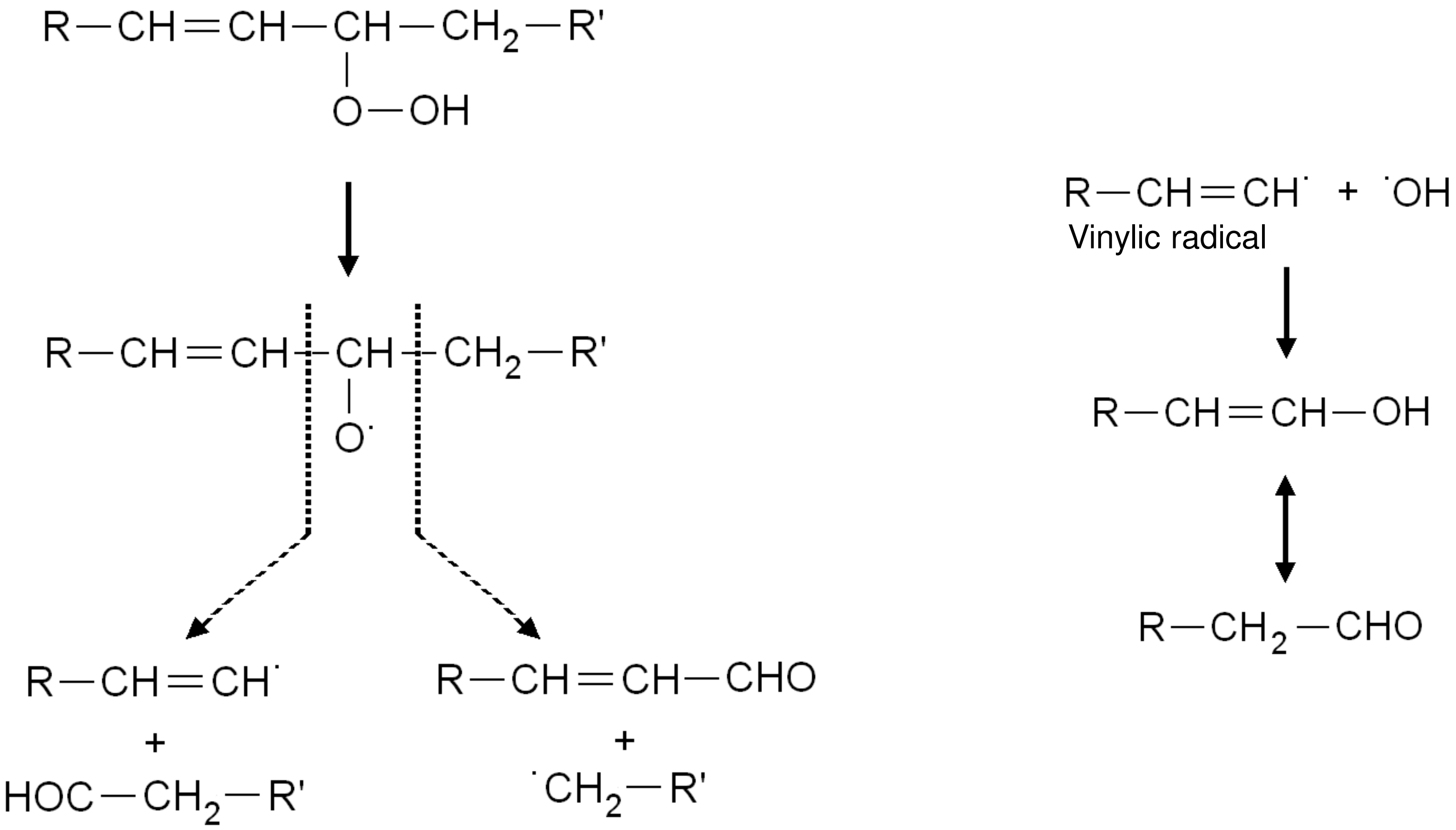
Hydrogen peroxide is then decomposed by Fenton reactions :

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^-$

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^{\cdot} + H^+$

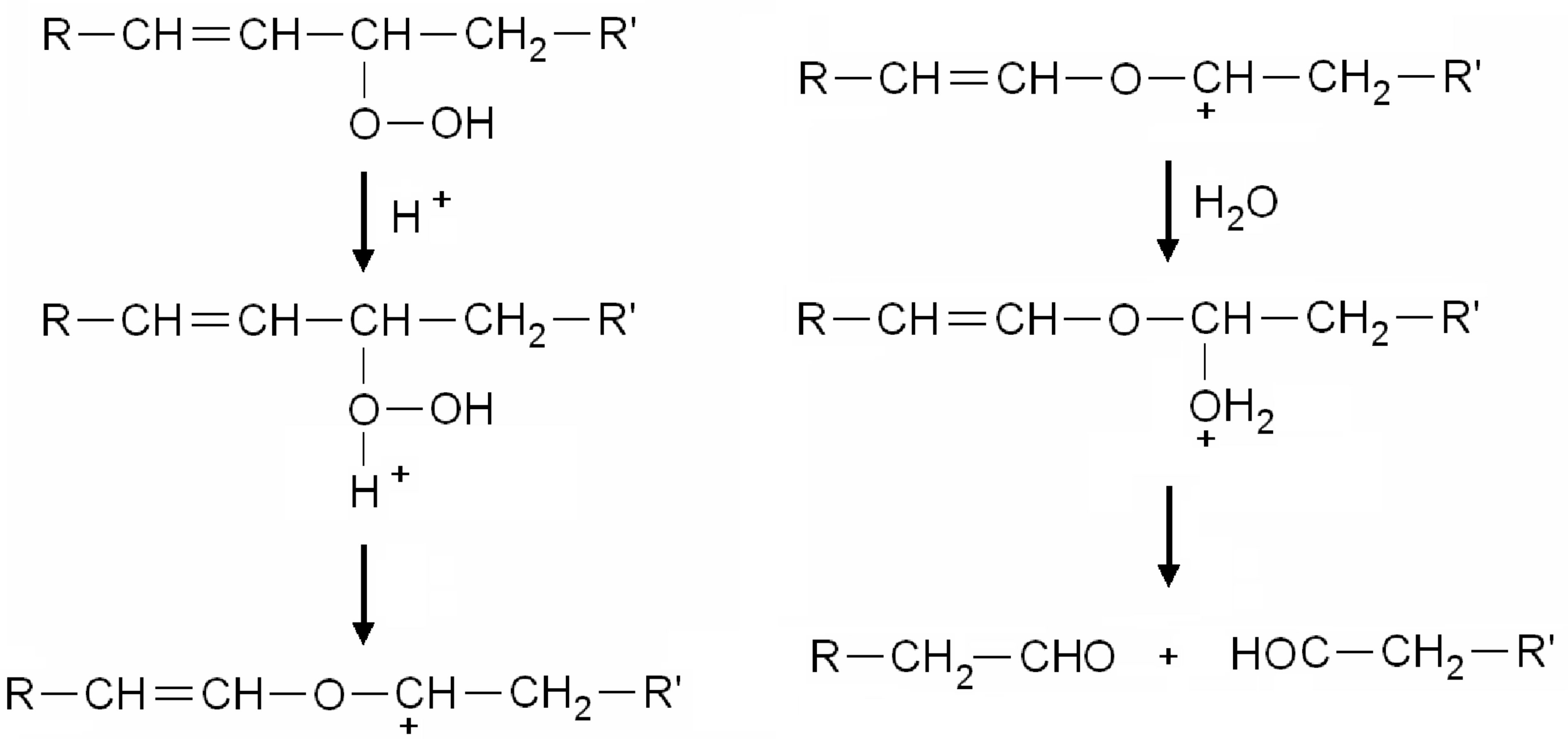
3.10 DEGRADATIONS

Homolytic cleavage of hydroperoxides



3.10 DEGRADATIONS

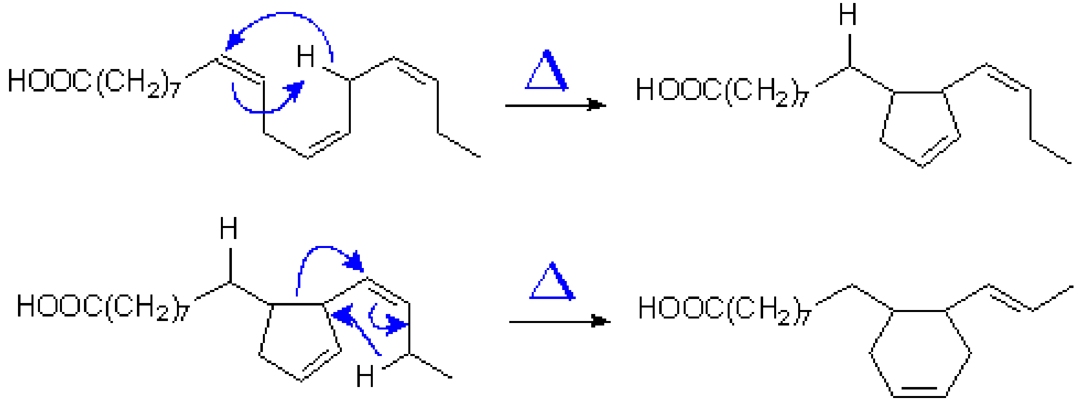
Heterolytic cleavage of hydroperoxides



3.10 DEGRADATIONS

Thermal reactions : formation of cyclic fatty acids in frying oil

C18:3 (n-3) α-linolenic acid



Cyclic fatty acid monomers (CFAM) are potentially toxic

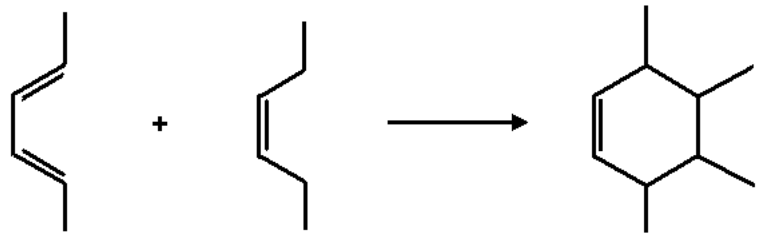
Thermally induced prototropic migrations in α-linolenate

Destaillats, F. and Angers, P. *Eur. J. Lipid Sci. Technol.*, **107**, 767-772 (2005)

3.10 DEGRADATIONS

Thermal reactions : formation of cyclic fatty acids in frying oil

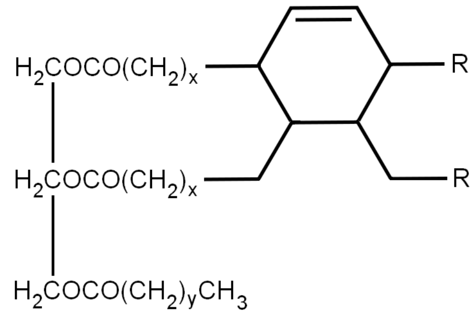
Diels-Alder cycloaddition



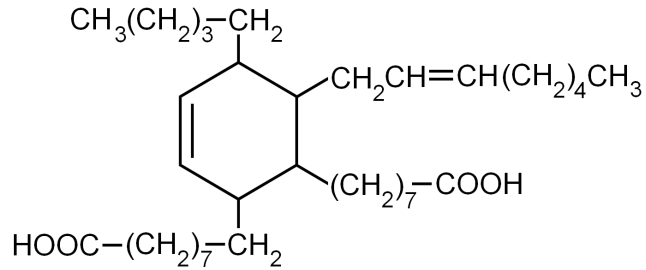
trans-diene FA
(Conjugated)

Monoene FA

Cyclic dimer of FA's
(cyclohexene tetrasubstituted structure)



Internal addition
(oleic-linoleic dimer)



Linoleic acid dimer

3.10 DEGRADATIONS
Enzymatic degradations

Formation of methyl-ketones due to lipases generation in blue cheese. (Penicillium roqueforti *Penicillium camemberti)*

Even-number FA gives odd-numbered methyl-ketones