Lipids

- **one of the major nutrients**
-

derivatives of fatty acids (FA) with >3 carbon atoms

free FA

+

- **homolipids - esters of glycerol**
- heterolipids - phospholipids — glycerophospholipids
  - glycolipids — natural / produced industrially
- complex lipids

in food technology and practice
(according to physical state – consistency)

fats, oils, waxes, lecithin, fatty acids

neutral lipids

polar lipids

function

- **major nutrient**
  - **source of energy**
  - **source of essentials fatty acids**

- **solvent of important compounds (lipophilic vitamins, etc.)**

content in foods

	% fresh weight	% dry matter
meat and meat products		
pork lean	18	51
pork fatty	41	75
beef	2-36	9-63
chicken	1-35	5-50
milk and milk products		
milk full-fat	3.8	30
butter	81	99
eggs		
yolk	33	66
white	0.02	0.15
cereals		
wheat flour	1-1.4	1.1-1.6
bread	0.8-1.1	1.3-1.7
fruits, vegetables		
fruits	0.2-0.7	1-2.8
beans	1.6	1.8
potatoes	0.2	0.8

sources of dietary fat

food	%
butter, spread fats	16, 9
milk, cream	15
cheeses	4
lard, oils	10
Bread, cereals	8
meat, eggs	20, 3

production of fats and oils

vegetal pressing extraction

animal melting extraction

plant fats and oils

refining

- deguming (hydration) $\xrightarrow{H_2O}$ lecithin removed
  (plant gums, proteins, their complexes with water)
- deacidification (neutralisation) $\xrightarrow{NaOH/Na_2CO_3}$ Na-salts
- bleaching $\xrightarrow{\text{hlinky}}$ carotenoids, chlorophylls
- deodoration $\xrightarrow{\text{pára}}$ tocopherols, sterols

source	oil	% fat
coconut palm	coconut	60-67
oil palm	palm	55
	palm kernel	60
groundnut	peanut	55
sunflower	sunflower	36
safflower	safflower	25
rape	rapeseed	47
soy	soy	25
olive tree	olive	70

Coconut palm
(*Cocos nucifera*)

Oil palm(*Elaeis guineensis)*

Rape (*Brassica napus)*

classification

according to consistence

- **oils** (liquid)
  - drying oils — linseed oil
  - semi-drying oils — sunflower,soy
  - nondrying oils — olive
- **fats** (plastic) — lard
- **waxes** (hard, nongreasing) — bee wax

according to structure

1. fatty acids and their soaps $R\text{-}[CH_2]_n\text{-}COOH$

2. homolipids (esters of fatty acids with alcohols)

2.1 monohydric alcohols (waxes)

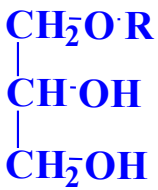
aliphatic (cerides)

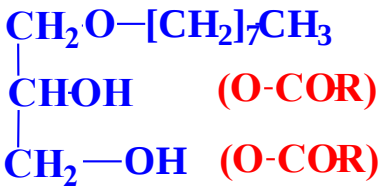
$CH_3\text{-}[CH_2]_{25}\text{-}OH$ cerylalcohol (bee wax, apples)

$CH_3\text{-}[CH_2]_{15}\text{-}OH$ hexadecan-1-ol, cetylalcohol

alicyclic (sterides) esters of sterols, triterpenic alcohols

2.2 dihydric alcohols (glycols), alkoxylipids

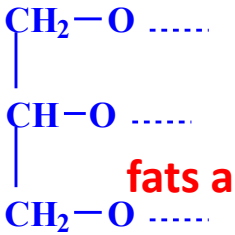




1-alkoxypropane-2,3-diols (glycerol ethers)

chimylalcohol (shark fat)

2.3 trihydric alcohol (glycerol)

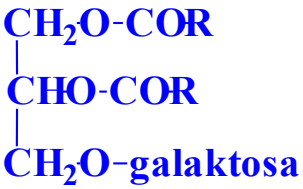


fats and oils

2.4 polyhydric alcohols

sugars - glycolipids

galaktosa (most often)



diacylglycerogalaktoside (diacylgalaktosylglycerol) ⇨ lipid membranes of chloroplasts of higher plants

saccharose

1-3 FA emulsifiers

6-8 FA low-energy fats (OLESTRA)

sorbitol (alcoholic sugar)

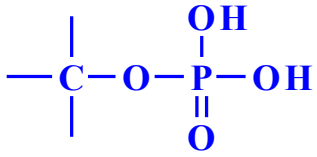
emulsifiers spans and tweens (additives E432-E436)

3. heterolipids

0.5-2%

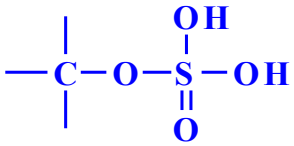
glycerol, FA, another component (mainly polar)

fosfolipids



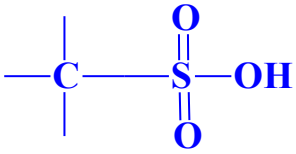
esters of FA

lipid sulfates



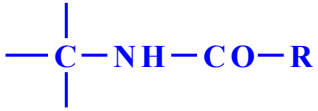
sulphuric acid bound

sulfolipids

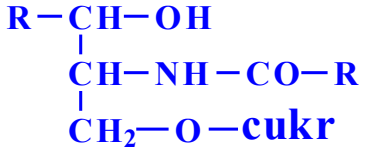


bound sulfonic acid

lipamides



amides of FA



e.g. cerebrosides (glykosides of ceramides)

ceramides=amides of sfingosine and FA

4. complex lipids

macromolecular compounds

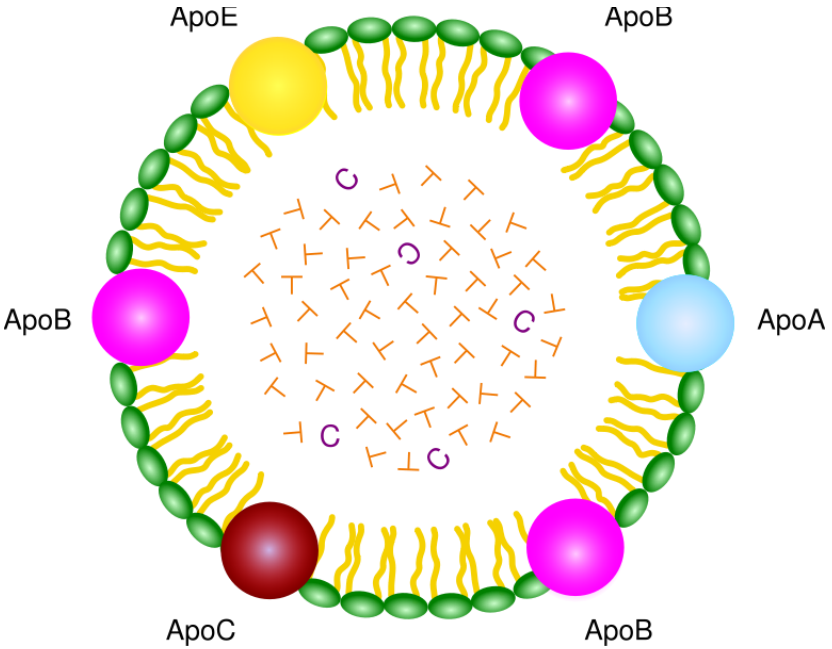
proteolipids (lipoproteins)

blood serum by density

chylomicrons and VLDL (very low density lipoproteins) higher amount of lipids

lipids are easily released and deposited in the arteries

LDL, MDL, HDL, VHDL



Chylomicron structure
ApoA, ApoB, ApoC, ApoE (apolipoproteins);
T (triacylglycerol); C (cholesterol);
green (phospholipids)

glycolipids (cerebrosides)

mucolipids (sialoglycosfingolipids = gangliosides)

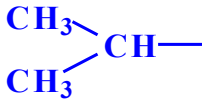
- **in neural tissues (brain up to 6%)**
- **bound sialic acid**

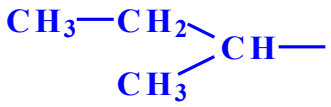
FATTY ACIDS (FA)

saturated $CH_3\text{-}[CH_2]_n\text{-}COOH$

straight chain

branched





iso- **anteiso-**

even number of C atoms

odd number of C atoms

fats, oils $C_4 - C_{22}$

waxes $C_{22} - C_{36}$

classification

- by the chain length:

• short-chain fatty acid - **SCFA**	C4 - C6
• medium-chain fatty acid – **MCFA**	C8 - C12
• long-chain fatty acid - **LCFA**	C14 - C18
• very long-chain fatty acid – **VLCFA**	C20 - C26
• ultra long-chain fatty acid – **ULCFA**	C28 - C38

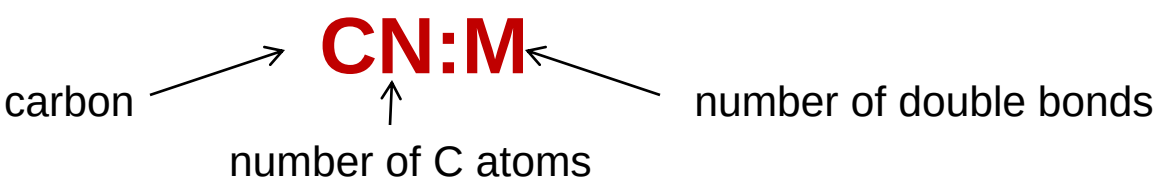
- according to saturation:
  - saturated fatty acid – **SFA**
  - unsaturated fatty acid – **UFA**
    - monounsaturated - **MUFA**
    - **with multiple double bonds** (polyunsaturated - **PUFA**)
      - highly unsaturated – **HUFA** - with 20 or more C atoms in the chain and with four or more double bonds

positional isomers *geometric isomers*

    - alkynic, branched and cyclic acids
    - with O-functional group: hydroxy, oxo, epoxy, furans
    - other FA (bound with sulfur, nitrogen or chlorine

shortened writing

physiological numbering x chemical numbering



C18:2

position of double bond:

-numbering carbons from the carboxyl end - carboxylic carbon is number 1

n n-1 n-2 3 2 1

CH_3-CH_2-CH_2…… CH_2-CH_2-COOH

CN:M $\Delta^{a,b,c}$ **C18:2** $\Delta^{9cis,12cis}$

CN:M (a,b,c) **C18:2 (9,12)**

- numbering from the methyl end of the FA – methyl carbon is labeled n or ω

ω1 ω2 ω3 β α

CH_3-CH_2-CH_2…… CH_2-CH_2-COOH

CN:M n - a **C18:2 n - 6**

CN:M ω - a **C18:2 ω - 6**

4:0	butyric (butanoic)
6:0	caproic (hexanoic)
8:0	caprylic (octanoic)
10:0	caprinic (decanoic)
12:0	lauric (dodecanoic)
14:0	myristic (tetradecanoic)
16:0	palmitic (hexadecanoic)
18:0	stearic (octadecanoic)
20:0	arachidic (eicosanoic)
22:0	behenic (docosanoic)

unsaturated (monoenoic) MUFA

CH_3-$[CH_2]_7$ -CH= CH-$[CH_2]_7$ –COOH

cis-9-octadecenoic oleic 18:1 Δ 9 *cis* ω-9

dienoic (polyenoic) PUFA

CH_3-$[CH_2]_4$ -CH= CH-CH_2-CH=CH-$[CH_2]_7$ –COOH

cis, cis-9,12-octadecadienoic linoleic 18:2 Δ 9,12 all-*cis* ω-6

trienoic PUFA

CH_3-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-$[CH_2]_7$ –COOH

cis,cis,cis-9,12,15-octadecatrienoic linolenic (α) 18:3 Δ 9,12,15 all-*cis* ω-3

polyenoic FA

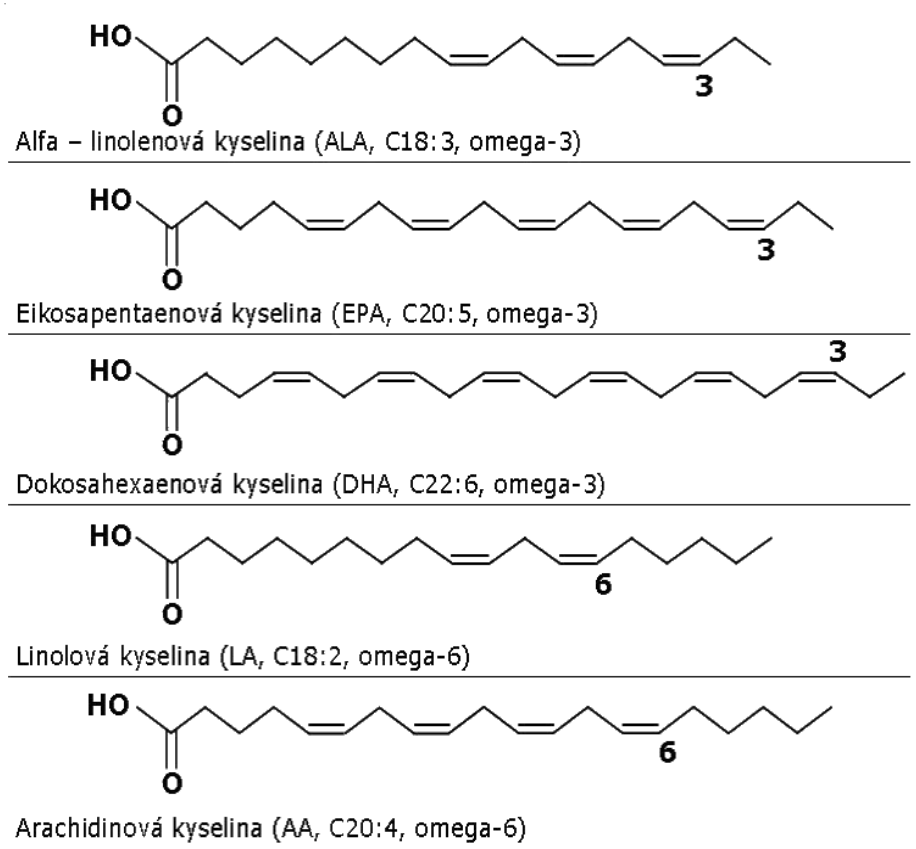
Isolated double bonds *cis* isomers

FA n-6

linoleic acid (LA)
γ-linolenic acid (GLA)
arachidonic acid (AA)

FA n-3

α-linolenic acid (ALA)
eicosapentaenoic acid (EPA)
docosahexaenoic acid (DHA)



other fatty acids

unsaturated in unusual positions

petroselinic	18:1 Δ 11 *cis*
erucic (rapeseed oil)	22:1 Δ 13 *cis*

trans

elaidic	18:1 Δ 9 *trans*

occurrence

SFA C4-C10	butter (cow´s milk fat)
SFA C12, C14	coconut, palm kernel oil
SFA C16, C18	palm oil, animal fats
branched C19, C20	butter (cow´s milk fat)
C18:1 (oleic)	olive, rapeseed, groundnut oils, butter, lard, tallow
C22:1 (erucic)	rapeseed oil
C 18:2 (linoleic)	soy, sunflower oil
C18:3 (α-linolenic)	linseed oil
PUFA ω-3	fish oils
C18:3 (γ-linolenic)	primerose oil, borage seed oil
C20:4 (arachidonic) ω-6	meat, liver, lard, eggs
trans-isomers	fats of ruminants, partially hydrogenated fats

FA	tallow	lard	butter	cod liver oil	olive oil	cocoa butter
4:0			9			
6:0			5			
8:0			2			
10:0			4			
12:0			3			
14:0	4	2	10	4		
14:1	1		2			
15:0	2		1	1		
16:0	28	26	23	13	11	29
16:1	5	4	2	18	1	
17:0	1		1	2		
18:0	20	15	12	4	3	35
18:1	34	44	23	26	79	32
18:2	3	9	2	2	5	3
18:3	2		1	1	1	
18:4				3		
20:0						
20:1				9		
20:4				1		
20:5				6		
22:1				5		
22:5				1		
22:6				14		

Sources of FA n-6 a n-3

vegetal

Oils with majority of oleic acid

.	oil						
	olive	almond	hazelnut	avocado	sunflower „high oleic“	groundnut	safflower
olejová kys.	55-83	43-60	71.9-84.0	56-74	70-87	76	74-82
LA	3.5-21	20-34	5.7-22.2	10-17	3-20	4	7-18
ALA	0-1.5	0	0.0-0.2	0-2	0	0	< 0.2
n-6/n-3	9.5	>100	>100	13.5	>100	>100	>100

Safflower (*Carthamus tinctorius*)
Chemical analysis of ancient Egyptian textiles dated to the Twelfth dynasty identified dyes made from safflower

Oils with majority of linoleic acid

	oil						
	groundnut	sesame	corn	sunflower	safflower	cotton	poppy
olejová kys.	36.4-67.1	35-50	24.6-42.2	13-40	8.4-21.3	14.7-21.7	16-30
LA	14.0-43.0	35-50	39.4-60.4	40-74	67.8-83.2	46.7-58.2	62-73
ALA	0.0-0.1	0.-0.4	0.7-1.3	<0.3	0.0-0.1	0.0-0.4	-
n-6/n-3	>100	>100	50	>100	>100	>100	>100

Oils with higher amount of linolenic acid

	Oil				
	rape	mustard	soy	wheat (germ)	flaxseed (linseed)
olejová kys.	52.0-66.9	8-23	17.7-25.1	14-23	12-34
LA	16.1-24.8	10-24	49.8-57.1	50-56	7-27
ALA	6.4-14.1	6-18	5.5-9.5	3.5-7.0	35-65
n-6/n-3	2.1	1.4	7	10	0.27

<u>palm seeds and pericarp</u>

palm	10% LA
palmkernel	3% LA
coconut	2% LA

animal

	hovězí lůj	vepřové sádlo	kuřecí sádlo	mléčný tuk
olejová kys.	26-50	35-62	37	19-33
LA	0.5-5	3-16	20	0.9-3.7
ALA	<2.5	<1.5	1	0.1-1.4
AA	-	-	-	0.8-3
n-6/n-3	2	6	20	5

	sladkovodní ryby		mořské ryby	
	kapr	pstruh	makrela	tuňák
olejová kys.	36	26	17	16
LA	7.3	19	2.0	1.4
ALA	2.7	6.7	1.4	0.6
AA	1	0.5	1.0	3.0
EPA	2.4	4.0	7.0	3.3
DHA	1.4	6.5	14	14
n-6/n-3	1.2	1.0	0.1	0.3

phytoplankton
colonies of **cyanobacteria**
Nostoc pruniforme

zooplankton
Northern krill *(Meganyctiphanes norvegica)*
North Atlantic Ocean

Functional foods

nutritional value + component with positive effects on health and / or reducing the risk of disease

Eggs with an increased content of FA n-3

- egg yolk: 33% lipids - acylglycerols (2/3)
  - phospholipids (1/3)
- UFA **64-71%**
- n-6/n-3 **6-14 : 1**

Composition of FA

common eggs

FA	free breeding	Hisex brown	Shaver
Palmitic	24.7	21.8	20.8
Stearic	7.6	5.4	5.5
SFA sum	**33.2**	**28.1**	**27.0**
Palmitoleic	4.0	3.7	3.3
Oleic	49.0	50.6	51.9
MUFA sum	**55.8**	**57.5**	**58.6**
Linoleic	6.3	10.2	10.5
Arachidonic	0.4	0.4	0.4
Linolenic	0.7	0.6	0.5
EPA	0.05	0.03	0.02
DHA	0.2	0.3	0.3
PUFA sum	**11**	**14.4**	**14.4**
n-6/n-3	***6.1***	***10.5***	***13.6***

“Omega eggs”

FA	Omega white eggs	Omega brown eggs	Omega Columbus Belgium
Palmitic	24.1	22.8	19.3
Stearic	8.6	7.5	9.2
SFA sum	**33.6**	**31.3**	**28.5**
Palmitoleic	3.5	3.8	3.2
Oleic	36.0	35.5	37.7
MUFA sum	**43.8**	**45.0**	**40.9**
Linoleic	12.7	13.2	13.6
Arachidonic	0.7	0.8	0.8
Linolenic	3.8	4.1	11.7
EPA	0.4	0.4	0.3
DHA	3.1	3.2	1.9
PUFA sum	**22.6**	**23.7**	**28.7**
n-6/n-3	***1.8***	***1.7***	***1.0***

Biosynthesis of FA

from acetyl-CoA

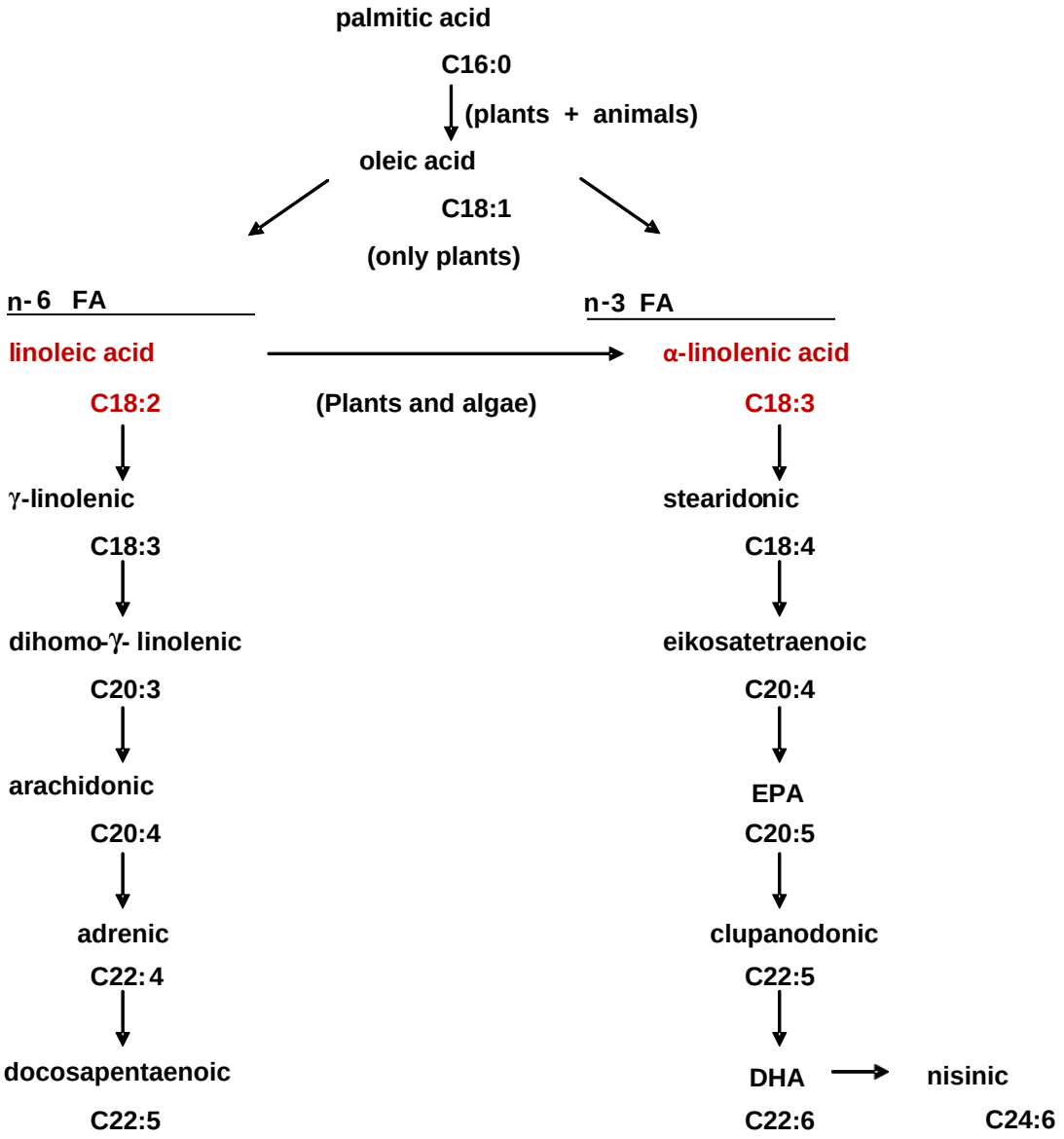
- stop after reaching C16 , C18
  - → SFA (C16:0 a C18:0)
    - → MUFA (C16:1, C18:1)

- humans are not able: - synthesize PUFA n-6 (LA)
  n-3 (ALA)
  → **essential**
  - convert n-6 to n-3
    (lacks proper desaturase)

Both rows have a different metabolic mechanism and often contradictory physiological function

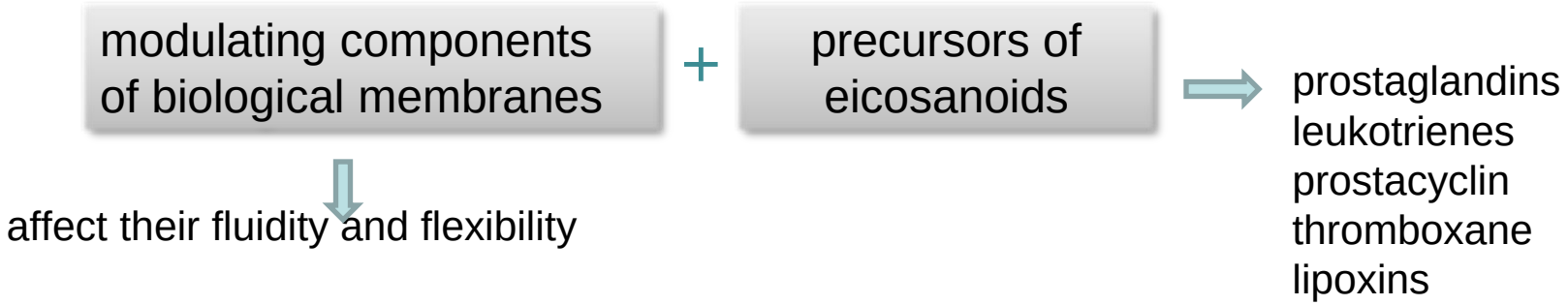
synthesis of HUFA:

- elongation
- desaturation
- retroconversion



The importance in nutrition

- FA are the source of cellular energy
- PUFA



prostacyclins – inhibits platelet activation and is also an effective vasodilator

lipoxins - have a number of proinflammatory and anti-inflammatory actions

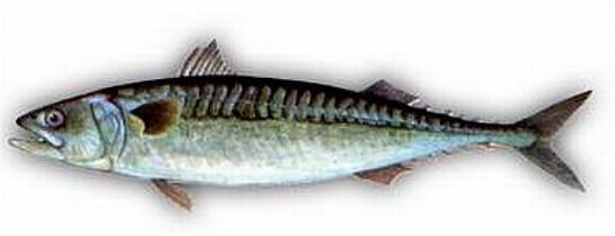
Scientific opinion on the nutritional value of fat

EFSA, 2010

*(*Scientific Opinion on Dietary Reference Values for fats, EFSA Journal 2010; 8(3):1461*)*

- fat intake 20 – 35 energy % (E%)
  - SFA - intake should be as low as is possible within the context of a nutritionally adequate diet
  - *trans-FA* - should be as low as is possible
  - *cis*-monoenové MK - not to set any Dietary Reference Value
  - *cis*-PUFA - not to set
  - rate n-6 / n-3 - not to set
  - linoleic acid – 4 E%
  - α-linolenic acid – 0.5 E%

Intake of EPA+DHA



EFSA, 2010

The human body can synthesise EPA and DHA from alpha-linolenic acid, but

- **1 g EPA+DHA/day** - intervention studies have demonstrated beneficial effects on recognised cardiovascular risk factors as
  - a reduction of plasma triacylglycerol concentrations
  - platelet aggregation
  - blood pressure

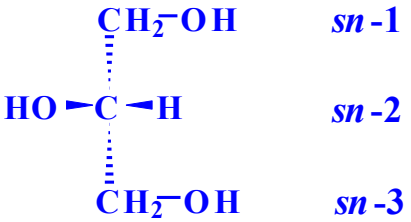
With respect to cardiovascular diseases (CVD), prospective epidemiological and dietary intervention studies indicate that oily fish consumption or dietary n-3 long-chain polyunsaturated fatty acids supplements (equivalent to a range of 250 to 500 mg of eicosapentaenoic acid plus docosahexaenoic acid daily) decrease the risk of mortality from coronary heart disease (CHD) and sudden cardiac death**.**

- **250 mg EPA+DHA/day** appears to be sufficient for primary prevention of CVD in healthy subjects

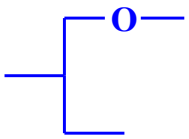
Advice for the adult population

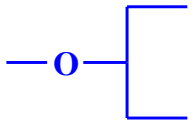
- **1 to 2** fatty fish meals per week or ~250 mg of eicosapentaenoic acid plus docosahexaenoic acid per day

esters of glycerol



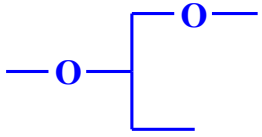
monoacylglycerols (monoglycerides)

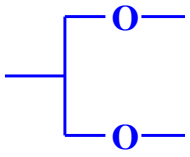




1-monoacyl-*sn*-glycerol **2- monoacyl-*sn*-glycerol**

diacylglycerols (diglycerides)

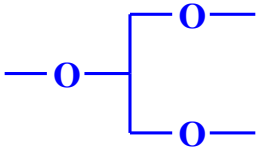




1,2-diacyl- **1,3-diacyl-**

triacylglycerols (triglycerides)

1,2,3-triacyl-



Lipid composition of refined oils

esters	%	
	rapeseed	sunflower
1-monoacylglycerols	0.6	0.2
2-monoacylglycerols	0.1	0.1
1,3-diacylglycerols	1.9	0.9
1,2-diacylglycerols	0.2	0.1
triacylglycerols	96.5	97.8

physical-chemical properties

melting point, thawing point, hardening point (in given range of temperature)

- structure of FA, TAG (number of C, multiple double bounds)
- configuration of crystals
- conformation of unsaturated fatty acid chain (lowers thawing point.)

	FA	Melting p. [°C]		FA	Melting p. [°C]
C4	butyric	-7.9	C18:1c	oleic	10.,5
C6	capronic	-3.4	C18:1t	elaidic	43.7
C8	caprylic	16.3			
C10	caprinic	31.6	C18:2	linoleic	-5.0
C12	lauric	44.2	C18:3	linolenic	-11.0
C14	myristic	54.1			
C16	palmitic	62.7	C20:4	arachidonic	-49.5
C18	stearic	69.6			

polymorphism **basic crystal modifications**

$\alpha \rightleftharpoons \beta \rightleftharpoons \beta'$

lowest melting point **highest melting point**

hexagonal **triclinic** **ortorhombical**

triacylglycerol	melting point [°C]		
	α	β	β´
tripalmitin	44	56	66
tristearin	54	64	73
triolein	-32	-13	4

β: lard, olive oil, cacao butter (symetric structure, large crystals, granular texture)

β´: tallow, butter, rapeseed oil (nesymetric structure, small crystals, plastic consistency)

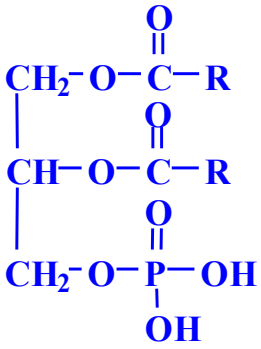
cacao butter 6 polymorphic modifications with melting p. 17.3-36.4 °C

melting point of chocolate 32-36 °C

phospholipids

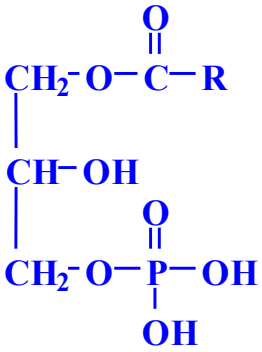
phosphatides and fospholipamides **stabilisation of emulsions**

phosphatides (phosphatidyl derivatives, lyso phosphatidyl derivatives, plasmalogens)



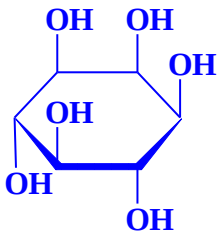
phosphatidyl acid

phosphatidylcholine



lysophosphatidyl acid

lysophosphatidylcholine



$(CH_3)_3N^+\text{-}CH_2\text{-}CH_2\text{-}OH$ **choline (lecithine)**

$H_2N\text{-}CH_2\text{-}CH_2\text{-}OH$ **ethanolamine**

serine

inositol (*myo*-inositol)

importance

- components of biomembranes (about 1% of dry matter even in nonfat food)
- emulsion stabilizers - oil in water (milk, mayonnaise)
  - water-in-oil (butter, margarine)

utilization

- in bakeries (substance improving the properties of dough)
- to reduce the viscosity of the chocolate
- for instantized powdered beverages (e.g. dairy)

instantized powdered beverages

several technologies can be used in order to produce instantized powders :

1) agglomeration, which results in an increased particle size and a more porous powder structure that improves the penetration of the liquid ;

2) use of a surface-active agent, which compensates the inconvenient powder surface behavior ;

3) combination of both agglomeration + surface-active agent

instantized whey protein

whole milk powder

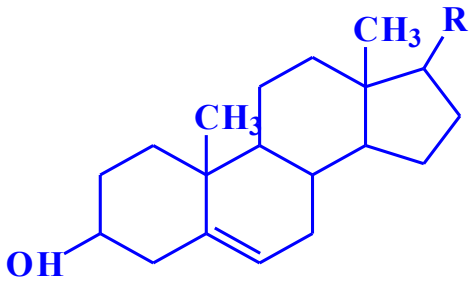
lipid accompanying compounds

lipoides, unsaponifiables

sterols **zoosterols** (cholesterol)

phytosterols (sitosterol)

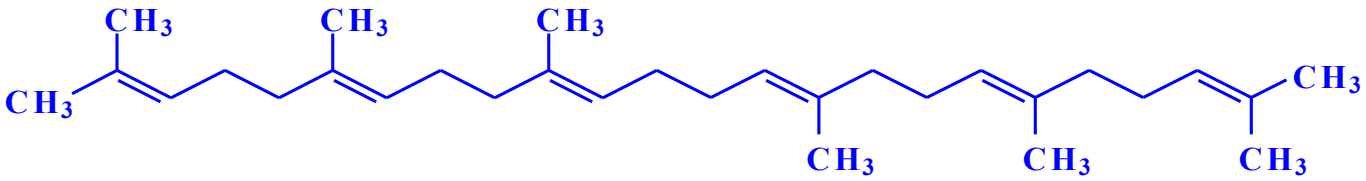
mycosterols (ergosterol) – from fungi



hydrocarbons

pentacosan C25, heptacosan C27, nonacosan C29

sum in olive oil = 30-100 mg/kg



higher terpenoic hydrocarbons - squalen C30 (precursor of steroides)

vitamins A, D, E, K

lipophilic pigments - carotenoids, chlorophylls

STEROLS

acetyl-CoA

↓

farnesylpyrophosphate

↓

squalen

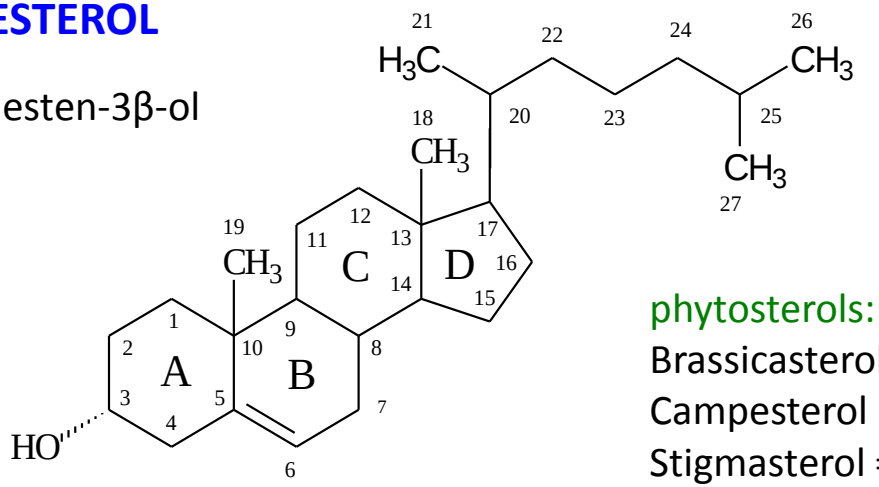
↙ ↘

lanosterol cycloartenol

other steroides

CHOLESTEROL

Δ^5-cholesten-3β-ol



phytosterols:

Brassicasterol = 24-methyl-$\Delta^{5,22}$-cholestadien-3β-ol

Campesterol = 24-methyl-Δ^5-cholesten-3β-ol

Stigmasterol = 24-ethyl-$\Delta^{5,22}$-cholestadien-3β-ol

β-Sitosterol = 24β-ethyl-Δ^5-cholesten-3β-ol

endogenic - metabolic processes (synthesized in the adrenal cortex)

exogenic - from food

importance:

+ production of adrenal cortical hormones and gonads
formation of bile acids
participation in the resorption of fat
structural element of biomembranes

- accumulation in the body, storing in blood vessels
formation of atherosclerosis

RDI: max. **300** mg/day

EFSA 2010: for cholesterol it was decided not to propose a reference value beside the limitation on the intake of SFA

Examples of cholesterol content in foods:

Food	(mg/100g fresh weight)
beef	70
liver	250
ham	70
sausages	100
herring	60
butter	240
cream	110
cheese Emmental	90
cheese Eidam (30%)	50
fruits, vegetables	traces
egg yolk (100 g)	1300
1 egg	220 - 240
mayonnaise	90 - 120

functional food

Flora pro.activ - margarine containing the active ingredient - plant sterols

plant sterols – it was clinically proven that the regular consumption of 2 - 2.5 grams per day reduced cholesterol levels by an average of 10% during 3 weeks / in combination with a varied balanced diet and a healthy lifestyle in diameter up to 15%