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Oils and Fats

Composition

Physico-chemical characteristics

Fat oxidation

Processing and refining

Extra-virgin olive oil

Unit 1 Lipids: chemical nature, nomenclature and classification. Compositional characteristics of edible fats: saponifiable and unsaponifiable fraction, constituents, biosynthetic characteristics, chemical-physical properties. Essential fatty acids: concept of essentiality.

Unit 2 Reactions involving the lipid fraction: oxidative, hydrolytic and ketone rancidity. Autoxidation and photoxidation. Changes induced by exposure to high temperatures (deep-frying) and due to ageing.

Unit 3 Outline of technology: food fat extraction techniques (squeezing and extraction), rectification, hydrogenation, trans-esterification and fractionation processes, characteristics of the derived products.
Learn more about palm oil.

Unit 4 Olive oil: botanical notes, reference legislation, production technology, compositional characteristics, quality and authenticity parameters. Analysis of olive oil: chemical and sensory analyses

Contents

Fats general overview

- ✓ FAO forecasts show world population growing sharply: 9.1 billion people will be reached in 2050 with a consequent increase in food production of 70% (World Agriculture Towards 2030/2050 FAO)

- ✓ The per capita consumption trend of vegetable oils is increasing FAO estimates an average annual growth rate of 2.2% for the global consumption of vegetable oils in the decade 2010-2020

- ✓ According to the report The Malaysian Palm Oil Sector – Overview (June 2015) the demand for vegetable oils is expected to double in the period 2010-2050 from 120 to 240 million tons per year (food consumption and biofuels)

Fats general overview

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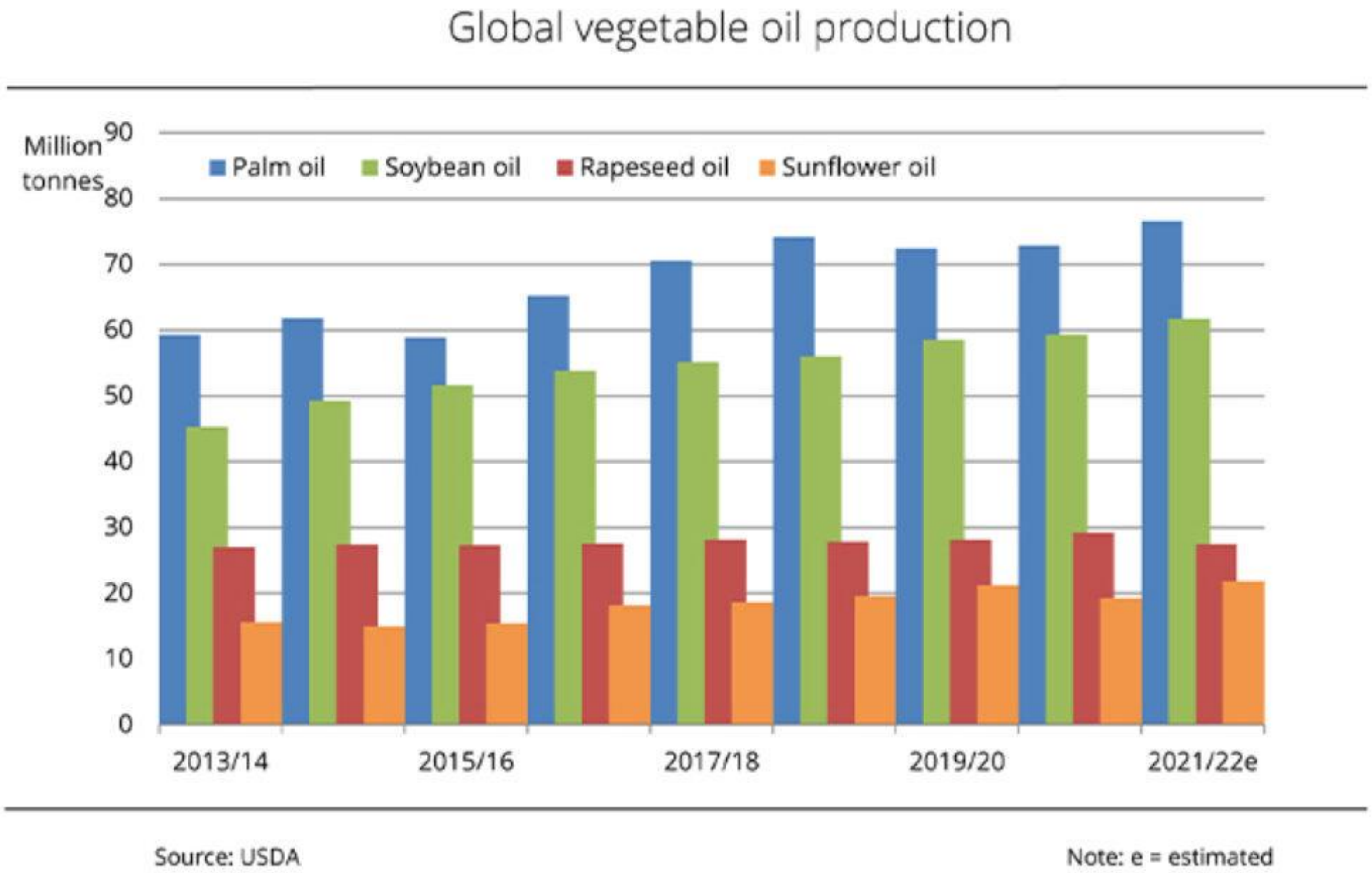

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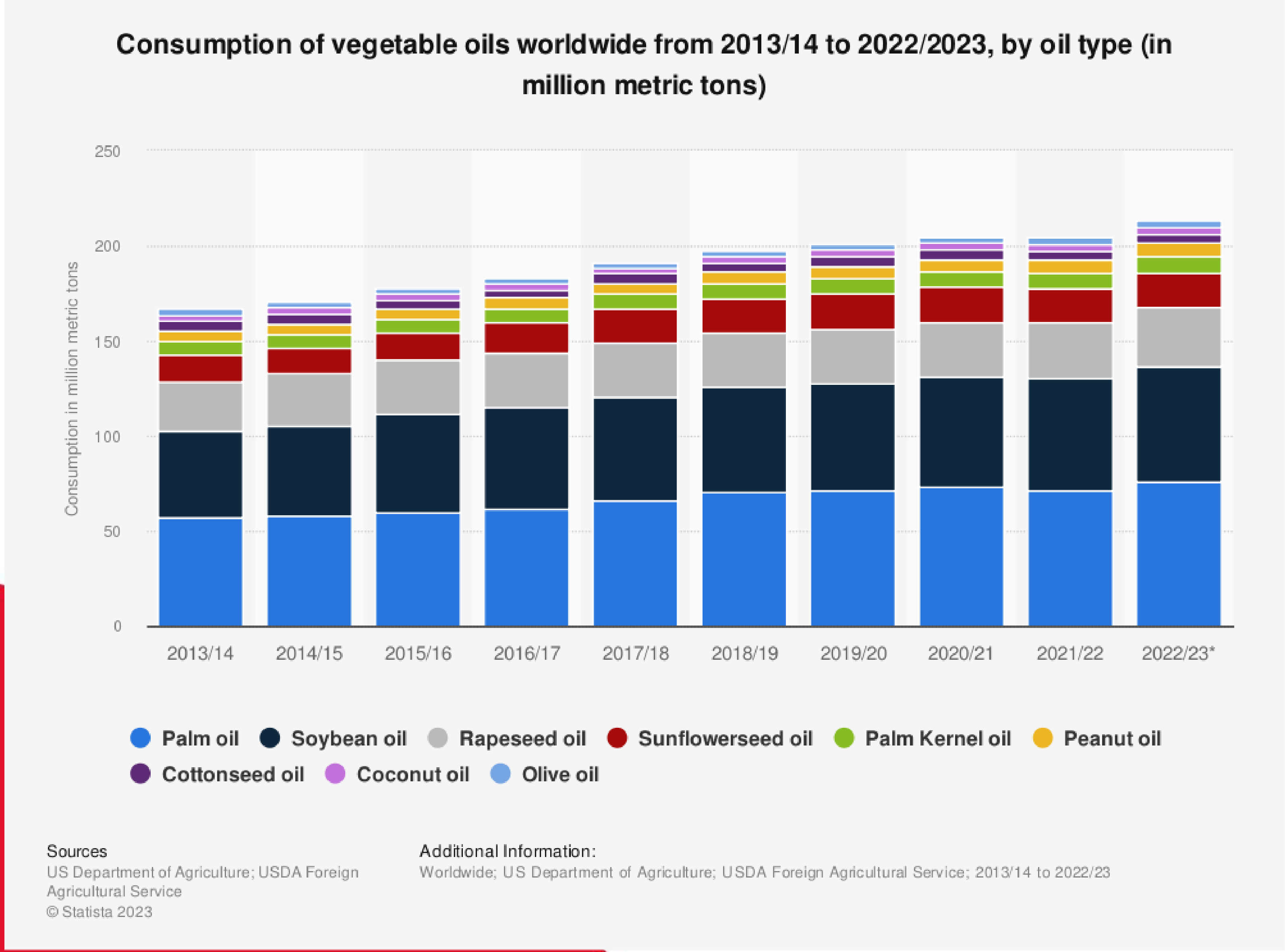


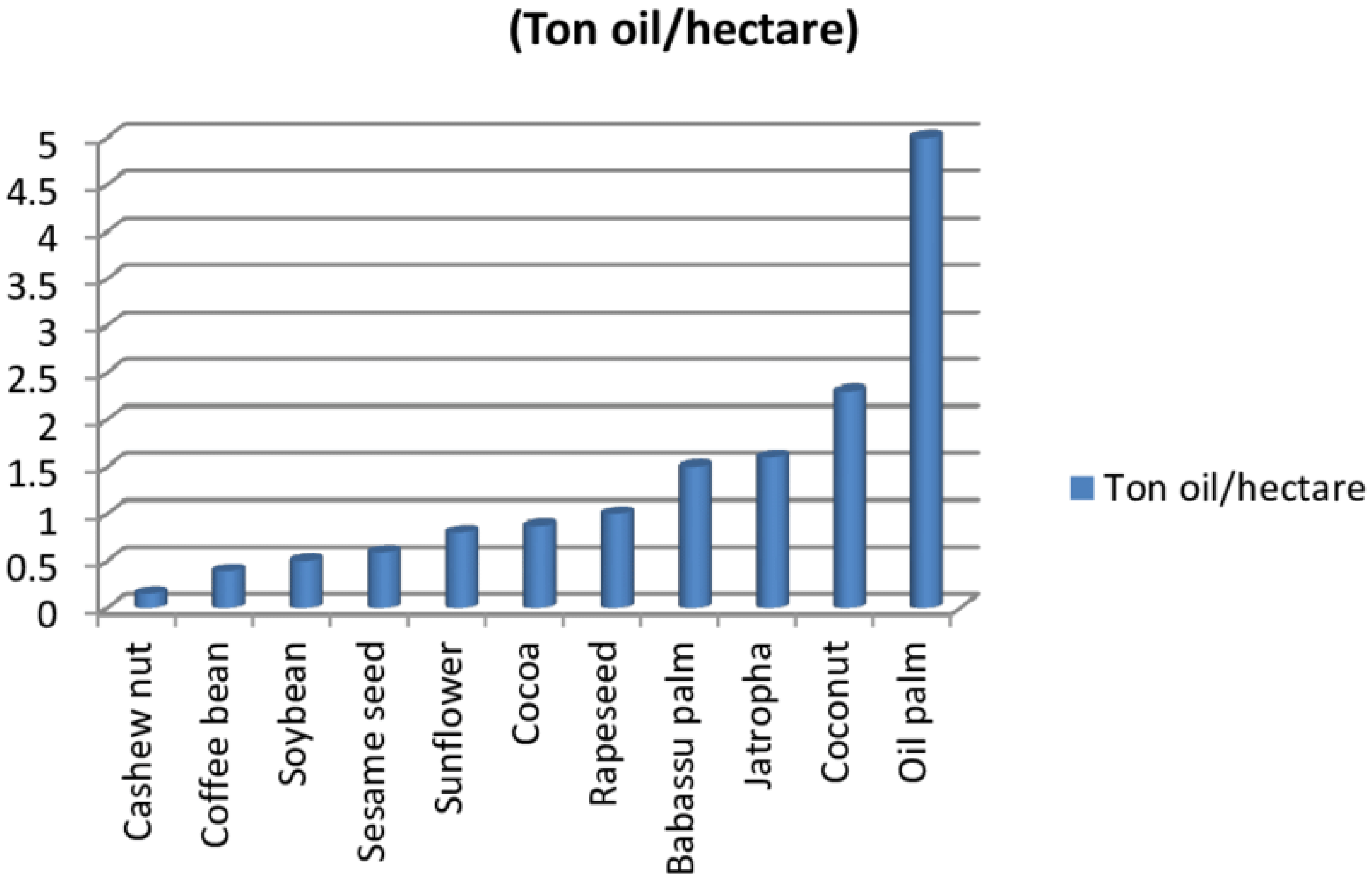
Consumption of vegetable oils worldwide from 2013/14 to 2022/2023, by oil type (in million metric tons)

Sources
US Department of Agriculture; USDA Foreign Agricultural Service
© Statista 2023

Additional Information:
Worldwide; US Department of Agriculture; USDA Foreign Agricultural Service; 2013/14 to 2022/23

Fats general overview

RESA IN OLIO



Characterization of genes related to oil palm (Elaeis guineensis Jacq.) drought stress responses
DO - 10.13140/RG.2.2.25686.75845

PALMA	3,47 t/ha
COLZA	0,65 t/ha
GIRASOLE	0,58 t/ha
SOIA	0,37 t/ha
OLIVA	0,32 t/ha

Fats composition and components

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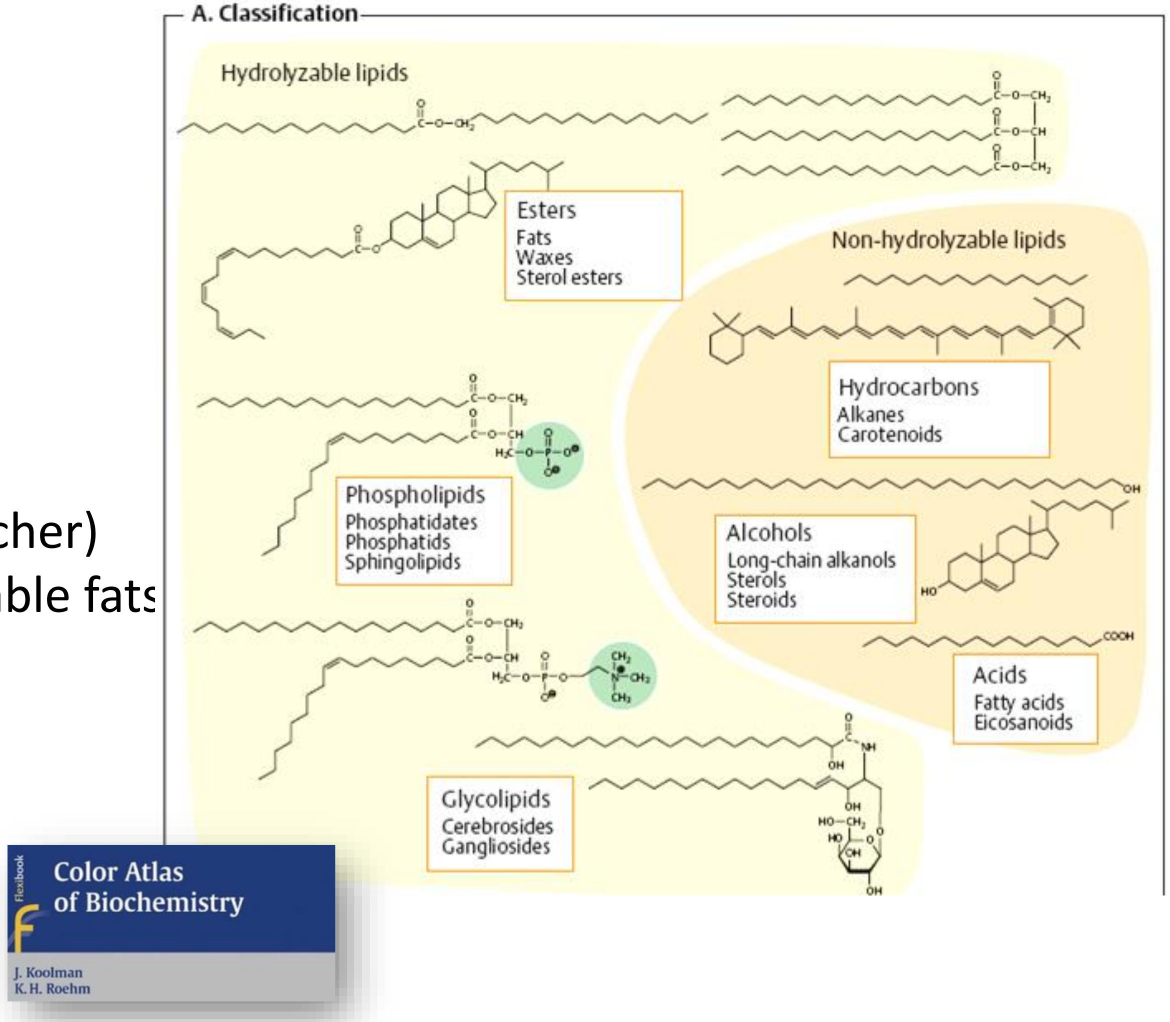
A) Fraction of glyceride nature (90 - 99%) - SAPONIFIABLE

- Mixed triglycerides (90 - 99%)
- Phospholipids (lecithins - traces)
- Diglycerides (traces / 4%)
- Monoglycerides (traces / 1%)
- Fatty acids (0.1 / 4% constitute the free acidity)

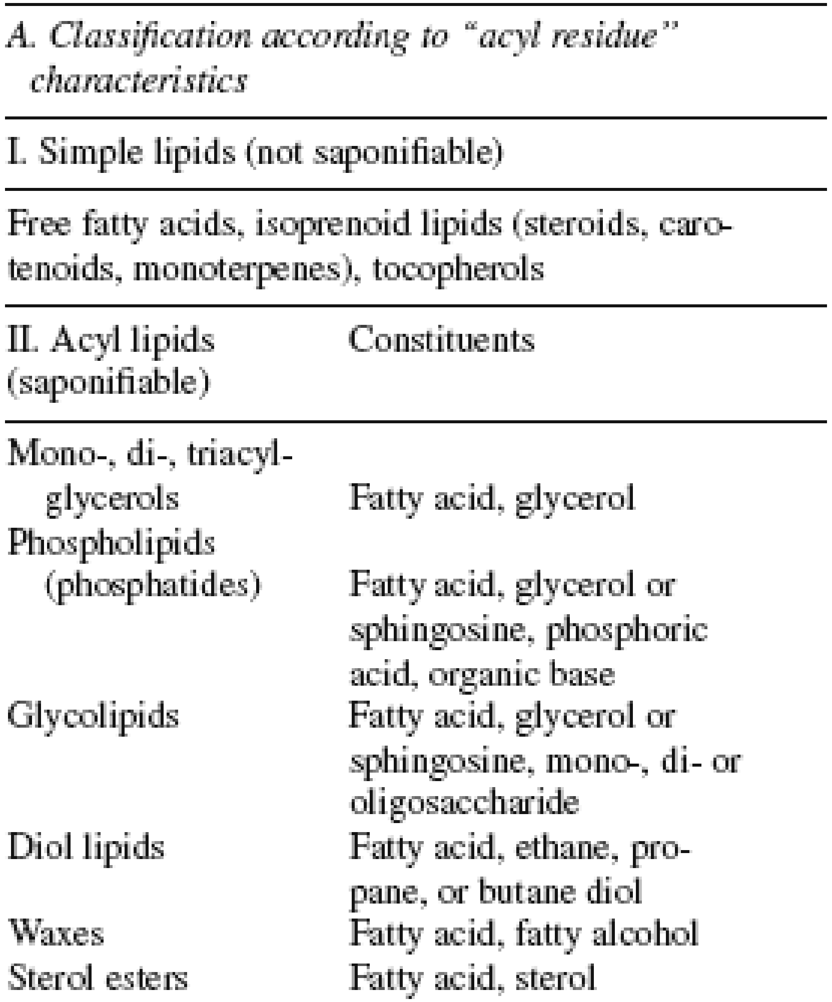
Waxes (esters of FA with long chain linear alcohols)

B) Non-glyceride fraction (0.5/4%) - UNSAPONIFIABLE
(very variable in function of origin, vegetable oils are richer)

- Sterols (cholesterol-animal fats, phytosterols-vegetable fats
- Vitamin A and E
- Carotenes, carotenoids and chlorophylls
- Phenolic substances
- Flavor components

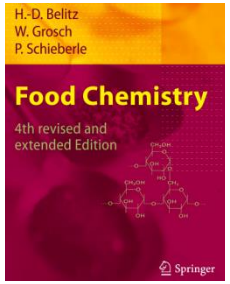


Fats composition and components



A. Classification according to "acyl residue" characteristics

I. Simple lipids (not saponifiable)	
Free fatty acids, isoprenoid lipids (steroids, carotenoids, monoterpenes), tocopherols	
II. Acyl lipids (saponifiable)	**Constituents**
Mono-, di-, triacylglycerols	Fatty acid, glycerol
Phospholipids (phosphatides)	Fatty acid, glycerol or sphingosine, phosphoric acid, organic base
Glycolipids	Fatty acid, glycerol or sphingosine, mono-, di- or oligosaccharide
Diol lipids	Fatty acid, ethane, propane, or butane diol
Waxes	Fatty acid, fatty alcohol
Sterol esters	Fatty acid, sterol



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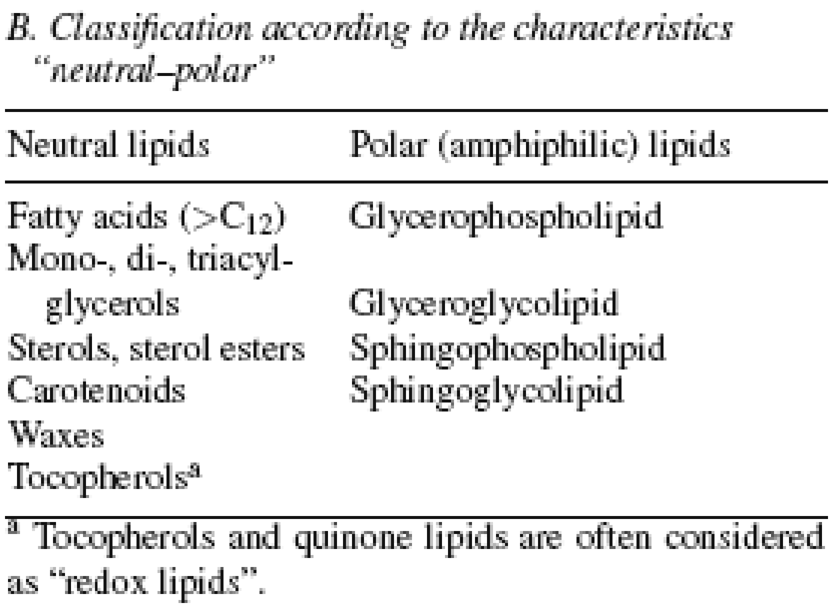

B. Classification according to the characteristics "neutral–polar"

Neutral lipids	Polar (amphiphilic) lipids
Fatty acids (>C_{12})	Glycerophospholipid
Mono-, di-, triacylglycerols	Glyceroglycolipid
Sterols, sterol esters	Sphingophospholipid
Carotenoids	Sphingoglycolipid
Waxes	
Tocopherols[a]	

[a] Tocopherols and quinone lipids are often considered as "redox lipids".

Fatty acids characteristics

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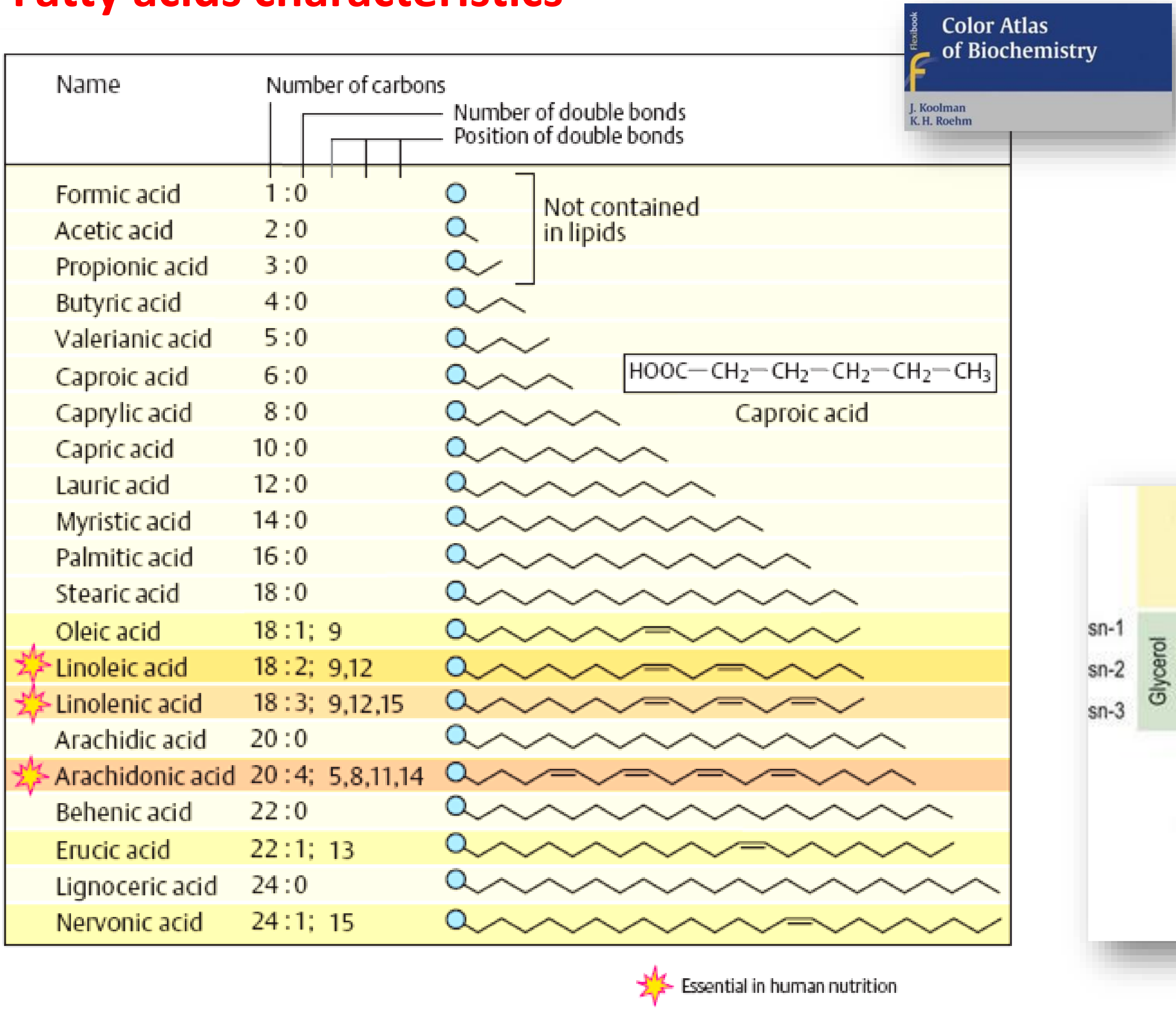
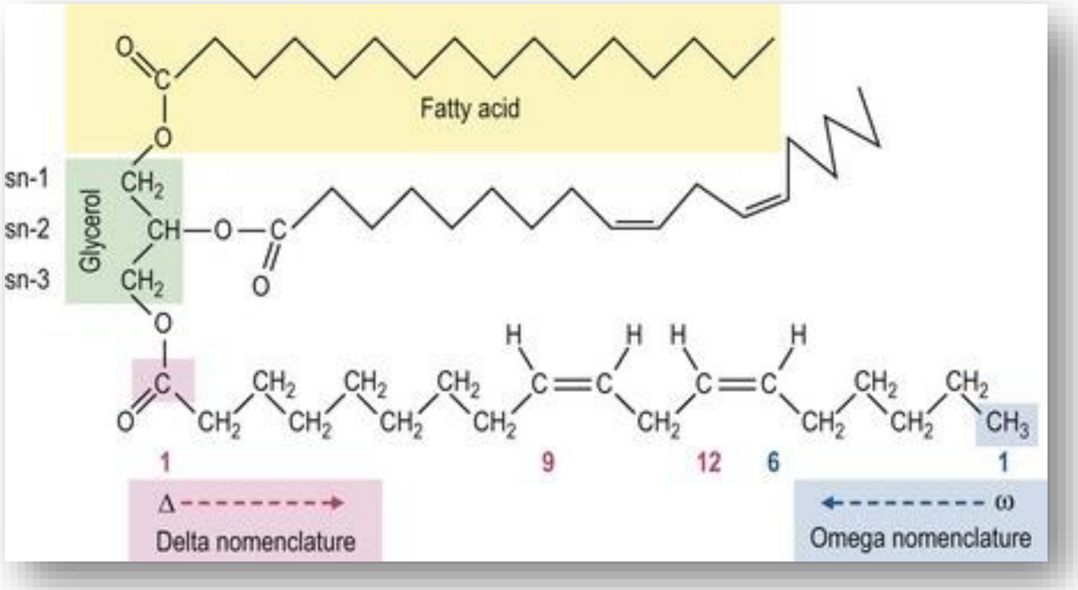


Color Atlas of Biochemistry
J. Koolman
K. H. Roehm

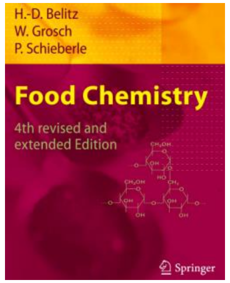
Name	Number of carbons	Number of double bonds	Position of double bonds	
Formic acid	1	0		Not contained in lipids
Acetic acid	2	0		Not contained in lipids
Propionic acid	3	0		Not contained in lipids
Butyric acid	4	0		
Valerianic acid	5	0		
Caproic acid	6	0		$HOOC-CH_2-CH_2-CH_2-CH_2-CH_3$ Caproic acid
Caprylic acid	8	0		
Capric acid	10	0		
Lauric acid	12	0		
Myristic acid	14	0		
Palmitic acid	16	0		
Stearic acid	18	0		
Oleic acid	18	1	9	
✷ Linoleic acid	18	2	9,12	
✷ Linolenic acid	18	3	9,12,15	
Arachidic acid	20	0		
✷ Arachidonic acid	20	4	5,8,11,14	
Behenic acid	22	0		
Erucic acid	22	1	13	
Lignoceric acid	24	0		
Nervonic acid	24	1	15	

✷ Essential in human nutrition

Nomenclature - RECAP!!!



Fatty acids characteristics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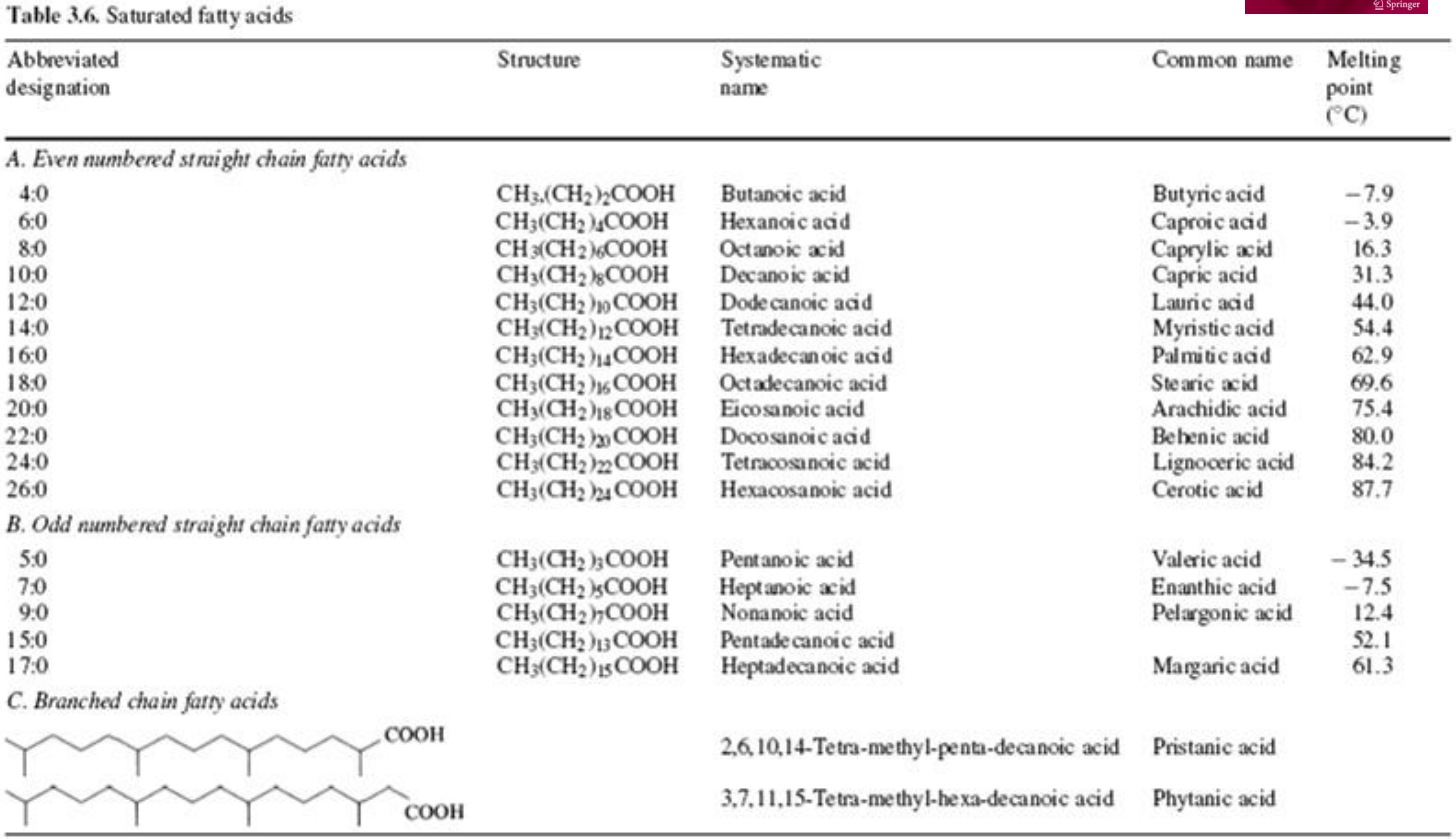
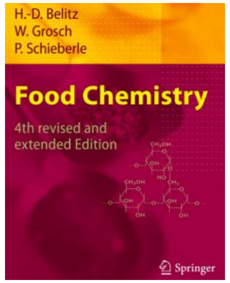


Table 3.6. Saturated fatty acids

Abbreviated designation	Structure	Systematic name	Common name	Melting point (°C)
A. Even numbered straight chain fatty acids				
4:0	$CH_3(CH_2)_2COOH$	Butanoic acid	Butyric acid	−7.9
6:0	$CH_3(CH_2)_4COOH$	Hexanoic acid	Caproic acid	−3.9
8:0	$CH_3(CH_2)_6COOH$	Octanoic acid	Caprylic acid	16.3
10:0	$CH_3(CH_2)_8COOH$	Decanoic acid	Capric acid	31.3
12:0	$CH_3(CH_2)_{10}COOH$	Dodecanoic acid	Lauric acid	44.0
14:0	$CH_3(CH_2)_{12}COOH$	Tetradecanoic acid	Myristic acid	54.4
16:0	$CH_3(CH_2)_{14}COOH$	Hexadecanoic acid	Palmitic acid	62.9
18:0	$CH_3(CH_2)_{16}COOH$	Octadecanoic acid	Stearic acid	69.6
20:0	$CH_3(CH_2)_{18}COOH$	Eicosanoic acid	Arachidic acid	75.4
22:0	$CH_3(CH_2)_{20}COOH$	Docosanoic acid	Behenic acid	80.0
24:0	$CH_3(CH_2)_{22}COOH$	Tetracosanoic acid	Lignoceric acid	84.2
26:0	$CH_3(CH_2)_{24}COOH$	Hexacosanoic acid	Cerotic acid	87.7
B. Odd numbered straight chain fatty acids				
5:0	$CH_3(CH_2)_3COOH$	Pentanoic acid	Valeric acid	−34.5
7:0	$CH_3(CH_2)_5COOH$	Heptanoic acid	Enanthic acid	−7.5
9:0	$CH_3(CH_2)_7COOH$	Nonanoic acid	Pelargonic acid	12.4
15:0	$CH_3(CH_2)_{13}COOH$	Pentadecanoic acid		52.1
17:0	$CH_3(CH_2)_{15}COOH$	Heptadecanoic acid	Margaric acid	61.3
C. Branched chain fatty acids				
COOH		2,6,10,14-Tetra-methyl-penta-decanoic acid	Pristanic acid	
COOH		3,7,11,15-Tetra-methyl-hexa-decanoic acid	Phytanic acid	

Fatty acids characteristics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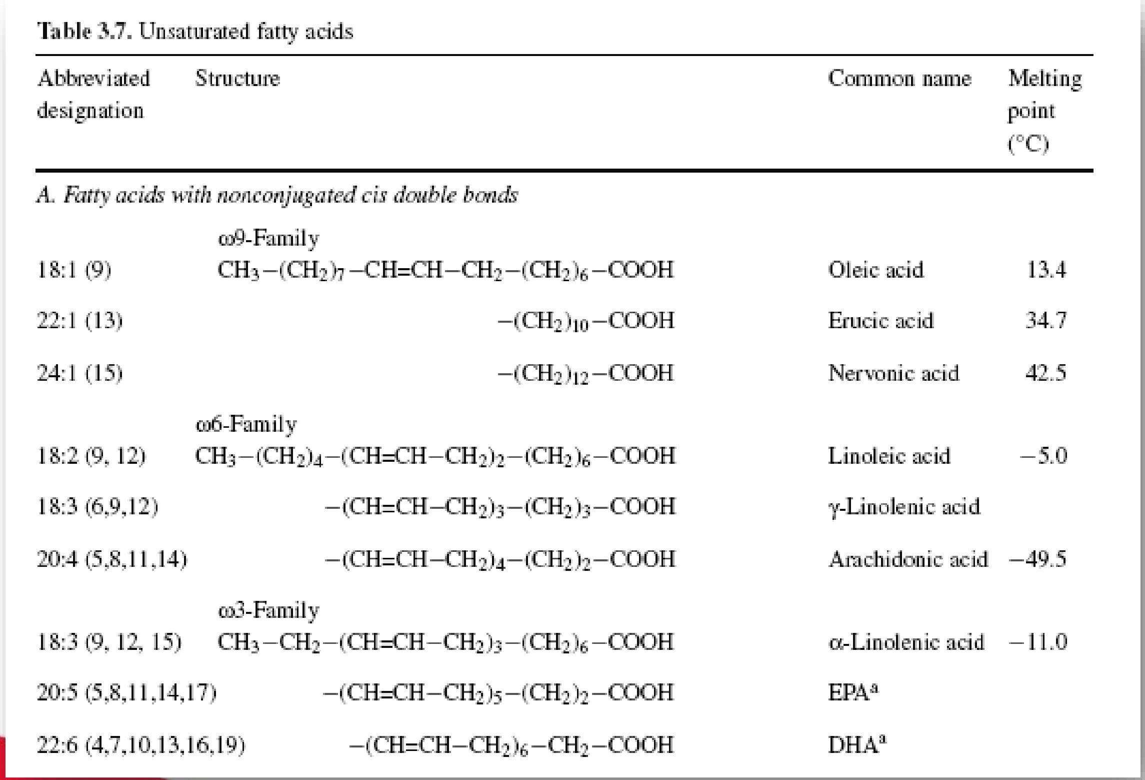
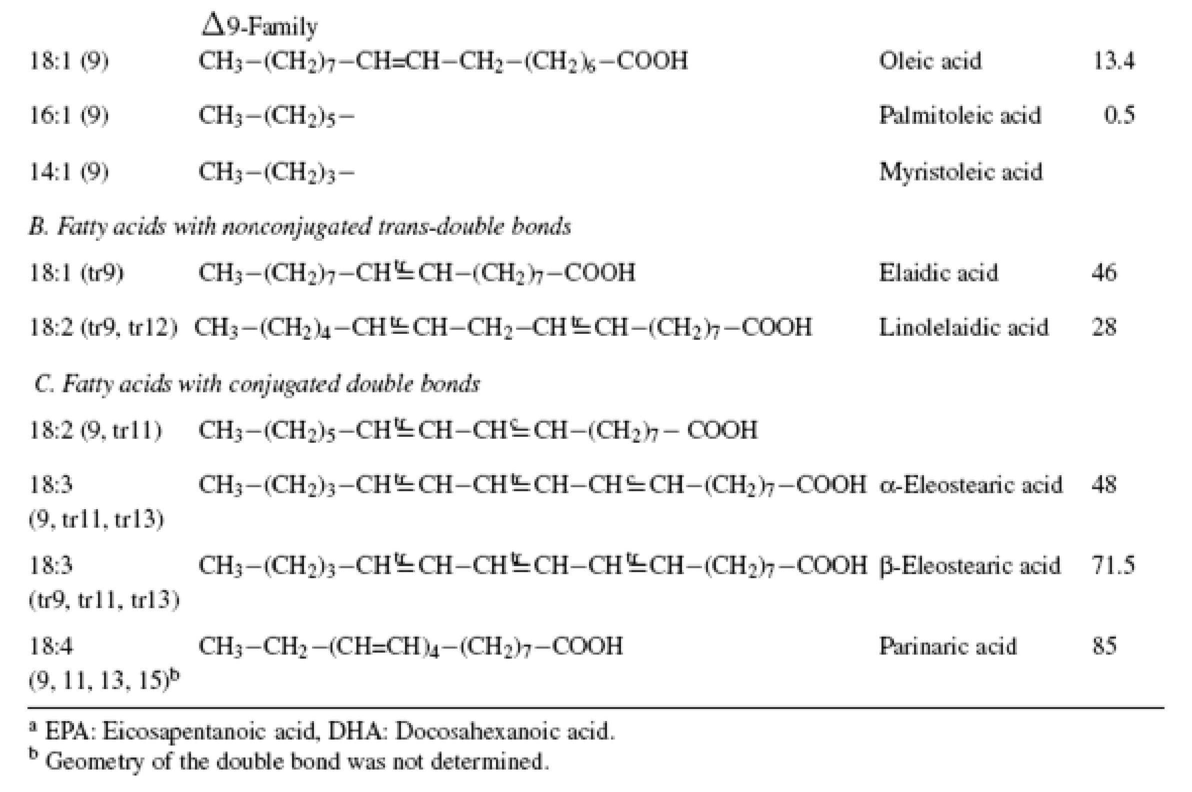


Table 3.7. Unsaturated fatty acids

Abbreviated designation	Structure	Common name	Melting point (°C)
A. Fatty acids with nonconjugated cis double bonds			
	ω9-Family		
18:1 (9)	$CH_3-(CH_2)_7-CH=CH-CH_2-(CH_2)_6-COOH$	Oleic acid	13.4
22:1 (13)	$-(CH_2)_{10}-COOH$	Erucic acid	34.7
24:1 (15)	$-(CH_2)_{12}-COOH$	Nervonic acid	42.5
	ω6-Family		
18:2 (9, 12)	$CH_3-(CH_2)_4-(CH=CH-CH_2)_2-(CH_2)_6-COOH$	Linoleic acid	−5.0
18:3 (6,9,12)	$-(CH=CH-CH_2)_3-(CH_2)_3-COOH$	γ-Linolenic acid	
20:4 (5,8,11,14)	$-(CH=CH-CH_2)_4-(CH_2)_2-COOH$	Arachidonic acid	−49.5
	ω3-Family		
18:3 (9, 12, 15)	$CH_3-CH_2-(CH=CH-CH_2)_3-(CH_2)_6-COOH$	α-Linolenic acid	−11.0
20:5 (5,8,11,14,17)	$-(CH=CH-CH_2)_5-(CH_2)_2-COOH$	EPA[a]	
22:6 (4,7,10,13,16,19)	$-(CH=CH-CH_2)_6-CH_2-COOH$	DHA[a]	


	Δ9-Family		
18:1 (9)	$CH_3-(CH_2)_7-CH=CH-CH_2-(CH_2)_6-COOH$	Oleic acid	13.4
16:1 (9)	$CH_3-(CH_2)_5-$	Palmitoleic acid	0.5
14:1 (9)	$CH_3-(CH_2)_3-$	Myristoleic acid	
B. Fatty acids with nonconjugated trans-double bonds			
18:1 (tr9)	$CH_3-(CH_2)_7-CH\overset{tr}{=}CH-(CH_2)_7-COOH$	Elaidic acid	46
18:2 (tr9, tr12)	$CH_3-(CH_2)_4-CH\overset{tr}{=}CH-CH_2-CH\overset{tr}{=}CH-(CH_2)_7-COOH$	Linolelaidic acid	28
C. Fatty acids with conjugated double bonds			
18:2 (9, tr11)	$CH_3-(CH_2)_5-CH\overset{tr}{=}CH-CH\overset{c}{=}CH-(CH_2)_7-COOH$		
18:3 (9, tr11, tr13)	$CH_3-(CH_2)_3-CH\overset{tr}{=}CH-CH\overset{tr}{=}CH-CH\overset{c}{=}CH-(CH_2)_7-COOH$	α-Eleostearic acid	48
18:3 (tr9, tr11, tr13)	$CH_3-(CH_2)_3-CH\overset{tr}{=}CH-CH\overset{tr}{=}CH-CH\overset{tr}{=}CH-(CH_2)_7-COOH$	β-Eleostearic acid	71.5
18:4 (9, 11, 13, 15)[b]	$CH_3-CH_2-(CH=CH)_4-(CH_2)_7-COOH$	Parinaric acid	85

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[a] EPA: Eicosapentanoic acid, DHA: Docosahexanoic acid.
[b] Geometry of the double bond was not determined.

Fatty acids characteristics

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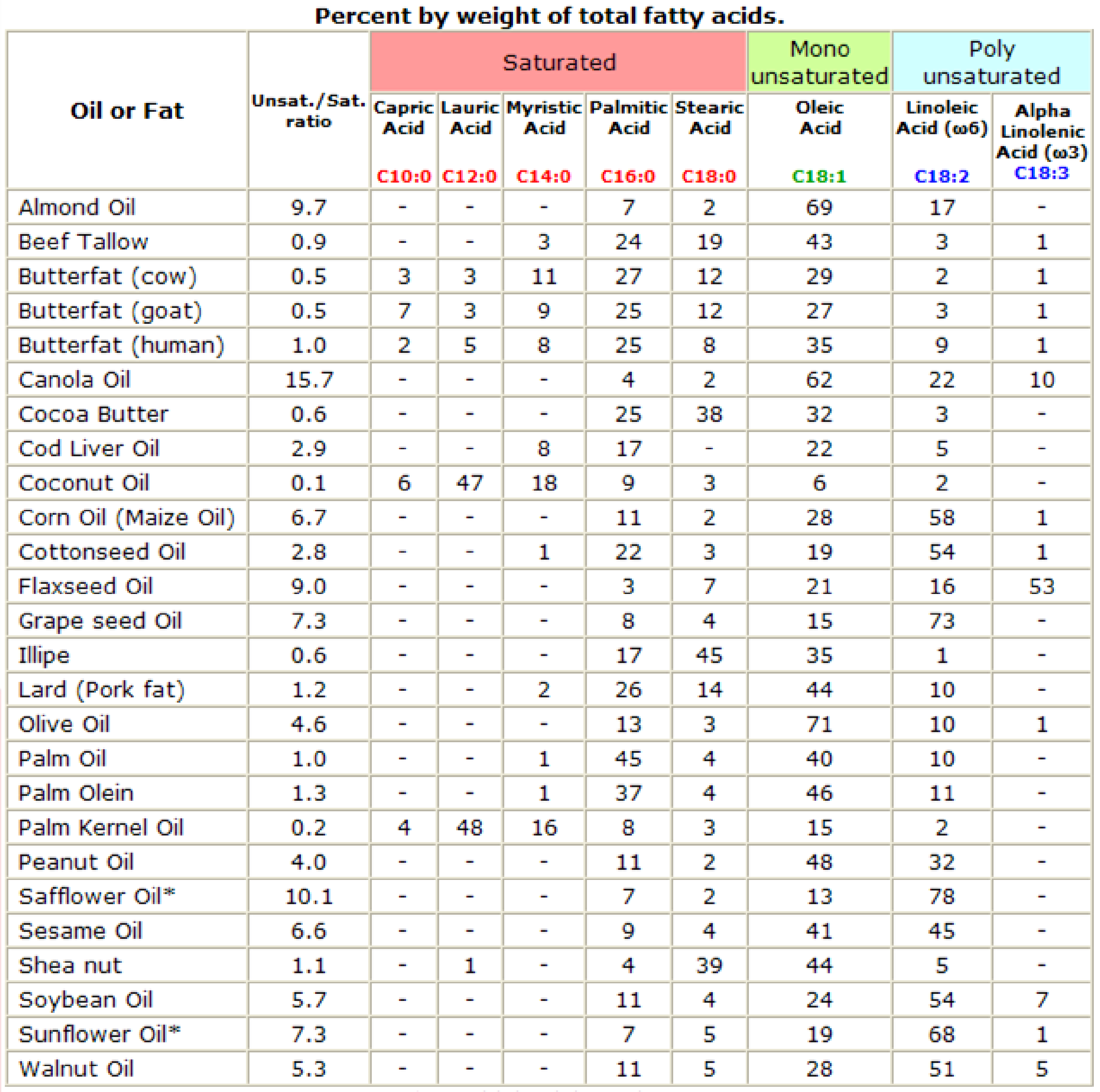
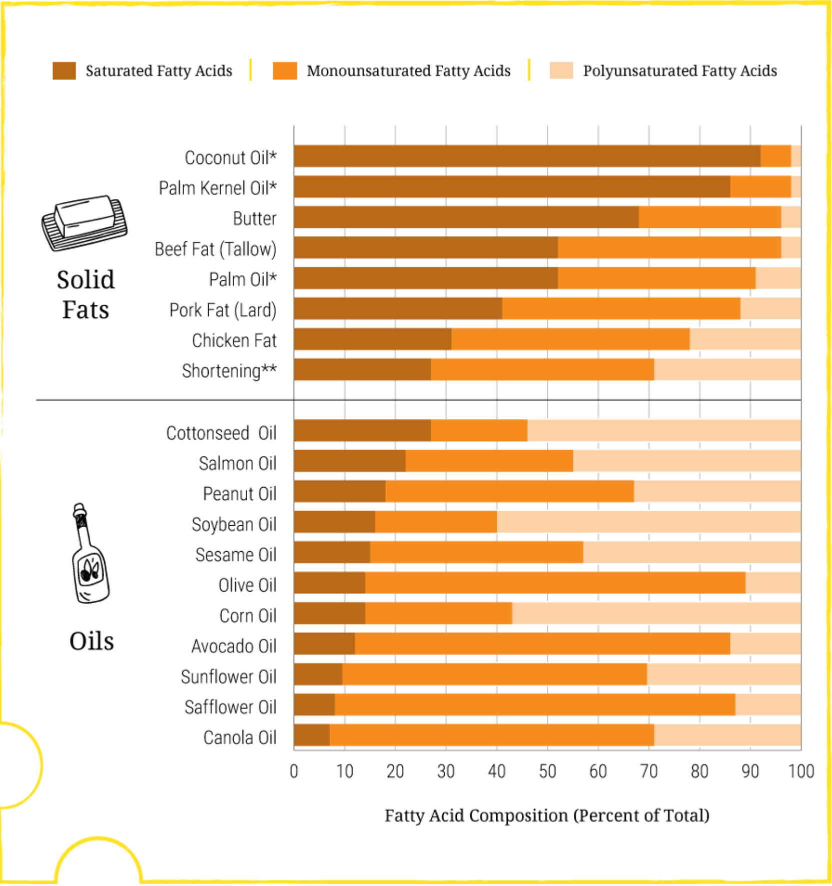
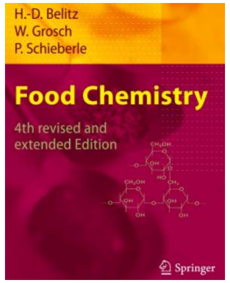


Percent by weight of total fatty acids.

Oil or Fat	Unsat./Sat. ratio	Saturated					Mono unsaturated	Poly unsaturated	
		Capric Acid C10:0	Lauric Acid C12:0	Myristic Acid C14:0	Palmitic Acid C16:0	Stearic Acid C18:0	Oleic Acid C18:1	Linoleic Acid (ω6) C18:2	Alpha Linolenic Acid (ω3) C18:3
Almond Oil	9.7	-	-	-	7	2	69	17	-
Beef Tallow	0.9	-	-	3	24	19	43	3	1
Butterfat (cow)	0.5	3	3	11	27	12	29	2	1
Butterfat (goat)	0.5	7	3	9	25	12	27	3	1
Butterfat (human)	1.0	2	5	8	25	8	35	9	1
Canola Oil	15.7	-	-	-	4	2	62	22	10
Cocoa Butter	0.6	-	-	-	25	38	32	3	-
Cod Liver Oil	2.9	-	-	8	17	-	22	5	-
Coconut Oil	0.1	6	47	18	9	3	6	2	-
Corn Oil (Maize Oil)	6.7	-	-	-	11	2	28	58	1
Cottonseed Oil	2.8	-	-	1	22	3	19	54	1
Flaxseed Oil	9.0	-	-	-	3	7	21	16	53
Grape seed Oil	7.3	-	-	-	8	4	15	73	-
Illipe	0.6	-	-	-	17	45	35	1	-
Lard (Pork fat)	1.2	-	-	2	26	14	44	10	-
Olive Oil	4.6	-	-	-	13	3	71	10	1
Palm Oil	1.0	-	-	1	45	4	40	10	-
Palm Olein	1.3	-	-	1	37	4	46	11	-
Palm Kernel Oil	0.2	4	48	16	8	3	15	2	-
Peanut Oil	4.0	-	-	-	11	2	48	32	-
Safflower Oil*	10.1	-	-	-	7	2	13	78	-
Sesame Oil	6.6	-	-	-	9	4	41	45	-
Shea nut	1.1	-	1	-	4	39	44	5	-
Soybean Oil	5.7	-	-	-	11	4	24	54	7
Sunflower Oil*	7.3	-	-	-	7	5	19	68	1
Walnut Oil	5.3	-	-	-	11	5	28	51	5



Fatty acids characteristics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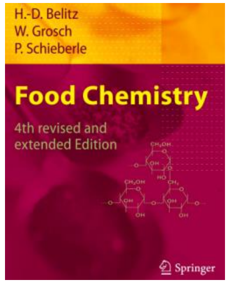
4.23. Fatty acid indicators suitable for determination of fat and oil origin

Fatty acid	Content (%)[a]	Indicator of
4:0	3.7	Milk fat
12:0	45	Coconut-, palm kernel-, and babassu fat
18:1 (9)	65–85[b]	Teaseed-, olive- and hazelnut oil
18:3 (9, 12, 15)	9	Soya-, rapeseed (also erucic acid free) oil
18:2 (9, 12)	50–70	Sunflower-, corn germ-, cottonseed-, wheat germ-, and soya oil
22:0	3	Peanut oil
20:4 (5, 8, 11, 14)	0.1–0.6	Animal fat
18:1 (9, 12-OH)	80	Castor bean oil
Trans-fatty acids		Partially or fully hydrogenated oil/fat[c]
Methyl-branched fatty acids	0.2–1.6	Animal fat[d]

[a] When value range is omitted fatty acid percentage composition is given as an average value.
[b] A high percentage of this acid is a characteristic indicator.
[c] Here precautions are needed: animal fat, e. g. from beef, might contain up to 10% trans fatty acids.
[d] It is relatively high in marine oils (approx. 1%).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Fatty acids characteristics
CLA: conjugated linoleic acids

The so-called CLA (Conjugated Linoleic Acids) are a series of fatty acids at 18 Carbon units in which the double bonds are found in a conjugated position and in a variable configuration (*cis* and/or *trans*).

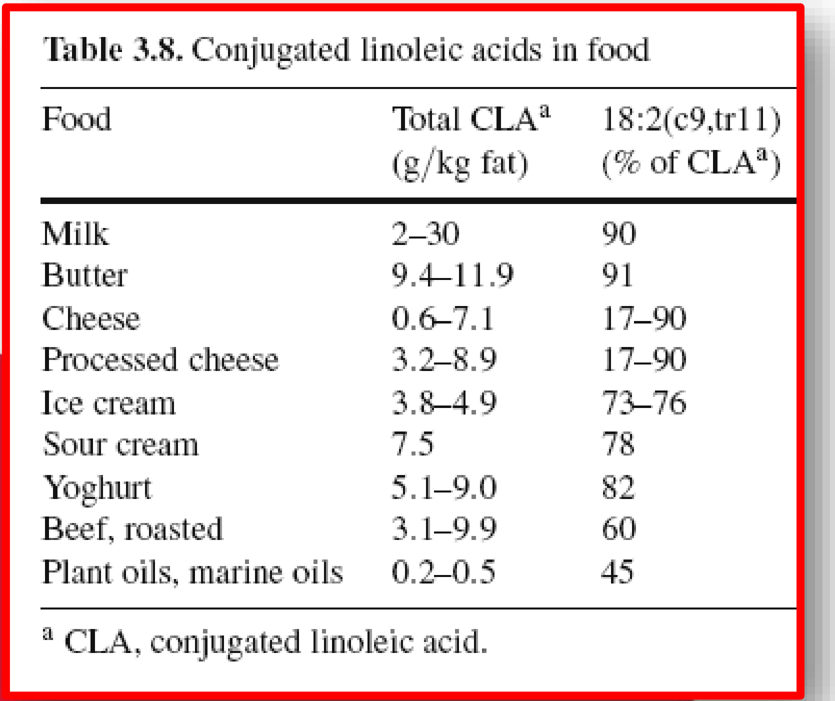


Table 3.8. Conjugated linoleic acids in food

Food	Total CLA[a] (g/kg fat)	18:2(c9,tr11) (% of CLA[a])
Milk	2–30	90
Butter	9.4–11.9	91
Cheese	0.6–7.1	17–90
Processed cheese	3.2–8.9	17–90
Ice cream	3.8–4.9	73–76
Sour cream	7.5	78
Yoghurt	5.1–9.0	82
Beef, roasted	3.1–9.9	60
Plant oils, marine oils	0.2–0.5	45

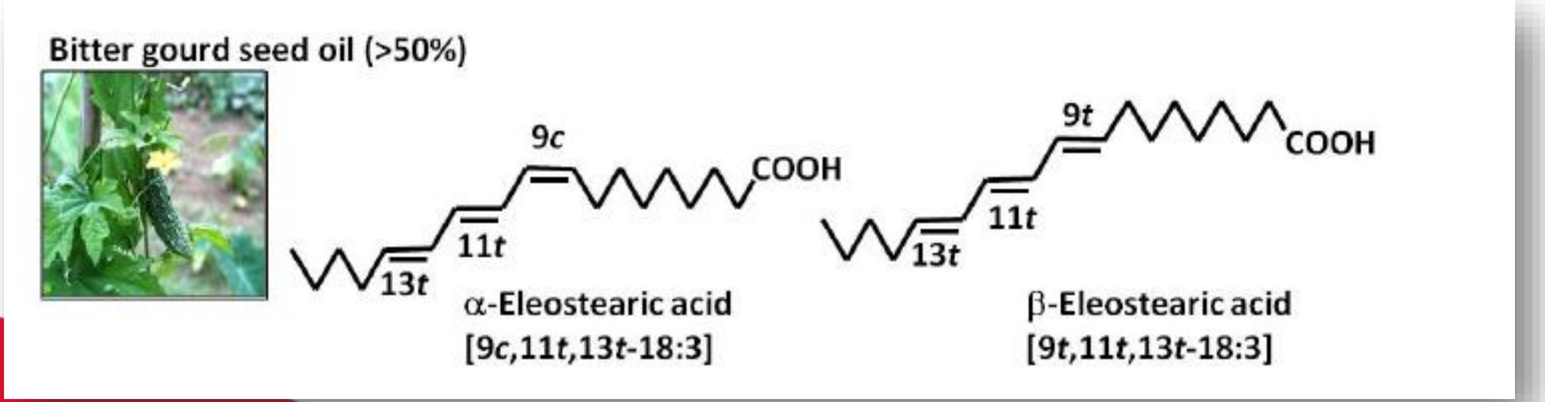
[a] CLA, conjugated linoleic acid.

In vitro anti-carcinogenic properties have been associated with them, therefore their presence in foods is of considerable interest. They are formed by bio-hydrogenation (reduction reactions) by rumen microorganisms and therefore their presence in milk and food meat is quite frequent.

They are particularly concentrated in cow milk when herbal silage or fresh herb dominates feeding.

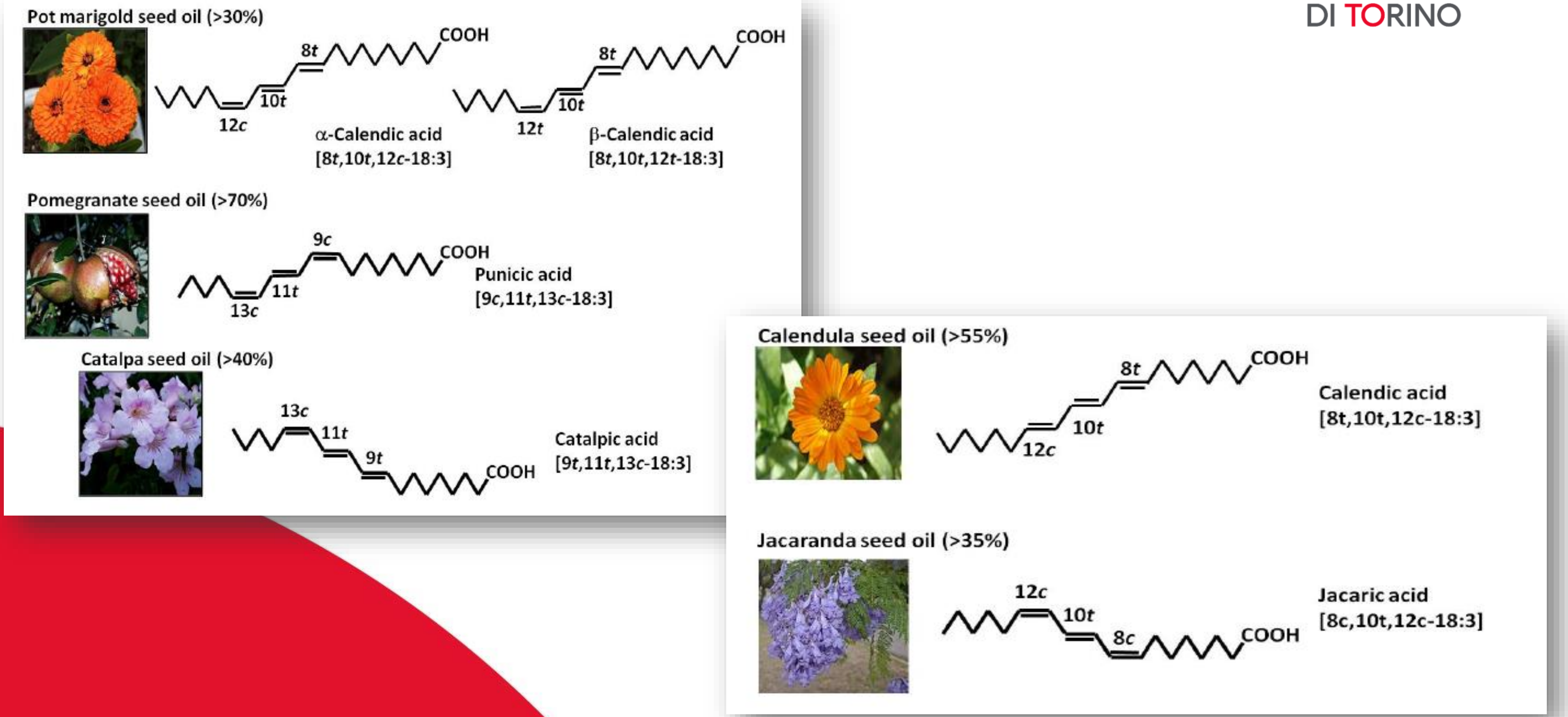
Fatty acids characteristics
CLN: conjugated linolenic acids

The so-called CLNs (Conjugated Linolenic Acids) are a series of fatty acids with 18 Carbon units in which the double bonds are found in a conjugated position and in a variable configuration (*cis* and/or *trans*).

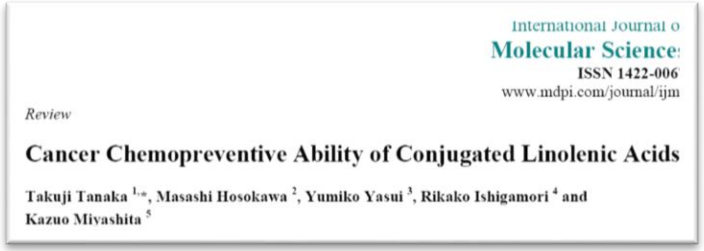


They are very abundant in vegetable sources of dietary fat and scientific studies have demonstrated a marked in vitro chemopreventive (anti-carcinogenic) activity. They bind to PPAR nuclear receptors (PPARα, PPARδ, and PPARγ) regulating gene transcription.

Fatty acids characteristics
CLN: conjugated linolenic acids



Fatty acids characteristics
CLN: conjugated linolenic acids



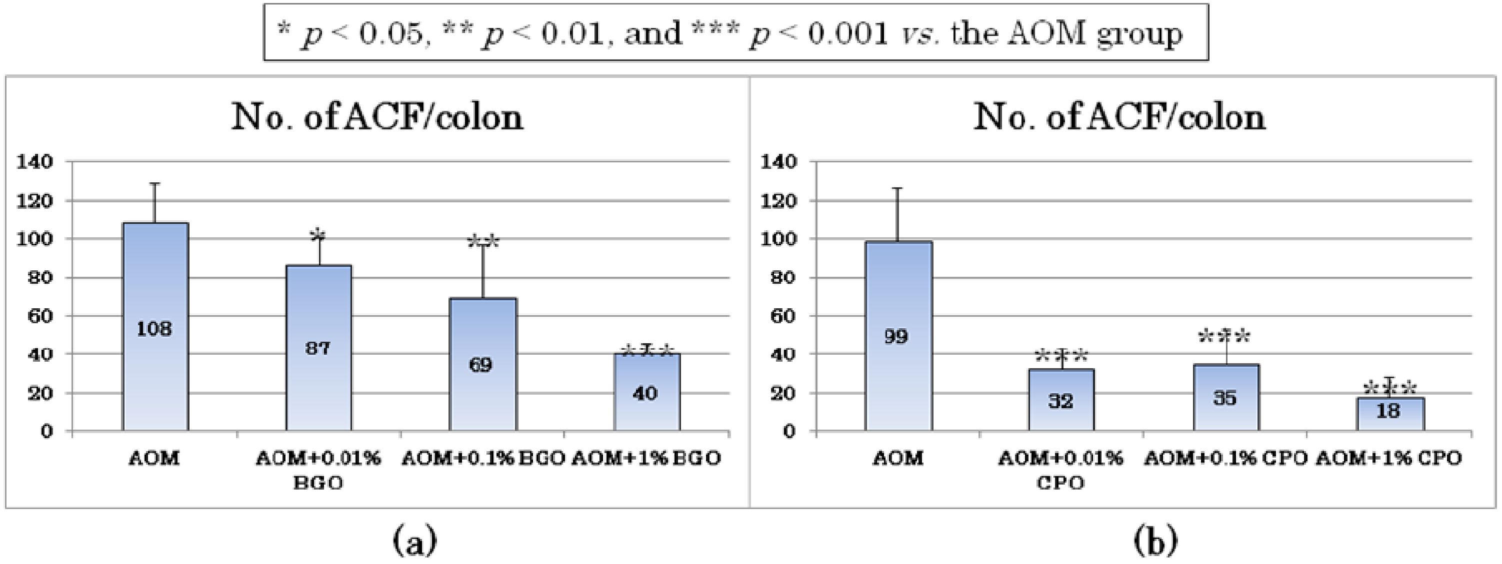
International Journal o
Molecular Science
ISSN 1422-006
www.mdpi.com/journal/ijm

Review

Cancer Chemopreventive Ability of Conjugated Linolenic Acids

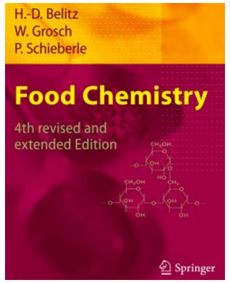
Takuji Tanaka [1,*], Masashi Hosokawa [2], Yumiko Yasui [3], Rikako Ishigamori [4] and Kazuo Miyashita [5]

Figure 3. The numbers of aberrant crypt foci (ACF) induced by azoxymethane (AOM) from *in vivo* short-term assays determining the effects of 5-week feeding with (**a**) Bitter gourd (*Momordica charantia*) seed oil (BGO) and (**b**) Catalpa (*Catalpa ovata*) seed oil (CPO) in rats.



* $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$ *vs.* the AOM group

Fatty acids characteristics
Some specific classes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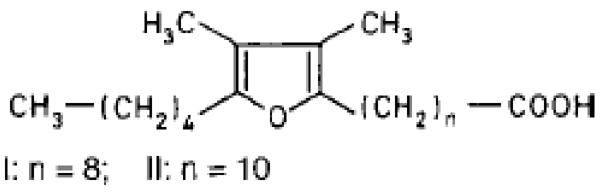
Hydroxy substituted FAs: among which the best known is ricinoleic acid (12-OH C18:1 (Δ9)) present in castor bean oil which is also optically active and naturally D(+)-ricinoleic acid prevails.
In the vegetable kingdom there are fatty acids with substitution in position 2. 2-OH derivatives of acid chains from C:16 to C:25 (odd and even) precursors of g and d lactones (very common aromas in fruits).

Ketoacids: they are less frequent but are present in milk.

Furan FAs: they are fatty acids in which a furan substructure is present in the side chain, they are particularly present in fish (fish liver oil and freshwater fish) where their presence ranges from 1-6% up to 25% of the total acid fraction.



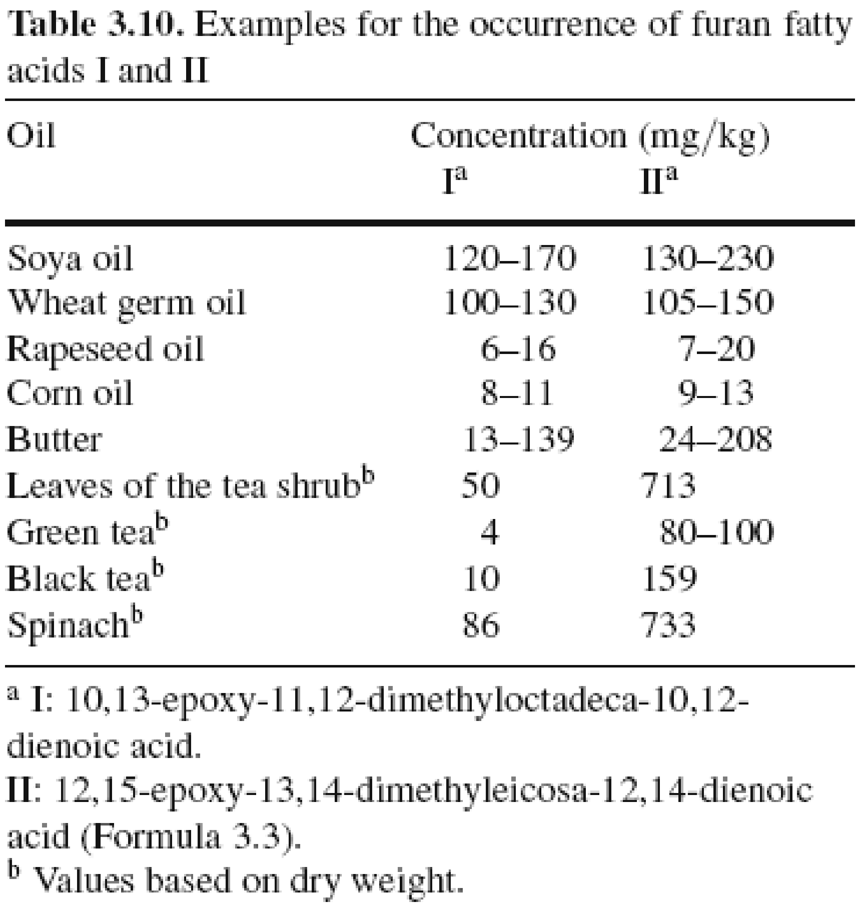


Table 3.10. Examples for the occurrence of furan fatty acids I and II

Oil	Concentration (mg/kg) I^a	II^a
Soya oil	120–170	130–230
Wheat germ oil	100–130	105–150
Rapeseed oil	6–16	7–20
Corn oil	8–11	9–13
Butter	13–139	24–208
Leaves of the tea shrub[b]	50	713
Green tea[b]	4	80–100
Black tea[b]	10	159
Spinach[b]	86	733

[a] I: 10,13-epoxy-11,12-dimethyloctadeca-10,12-dienoic acid.
II: 12,15-epoxy-13,14-dimethyleicosa-12,14-dienoic acid (Formula 3.3).
[b] Values based on dry weight.

Fatty acids characteristics
Physico-chemical properties of relevance

The **melting point** of the saturated series increases as the number of carbon units in the hydrocarbon chain increases: -7.9°C / 75.4°C between C4:0 and C20:0;

Fatty acids in *cis* (*Z*) configuration have lower melting points than the corresponding *trans* (E) isomers: C18:1 (cis oleic) 13.4°C / C18:1 (trans elaidinic) 46°C.

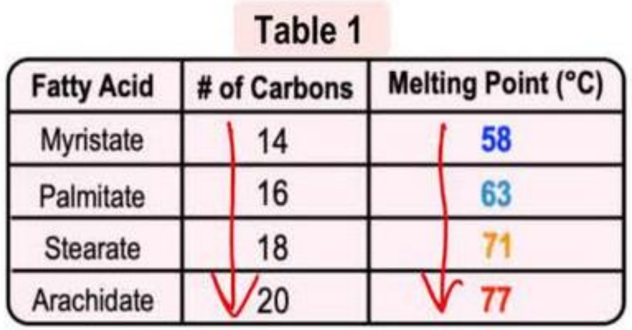


Table 1

Fatty Acid	# of Carbons	Melting Point (°C)
Myristate	14	58
Palmitate	16	63
Stearate	18	71
Arachidate	20	77

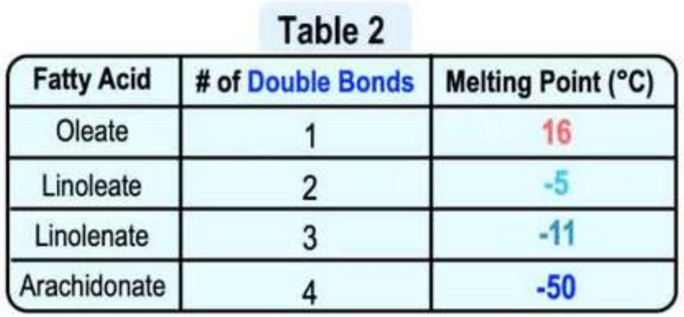
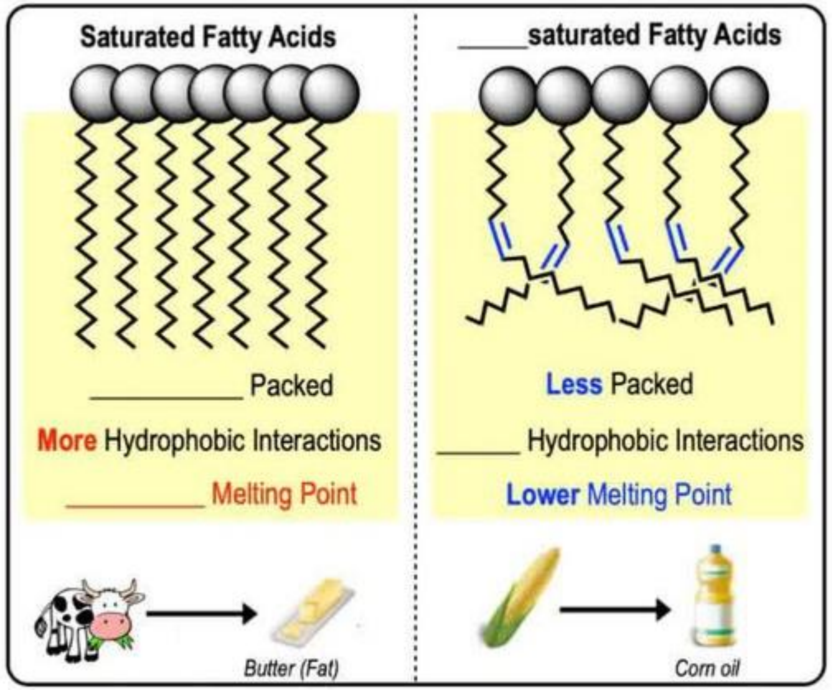


Table 2

Fatty Acid	# of Double Bonds	Melting Point (°C)
Oleate	1	16
Linoleate	2	-5
Linolenate	3	-11
Arachidonate	4	-50



Glycerides compositional characteristics

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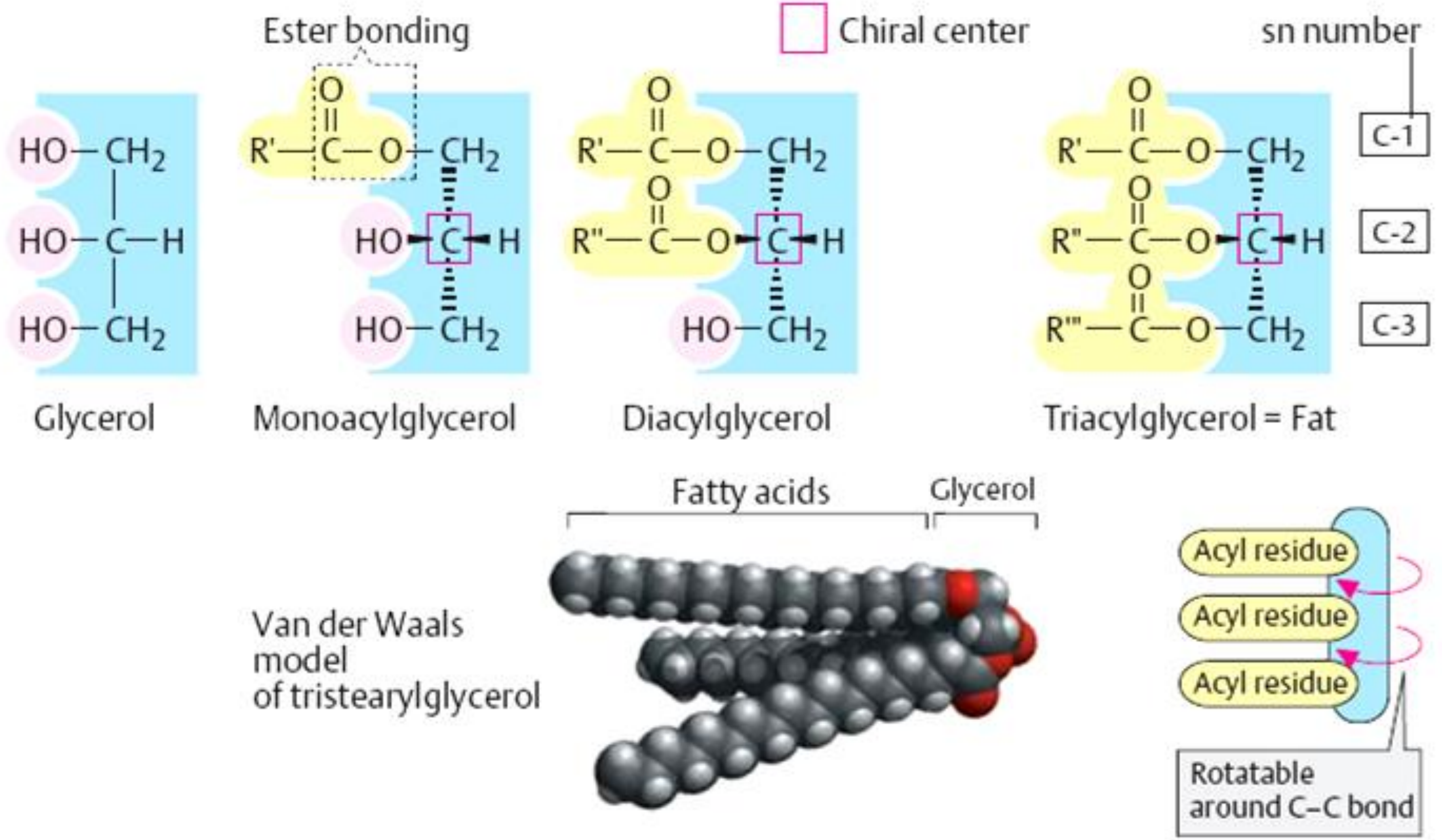
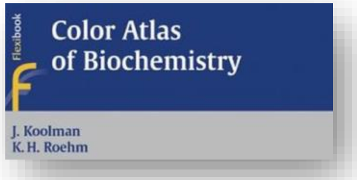



Color Atlas of Biochemistry

J. Koolman
K. H. Roehm

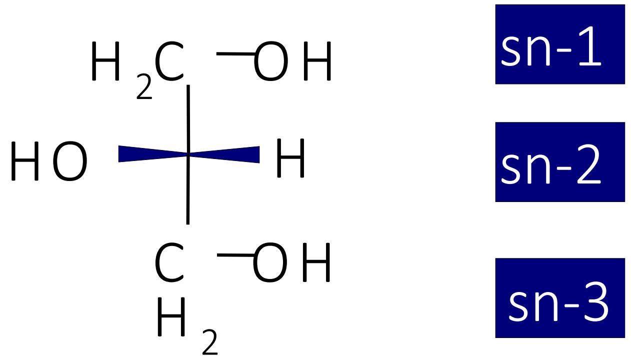
Glycerides compositional characteristics

The fatty acids in dietary fats are found esterified with glycerol to form mono-, di-, and tri-acylglycerols.

- ✓ The position of specific fatty acids on glycerol is determined by the specific biosynthetic pathway and in the case of animal fats it is strongly influenced by diet while in vegetable fats by pedoclimatic variations.
- ✓ Rule 1,3-random-2-restricted: in fats of vegetable origin generally in positions 1,3 there are residues of ac saturated fats while in position 2 ac unsaturated or poly-unsaturated fats.
- ✓ Mono- and diglycerides can derive from incomplete biosynthesis of triglycerides (they generally have position 1 (or 3) and 2 esterified) or from their hydrolysis by lipases (they generally have position 1 and 3 esterified).
- ✓ Triglycerides made up of different fatty acids are defined as mixed.
  PPO=DipalmitylOlein, POO=PalmitylDiolein, SSS=Tristearin, POL=PalmitylOleylLinolein…

Glycerides compositional characteristics
SN- stereospecific numbering

Depending on the distribution of fatty acids on the molecule, triglycerides can have optical properties (center of asymmetry - Chiral carbon)



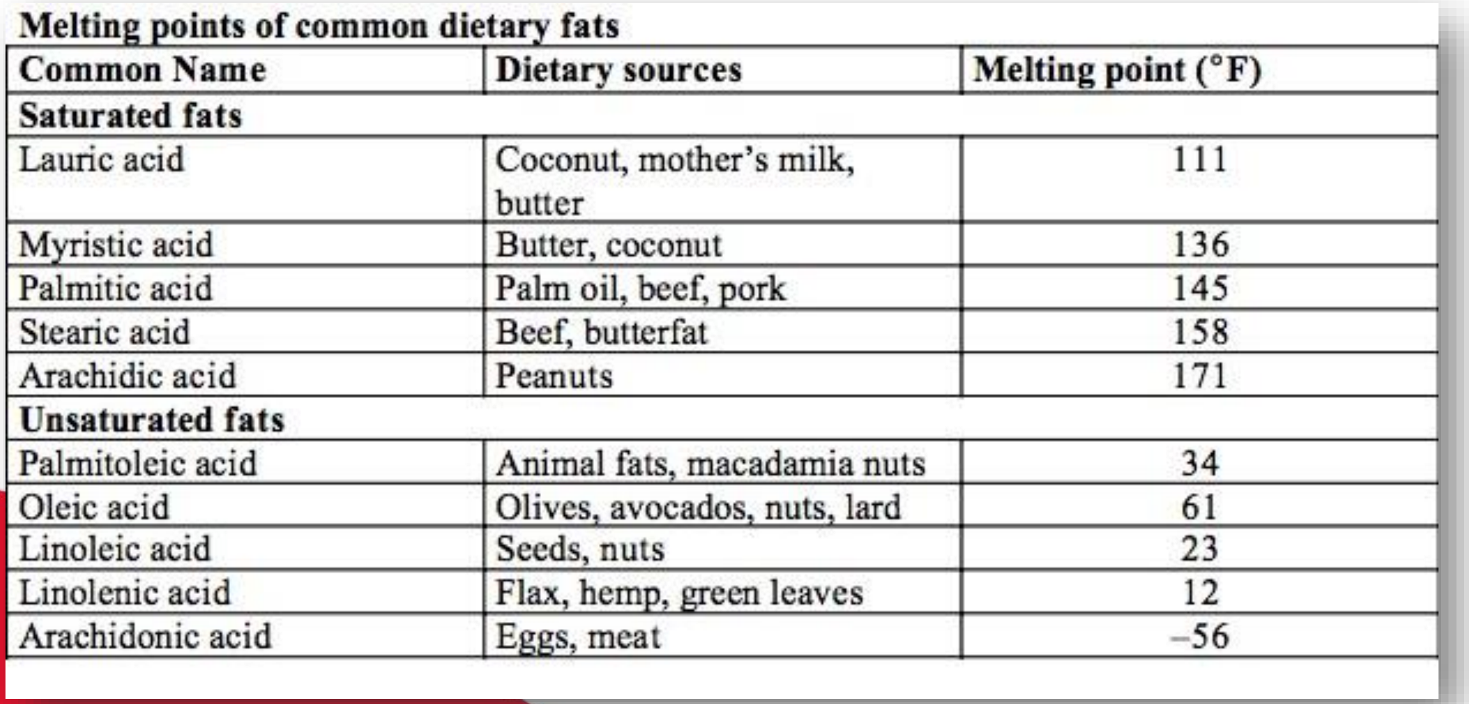
Fisher projection
L-glicerol
sn= stereospecific numbering

Es: sn-POS
sn-1-Palmito-2-oleo-3-stearin

It is possible to assign a sn configuration only through a stereospecific chemical analysis.

Glycerides characteristics
Physico-chemical properties of relevance

The **melting point** of triglycerides depends of the FA composition

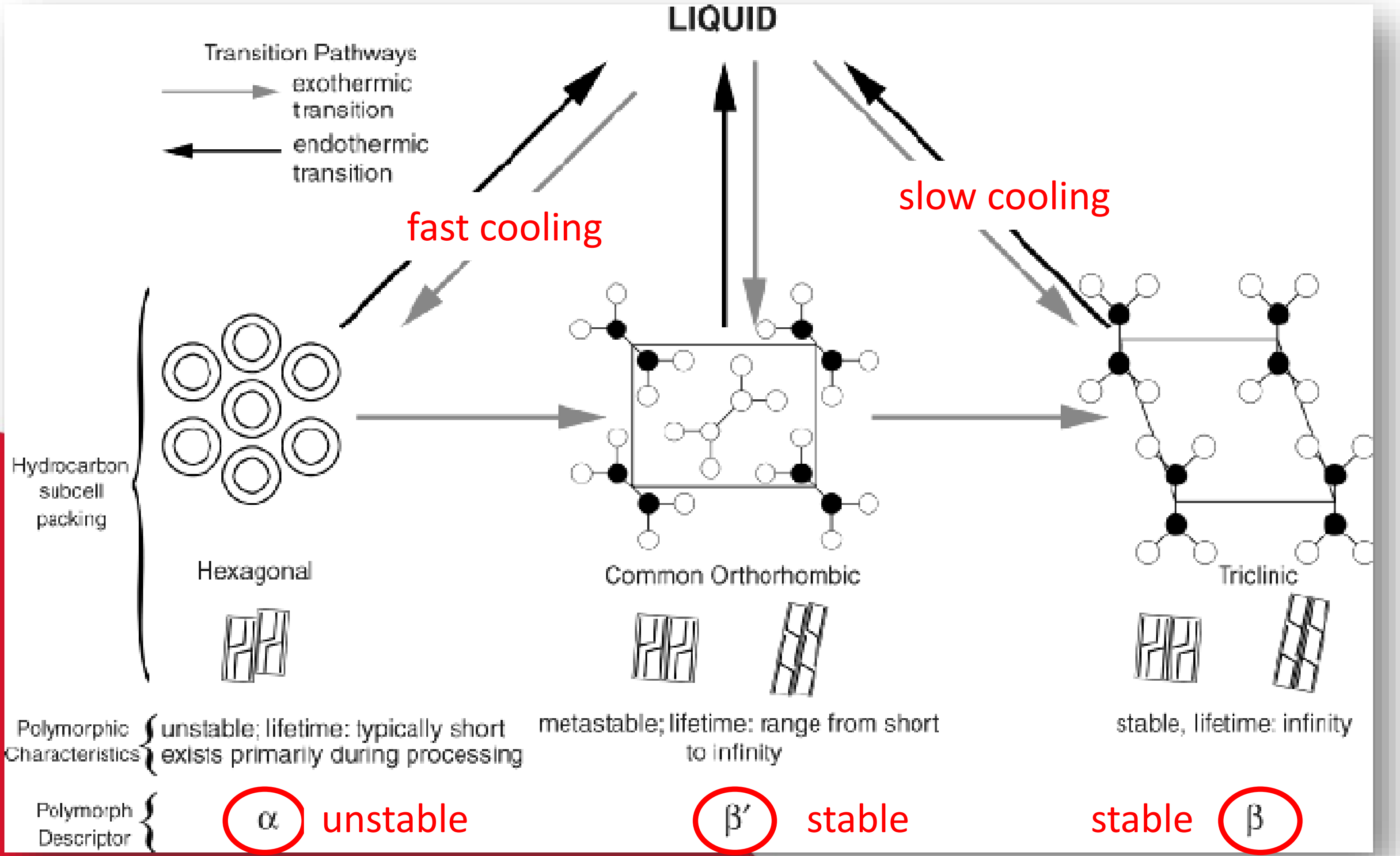


Melting points of common dietary fats

Common Name	Dietary sources	Melting point (°F)
Saturated fats		
Lauric acid	Coconut, mother's milk, butter	111
Myristic acid	Butter, coconut	136
Palmitic acid	Palm oil, beef, pork	145
Stearic acid	Beef, butterfat	158
Arachidic acid	Peanuts	171
Unsaturated fats		
Palmitoleic acid	Animal fats, macadamia nuts	34
Oleic acid	Olives, avocados, nuts, lard	61
Linoleic acid	Seeds, nuts	23
Linolenic acid	Flax, hemp, green leaves	12
Arachidonic acid	Eggs, meat	–56

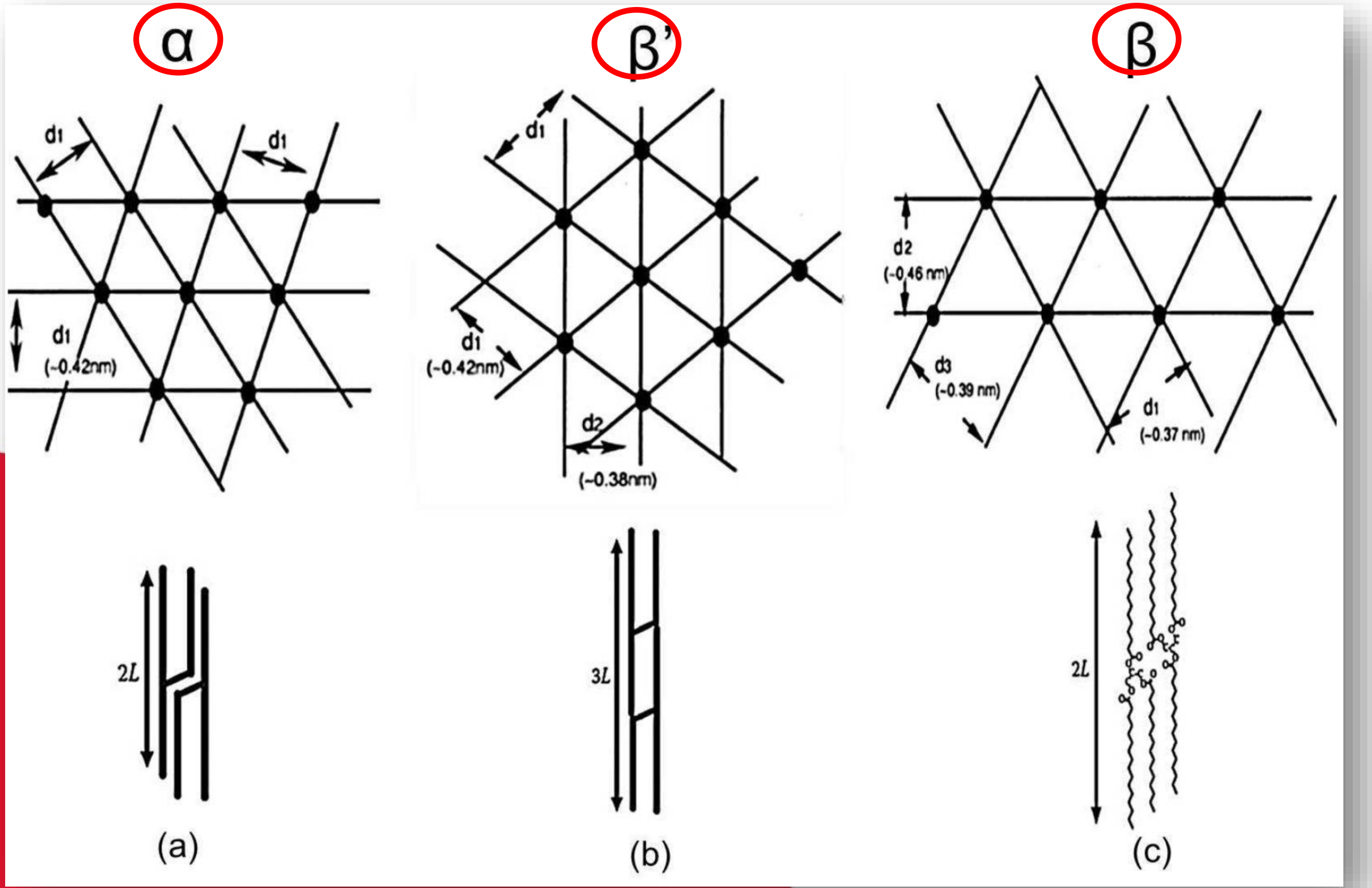
Glycerides characteristics
Physico-chemical properties of relevance

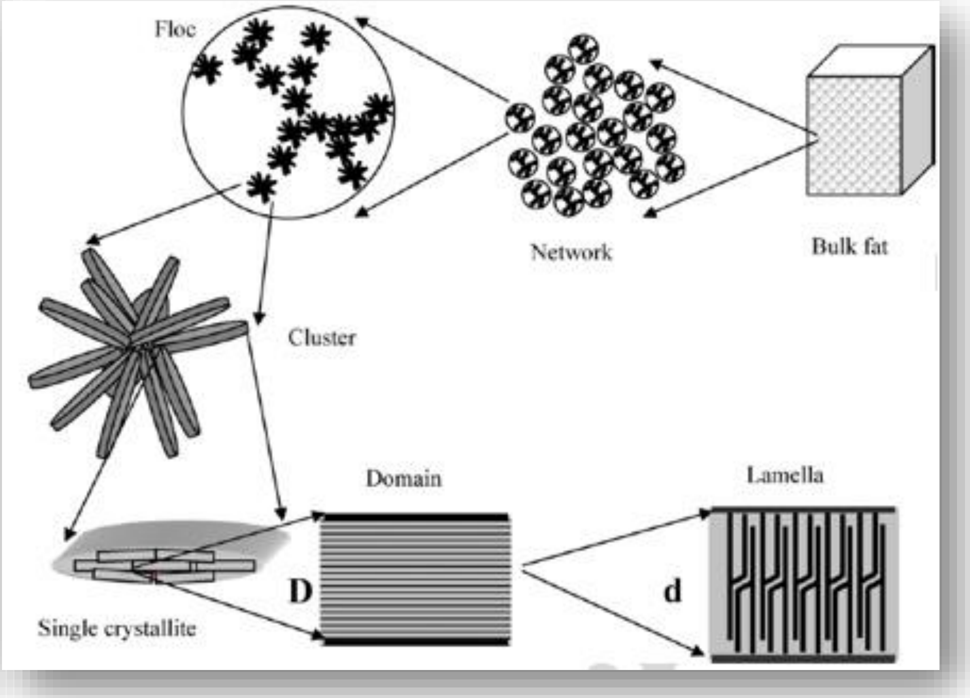
The **polymorphism** of triglycerides depends of the FA composition and on the crystallization dynamics



Glycerides characteristics
Physico-chemical properties of relevance

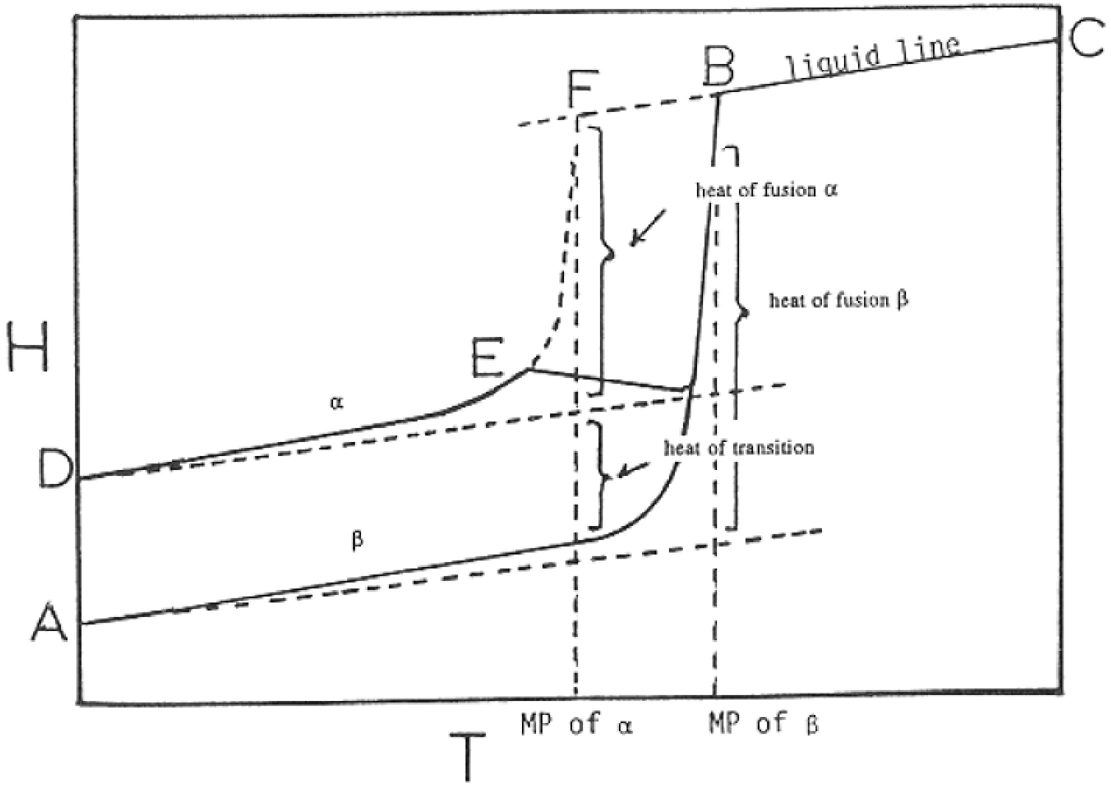
The **polymorphism** of triglycerides depends of the FA composition and on the crystallization dynamics





Glycerides characteristics
Physico-chemical properties of relevance

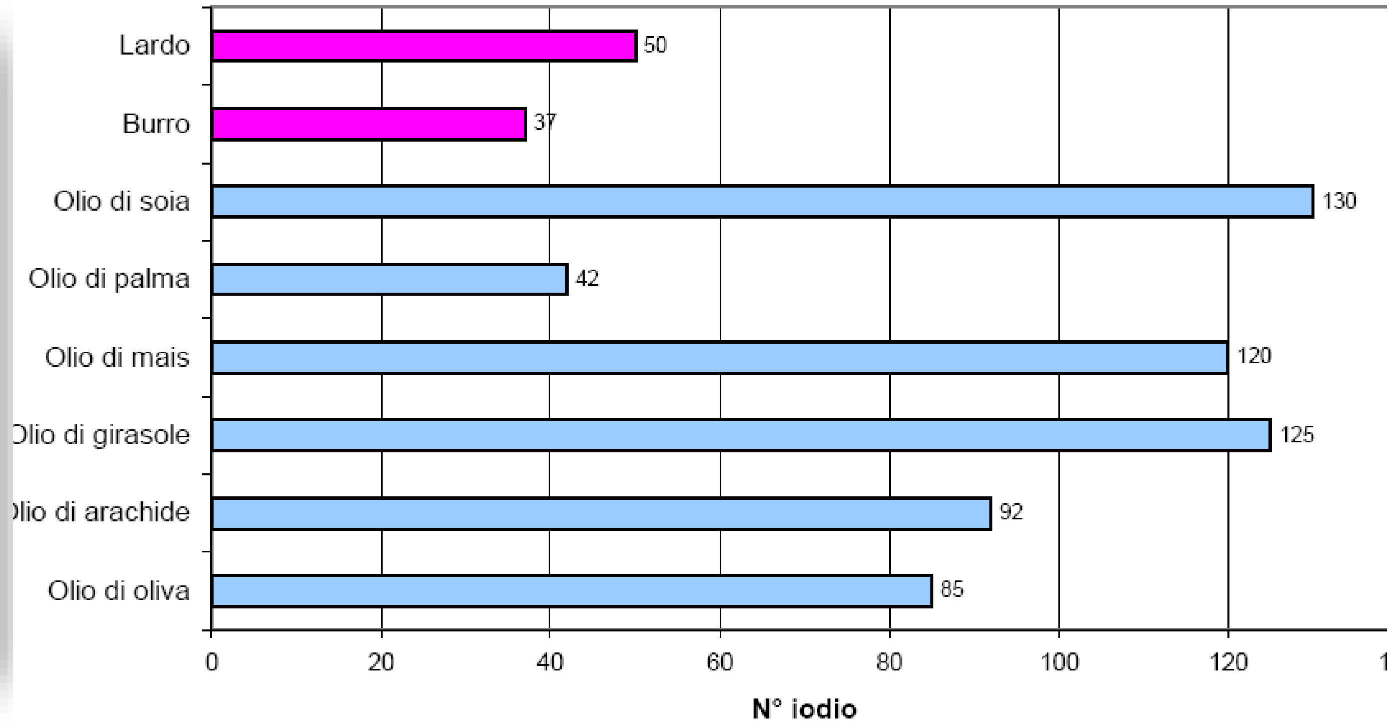
The **polymorphism** of triglycerides depends of the FA composition and on the crystallization dynamics



Glycerides characteristics
Physico-chemical properties of relevance

The **Iodine value (Numero di Iodio)** (IV) indicates the degree of unsaturation of a fat or oil.
It is defined as the grams of iodine absorbed by 100 g of fat

Oil	Iodine Value
Coconut oil	7.5-10.5
Olive oil	79-90
Palm oil	4-22
Sunflower oil	125-140
Ghee	26-38
Groundnut oil	84-100
Mustard oil	98-110
Sesame oil	103-116



Minor unsaponifiable components characteristics

1. Saturated hydrocarbons
2. Unsaturated and polyunsaturated hydrocarbons
3. Tocopherols and tocotrienols
4. Higher aliphatic alcohols
5. Sterols
6. Methyl sterols
7. Di- and tri-terpenic alcohols
8. Fat-soluble vitamins
9. Pigments, ubiquinones, phenols

4. Higher aliphatic alcohols abundant especially in solvent-extracted oils, they probably derive from waxes. Examples are docosanol ($C_{22}H_{45}OH$), tetracosanol ($C_{24}H_{49}OH$) and hexacosanol $C_{26}H_{53}OH$)

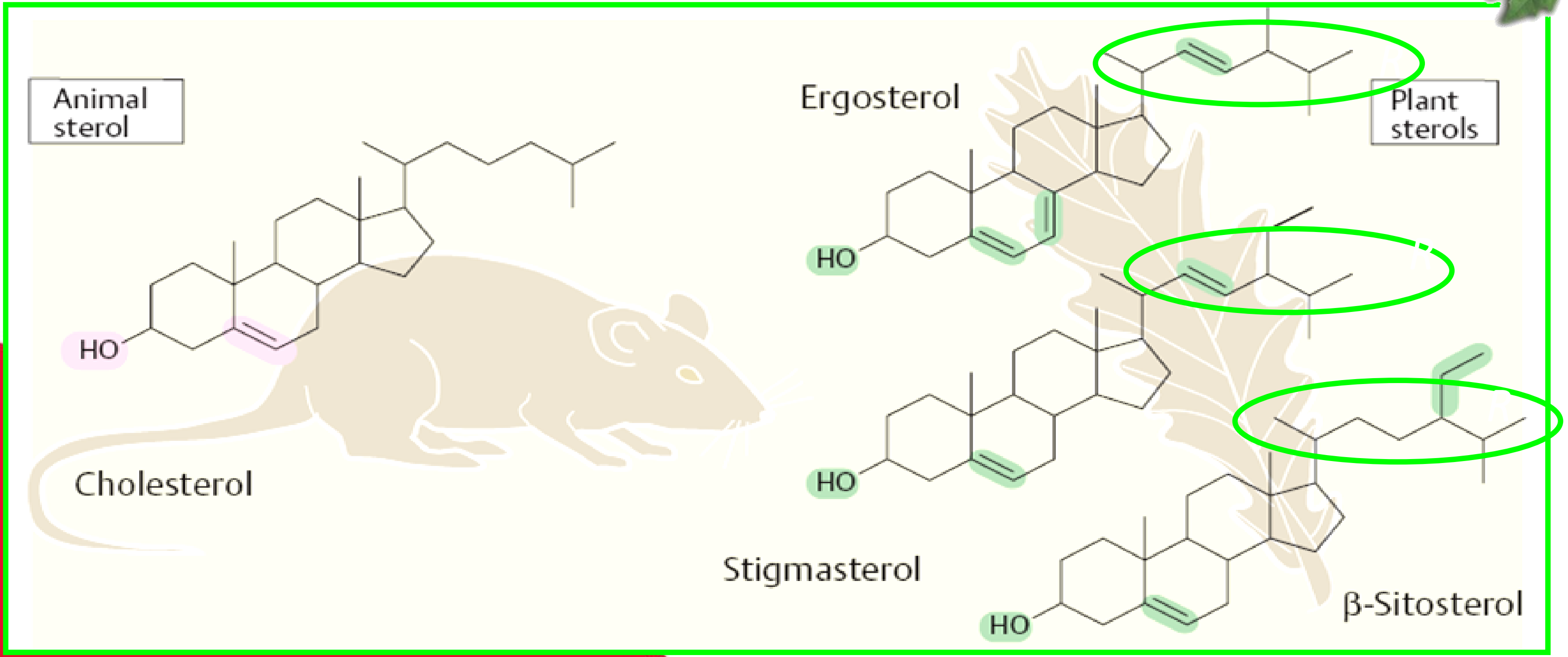
2. Unsaturated and polyunsaturated hydrocarbons
the main one is squalene, a terpenic hydrocarbon with 6 isoprene units.

3. Tocopherols and tocotrienols
benzohydropyran derivatives.
If the side chain is unsaturated, they are called tocotrienols. Tocopherols have vitamin action (Vitamin E) and are natural antioxidants. The antioxidant activity is α-T < α-T3 < γ-T < γ-T3 < β-T < β-T3 < δ-T < δ-T3

Minor unsaponifiable components characteristics

5. Sterols

cholesterol is present in animal fats while in vegetable fats phytosterols prevail. Cholesterol is practically absent in vegetable fats except in tomato seed oil.



The main phytosterols are: brassicasterol, campesterol, stigmasterol, β- sitosterol, Δ5-avenasterol, Δ7-avenasterol, Δ7-stigmastenol

Minor unsaponifiable components characteristics

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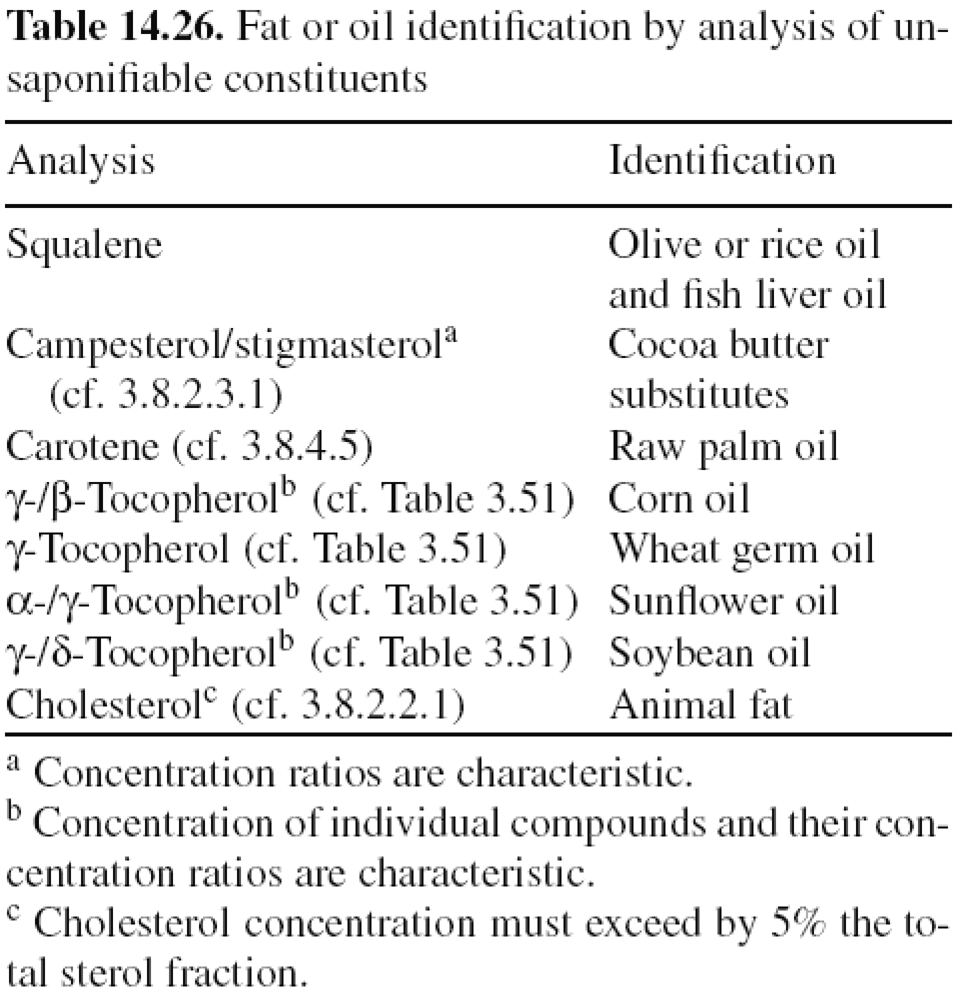

Table 14.26. Fat or oil identification by analysis of unsaponifiable constituents

Analysis	Identification
Squalene	Olive or rice oil and fish liver oil
Campesterol/stigmasterol[a] (cf. 3.8.2.3.1)	Cocoa butter substitutes
Carotene (cf. 3.8.4.5)	Raw palm oil
γ-/β-Tocopherol[b] (cf. Table 3.51)	Corn oil
γ-Tocopherol (cf. Table 3.51)	Wheat germ oil
α-/γ-Tocopherol[b] (cf. Table 3.51)	Sunflower oil
γ-/δ-Tocopherol[b] (cf. Table 3.51)	Soybean oil
Cholesterol[c] (cf. 3.8.2.2.1)	Animal fat

[a] Concentration ratios are characteristic.

[b] Concentration of individual compounds and their concentration ratios are characteristic.

[c] Cholesterol concentration must exceed by 5% the total sterol fraction.

Minor unsaponifiable components characteristics

7. Tri-Terpenic Alcohols:

present in modest quantities, but with different compositions for each oil. In the olive oil obtained by extraction with solvent there are erythrodiol and uvaol which are also found in grape seed oil.
Also present are diterpene alcohols (phytol and geranylgeraniol)

8. Vitamins:

vitamins A, D, K and E are present. The richest fats in vitamins A are fish liver oils and in particular cod. In the others fats, on the other hand, β-carotene, its precursor, is present.

9. Pigments: chlorophylls and carotenoids are present. Chlorophyll is particularly present in olive oil and its presence depends on the variety of the olives, the degree of ripeness and the extraction technology.
Among the particularly abundant carotenoids are β-carotene and lycopene. Palm oil is the richest in carotenoids (about 400 mg/100 g).
Ubiquinones: are represented by coenzyme Q

Reactions on fats

Oxidative rancidity
It is a predominantly chemical phenomenon and consists of an absorption of oxygen by unsaturated fatty acids. It is an autocatalytic reaction. Hydroperoxides are primary products from which various compounds derive (aldehydes, acids, ketones and hydrocarbons)

Hydrolytic rancidity
It is exclusively an enzymatic phenomenon caused by the lipases present in the fat matrix (native or microbial or added origin) which cause the breakage of the ester binding of lipids with release of glycerin and fatty acids

Ketonic rancidity
It is a phenomenon of oxidation of the methylene group in position β with respect to the carboxyl of the fatty acid and the formation of a ketoacid which by subsequent oxidation leads to a methyl ketone. It is catalysed by an enzyme, the β-oxidase produced for example by mushrooms (Gorgonzola)

Reactions on fats: oxidation

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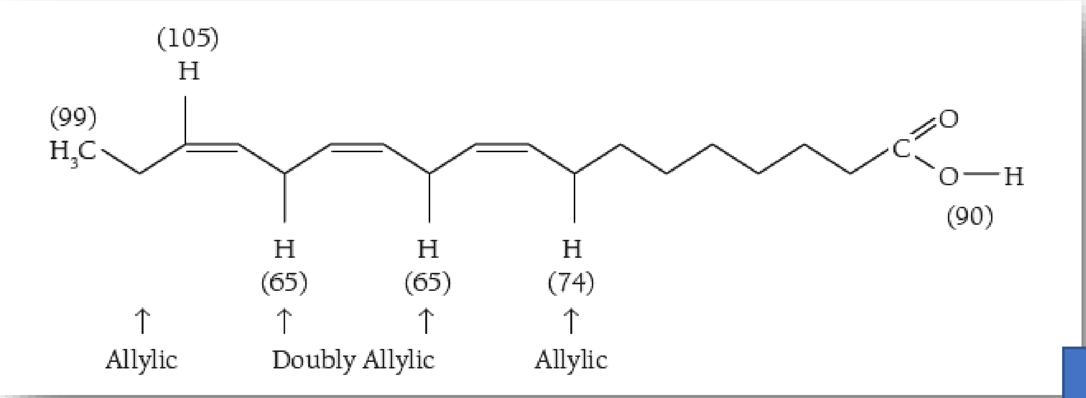
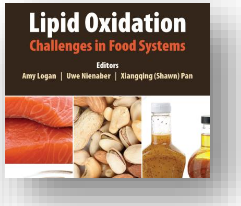
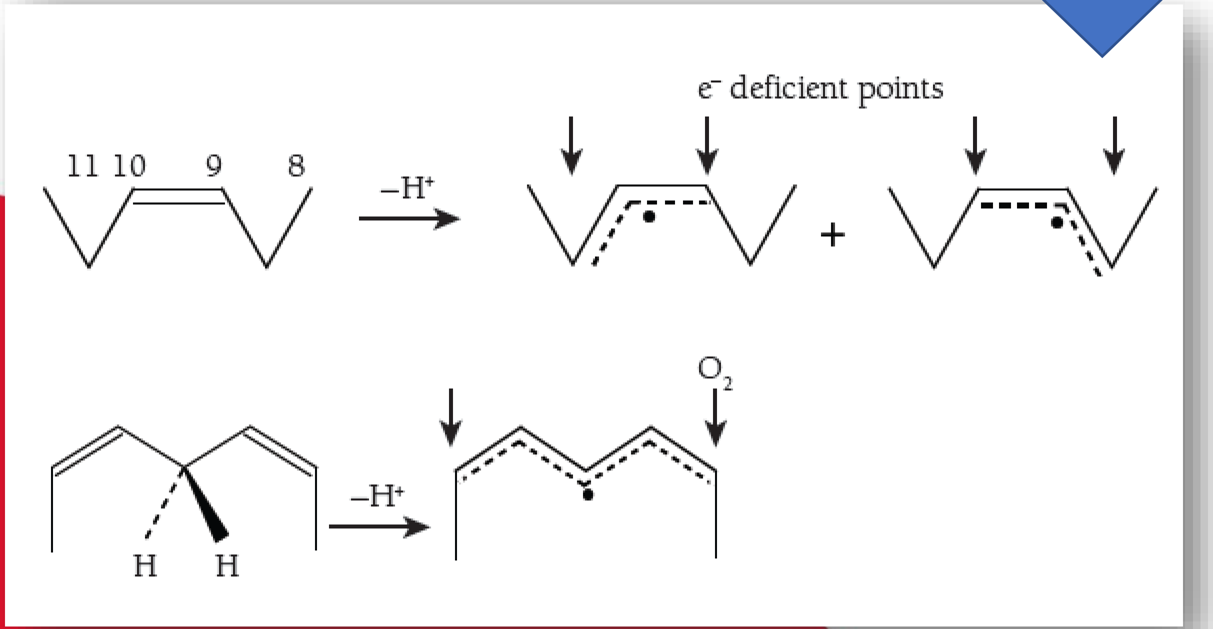



Lipid Oxidation
Challenges in Food Systems
Editors
Amy Logan | Uwe Nienaber | Xiangqing (Shawn) Pan



The -CH2- groups between two double bonds in lipids (called doubly allylic) are doubly activated for hydrogen abstraction so C-H bond energies drop dramatically as shown in the structure on the left. Numbers in parentheses are bond energies in kcal/mol.

The order of reactivity, then, is doubly allylic H between two double bonds > singly allylic H next to double bonds >> H α to the -COOH group > H on methylene groups farther down the acyl chains.

Reactions on fats: oxidation

All types of biological molecules are damaged by ROS, but lipid oxidation plays a special role in this process because the energy barrier to initiate lipid peroxidation is lower than those to initiate oxidation of proteins, carbohydrates, or nucleic acids.

There is interplay between oxidative reactions of various biomolecules. Free radicals of other molecules may initiate lipid oxidation while products of lipid oxidation modify proteins and nucleic acids and deplete antioxidants.

Different mechanisms are able to induce lipid peroxidation: free-radical reactions, photoxidation, enzyme action, and oxidation catalyzed by trace metals.

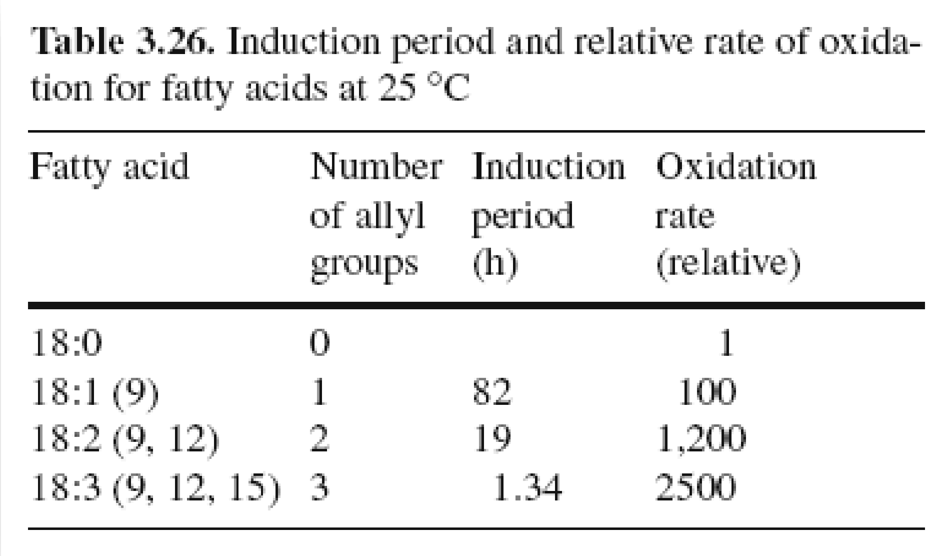
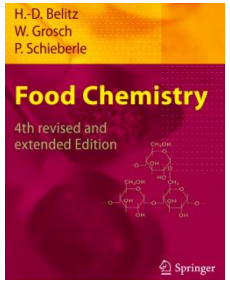
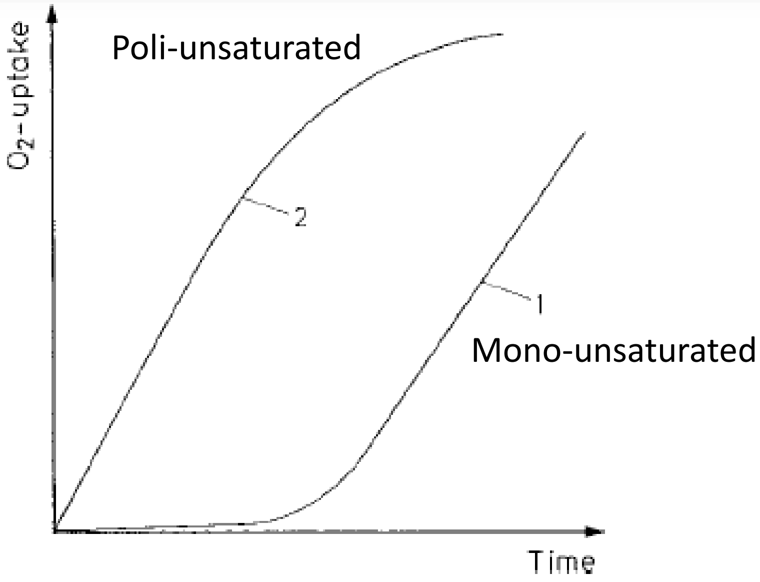


Table 3.26. Induction period and relative rate of oxidation for fatty acids at 25 °C

Fatty acid	Number of allyl groups	Induction period (h)	Oxidation rate (relative)
18:0	0		1
18:1 (9)	1	82	100
18:2 (9, 12)	2	19	1,200
18:3 (9, 12, 15)	3	1.34	2500

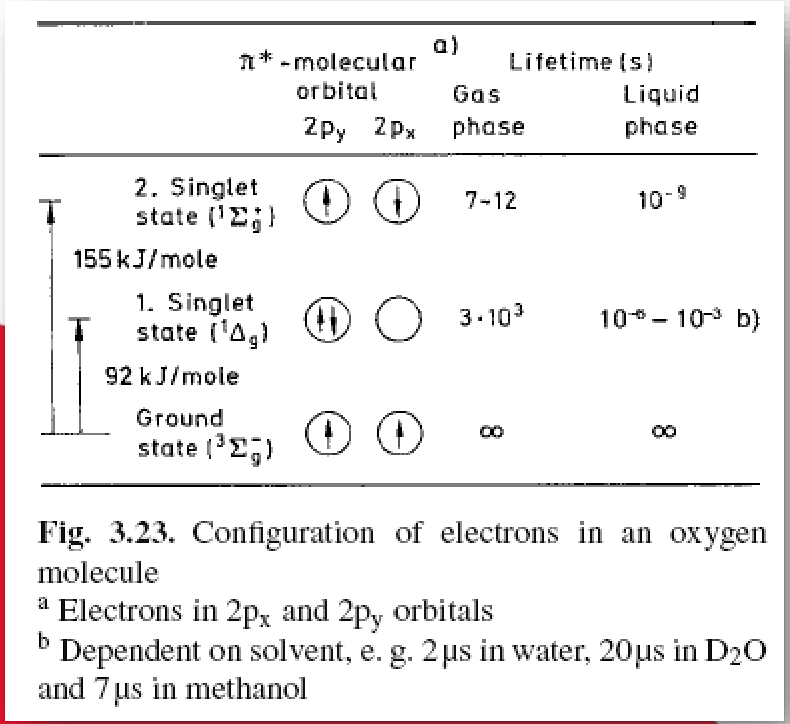




Reactions on fats: oxidation

!

Oxigen reactive species
Oxigen in singlet state has more energy thereby the oxidation reaction is favored thanks to a smaller activation energy

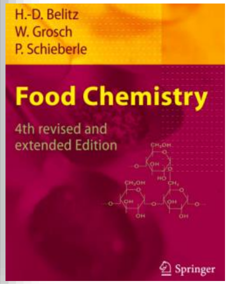


	π^*-molecular orbital[a]		Lifetime (s)	
	$2p_y$	$2p_x$	Gas phase	Liquid phase
2. Singlet state ($^1\Sigma_g^+$)	↑	↓	7–12	10^{-9}
155 kJ/mole				
1. Singlet state ($^1\Delta_g$)	↑↓	○	$3 \cdot 10^3$	$10^{-6} - 10^{-3}$ b)
92 kJ/mole				
Ground state ($^3\Sigma_g^-$)	↑	↑	∞	∞

Fig. 3.23. Configuration of electrons in an oxygen molecule

[a] Electrons in $2p_x$ and $2p_y$ orbitals

[b] Dependent on solvent, e. g. 2 µs in water, 20 µs in D_2O and 7 µs in methanol



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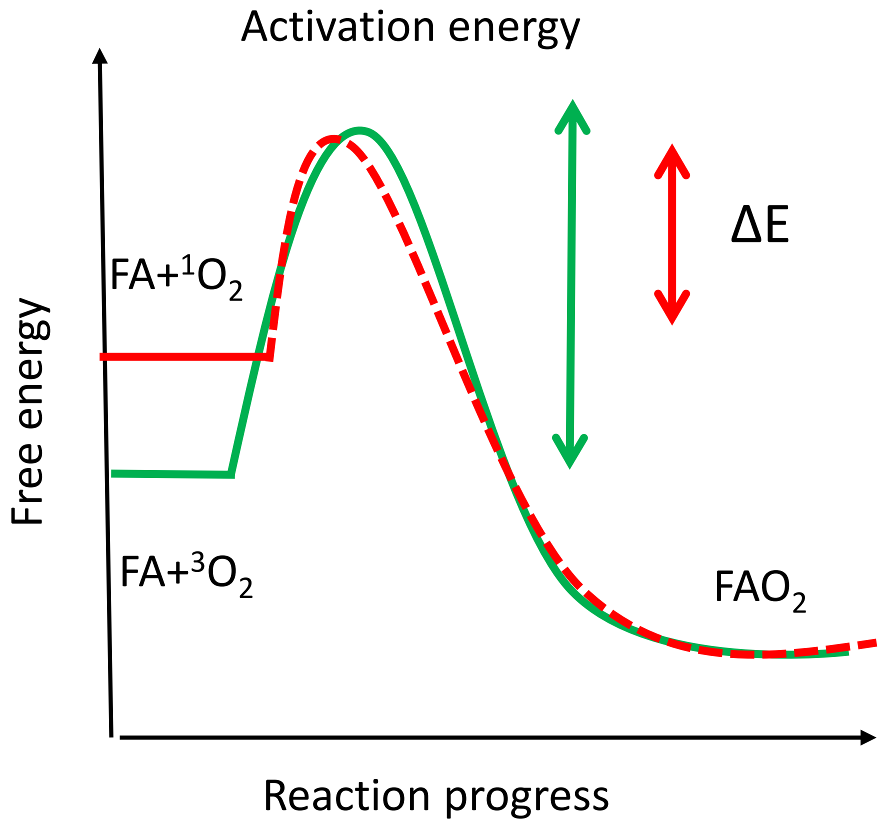
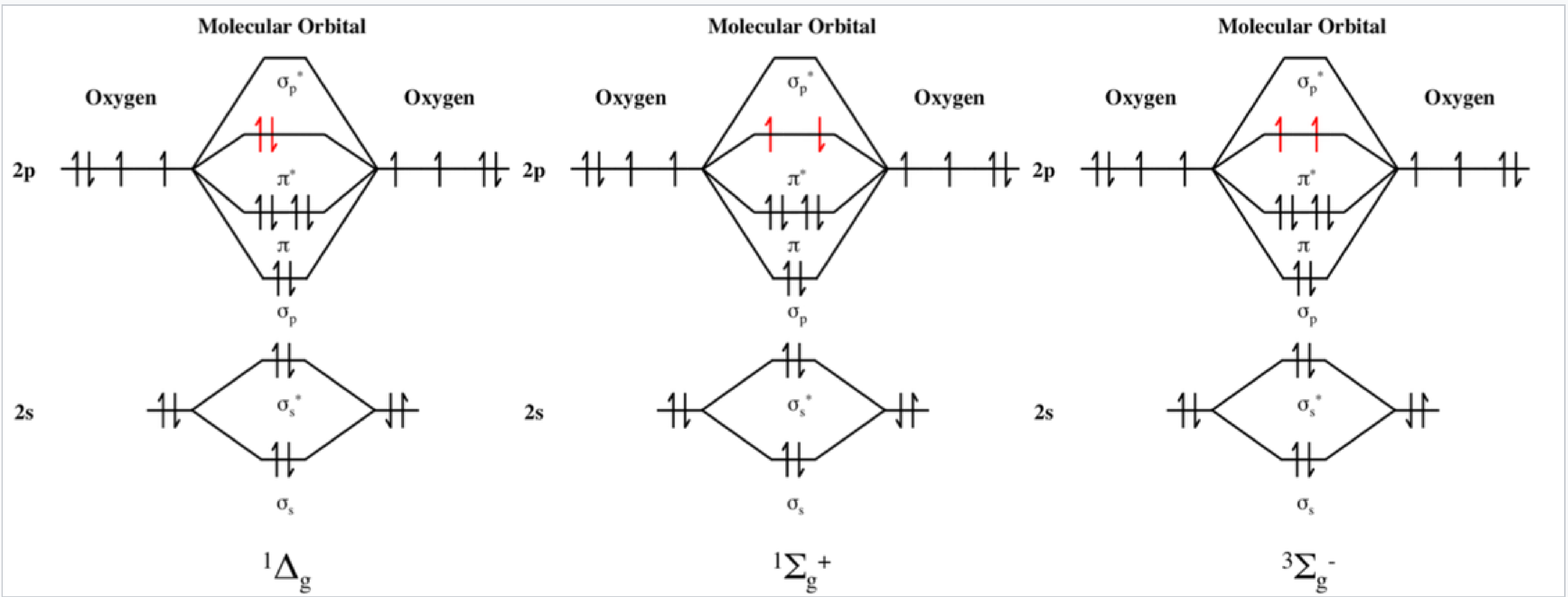


Reactions on fats: oxidation

Singlet oxygen ($^1O_2$) is the first electronic excited state of molecular oxygen (O_2).

Considered as a **distinct chemical entity**, its electronic configuration is responsible for its **unusual thermodynamic stability but remarkably enhanced reactivity** towards other molecules in the singlet state.



Molecular orbital diagram of two singlet excited states as well as the triplet ground state of molecular dioxygen. From left to right, the diagrams are for: $^1\Delta_g$ singlet oxygen (first excited state), $^1\Sigma_g^+$ singlet oxygen (second excited state), and $^3\Sigma_g^-$ triplet oxygen (ground state). The lowest energy 1s molecular orbitals are uniformly filled in all three and are omitted for simplicity. The broad horizontal lines labelled π and π* each represent two molecular orbitals (for filling by up to 4 electrons in total). The three states only differ in the occupancy and spin states of electrons in the two degenerate π* antibonding orbitals.

Reactions on fats: oxidation

CRITICAL REVIEW www.rsc.org/csr | Chemical Society Reviews

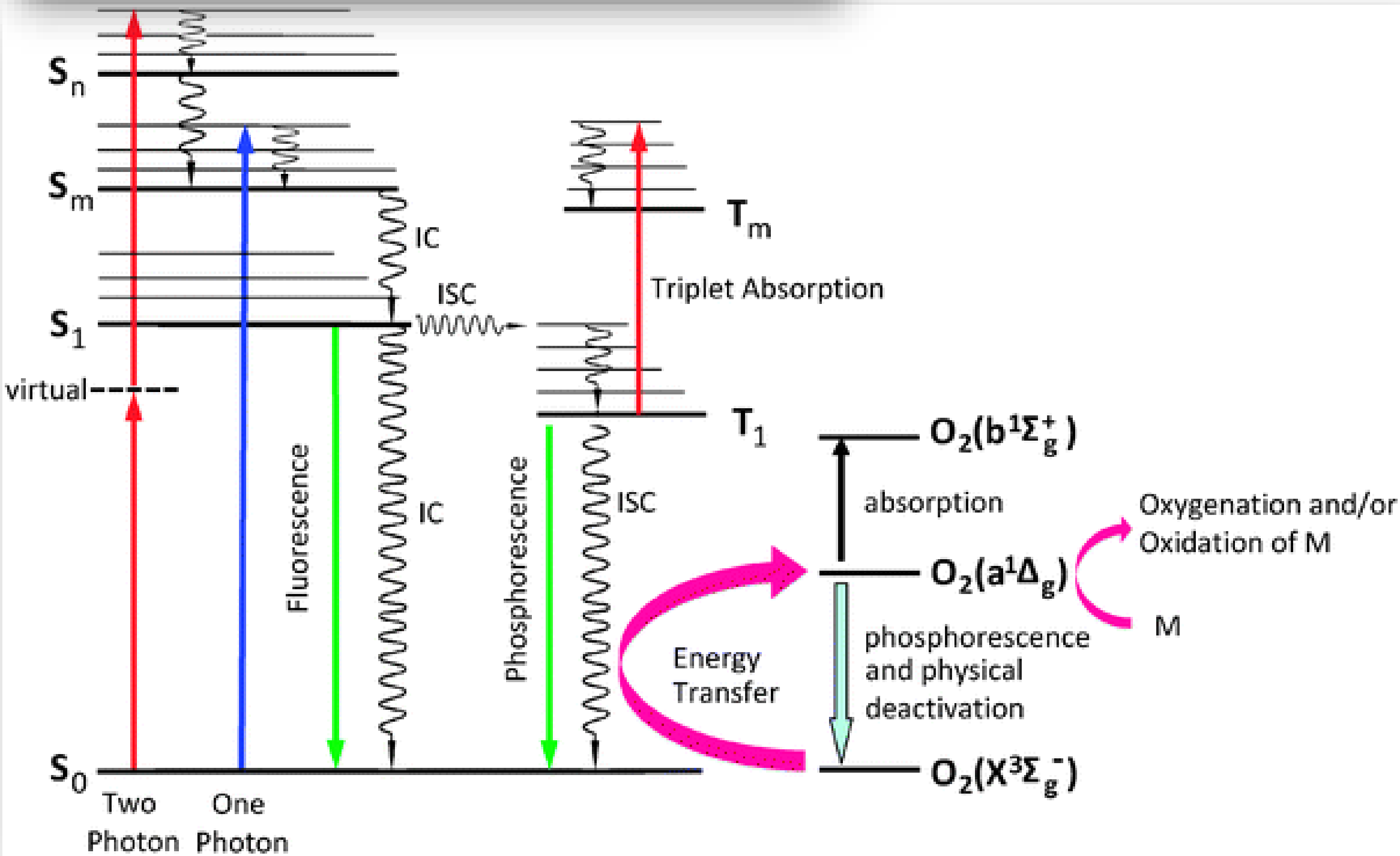
Singlet oxygen: there is indeed something new under the sun

Peter R. Ogilby

Received 4th February 2010, Accepted 23rd March 2010
First published as an Advance Article on the web 22nd June 2010
DOI: 10.1039/b926014p

Diagram illustrating the one- and two-photon-initiated, triplet-state photosensitized production of singlet oxygen, $O_2(a^1\Delta g)$.
The letter S denotes discrete states of the sensitizer with singlet spin multiplicity, and T denotes states with triplet spin multiplicity.

IC (Internal Conversion) and ISC (Inter System Crossing). Depending on the sensitizer, the simultaneous absorption of two photons may or may not populate the same state as that created upon the absorption of a single higher-energy photon.



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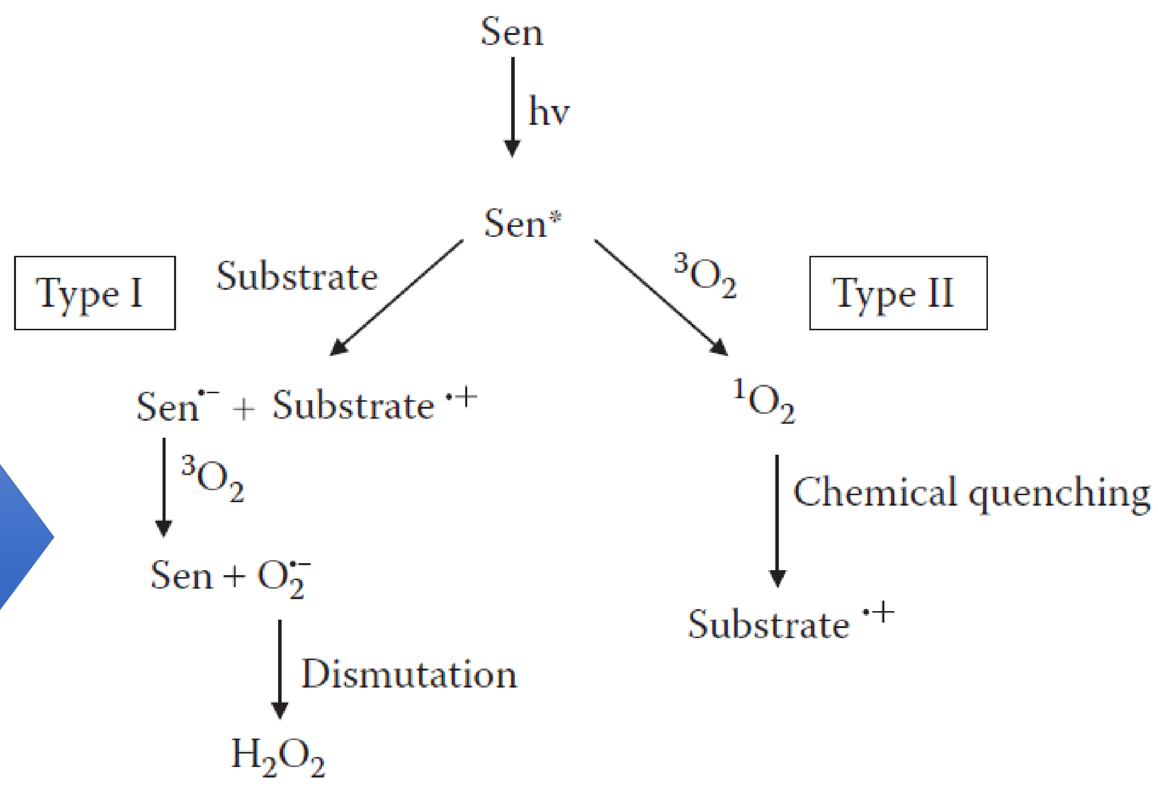
Reactions on fats: oxidation

Riboflavin, porphyrins, and chlorophyll derivatives are photosensitizers naturally occurring in foods.
Meat, fruit juice, and vegetable oils, together with dairy products, such as cheese, butter, and milk, are susceptible to photoxidation resulting
from their natural content of photosensitizers.

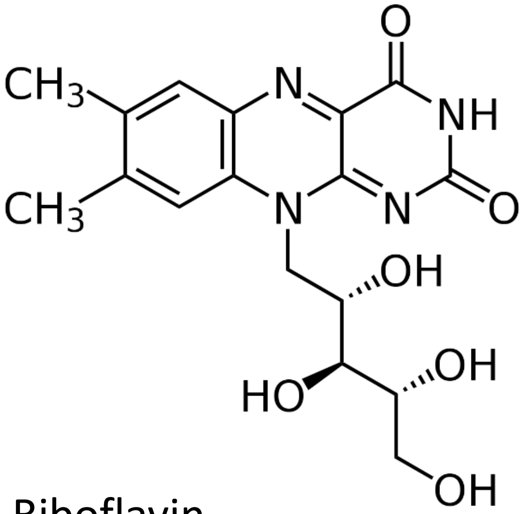
Photosensitizers absorb light, becoming excited to one or more energy-rich state(s). The excited sensitizer (Sen*) undergoes internal reactions that ultimately result in the oxidative alteration of a second molecule.



Type I and type II photosensitization process.

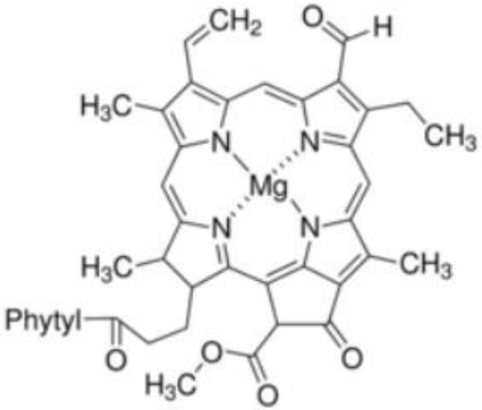
Reactions on fats: oxidation

Riboflavin has been traditionally considered as the active photosensitizer in dairy products.
Riboflavin can initiate photooxidation of types I and II by exposure to UV radiation or visible light up to approximately 500 nm.
Recent studies have shown the presence of five other photosensitizers in butter:
protoporphyrin,
hematoporphyrin,
a chlorophyll a-like molecule,
and two unidentified tetrapyrrols.



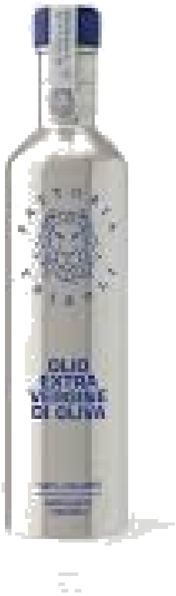
Riboflavin
Vitamin B2

Chlorophyll and porphyrin molecules absorb light in the UV and violet region with absorption peaks of approximately 410 nm (the Soret band).
In addition, they absorb light pronouncedly in the red above 600 nm, and therefore, they may be responsible for the formation of off-flavors in dairy products exposed to light of wavelengths longer than 500 nm.



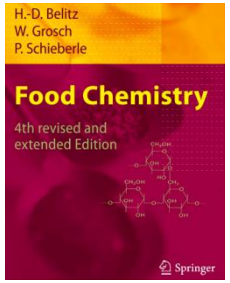
Chlorophyll

Reactions on fats: oxidation



Reactions on fats: oxidation

U2



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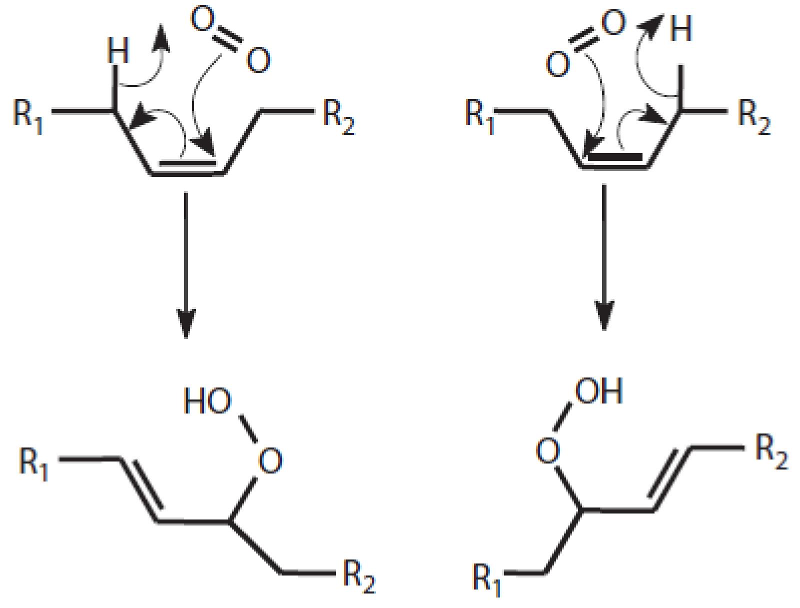
Formation of fatty acids hydroperoxides through the mechanism of ene-addition.
Oxigen in singlet state.



"ene" addition

Start: Formation of peroxy ($RO_2^\cdot$), alkoxy ($RO^\cdot$) or alkyl ($R^\cdot$) radicals

Chain propagation:

(1) $R^\cdot + O_2 \longrightarrow RO_2^\cdot$ k_1: $10^9\ l\,mol^{-1}\,s^{-1}$

(2) $RO_2^\cdot + RH \longrightarrow ROOH + R^\cdot$ k_2: $10-60\ l\,mol^{-1}\,s^{-1}$

(3) $RO^\cdot + RH \longrightarrow ROH + R^\cdot$

Chain branching:

(4) $ROOH \longrightarrow RO^\cdot + {}^\cdot OH$

(5) $2\,ROOH \longrightarrow RO_2^\cdot + RO^\cdot + H_2O$

Chain termination:

$$\left.\begin{array}{l} (6)\ 2\,R^\cdot \longrightarrow \\ (7)\ R^\cdot + RO_2^\cdot \longrightarrow \\ (8)\ 2\,RO_2^\cdot \longrightarrow \end{array}\right\}\ \text{Stable products}$$

Reactions on fats: oxidation

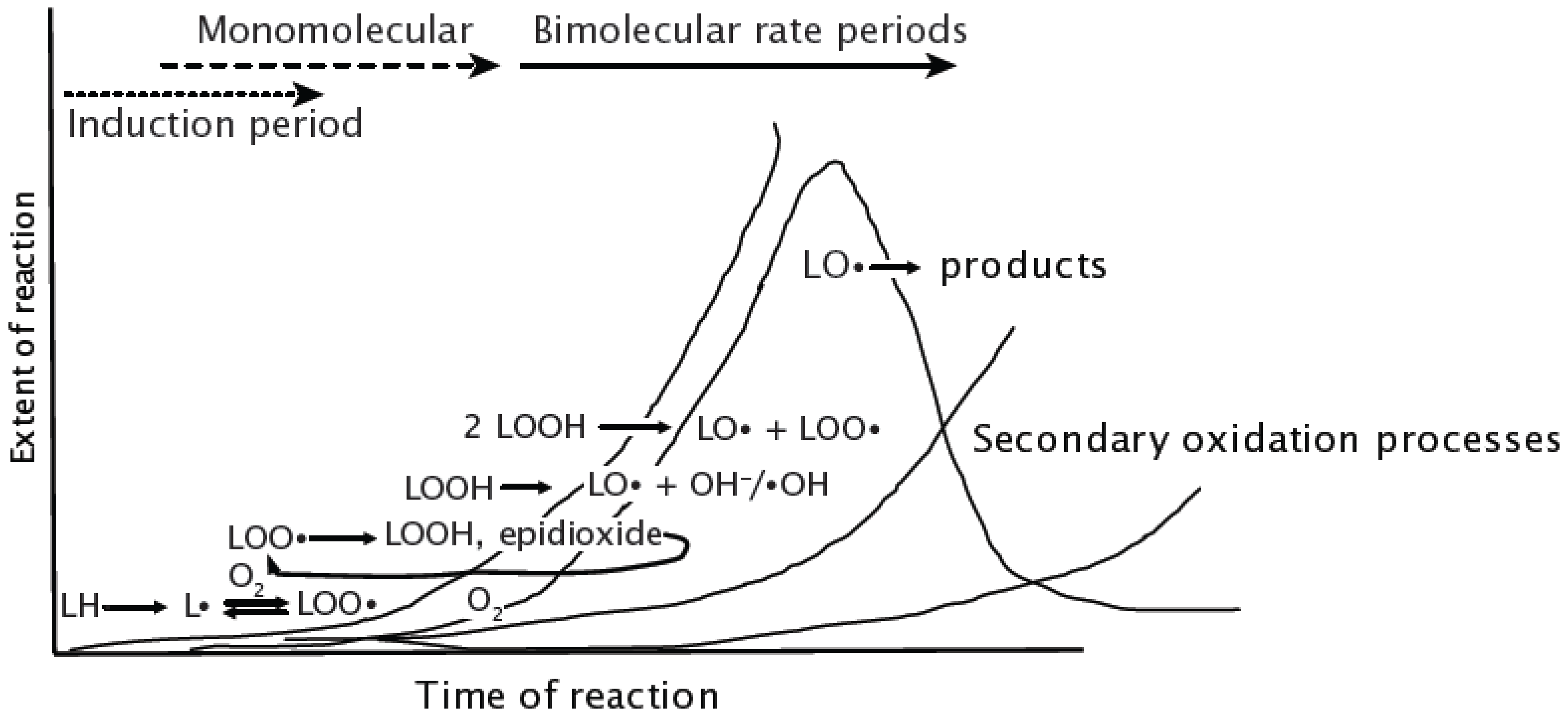
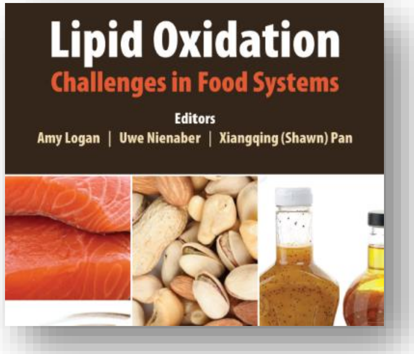


Fig. 1.8. Conceptual diagram of time course of product development in lipid oxidation as has been traditionally depicted.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Challenges in Food Systems
Editors
Amy Logan | Uwe Nienaber | Xiangqing (Shawn) Pan

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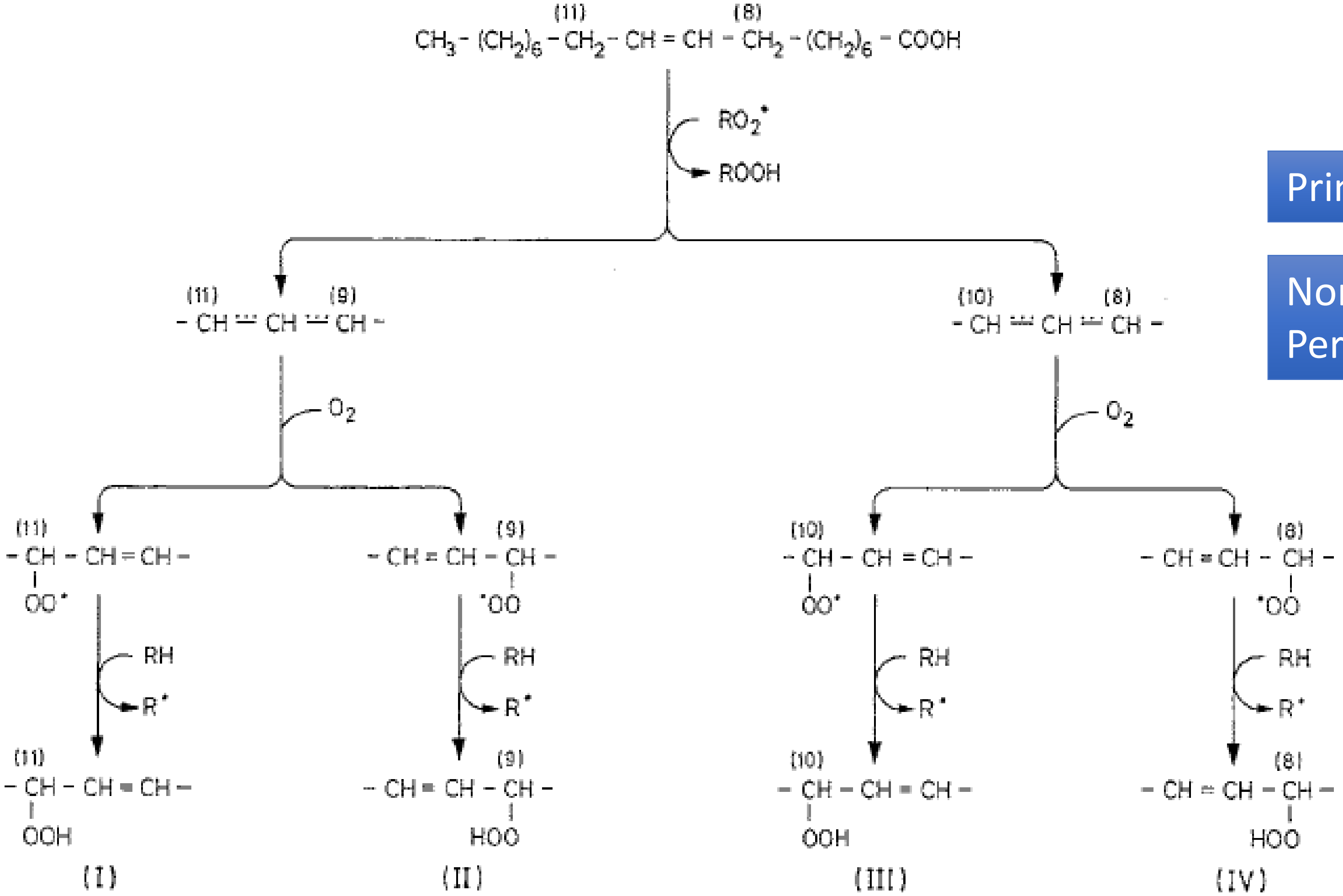
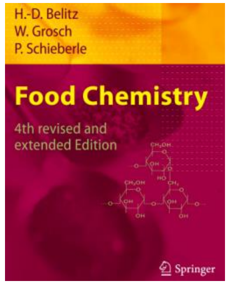


Fig. 3.20. Autoxidation of oleic acid. Primary reaction products: I 11-Hydroperoxyoctadec-9-enoic acid; II 9-hydroperoxyoctadec-10-enoic acid, III 10-hydroperoxyoctadec-8-enoic acid, IV 8-hydroperoxyoctadec-9-enoic acid

Primary products of lipid oxidation

Non volatile, relatively unstable
Peroxide value (mEq of O_2/kg)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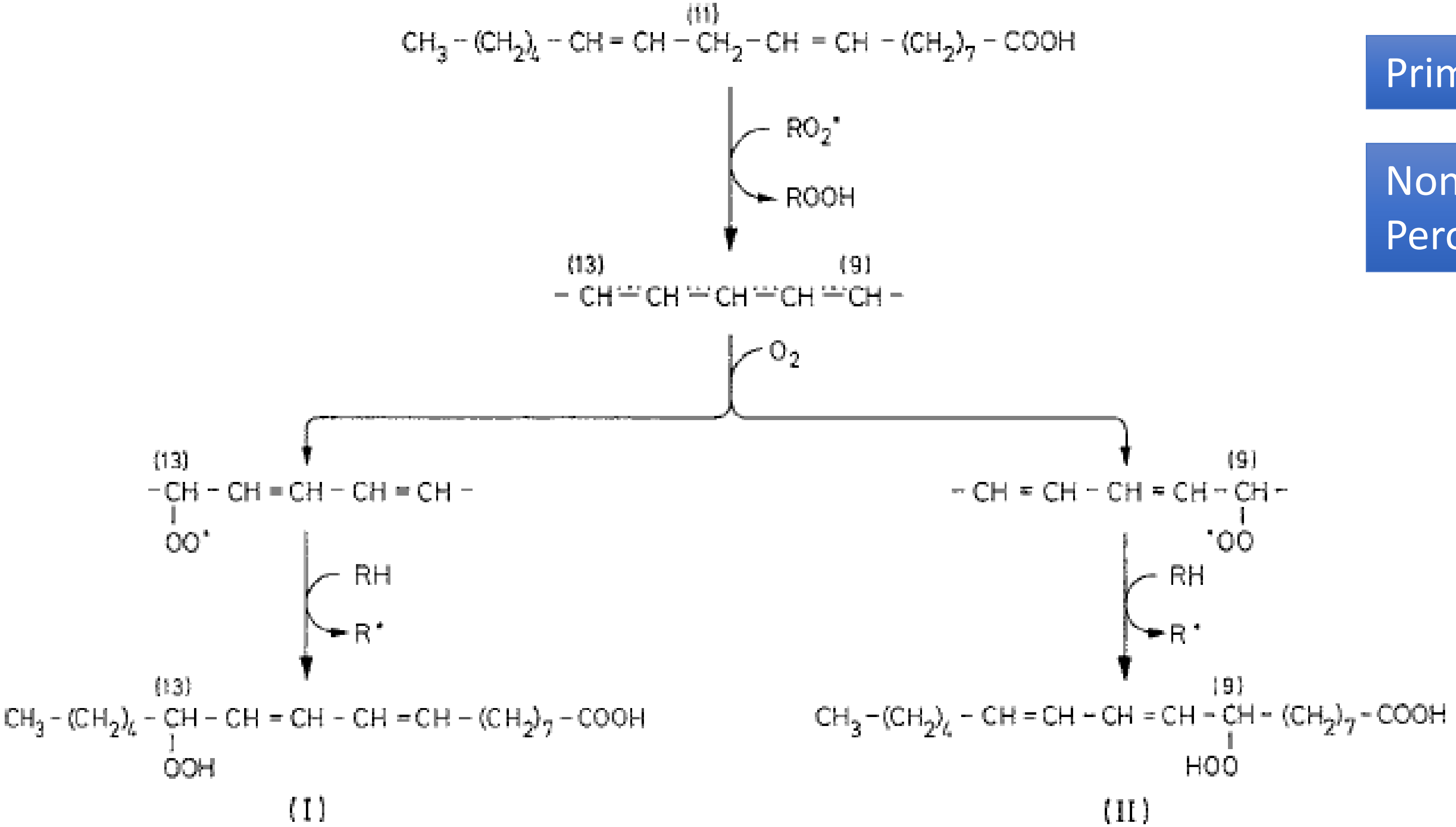
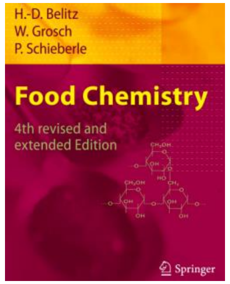


Fig. 3.21. Autoxidation of linoleic acid. Primary reaction products: I 13-Hydroperoxyoctadeca-9,11-dienoic acid, II 9-hydroperoxyoctadeca-10,12-dienoic acid

Primary products of lipid oxidation

Non volatile, relatively unstable
Peroxide value (mEq of O_2/kg)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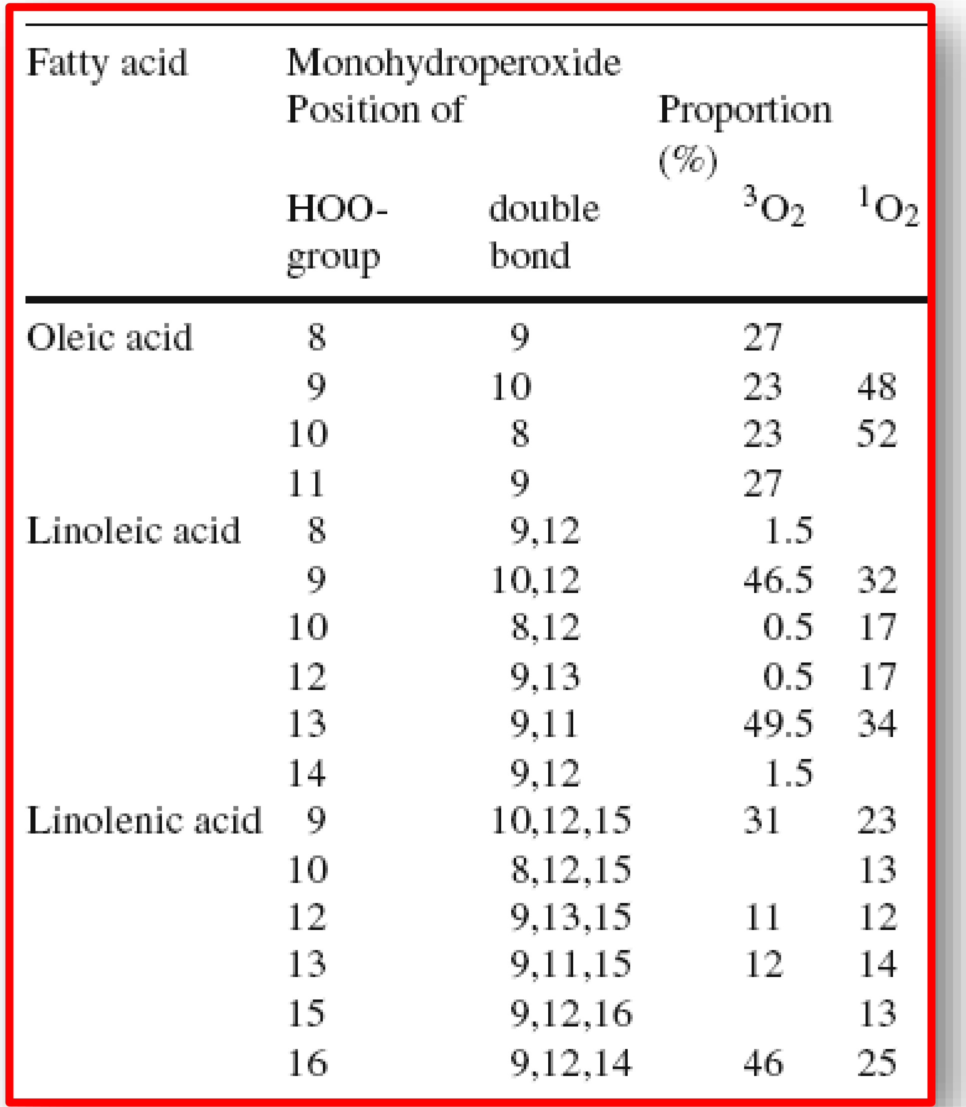
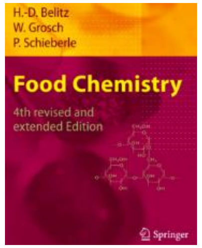
Reaction products yields **follows thermodynamic stability profiles.**
Double bonds position might change due to resonance equilibria.

At temperatures below 40°C *Z* (cis) isomers prevail over *E* (*trans*) while at higher temperatures the more stable *E* forms are more abundant.



Fatty acid	Monohydroperoxide Position of		Proportion (%)	
	HOO-group	double bond	$^3O_2$	$^1O_2$
Oleic acid	8	9	27	
	9	10	23	48
	10	8	23	52
	11	9	27	
Linoleic acid	8	9,12	1.5	
	9	10,12	46.5	32
	10	8,12	0.5	17
	12	9,13	0.5	17
	13	9,11	49.5	34
	14	9,12	1.5	
Linolenic acid	9	10,12,15	31	23
	10	8,12,15		13
	12	9,13,15	11	12
	13	9,11,15	12	14
	15	9,12,16		13
	16	9,12,14	46	25



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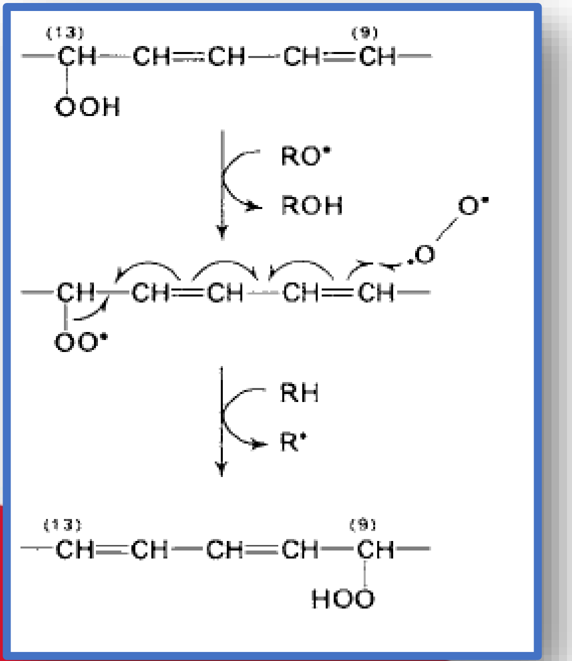
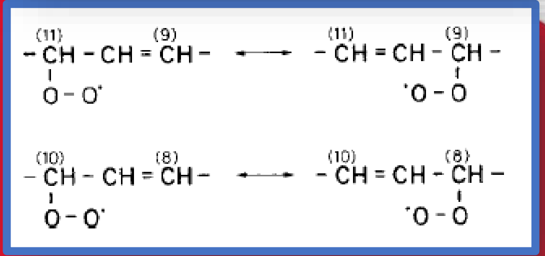
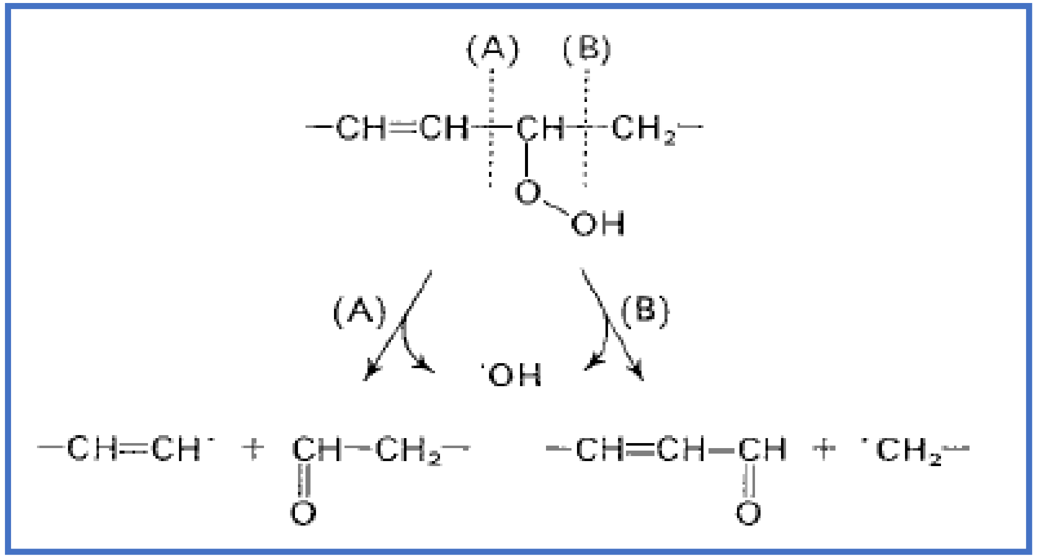


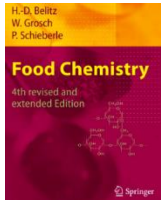


Fatty acids hydroperoxides undergo to various re-arrangements where hydroperoxyl group shifts through various positions along the alkyl-chain.

These re-arrangements contribute to the complexity of the primary products mixture -> secondary products will reflects this great "chemical dimensionality"

Primary products breakdown through different mechanisms

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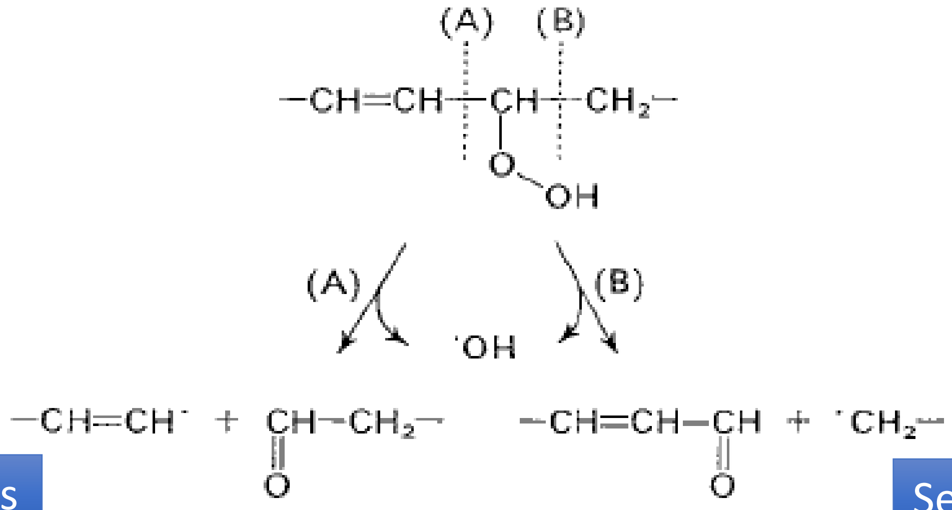
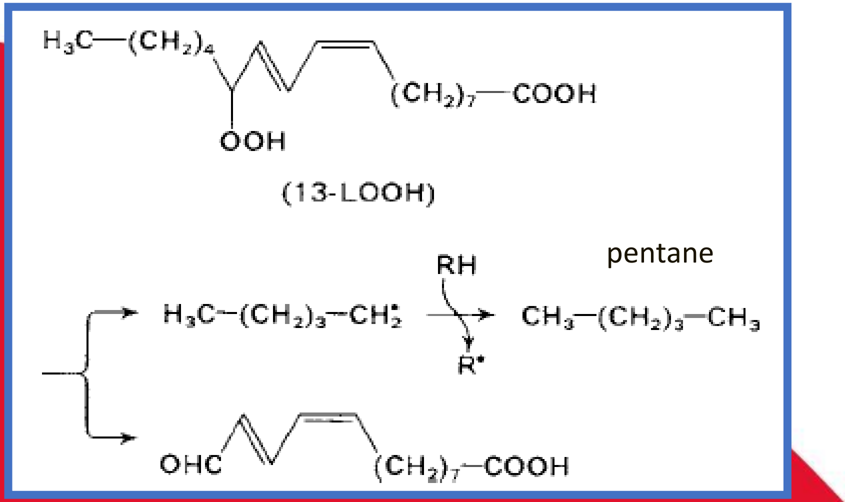
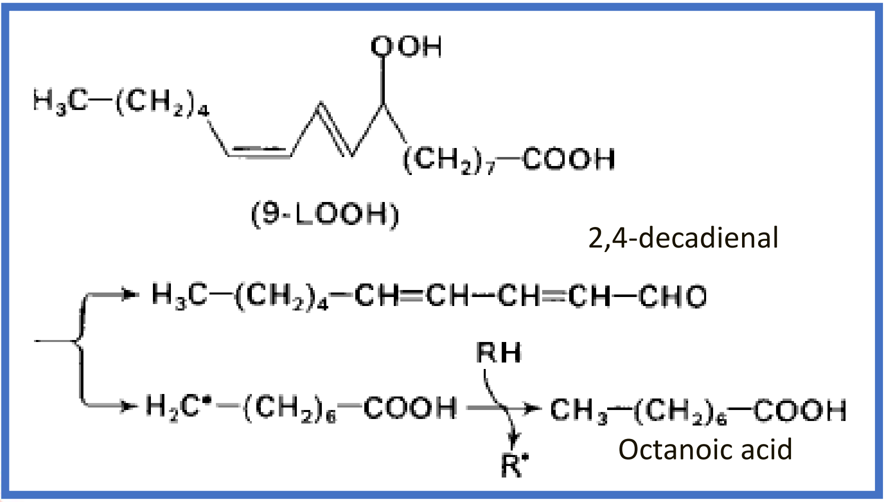


Secondary products



Secondary products



Secondary products

Fatty acids hydroperoxides are unstable, their breakdown occurs to form the so-called “secondary products” of lipid oxidation.

Various chemical classes are represented: hydrocarbons (saturated and unsaturated), aldehydes (saturated and unsaturated), ketones and carboxylic acids.

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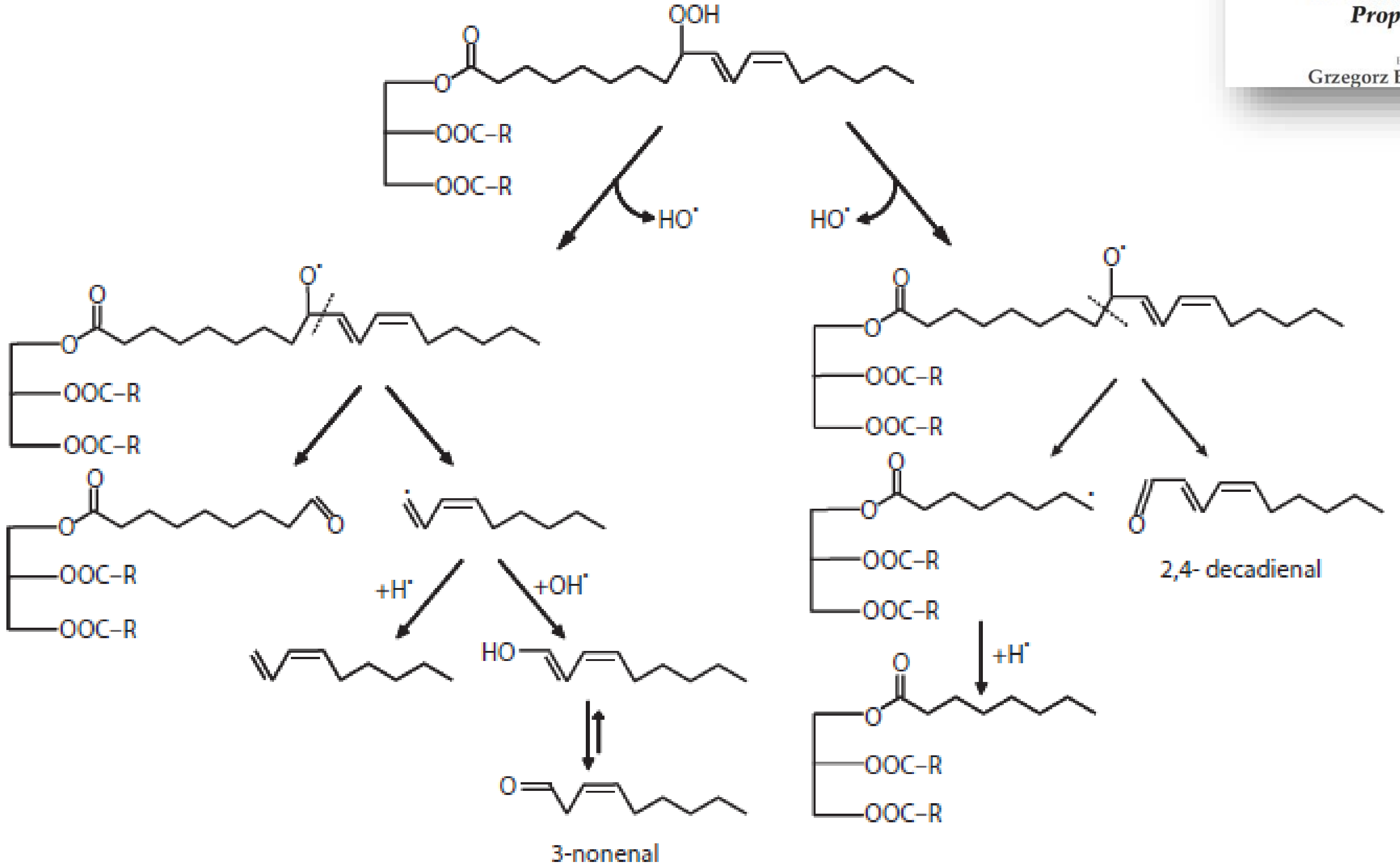

Reactions of β-scission of the diene 9-hydroperoxide in linoleyl acyl of TAGs involved in formation of volatile products.

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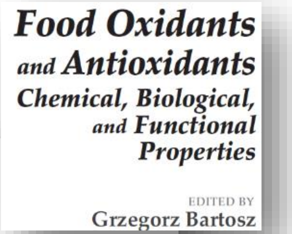

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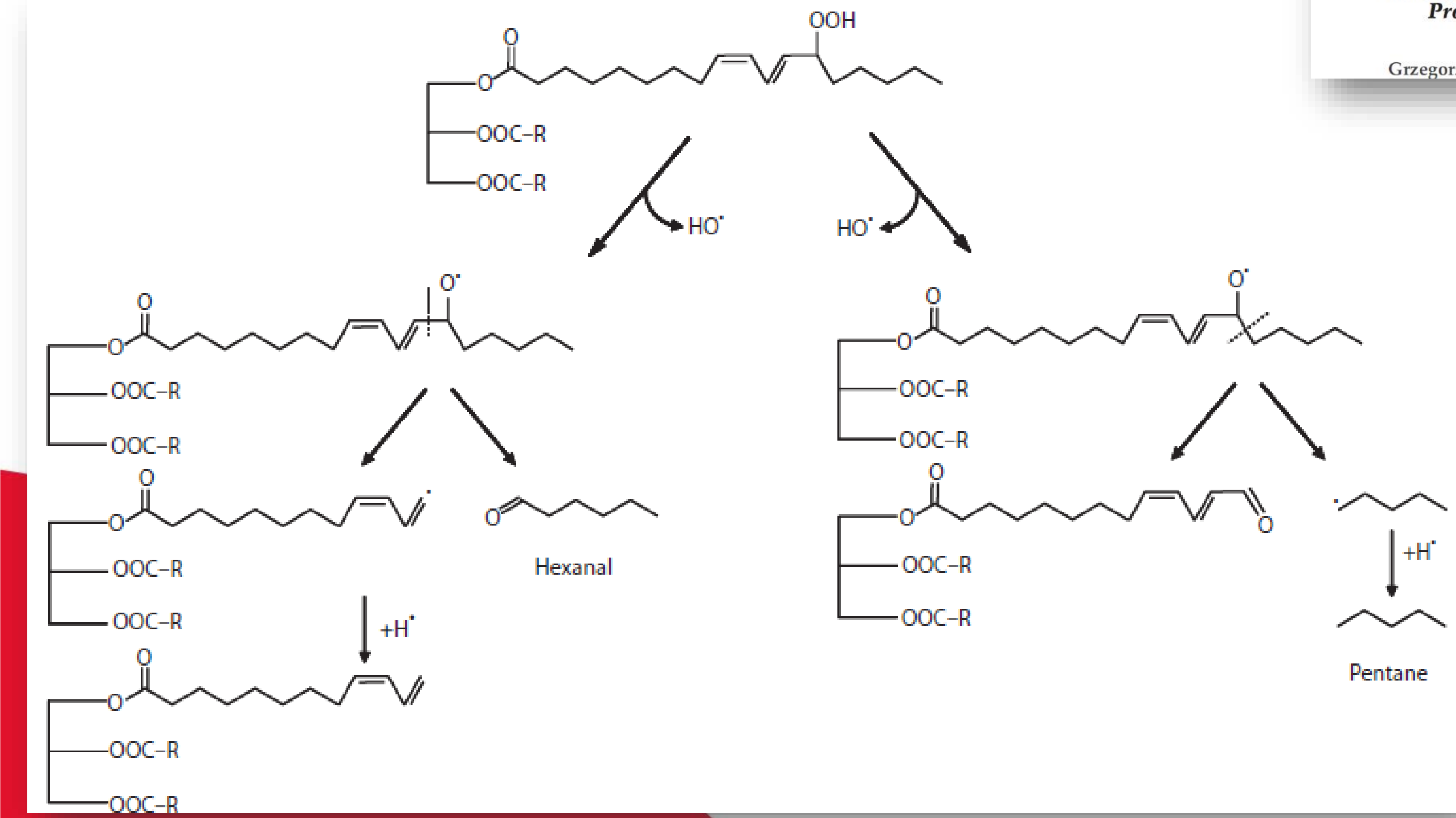

Reactions of β-scission of diene 13-hydroperoxide in linoleyl acyl of TAGs involved in formation of volatile products.

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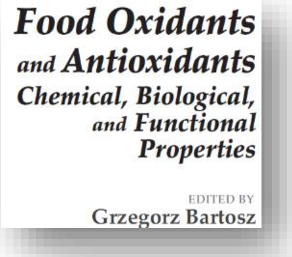

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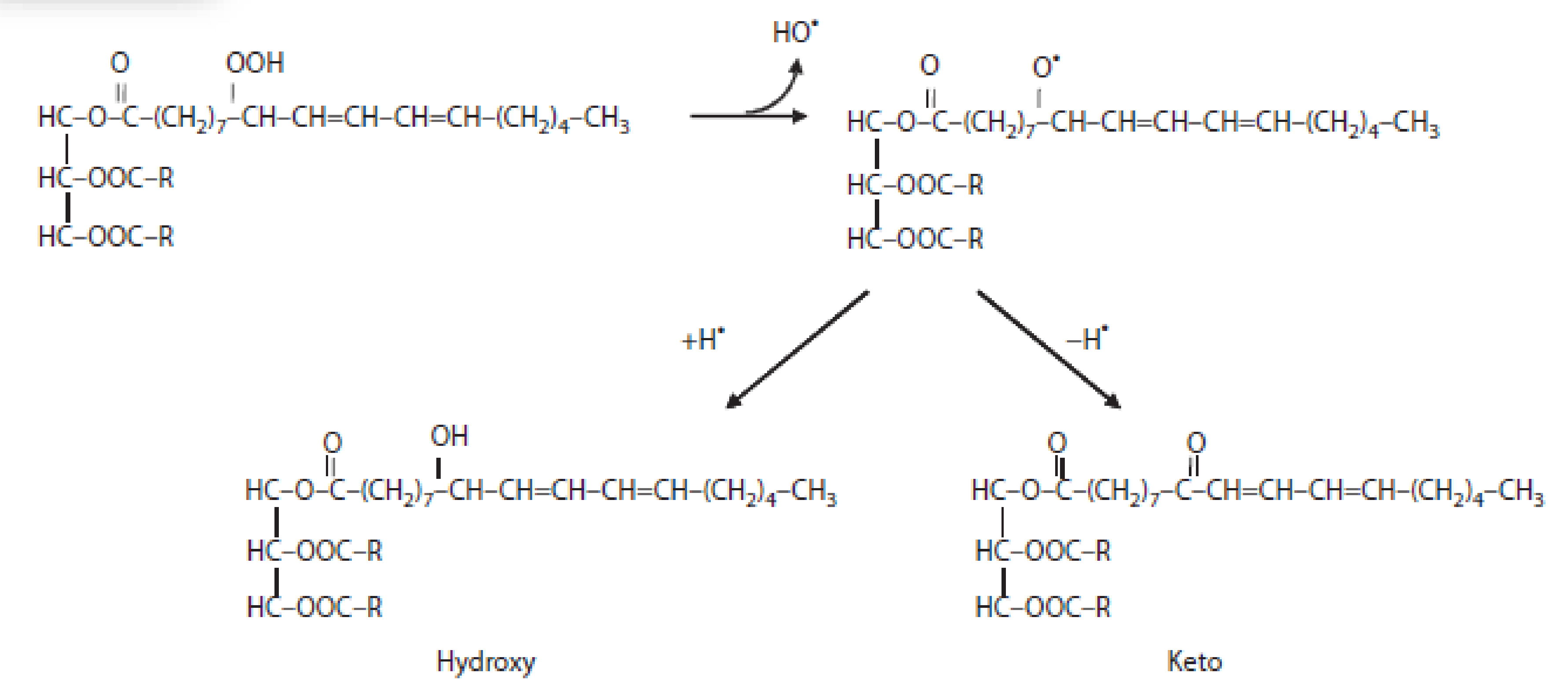

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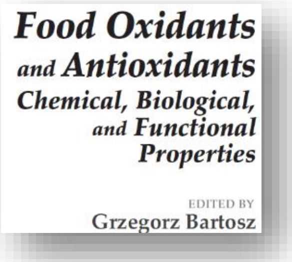

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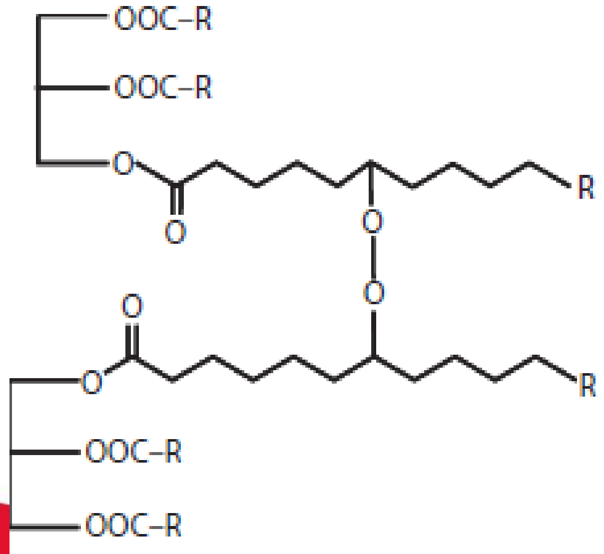
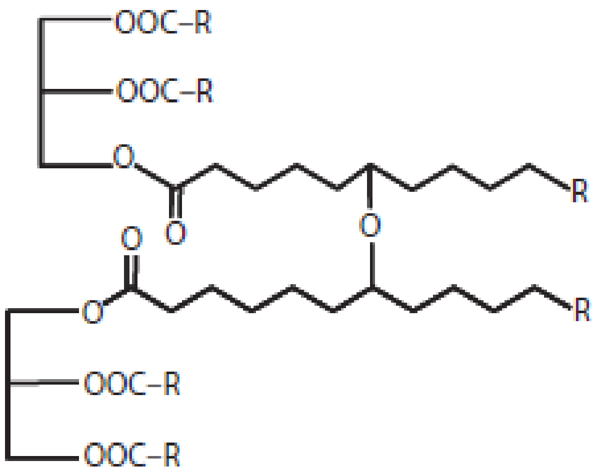
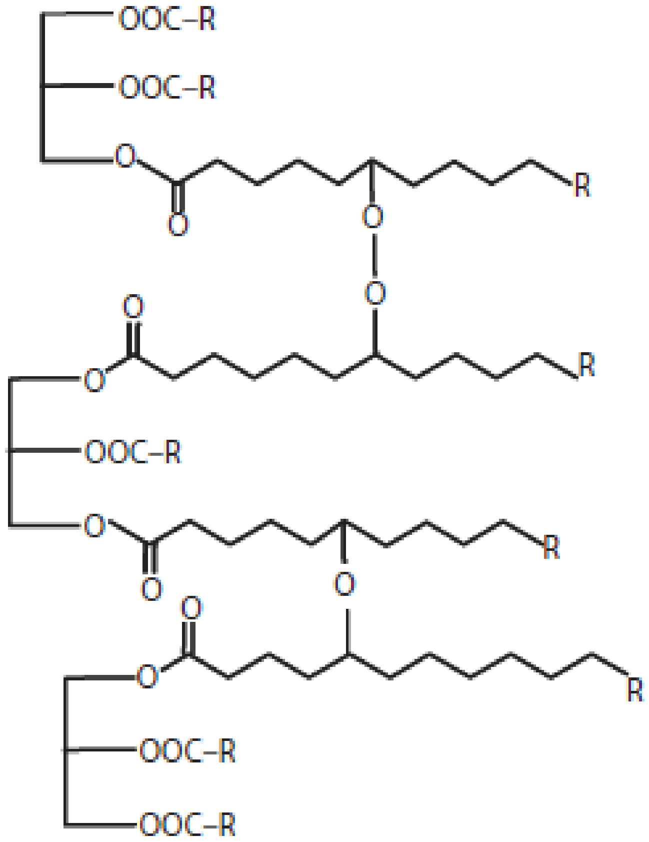


Peroxy-linked dimers



Ether-linked dimers



Oligomers

Representative structures of TAG dimers and oligomers linked by peroxide (C–O–O–C) or ether (C–O–C) linkages

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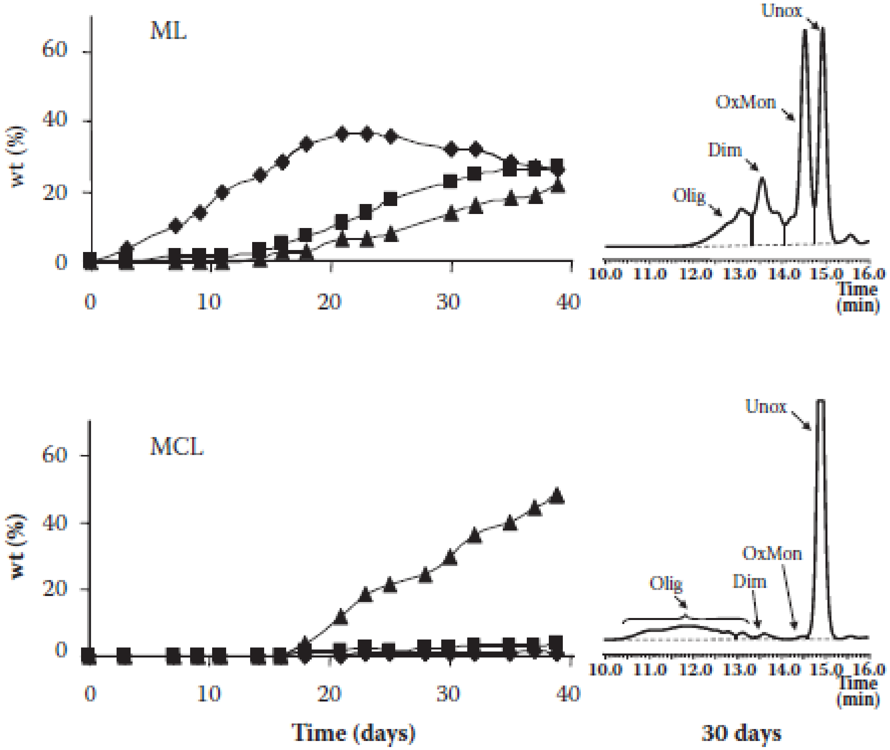
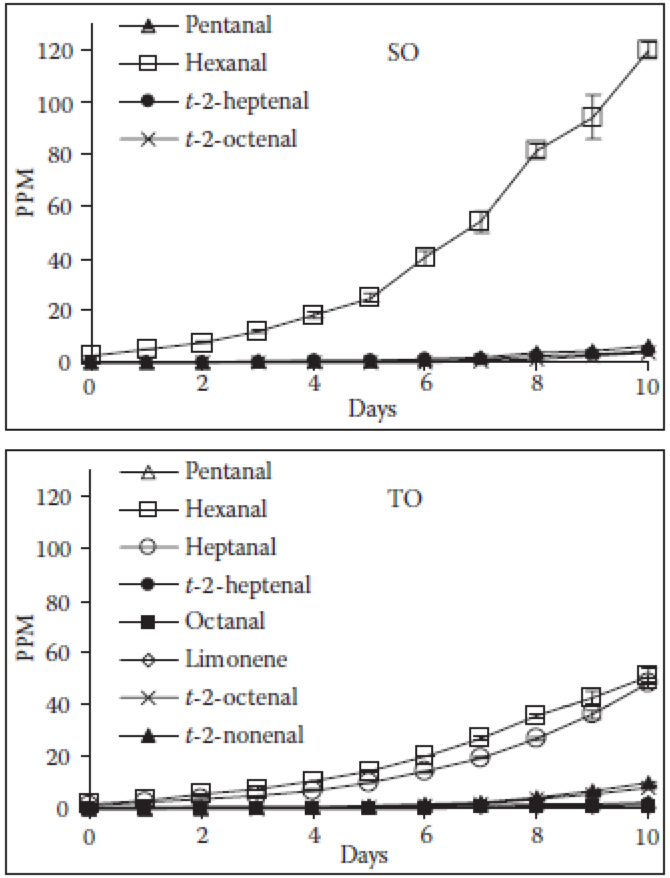
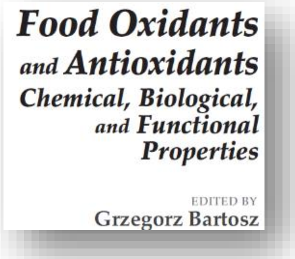


Time course of formation of oxidized monomers (♦), dimers (▪), and oligomers (▴) by HPSEC analysis in methyl linoleate (ML) and methyl conjugated linoleate (MCL) during oxidation at 30ºC.

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Time course of formation of main volatile compounds in SO (safflower oil) and TO (Tonalin™ oil) during oxidation at 30ºC.

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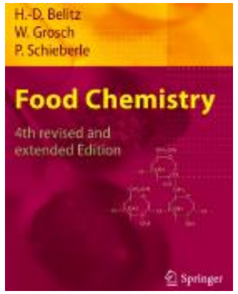

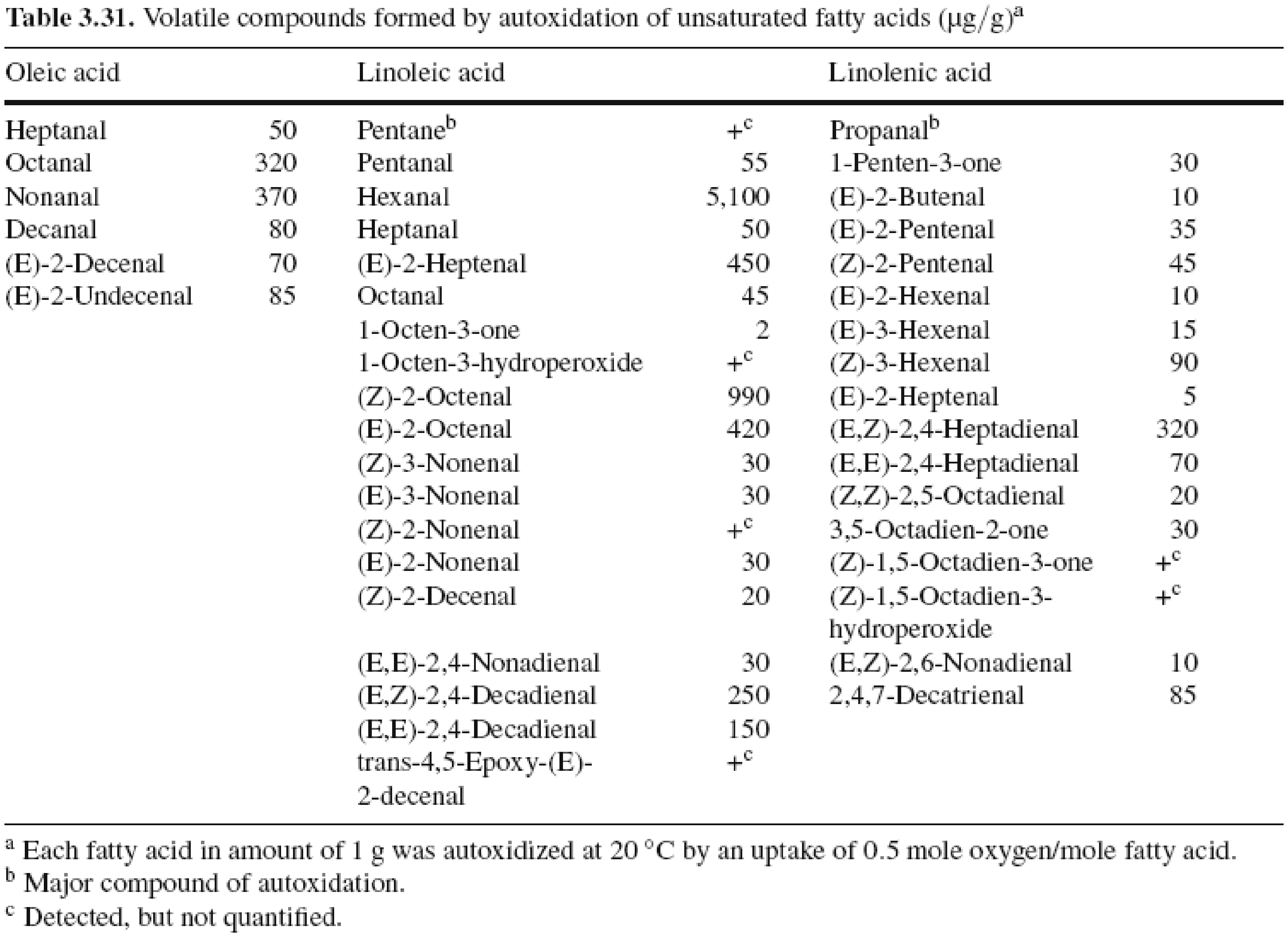

Table 3.31. Volatile compounds formed by autoxidation of unsaturated fatty acids (μg/g)[a]

Oleic acid		Linoleic acid		Linolenic acid	
Heptanal	50	Pentane[b]	+[c]	Propanal[b]	
Octanal	320	Pentanal	55	1-Penten-3-one	30
Nonanal	370	Hexanal	5,100	(E)-2-Butenal	10
Decanal	80	Heptanal	50	(E)-2-Pentenal	35
(E)-2-Decenal	70	(E)-2-Heptenal	450	(Z)-2-Pentenal	45
(E)-2-Undecenal	85	Octanal	45	(E)-2-Hexenal	10
		1-Octen-3-one	2	(E)-3-Hexenal	15
		1-Octen-3-hydroperoxide	+[c]	(Z)-3-Hexenal	90
		(Z)-2-Octenal	990	(E)-2-Heptenal	5
		(E)-2-Octenal	420	(E,Z)-2,4-Heptadienal	320
		(Z)-3-Nonenal	30	(E,E)-2,4-Heptadienal	70
		(E)-3-Nonenal	30	(Z,Z)-2,5-Octadienal	20
		(Z)-2-Nonenal	+[c]	3,5-Octadien-2-one	30
		(E)-2-Nonenal	30	(Z)-1,5-Octadien-3-one	+[c]
		(Z)-2-Decenal	20	(Z)-1,5-Octadien-3-hydroperoxide	+[c]
		(E,E)-2,4-Nonadienal	30	(E,Z)-2,6-Nonadienal	10
		(E,Z)-2,4-Decadienal	250	2,4,7-Decatrienal	85
		(E,E)-2,4-Decadienal	150		
		trans-4,5-Epoxy-(E)-2-decenal	+[c]		

---

[a] Each fatty acid in amount of 1 g was autoxidized at 20 °C by an uptake of 0.5 mole oxygen/mole fatty acid.
[b] Major compound of autoxidation.
[c] Detected, but not quantified.

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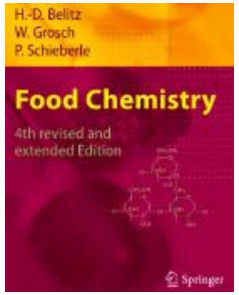
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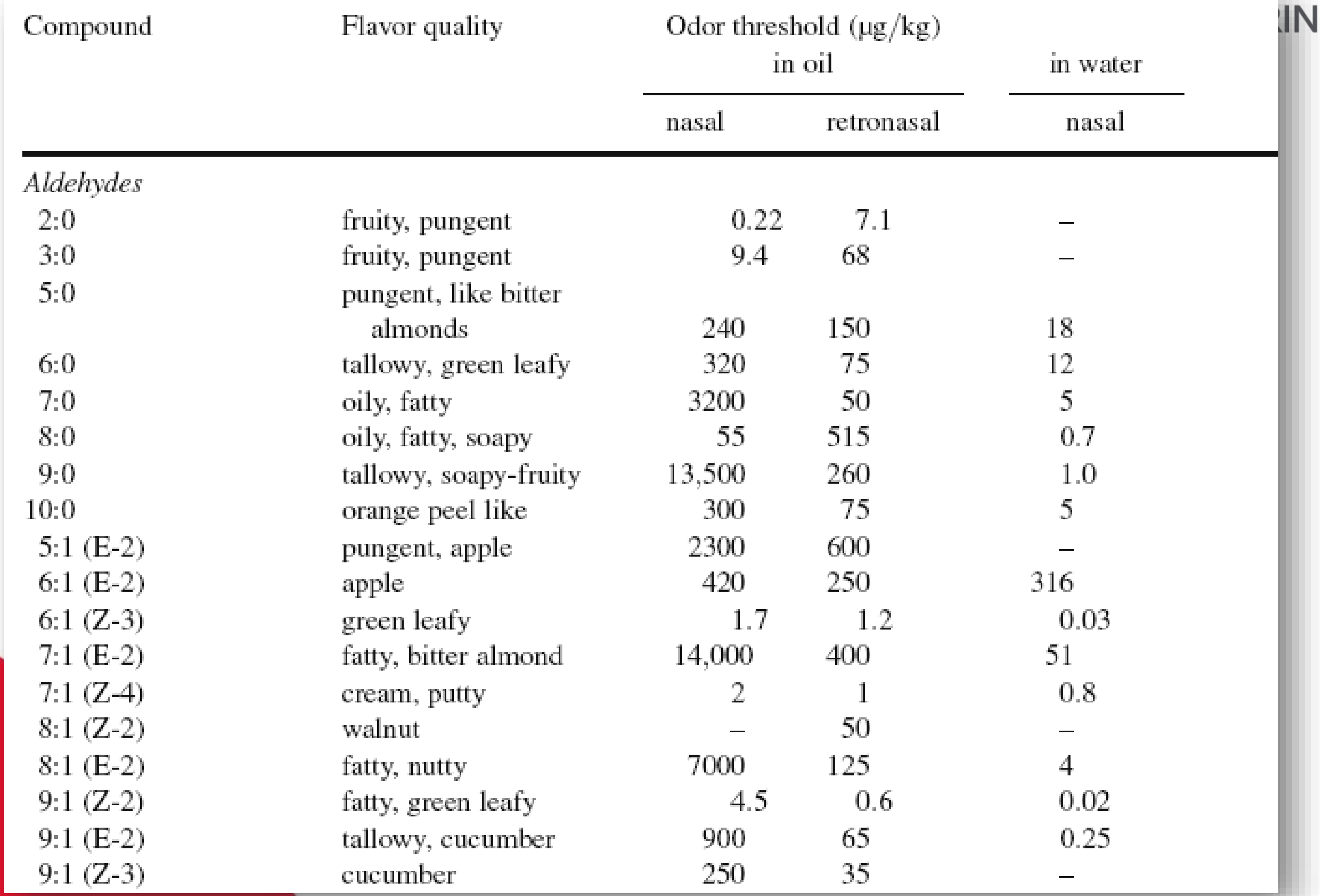

Compound	Flavor quality	Odor threshold (µg/kg) in oil		in water
		nasal	retronasal	nasal
Aldehydes				
2:0	fruity, pungent	0.22	7.1	–
3:0	fruity, pungent	9.4	68	–
5:0	pungent, like bitter almonds	240	150	18
6:0	tallowy, green leafy	320	75	12
7:0	oily, fatty	3200	50	5
8:0	oily, fatty, soapy	55	515	0.7
9:0	tallowy, soapy-fruity	13,500	260	1.0
10:0	orange peel like	300	75	5
5:1 (E-2)	pungent, apple	2300	600	–
6:1 (E-2)	apple	420	250	316
6:1 (Z-3)	green leafy	1.7	1.2	0.03
7:1 (E-2)	fatty, bitter almond	14,000	400	51
7:1 (Z-4)	cream, putty	2	1	0.8
8:1 (Z-2)	walnut	–	50	–
8:1 (E-2)	fatty, nutty	7000	125	4
9:1 (Z-2)	fatty, green leafy	4.5	0.6	0.02
9:1 (E-2)	tallowy, cucumber	900	65	0.25
9:1 (Z-3)	cucumber	250	35	–

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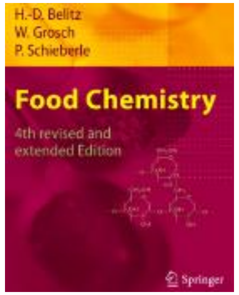
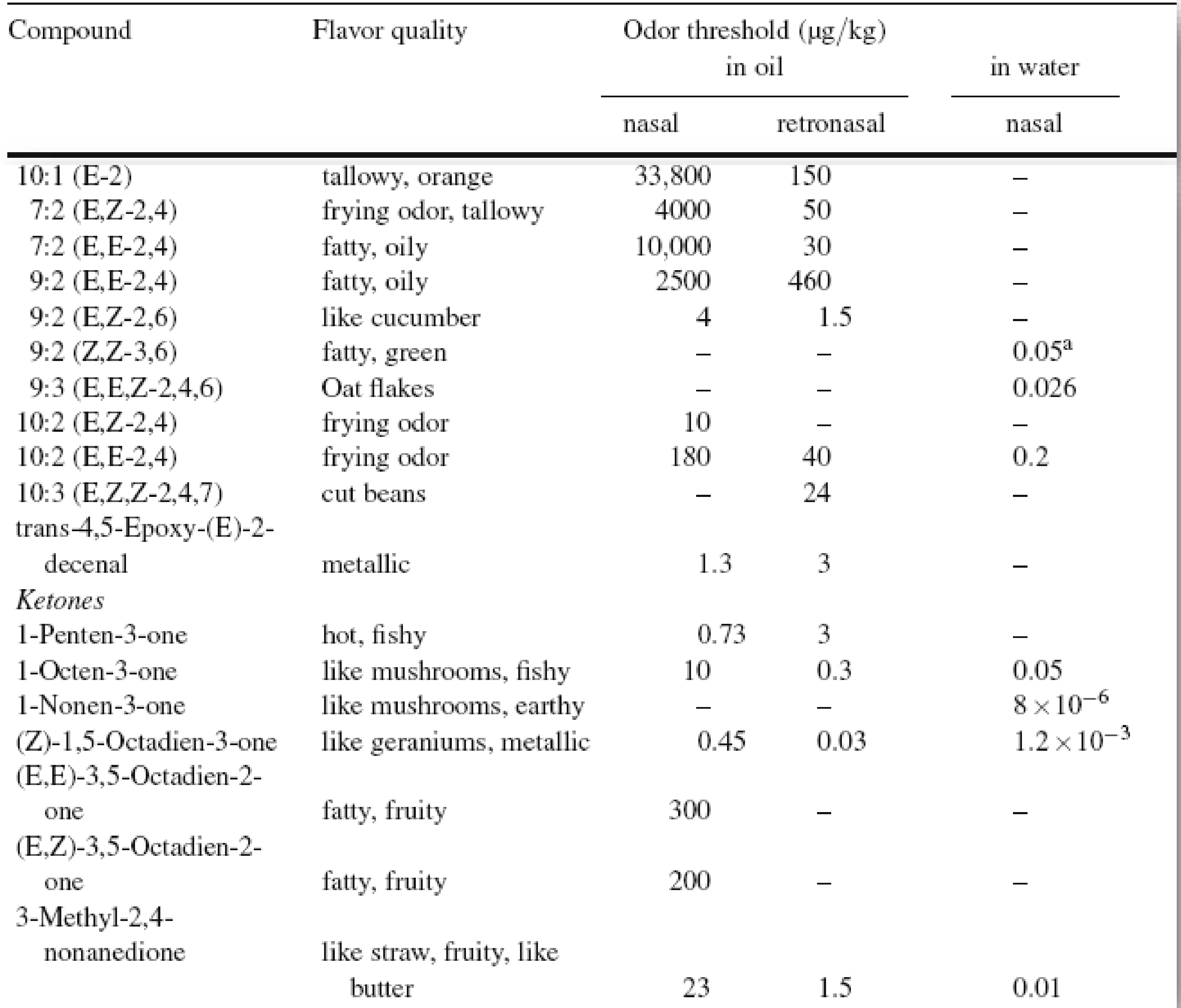
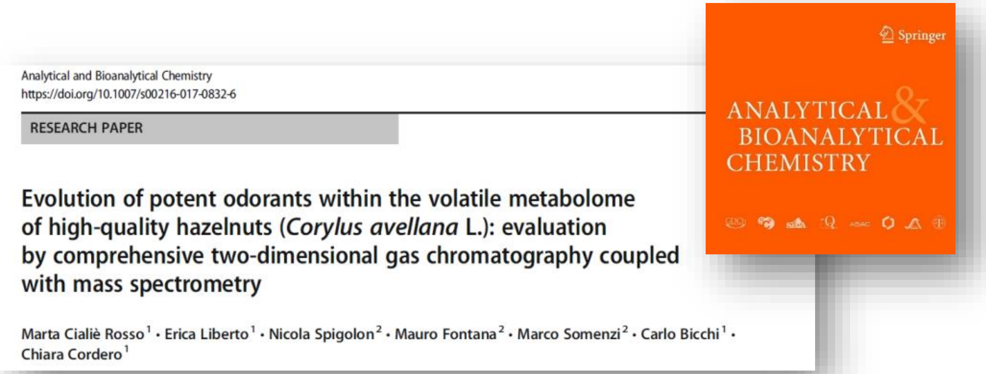




Compound	Flavor quality	Odor threshold (µg/kg)		
		in oil		in water
		nasal	retronasal	nasal
10:1 (E-2)	tallowy, orange	33,800	150	–
7:2 (E,Z-2,4)	frying odor, tallowy	4000	50	–
7:2 (E,E-2,4)	fatty, oily	10,000	30	–
9:2 (E,E-2,4)	fatty, oily	2500	460	–
9:2 (E,Z-2,6)	like cucumber	4	1.5	–
9:2 (Z,Z-3,6)	fatty, green	–	–	0.05^a
9:3 (E,E,Z-2,4,6)	Oat flakes	–	–	0.026
10:2 (E,Z-2,4)	frying odor	10	–	–
10:2 (E,E-2,4)	frying odor	180	40	0.2
10:3 (E,Z,Z-2,4,7)	cut beans	–	24	–
trans-4,5-Epoxy-(E)-2-decenal	metallic	1.3	3	–
Ketones				
1-Penten-3-one	hot, fishy	0.73	3	–
1-Octen-3-one	like mushrooms, fishy	10	0.3	0.05
1-Nonen-3-one	like mushrooms, earthy	–	–	8×10^{-6}
(Z)-1,5-Octadien-3-one	like geraniums, metallic	0.45	0.03	1.2×10^{-3}
(E,E)-3,5-Octadien-2-one	fatty, fruity	300	–	–
(E,Z)-3,5-Octadien-2-one	fatty, fruity	200	–	–
3-Methyl-2,4-nonanedione	like straw, fruity, like butter	23	1.5	0.01

Case Study



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RESEARCH PAPER

Evolution of potent odorants within the volatile metabolome of high-quality hazelnuts (*Corylus avellana* L.): evaluation by comprehensive two-dimensional gas chromatography coupled with mass spectrometry

Marta Cialiè Rosso[1] • Erica Liberto[1] • Nicola Spigolon[2] • Mauro Fontana[2] • Marco Somenzi[2] • Carlo Bicchi[1] • Chiara Cordero[1]

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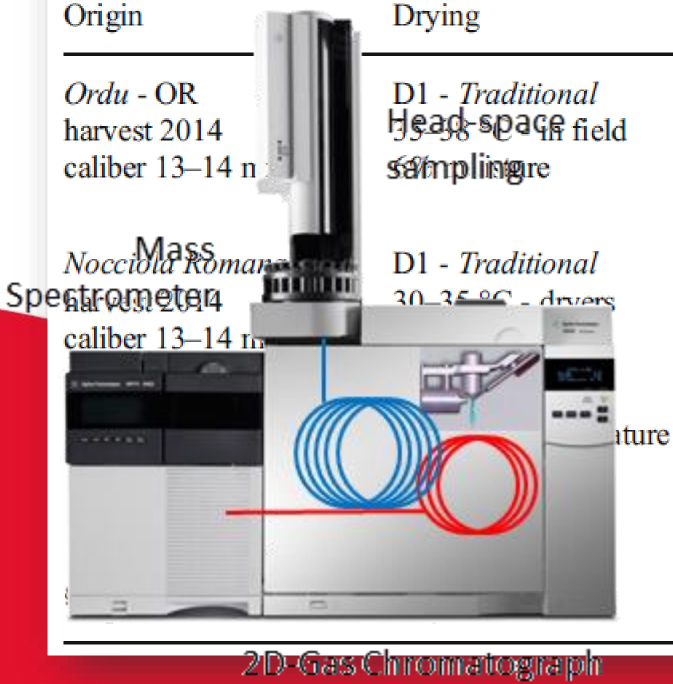
Profiling and Fingerprinting

Accurate comparative analysis

Single analyte information

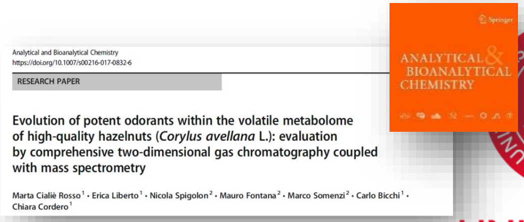
Origin	Drying	Storage	Temperature	Timing
Ordu - OR harvest 2014 caliber 13–14 m	D1 - *Traditional* 35–38 °C - in field	NA - Normal atmosphere (78% N_2–21% O_2 65% of ERH§)	5 (±0.1)°C 18 (±0.1)°C	(T) 4-9-12 months
		MA - Modified atmosphere (99% N_2–1% O_2 65% of ERH§)	5 (±0.1)°C	
Nocciola Romana harvest 2014 caliber 13–14 m	D1 - *Traditional* 30–35 °C - dryers	NA - Normal atmosphere (78% N_2–21% O_2 65% of ERH§)	5 (±0.1)°C 18 (±0.1)°C	
		MA - Modified atmosphere (99% N_2–1% O_2 65% of ERH§)	5 (±0.1)°C	
	ature	NA - Normal atmosphere (78% N_2–21% O_2 65% of ERH§)	5 (±0.1)°C 18 (±0.1) °C	
		MA - Modified atmosphere (99% N_2–1% O_2 65% of ERH§)	5 (±0.1)°C	



- ✓ Origin - botanical / geographical
- ✓ Post-harvest drying (traditional in field, traditional under controlled conditions and at low temperature)
- ✓ Storage 0-12 months at different conditions: normal or modified atmosphere, 5 and 18°C

Volatiles formed by lipid oxidation and enzymatic activity (endogenous or exogenous - bacteria, moulds)

Case Study



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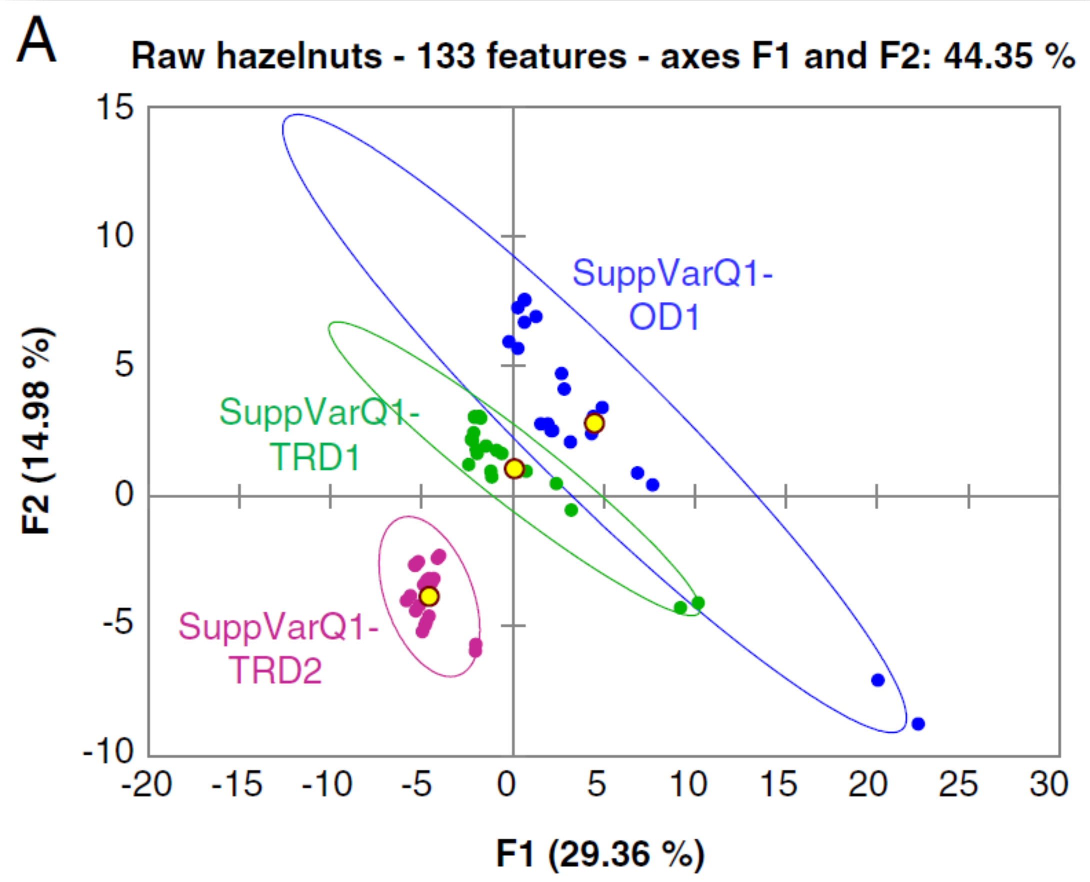
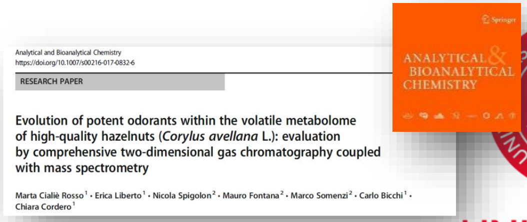


133 volatiles belonging to different chemical classes and formation pahways enable a clear clusterization of samples according to origin and post-harves treatment

<u>Fisher ratio</u> (F), driven by post-harvest drying (**<u>D1 vs. D2</u>**). Fisher critical value at the 95% of confidence level (α = 0.05 Fcrit) for the data matrix dimensions was 2.16.
The results indicate the **most informing variables** with a F value between 202 and 22, as being a <u>series of linear and branched alcohols</u> (2-heptanol, 2-methyl-1-propanol, 3-methyl-1-butanol, 2-ethyl-1-hexanol, benzyl alcohol), <u>esters</u> (ethyl acetate, butyl butanoate, 2-methyl-butyl propanoate) and <u>acetic acid</u>.

Case Study



Analytical and Bioanalytical Chemistry
https://doi.org/10.1007/s00216-017-0832-6

RESEARCH PAPER

Evolution of potent odorants within the volatile metabolome of high-quality hazelnuts (*Corylus avellana* L.): evaluation by comprehensive two-dimensional gas chromatography coupled with mass spectrometry

Marta Cialiè Rosso[1] · Erica Liberto[1] · Nicola Spigolon[2] · Mauro Fontana[2] · Marco Somenzi[2] · Carlo Bicchi[1] · Chiara Cordero[1]

UNIVERSITÀ DI TORINO

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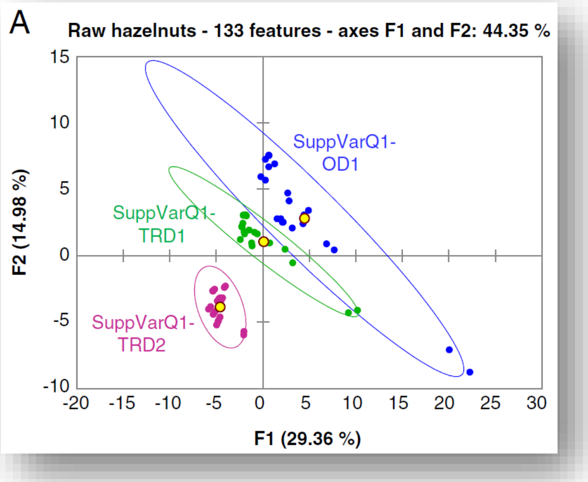
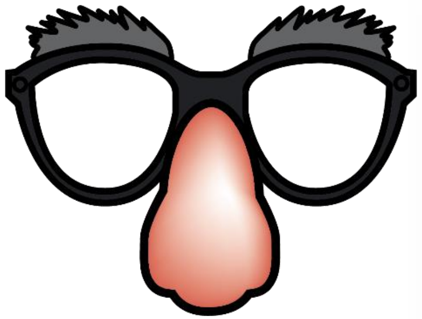
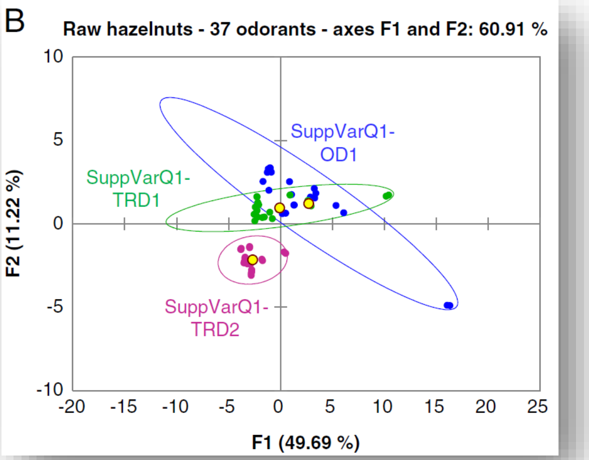


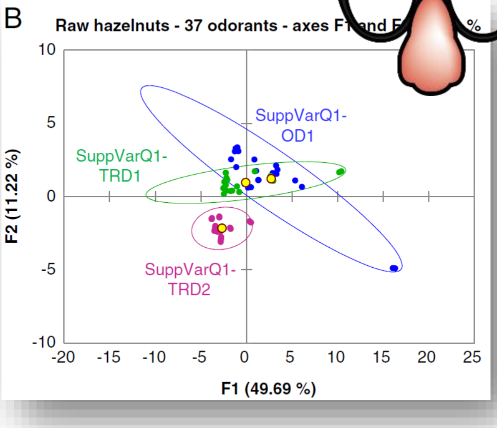
Most of the informative compounds have been correlated with nut **ripening** and/or **fermentation processes** occurring in vegetables. For instance, 3-methyl-1-butanol (i.e., isoamyl alcohol) is a fermentation product in grapes and wines, where it is formed from L-leucine, and 2-methyl-1-propanol has L-valine as precursor.
2-Heptanol is formed during tomato ripening, from β-ketoacids hydrolysis and subsequent decarboxylation, while 2-ethyl-1-hexanol has been found in fermented soybean foods.





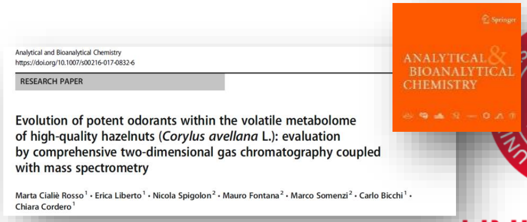
The **most potent odorants** (OT values up to 2500 µg/L) correlated closely (> 0.800) with storage time were: 1-heptanol (*green*, *chemical*), 2-octanol (*metal*, *burnt*), 1-octen-3-ol (*mushroom*), (E)-2-heptenal (*fatty*, *almond*), hexanal (*leaf-like, green*), heptanal (*fatty*), octanal (*fatty*) and nonanal (*tallowy*, *fruity*).

Case Study



Eight-carbon-atom alcohols, 2-octanol and 1-octen-3-ol, are known products of linoleic acid cleavage, which are generally promoted by fungal lipoxygenase/hydroperoxide liase enzymes.

With the exception of 1-octen-3-ol, which was not detected in Tonda Romana hazelnuts and was below the LOD in TR D2 samples, the increasing trend of these alcohols was quite informative, and might be correlated to the occurrence of off-odors related to *metallic* and *mushroom-like* notes.



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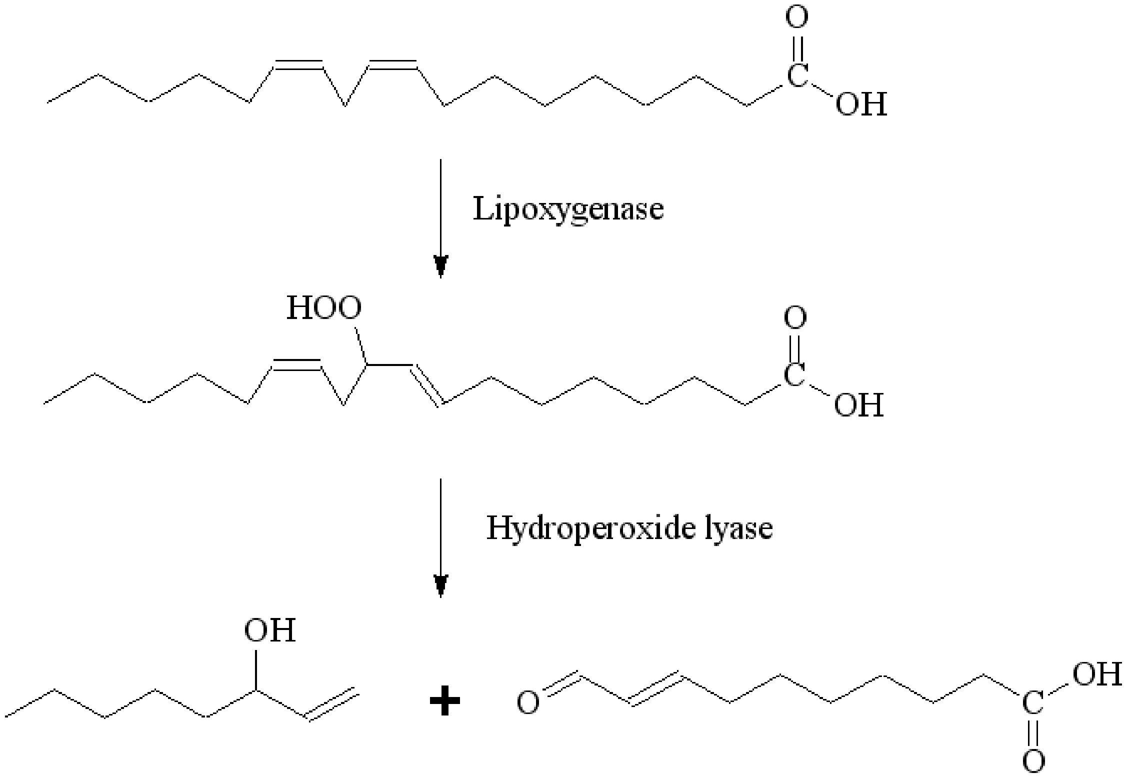
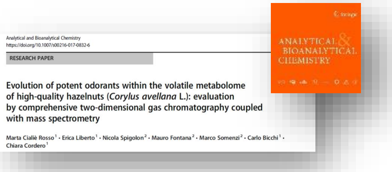


Case Study



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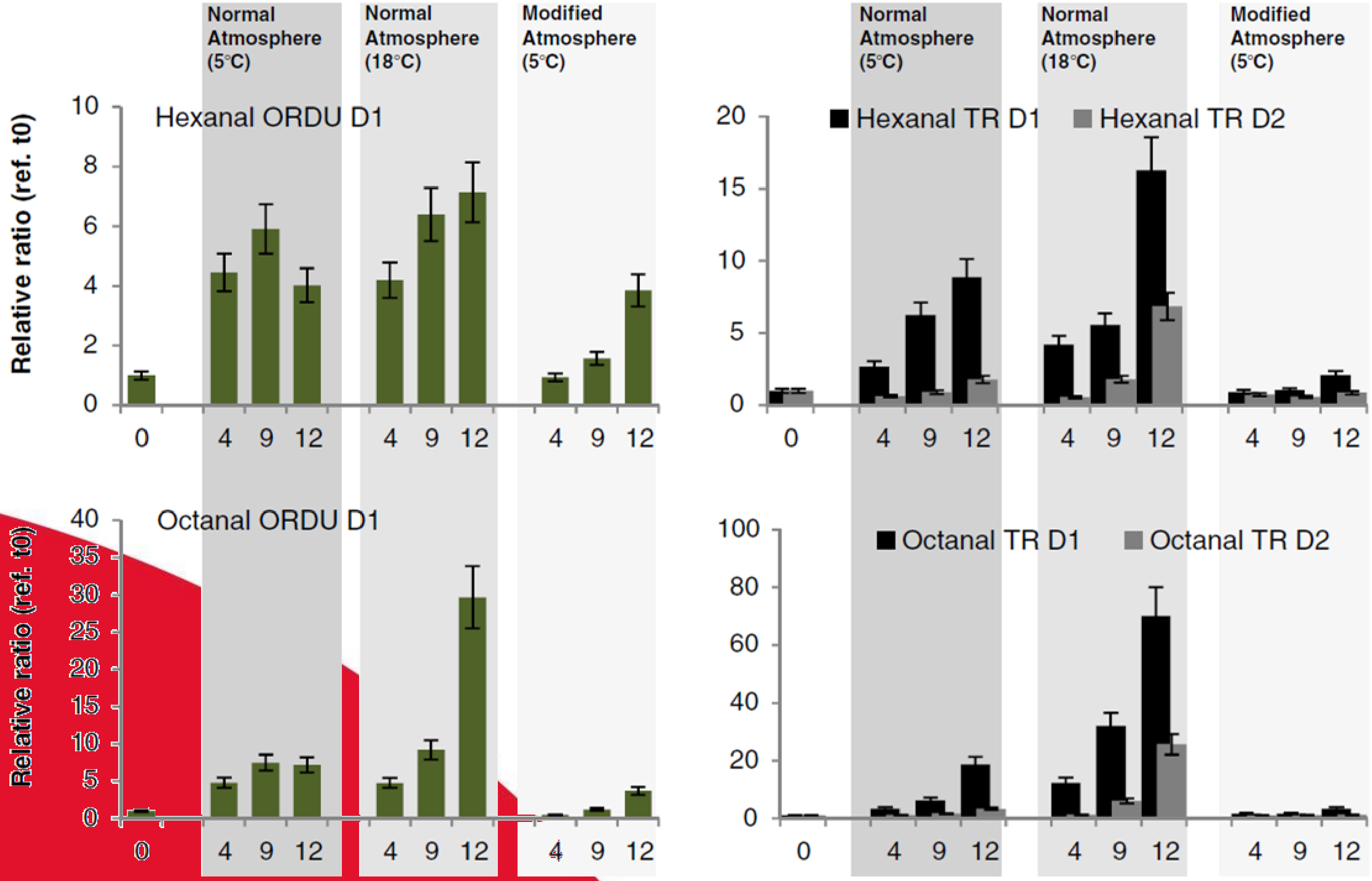
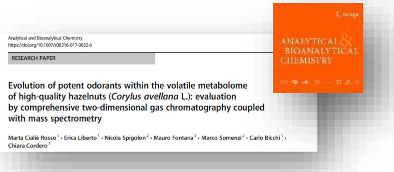


leaf-like, green

fatty

Case Study



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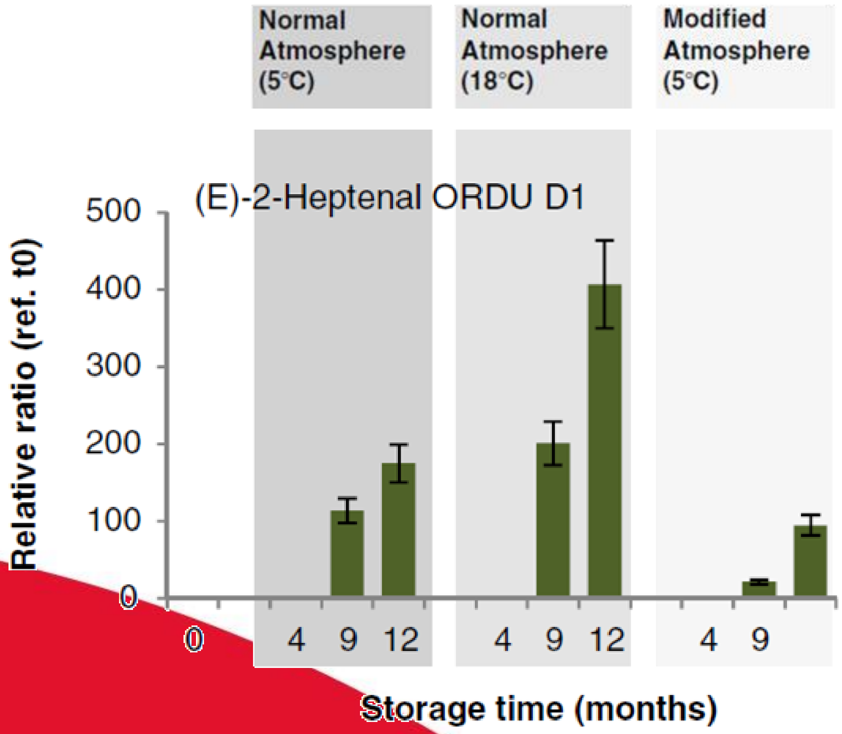
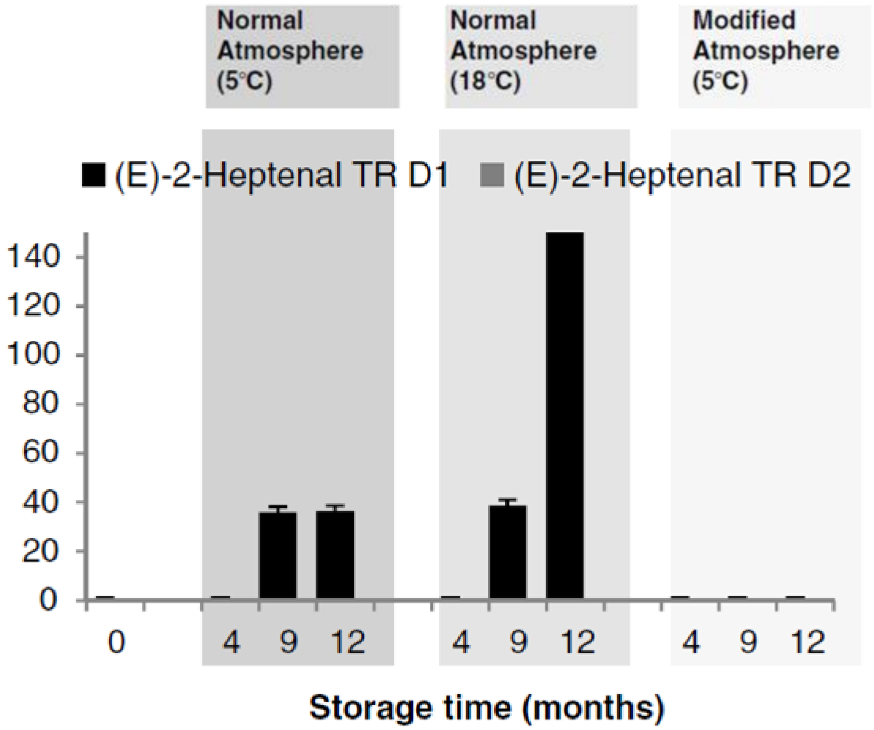
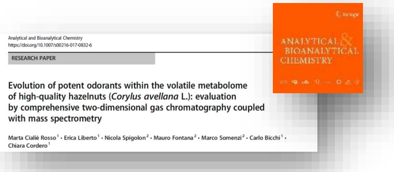
fatty, almond





Case Study



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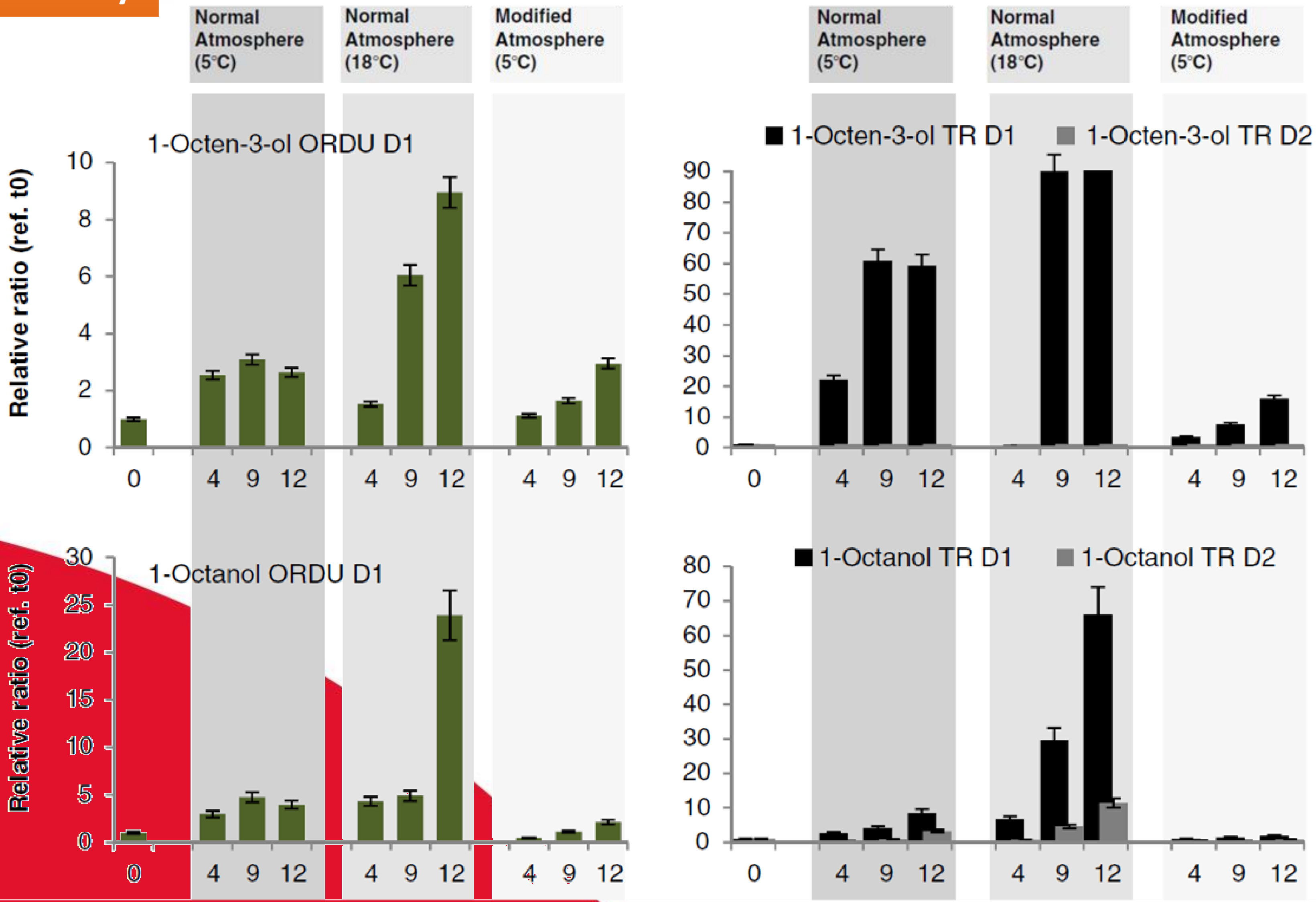


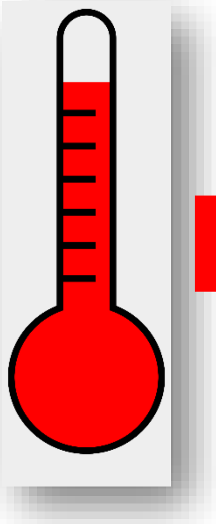
mushroom

metal, mushroom

Reactions on fats: deep frying and thermoxidation

High-temperatures Thermoxidation

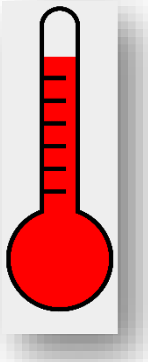
The chemistry of lipid oxidation at the high temperatures of food processes such as baking and frying is highly complex because both oxidative and thermal reactions are involved simultaneously.



At **low or moderate temperatures**, formation of oxidation compounds during the induction period is slow; hydroperoxides are the major compounds formed, and their concentration increases until advanced stages of oxidation.
Polymerization compounds only become significant in the accelerated stage of oxidation after the end of the induction period.

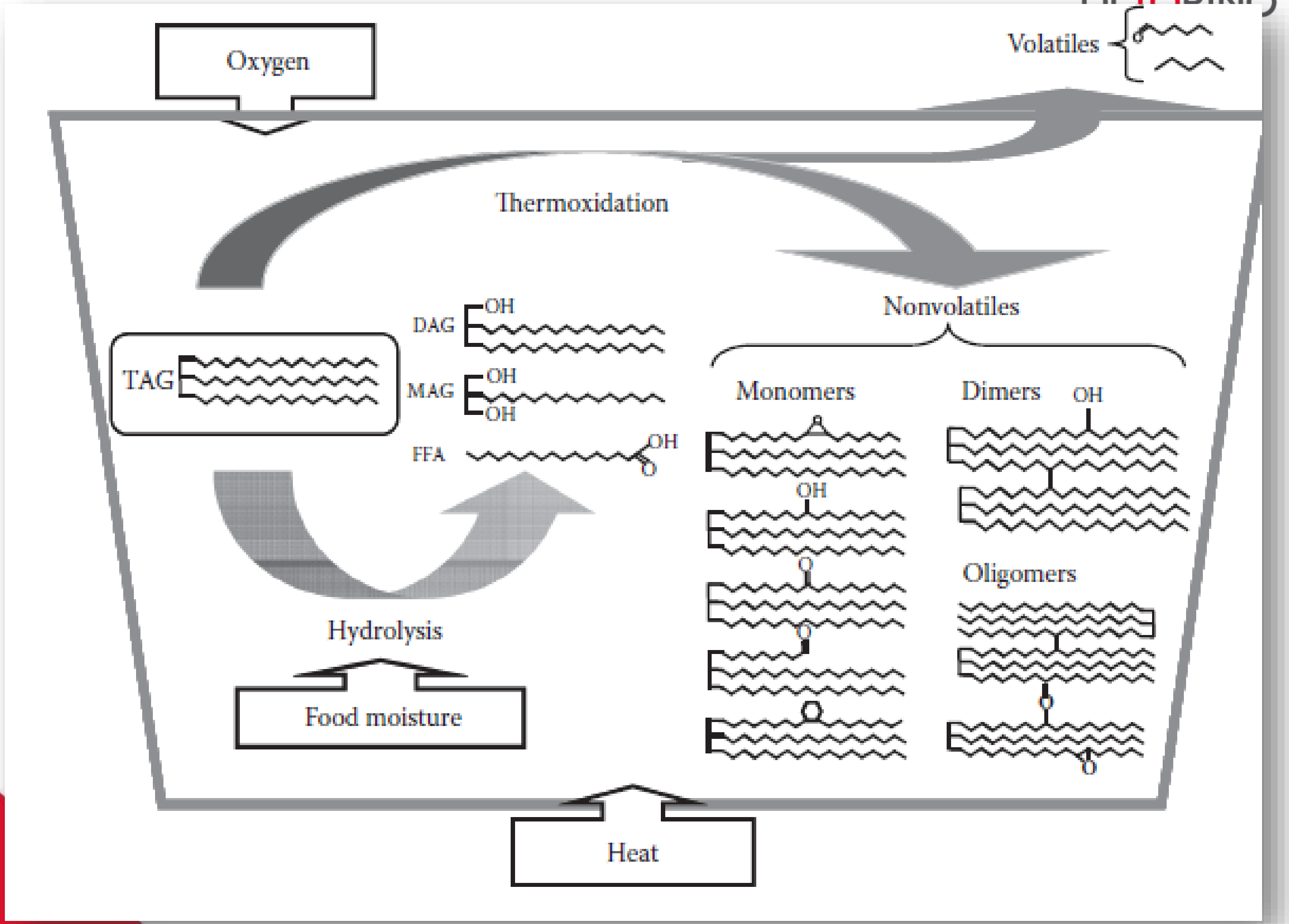
At **high temperatures**, formation of new compounds is very rapid; the oxygen pressure is reduced, and consequently, the initiation reaction becomes more important and gives rise to an increase in the concentration of alkyl radicals (R•) with respect to alkylperoxyl radicals (ROO•). Hydroperoxides decompose rapidly and are practically absent above 150ºC, indicating that decomposition of hydroperoxides becomes faster than formation. As a result, polymeric compounds form from the very early stages of heating through termination reactions that mainly involve alkyl (R•) and alkoxyl (RO•) radicals. In addition, because of the low oxygen concentration, significant amounts of nonpolar TG dimers (C-C linkages) are also produced.

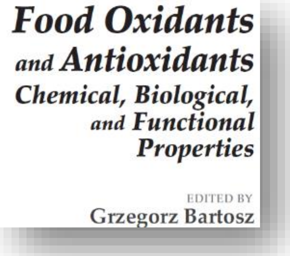
Reactions on fats: deep frying and thermoxidation



Schematic representation of main groups of alteration compounds formed during frying.

Abbreviations: TAG, triacylglycerols; DAG, diacylglycerols; MAG, monoacylglycerols; and FFA, free fatty acids.




Food Oxidants and Antioxidants
Chemical, Biological, and Functional Properties
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Reactions on fats: formation of oxysterols

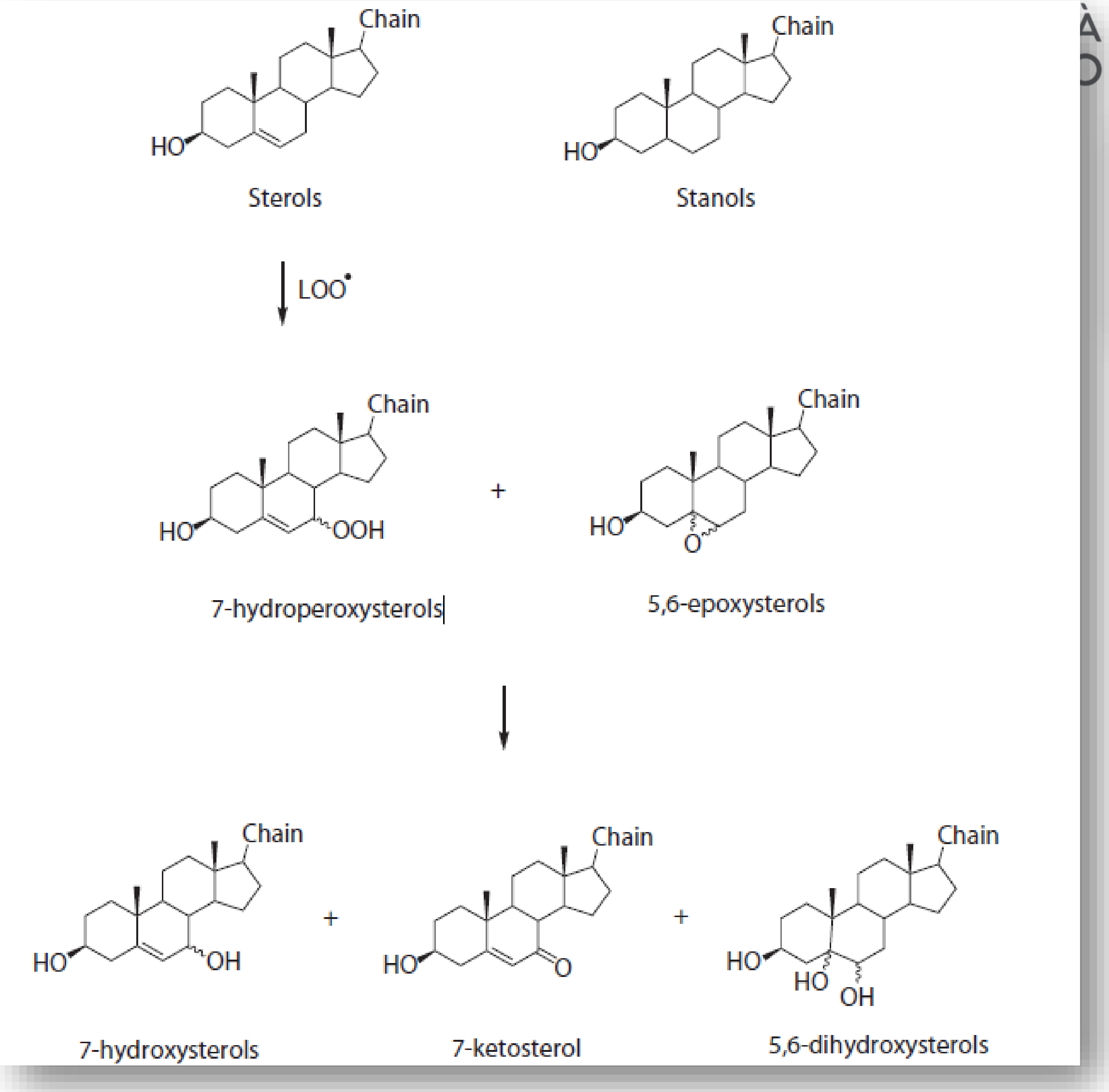
U2

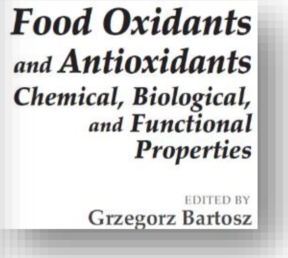
Oxysterols

Sterols are susceptible to oxidation. Common steroid (ring) oxidation products are hydroxyl-, keto-, epoxy-, and dihydroxy-derivative.

Side-chain oxidation is believed to be mainly a result of enzymatic reactions.

Accumulating experimental evidence suggests that autoxidation of sterols follows a free-radical mechanism.
The major primary autoxidation products of cholesterol are 5,6-epoxysterols and 7-hydroperoxysterols, which are lately converted into 5,6-dihydroxysterols, 7-hydroxysterols, and 7-ketosterol.

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Reactions on fats: formation of oxysterols

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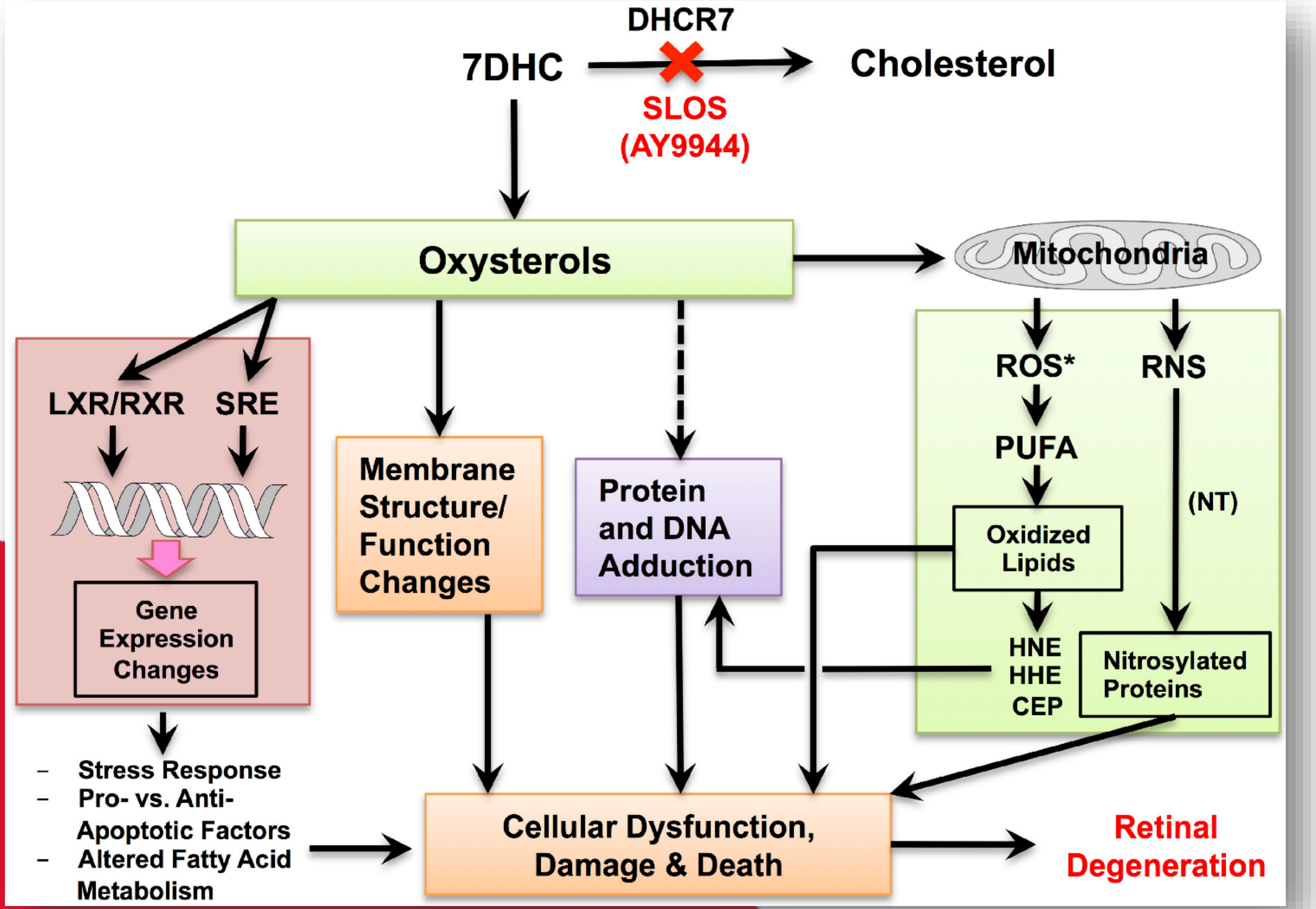
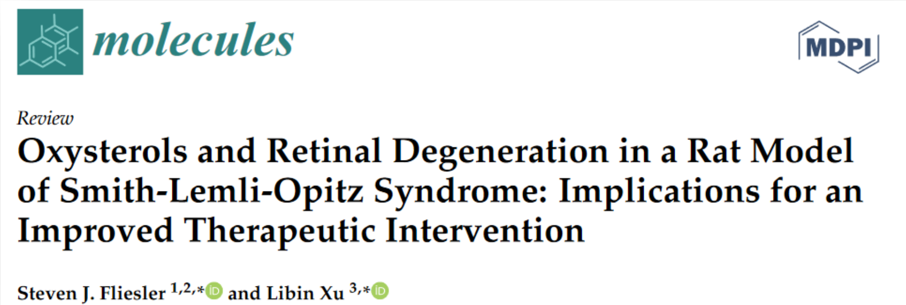
Oxysterols


DHCR7
7DHC
Cholesterol
SLOS
(AY9944)
Oxysterols
Mitochondria
LXR/RXR
SRE
Gene Expression Changes
Membrane Structure/ Function Changes
Protein and DNA Adduction
ROS*
RNS
PUFA
Oxidized Lipids
(NT)
HNE
HHE
CEP
Nitrosylated Proteins

- Stress Response
- Pro- vs. Anti-Apoptotic Factors
- Altered Fatty Acid Metabolism

Cellular Dysfunction, Damage & Death
Retinal Degeneration


molecules MDPI

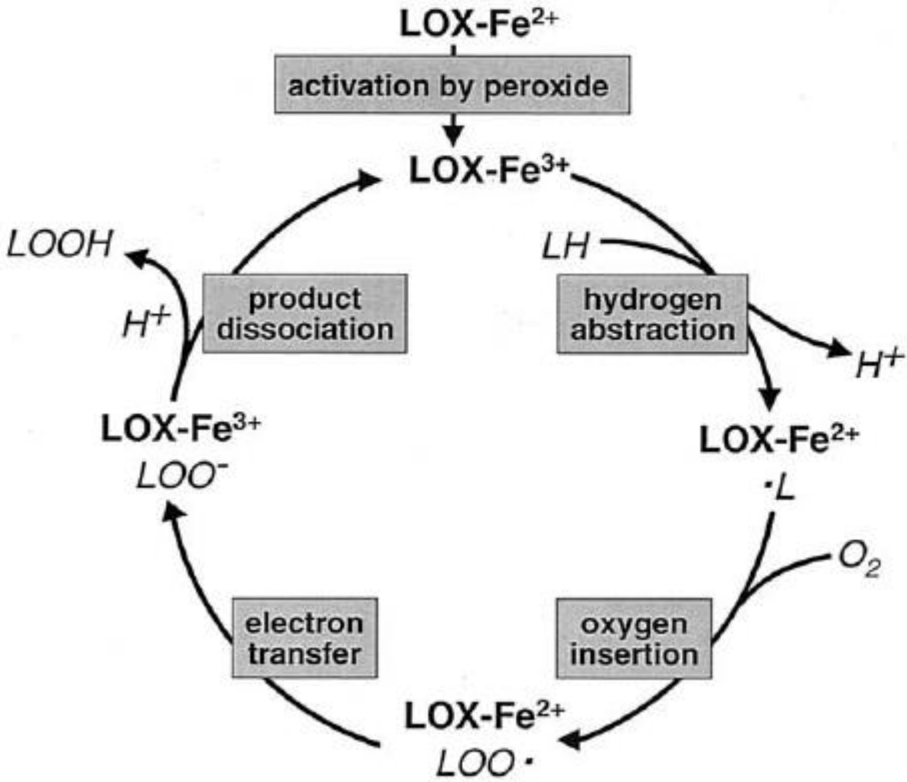
Review

Oxysterols and Retinal Degeneration in a Rat Model of Smith-Lemli-Opitz Syndrome: Implications for an Improved Therapeutic Intervention

Steven J. Fliesler [1,2,*] and Libin Xu [3,*]

Reactions on fats: lypoxygenase

Enzyme catalysis



Primary products

Fatty acids hydroperoxides can be also formed by enzymatic catalysis - no need to activate O_2; in this case the enzymes (lypoxygenases - LOX) lower the reaction energy barrier.

Lypoxygenases - LOX are substrate specific (linoleic and linolenic acids are preferably oxidated) and recognize the 1-*Z*-4-*Z*-pentadienic sub-structure.

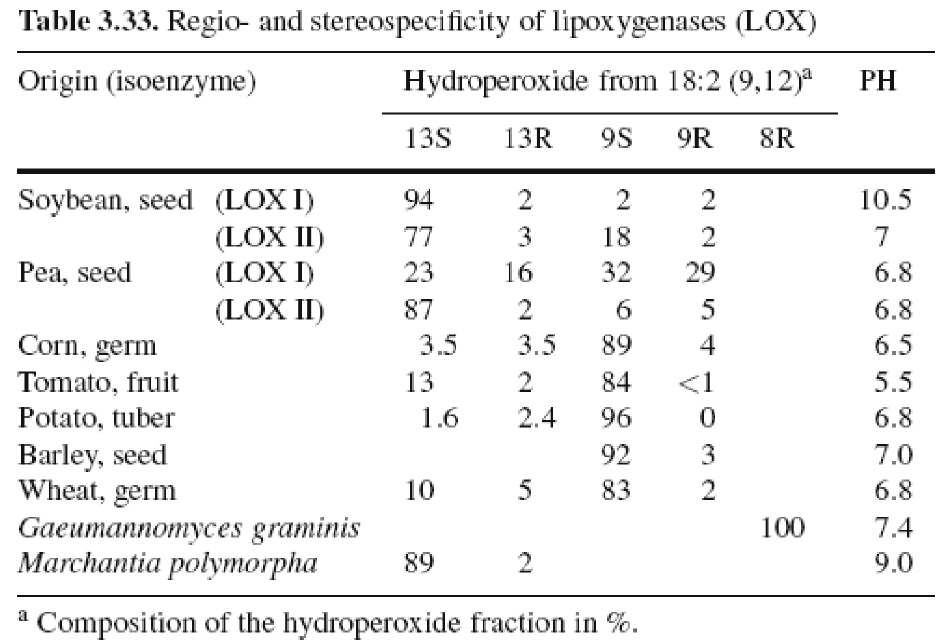


Table 3.33. Regio- and stereospecificity of lipoxygenases (LOX)

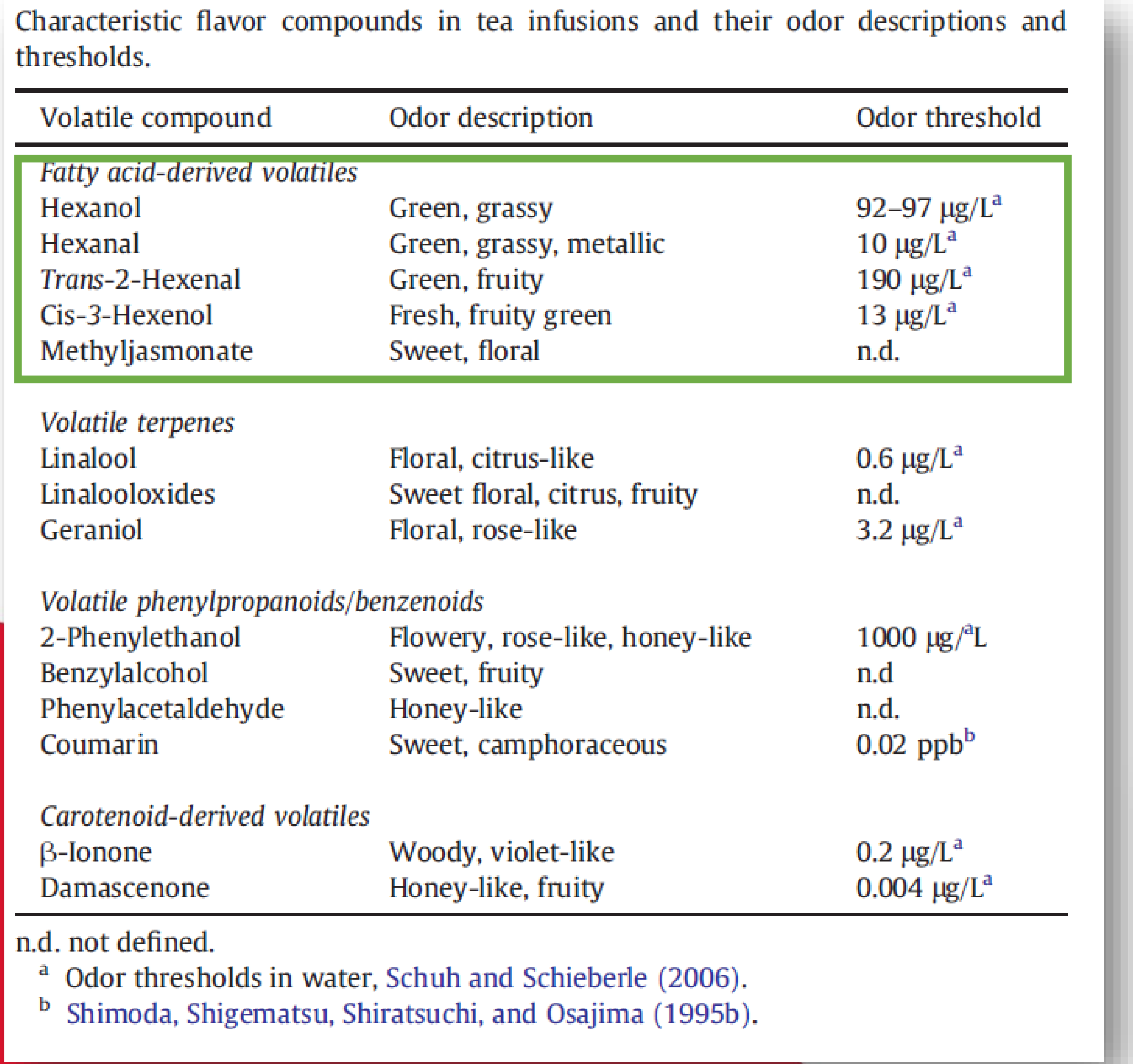
Origin (isoenzyme)		Hydroperoxide from 18:2 (9,12)[a]					PH
		13S	13R	9S	9R	8R	
Soybean, seed	(LOX I)	94	2	2	2		10.5
	(LOX II)	77	3	18	2		7
Pea, seed	(LOX I)	23	16	32	29		6.8
	(LOX II)	87	2	6	5		6.8
Corn, germ		3.5	3.5	89	4		6.5
Tomato, fruit		13	2	84	<1		5.5
Potato, tuber		1.6	2.4	96	0		6.8
Barley, seed				92	3		7.0
Wheat, germ		10	5	83	2		6.8
Gaeumannomyces graminis						100	7.4
Marchantia polymorpha		89	2				9.0

[a] Composition of the hydroperoxide fraction in %.

Some LOX are region- and stereospecific and consequently the spectrum of possible products is quite limited.

Reactions on fats: lipoxygenase

Insight - Tea aroma and lipid oxidation



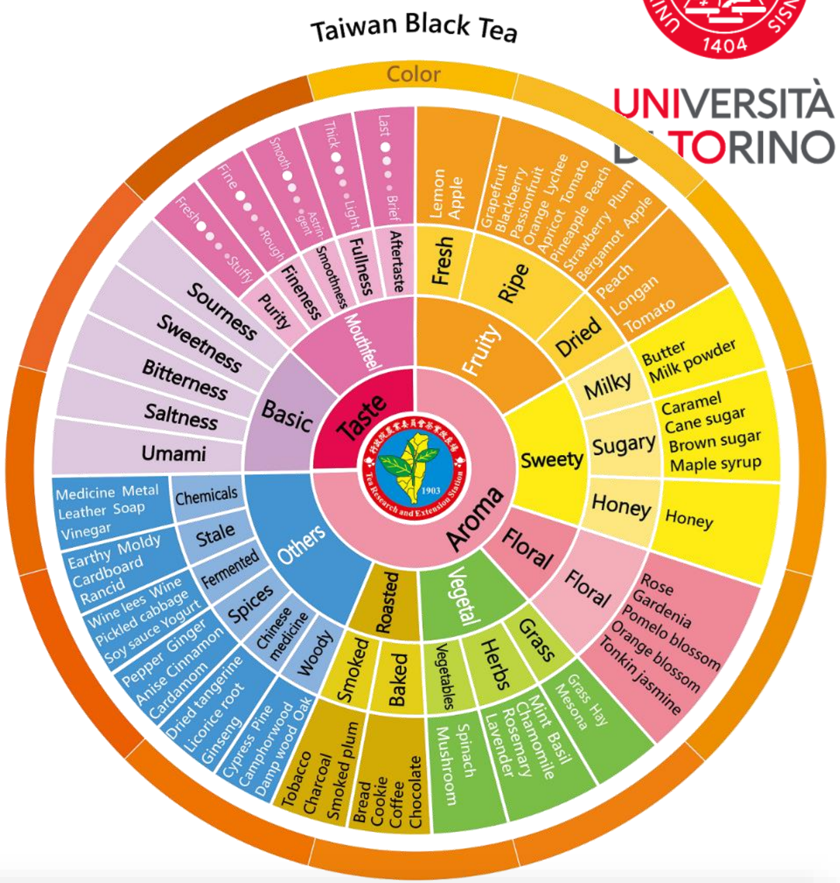
Characteristic flavor compounds in tea infusions and their odor descriptions and thresholds.

Volatile compound	Odor description	Odor threshold
Fatty acid-derived volatiles		
Hexanol	Green, grassy	92–97 µg/L[a]
Hexanal	Green, grassy, metallic	10 µg/L[a]
Trans-2-Hexenal	Green, fruity	190 µg/L[a]
Cis-3-Hexenol	Fresh, fruity green	13 µg/L[a]
Methyljasmonate	Sweet, floral	n.d.
Volatile terpenes		
Linalool	Floral, citrus-like	0.6 µg/L[a]
Linalooloxides	Sweet floral, citrus, fruity	n.d.
Geraniol	Floral, rose-like	3.2 µg/L[a]
Volatile phenylpropanoids/benzenoids		
2-Phenylethanol	Flowery, rose-like, honey-like	1000 µg/[a]L
Benzylalcohol	Sweet, fruity	n.d
Phenylacetaldehyde	Honey-like	n.d.
Coumarin	Sweet, camphoraceous	0.02 ppb[b]
Carotenoid-derived volatiles		
β-Ionone	Woody, violet-like	0.2 µg/L[a]
Damascenone	Honey-like, fruity	0.004 µg/L[a]

n.d. not defined.

[a] Odor thresholds in water, Schuh and Schieberle (2006).

[b] Shimoda, Shigematsu, Shiratsuchi, and Osajima (1995b).



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Recent studies of the volatile compounds in tea

Ziyin Yang [a,1], Susanne Baldermann [b,c,1], Naoharu Watanabe [d,*]

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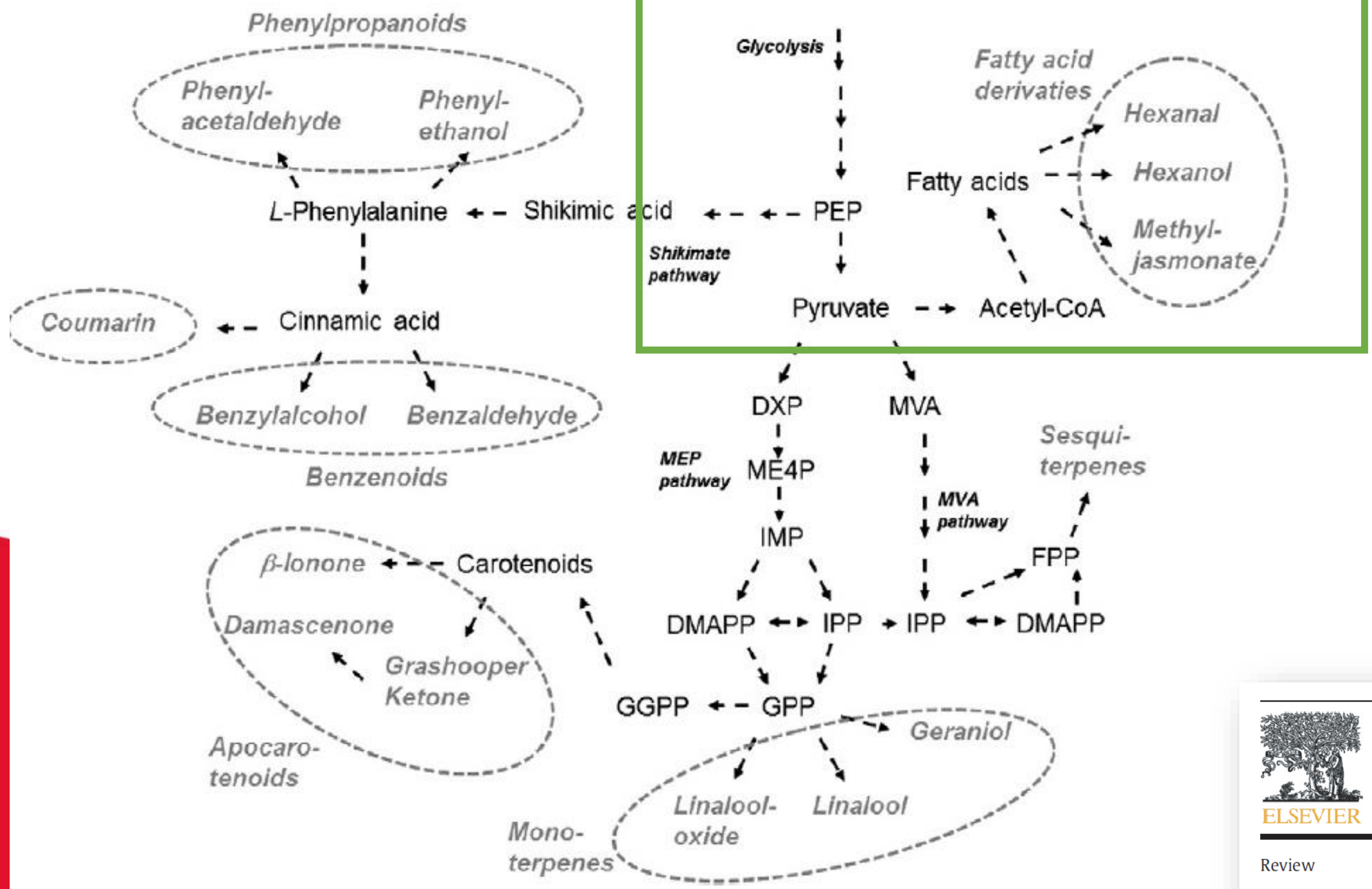


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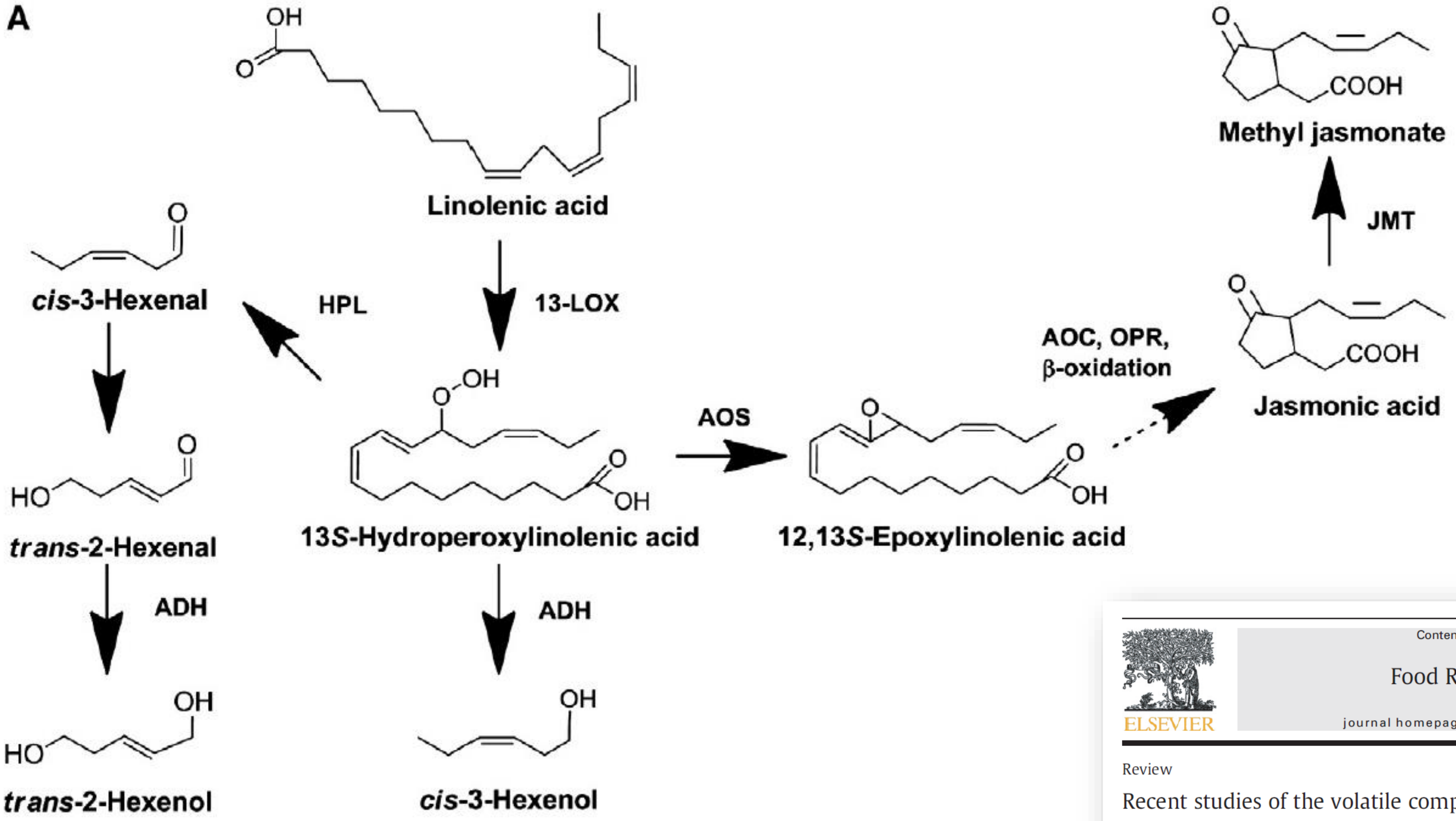

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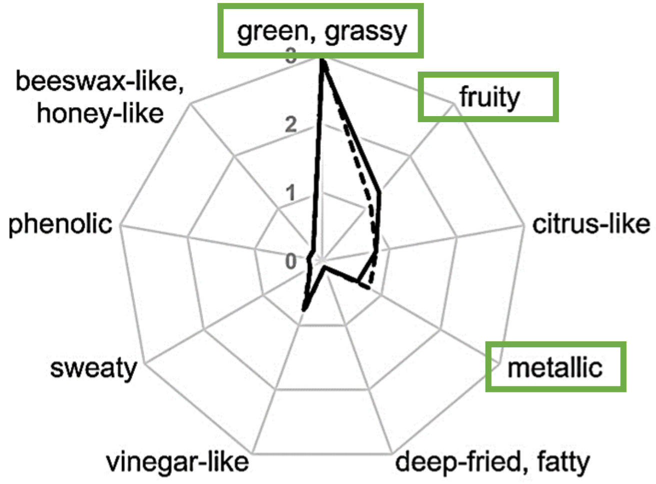
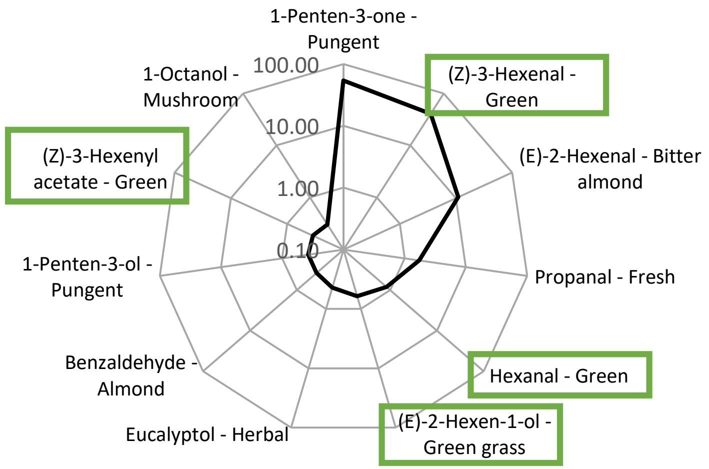


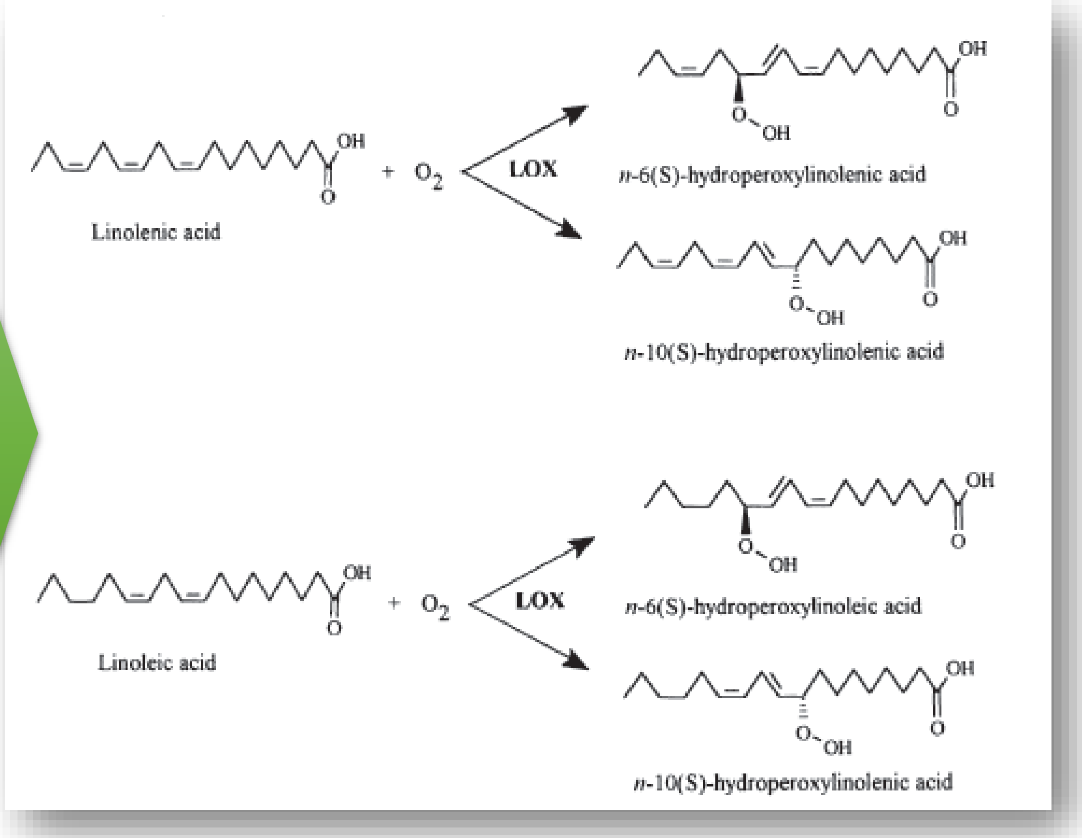


Human panel

https://www.solagrifood.com

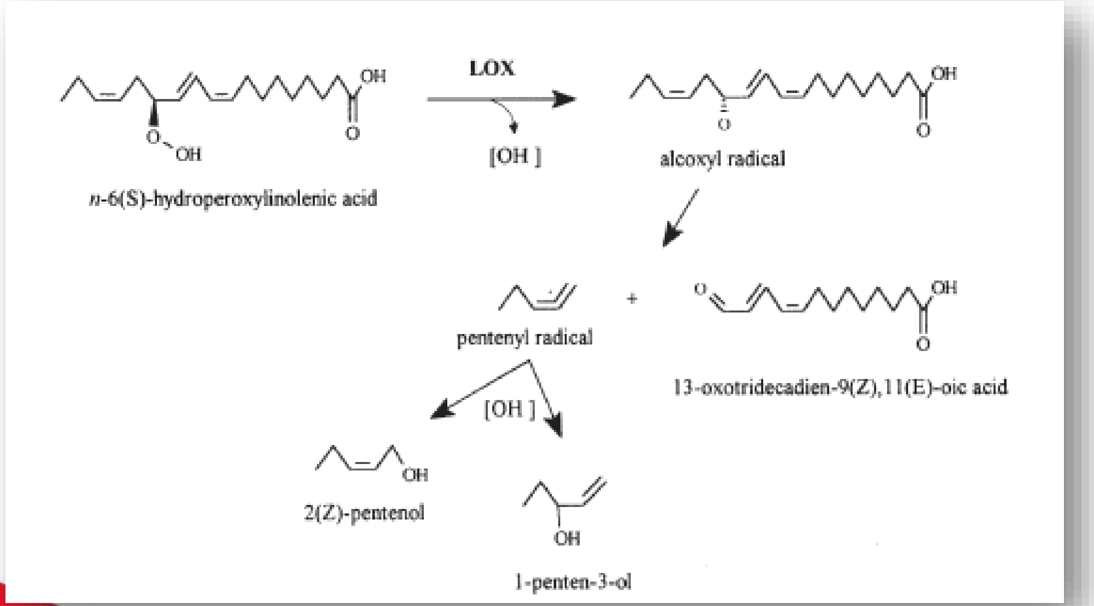
Biogenesis of Olive Oil Aroma

Juan Sánchez and Joaquín J. Salas



Reactions on fats: lipoxygenase

Insight - Extra-virgin olive oil aroma



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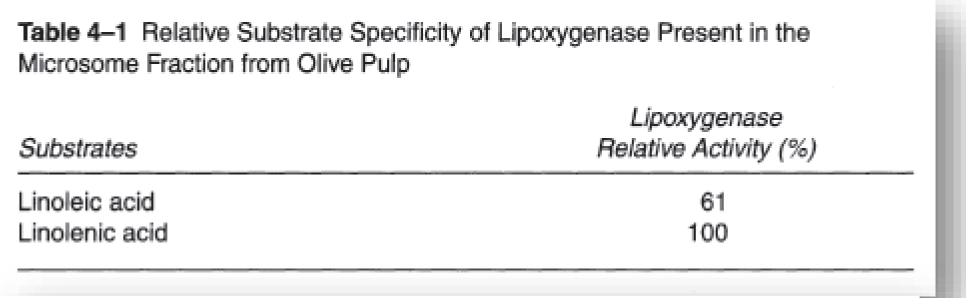

Table 4–1 Relative Substrate Specificity of Lipoxygenase Present in the Microsome Fraction from Olive Pulp

Substrates	*Lipoxygenase Relative Activity (%)*
Linoleic acid	61
Linolenic acid	100

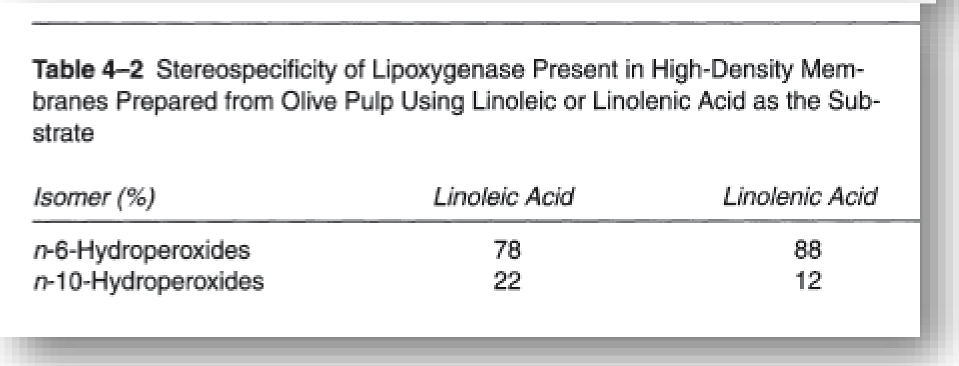

Table 4–2 Stereospecificity of Lipoxygenase Present in High-Density Membranes Prepared from Olive Pulp Using Linoleic or Linolenic Acid as the Substrate

Isomer (%)	*Linoleic Acid*	*Linolenic Acid*
n-6-Hydroperoxides	78	88
n-10-Hydroperoxides	22	12

Reactions on fats: lipoxygenase

Insight - Extra-virgin olive oil aroma

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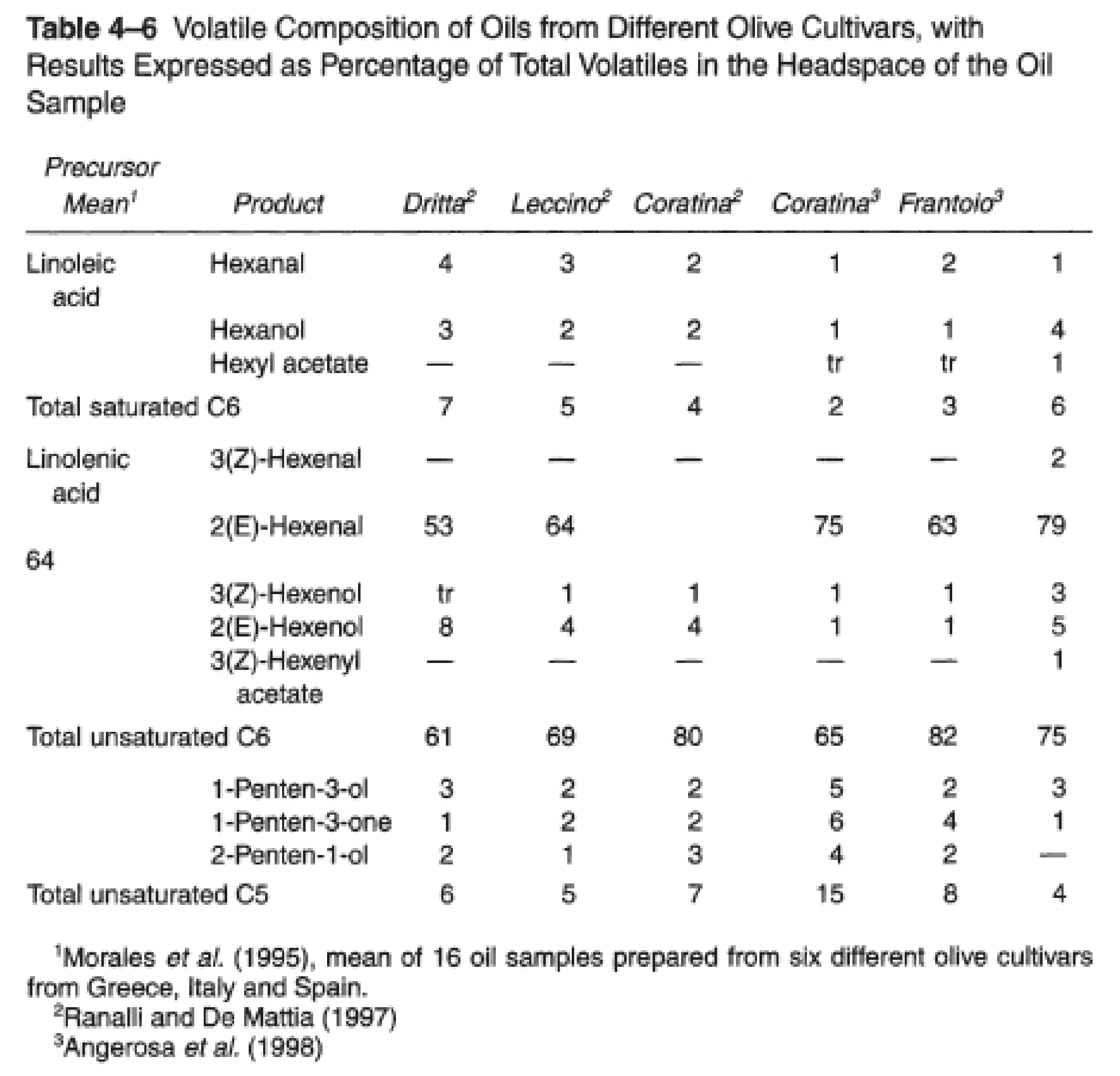


Table 4–6 Volatile Composition of Oils from Different Olive Cultivars, with Results Expressed as Percentage of Total Volatiles in the Headspace of the Oil Sample

Precursor Mean[1]	*Product*	*Dritta*[2]	*Leccino*[2]	*Coratina*[2]	*Coratina*[3]	*Frantoio*[3]	
Linoleic acid	Hexanal	4	3	2	1	2	1
	Hexanol	3	2	2	1	1	4
	Hexyl acetate	—	—	—	tr	tr	1
Total saturated C6		7	5	4	2	3	6
Linolenic acid	3(Z)-Hexenal	—	—	—	—	—	2
	2(E)-Hexenal	53	64		75	63	79
64							
	3(Z)-Hexenol	tr	1	1	1	1	3
	2(E)-Hexenol	8	4	4	1	1	5
	3(Z)-Hexenyl acetate	—	—	—	—	—	1
Total unsaturated C6		61	69	80	65	82	75
	1-Penten-3-ol	3	2	2	5	2	3
	1-Penten-3-one	1	2	2	6	4	1
	2-Penten-1-ol	2	1	3	4	2	—
Total unsaturated C5		6	5	7	15	8	4

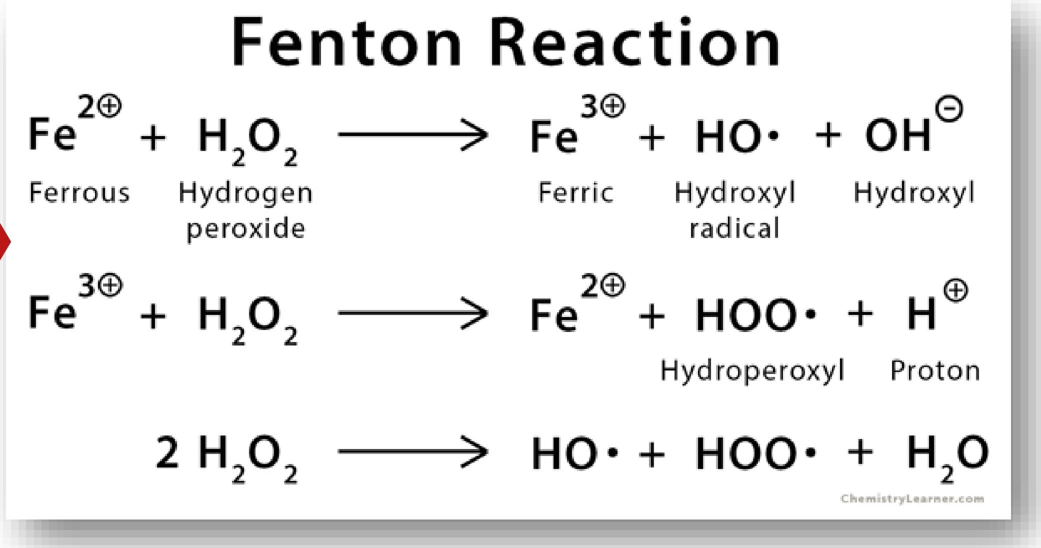
[1] Morales *et al.* (1995), mean of 16 oil samples prepared from six different olive cultivars from Greece, Italy and Spain.
[2] Ranalli and De Mattia (1997)
[3] Angerosa *et al.* (1998)

Biogenesis of Olive Oil Aroma

Juan Sánchez and Joaquín J. Salas

Reactions on fats: trace metals catalysis

Transition metal ions, first, participate in the Fenton reaction believed to be the main source of the hydroxyl radical (•OH) in biological systems.
Another contribution of transition metal ions to lipid peroxidation is a result of their role in the decomposition of lipid hydroperoxides.



Fenton Reaction

$$Fe^{2\oplus} + H_2O_2 \longrightarrow Fe^{3\oplus} + HO\cdot + OH^{\ominus}$$

Ferrous, Hydrogen peroxide, Ferric, Hydroxyl radical, Hydroxyl

$$Fe^{3\oplus} + H_2O_2 \longrightarrow Fe^{2\oplus} + HOO\cdot + H^{\oplus}$$

Hydroperoxyl, Proton

$$2\,H_2O_2 \longrightarrow HO\cdot + HOO\cdot + H_2O$$

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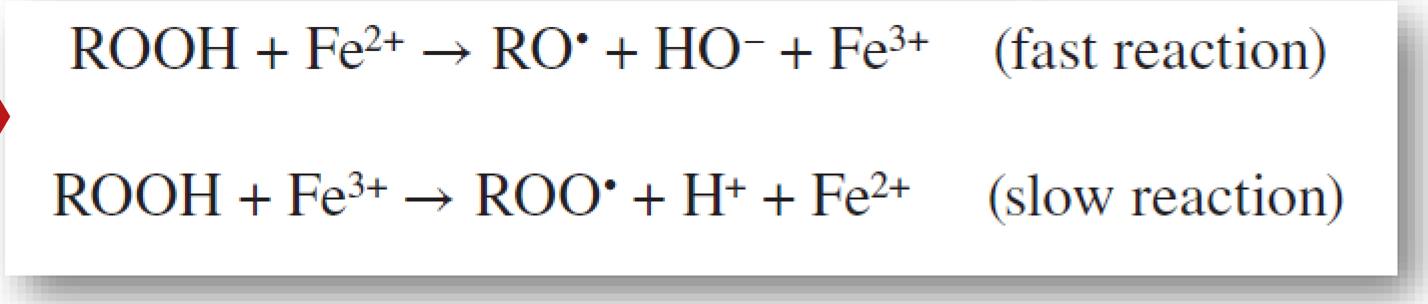
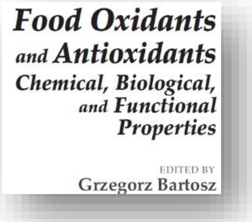
These primary products of peroxidation may slowly decompose spontaneously, especially at elevated temperatures, but transition metal ions accelerate their decomposition, resulting in formation of alkoxyl (RO•) and peroxyl (ROO•) radicals.



$$ROOH + Fe^{2+} \rightarrow RO^{\bullet} + HO^{-} + Fe^{3+} \quad \text{(fast reaction)}$$

$$ROOH + Fe^{3+} \rightarrow ROO^{\bullet} + H^{+} + Fe^{2+} \quad \text{(slow reaction)}$$

Reactions on fats: trace metals catalysis



Food Oxidants and Antioxidants
Chemical, Biological, and Functional Properties
EDITED BY Grzegorz Bartosz

UNIVERSITÀ DI TORINO

Dipartimento
Scienza e Tecnologia
del Farmaco

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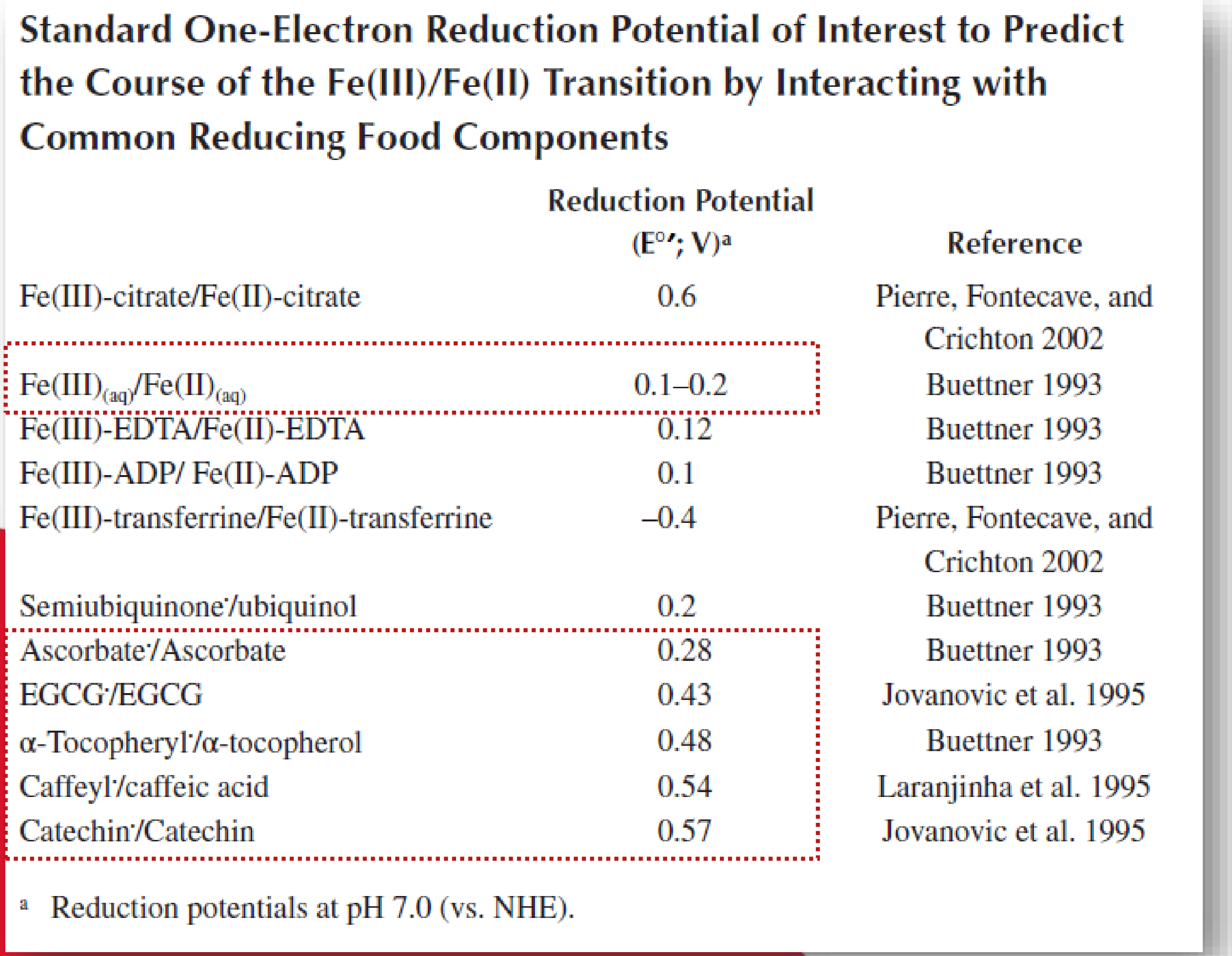


Standard One-Electron Reduction Potential of Interest to Predict the Course of the Fe(III)/Fe(II) Transition by Interacting with Common Reducing Food Components

	Reduction Potential ($E^{o\prime}$; V)^{a}	Reference
Fe(III)-citrate/Fe(II)-citrate	0.6	Pierre, Fontecave, and Crichton 2002
Fe(III)$_{(aq)}$/Fe(II)$_{(aq)}$	0.1–0.2	Buettner 1993
Fe(III)-EDTA/Fe(II)-EDTA	0.12	Buettner 1993
Fe(III)-ADP/ Fe(II)-ADP	0.1	Buettner 1993
Fe(III)-transferrine/Fe(II)-transferrine	–0.4	Pierre, Fontecave, and Crichton 2002
Semiubiquinone$^{\bullet}$/ubiquinol	0.2	Buettner 1993
Ascorbate$^{\bullet}$/Ascorbate	0.28	Buettner 1993
EGCG$^{\bullet}$/EGCG	0.43	Jovanovic et al. 1995
α-Tocopheryl$^{\bullet}$/α-tocopherol	0.48	Buettner 1993
Caffeyl$^{\bullet}$/caffeic acid	0.54	Laranjinha et al. 1995
Catechin$^{\bullet}$/Catechin	0.57	Jovanovic et al. 1995

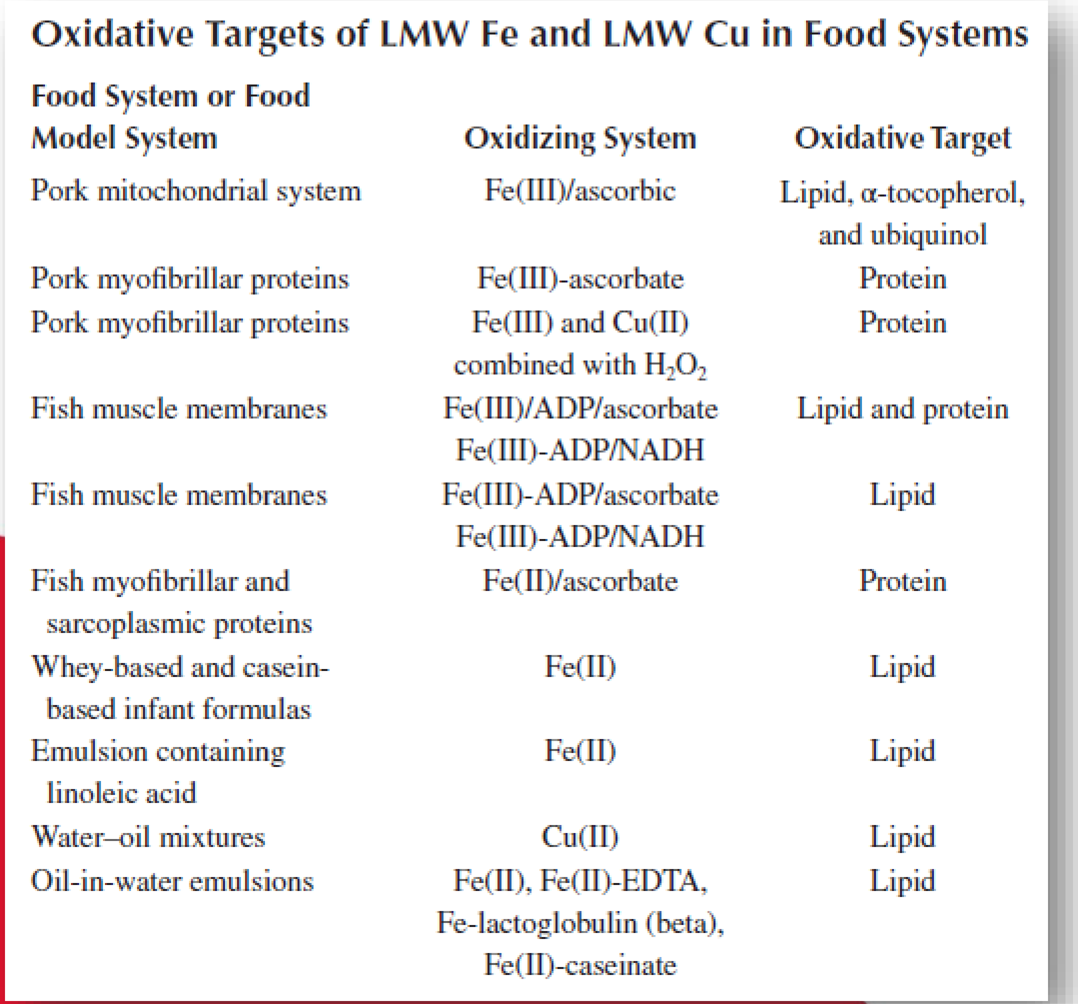
[a] Reduction potentials at pH 7.0 (vs. NHE).

The redox state of metals is crucial for the oxidative stability of foods.
The most common redox state for iron, the oxidized ferric [Fe(III)] ion, is significantly less pro-ooxidant than the reduced ferrous [Fe(II)] state.
However, several enzymatic and nonenzymatic food components or additives may convert the ferric iron to the more oxidizing ferrous form: enzymatic iron-reductase systems, ascorbic acid, glutathione, and phenolic compounds.

The reduction of the ferric to the ferrous state is the driving force for the catalysis of oxidation by iron, being thermodynamically possible for reductants whose one-electron reduction potential is lower than that of ferric iron.

The redox potential of the Fe(III)/Fe(II) transition depends strongly on the chelating agent and pH. Iron coverts a wide physiological range of redox potentials, from approximately −0.5 to 0.6 V, depending on the ligand complexed to the metal.

Reactions on fats: trace metals catalysis



Oxidative Targets of LMW Fe and LMW Cu in Food Systems

Food System or Food Model System	Oxidizing System	Oxidative Target
Pork mitochondrial system	Fe(III)/ascorbic	Lipid, α-tocopherol, and ubiquinol
Pork myofibrillar proteins	Fe(III)-ascorbate	Protein
Pork myofibrillar proteins	Fe(III) and Cu(II) combined with H_2O_2	Protein
Fish muscle membranes	Fe(III)/ADP/ascorbate Fe(III)-ADP/NADH	Lipid and protein
Fish muscle membranes	Fe(III)-ADP/ascorbate Fe(III)-ADP/NADH	Lipid
Fish myofibrillar and sarcoplasmic proteins	Fe(II)/ascorbate	Protein
Whey-based and casein-based infant formulas	Fe(II)	Lipid
Emulsion containing linoleic acid	Fe(II)	Lipid
Water–oil mixtures	Cu(II)	Lipid
Oil-in-water emulsions	Fe(II), Fe(II)-EDTA, Fe-lactoglobulin (beta), Fe(II)-caseinate	Lipid

Table on the left collects some of the food systems or food model systems in which the **ascorbic acid combined with traces of iron causes oxidation of important food components, for example, lipids, proteins, α-tocopherol, or ubiquinol**

Iron-reducing enzymatic systems are also a relevant font of the reactive ferrous ions in meat-based foods not subjected to thermal treatments.
Cellular membranes of muscle foods contain NAD(P)H-dependent enzymatic systems with the capacity to transfer one electron to convert ferric to ferrous iron, such as ferredoxin, thioredoxin, and cytochrome P450.

Reactions on fats: lipases and hydrolytic rancidity

Lipases attack triglyceride emulsions at the interface. The greater the surface area of the oil/water emulsion, the faster the activity of the lipases will be.

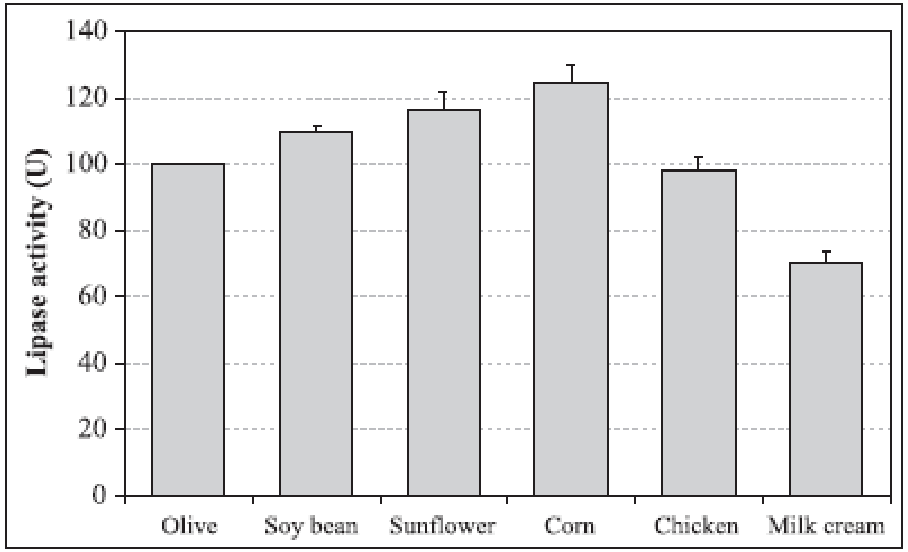


Figure 4. Level of hydrolysis activity from different fatty and oil compared with olive oil (olive oil was taken as 100%). The lipolytic assay was determined at 50ºC, pH 8.0, 30 min incubation. The experiments were performed in triplicate and bars represent the standard derivation.

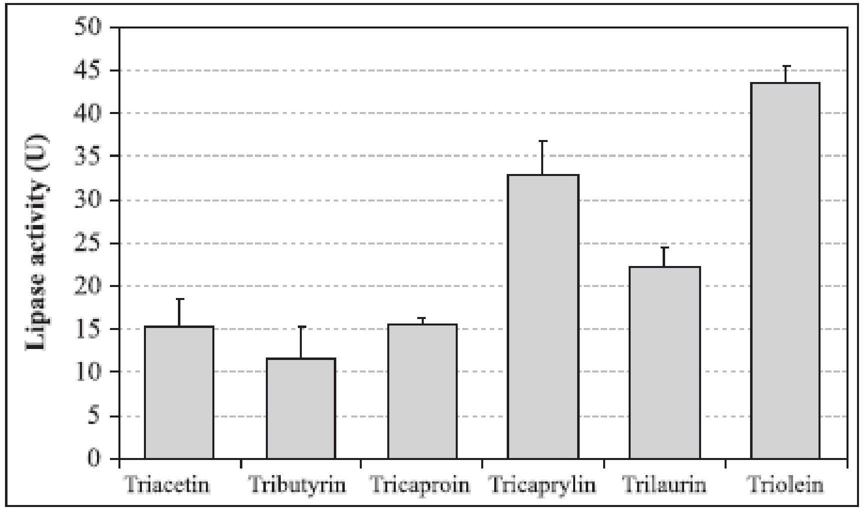


Figure 3. Substrate specificities of alkaline lipase toward several triglycerides. The lipolytic assay was determined at 50ºC, pH 8.0, 30 min incubation. The experiments were performed in triplicate and bars represent the standard derivation.

Reactions on fats: lipases and hydrolytic rancidity

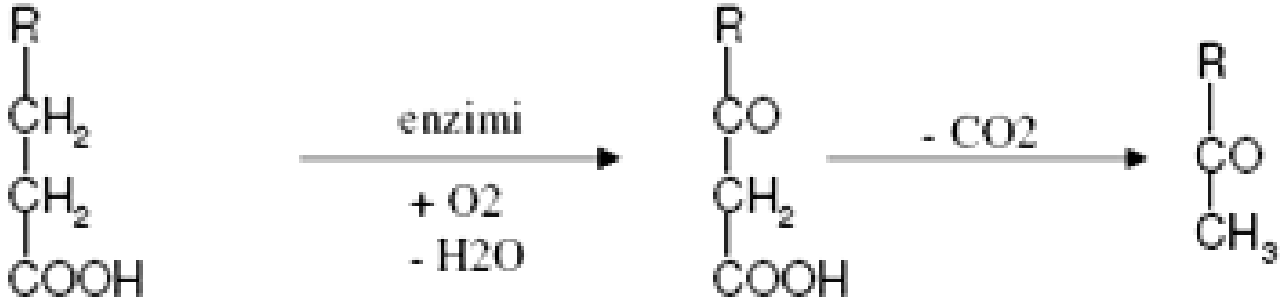
Free acidity (acidità libera) is not an organoleptic "defect" since, especially with regard to vegetable fats, the long-chain fatty acids released are not perceived. Rather, it is a parameter that indicates the quality, degree of conservation and handling of a substrate which also falls under current legislation.

Free acidity: g oleic acid / 100 g oil

Reactions on fats: ketonic rancidity

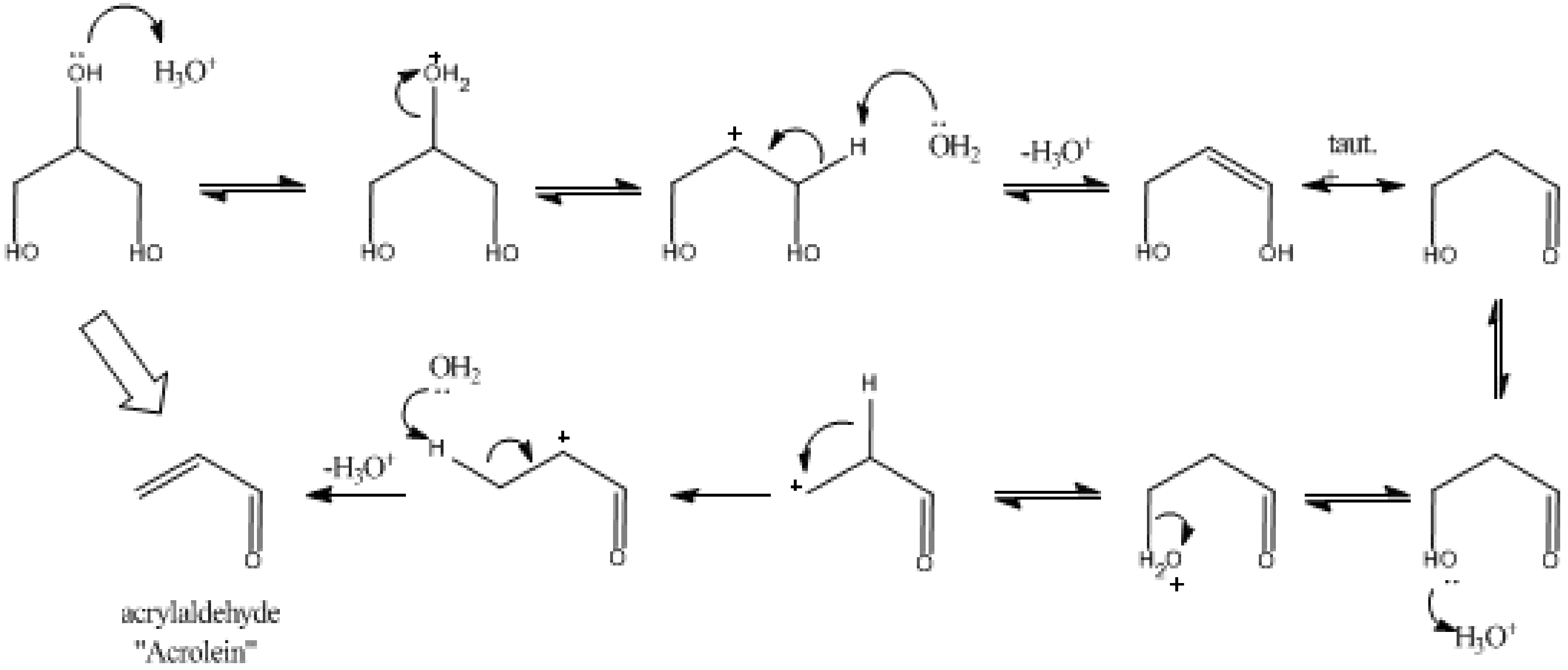
It is a phenomenon of oxidation of the methylene group in β position with respect to the carboxyl of the fatty acid with formation of a keto acid which, by subsequent oxidation, forms a methyl ketone.

It is catalyzed by an enzyme, the β -oxidase present in some penicilli (*Penicillum roqueforti* - Gorgonzola)



Smoke point of fats and acrolein formation

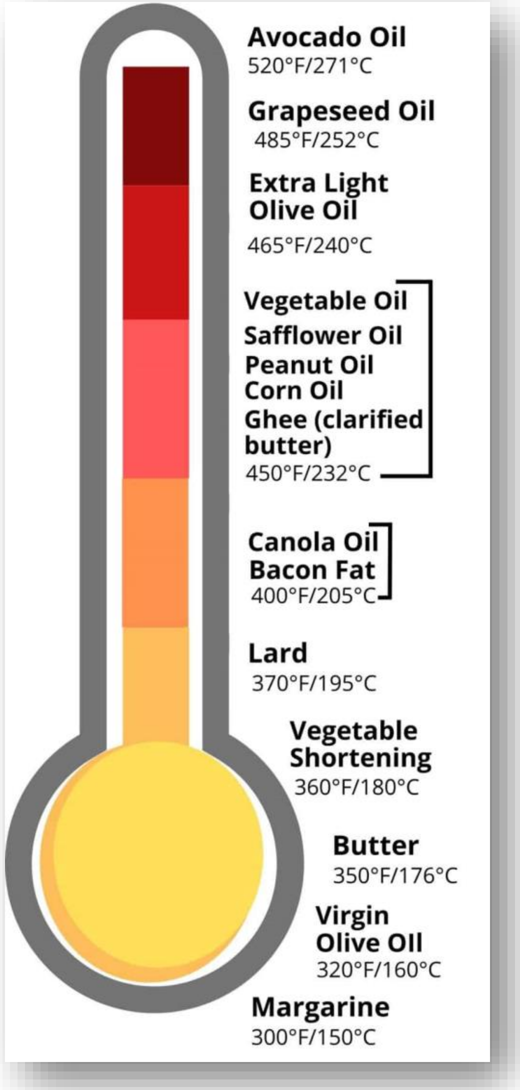
The smoking point is the temperature at which a heated fat undergoes hydrolysis of the triglyceride component with consequent release of glycerol. The latter, due to the effect of the high temperature, dehydrates and forms acrolein, a compound with irritating properties (IARC Group 3, not carcinogenic for humans).



Smoke point of fats and acrolein formation

SMOKING POINTS OF OILS

FAT	QUALITY	SMOKE POINT ° C
Almond Oil		216°C
Avocado Oil		270°C
Butter		150°C
Canola Oil (Rapeseed)	Expeller Press	190-230°C
Canola Oil (Rapeseed)	High	245°C
Canola Oil (Rapeseed)	Refined	200°C
Canola Oil (Rapeseed)	Unrefined	105°C
Coconut Oil	Dry Expeller Pressed Virgin (unrefined)	177°C
Coconut Oil	Dry Refined	204°C
Corn Oil	Unrefined	177°C
Corn Oil	Refined	232°C
Flaxseed Oil		105°C
Hazelnut Oil		220°C
Hemp Oil		165°C
Lard		190°C
Olive Oil	Generic	160°C
Olive Oil	Virgin	210°C
Olive Oil	Extra Virgin	207°C
Olive Pomace Oil		238°C
Palm Oil		235°C
Peanut Oil	Unrefined	160°C
Peanut Oil	Refined	232°C
Safflower Oil	Unrefined	107°C
Safflower Oil	Semirefined	160°C
Safflower Oil	Refined	266°C
Sesame Oil	Unrefined	177°C
Sesame Oil	Semirefined	232°C
Soybean Oil	Unrefined	160°C
Soybean Oil	Semirefined	177°C
Soybean Oil	Refined	238°C
Sunflower Oil	Unrefined	107°C
Sunflower Oil	Refined	232°C
Walnut Oil	Unrefined	160°C
Walnut Oil	Refined	204°C



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