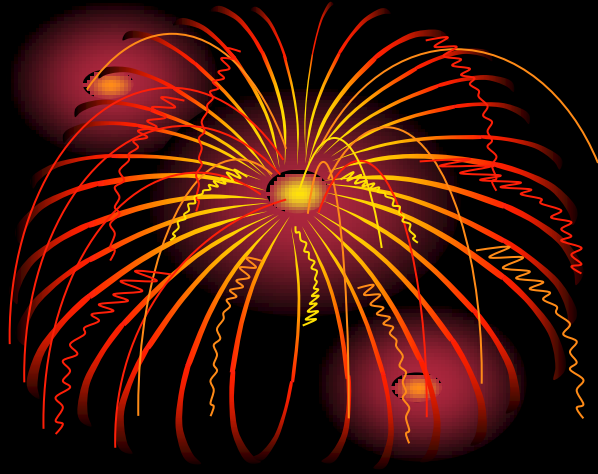


Fats :

Lipids / Phospholipids

Dr.Sulieman Al-Khalil

Lipids

- Lipids: a heterogeneous class of naturally occurring organic compounds classified together on the basis of common solubility properties.
- they are insoluble in water, but soluble in aprotic organic solvents, including diethyl ether, chloroform, methylene chloride, and acetone.
- Lipids include:

triacylglycerols, phosphodiacylglycerols, sphingolipids, glycolipids, lipid-soluble vitamins, and prostaglandins.

cholesterol, steroid hormones, and bile acids

- Lipids are efficient as energy-storage molecules
- Properties of lipids are strongly influenced by their melting temperature, which depends on their lengths and the number of double bonds (degree of unsaturation)
- Lipids also play a variety of other roles, from structural (membranes) to signaling (hormones)
- The defining feature of lipids is that they are insoluble in water.

- There are four major functions of lipids:

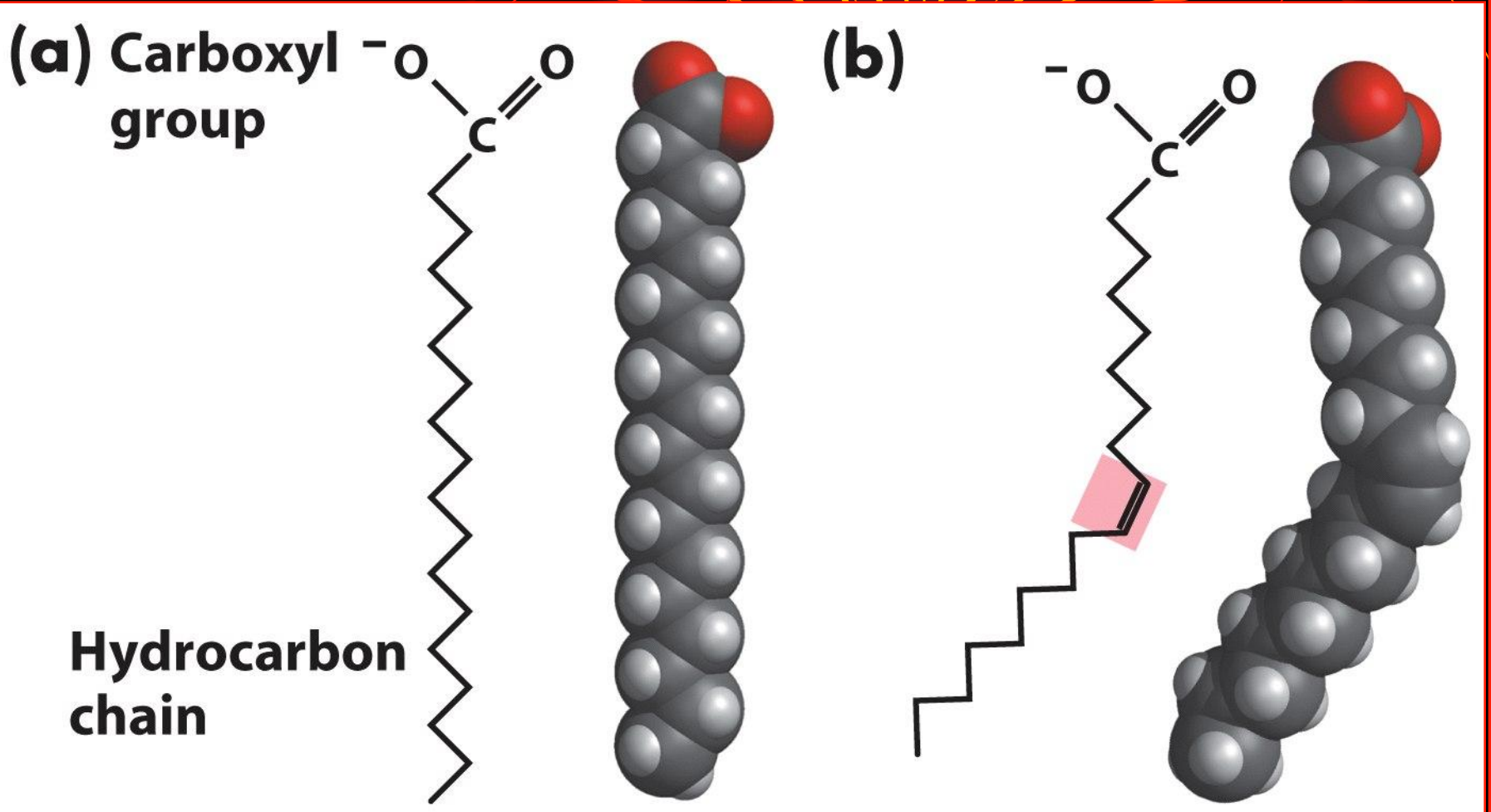
1. Energy storage (*e.g.* triacylgycerols)
2. structural (membranes)
3. vitamins and hormones (*e.g.* vitamins A,D; steroids)
4. solubilization of other lipids (*e.g.* bile acids)

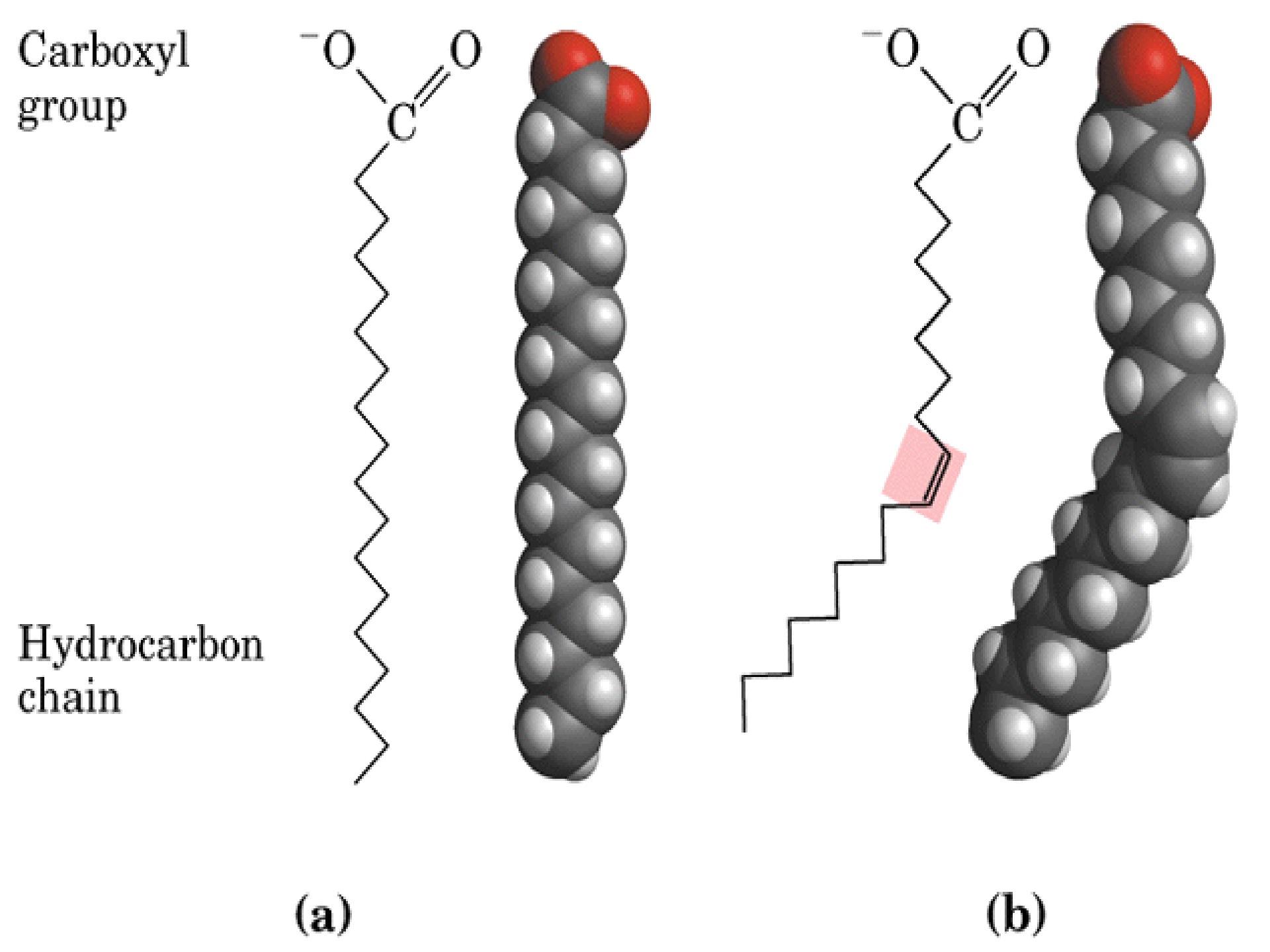
1. Energy Storage lipids: fatty acids and triacylglycerols

Fatty acids

- – carboxylic acids with long hydrocarbon chains .
  - $CH_3(CH_2)_nCOOH$ structural formula
  - chains range from four to 36 carbons
  - Can be branched or unbranched
  - Can be saturated or unsaturated (if unsaturated, there are double bonds)

Basic Structure of Fatty Acids




Carboxyl group
Hydrocarbon chain
(a)
(b)

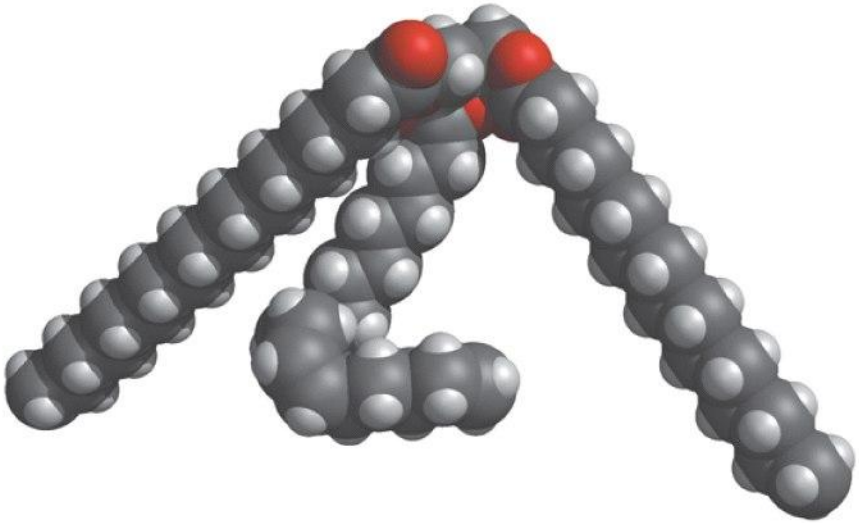
Fatty Acids

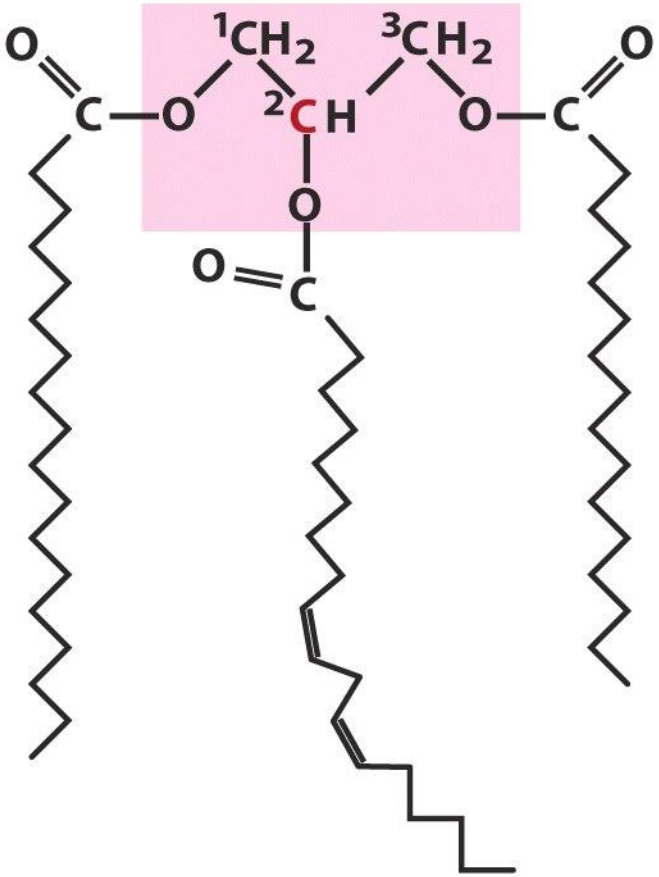
- Fatty acid: a long, unbranched chain carboxylic acid, most commonly of 12 - 20 carbons, derived from hydrolysis of animal fats, vegetable oils, or phosphodiacylglycerols of biological membranes

- In the shorthand notation for fatty acids

  - the number of carbons and the number of double bonds in the chain are shown by two numbers, separated by a colon

Fatty Acids Are Present in Triacylglycerols





1-Stearoyl, 2-linoleoyl, 3-palmitoyl glycerol, a mixed triacylglycerol

- **Fatty Acids**
  - Among the fatty acids most abundant in plants and animals
  - nearly all have an even number of carbon atoms, most between 12 and 20, in an unbranched chain
  - the three most abundant are palmitic (16:0), stearic acid (18:0), and oleic acid (18:1)
  - in most unsaturated fatty acids, the cis isomer predominates; the trans isomer is rare
  - unsaturated fatty acids have lower melting points than their saturated counterparts; the greater the degree of unsaturation, the lower the melting point

TABLE 10–1 Some Naturally Occurring Fatty Acids: Structure, Properties, and Nomenclature

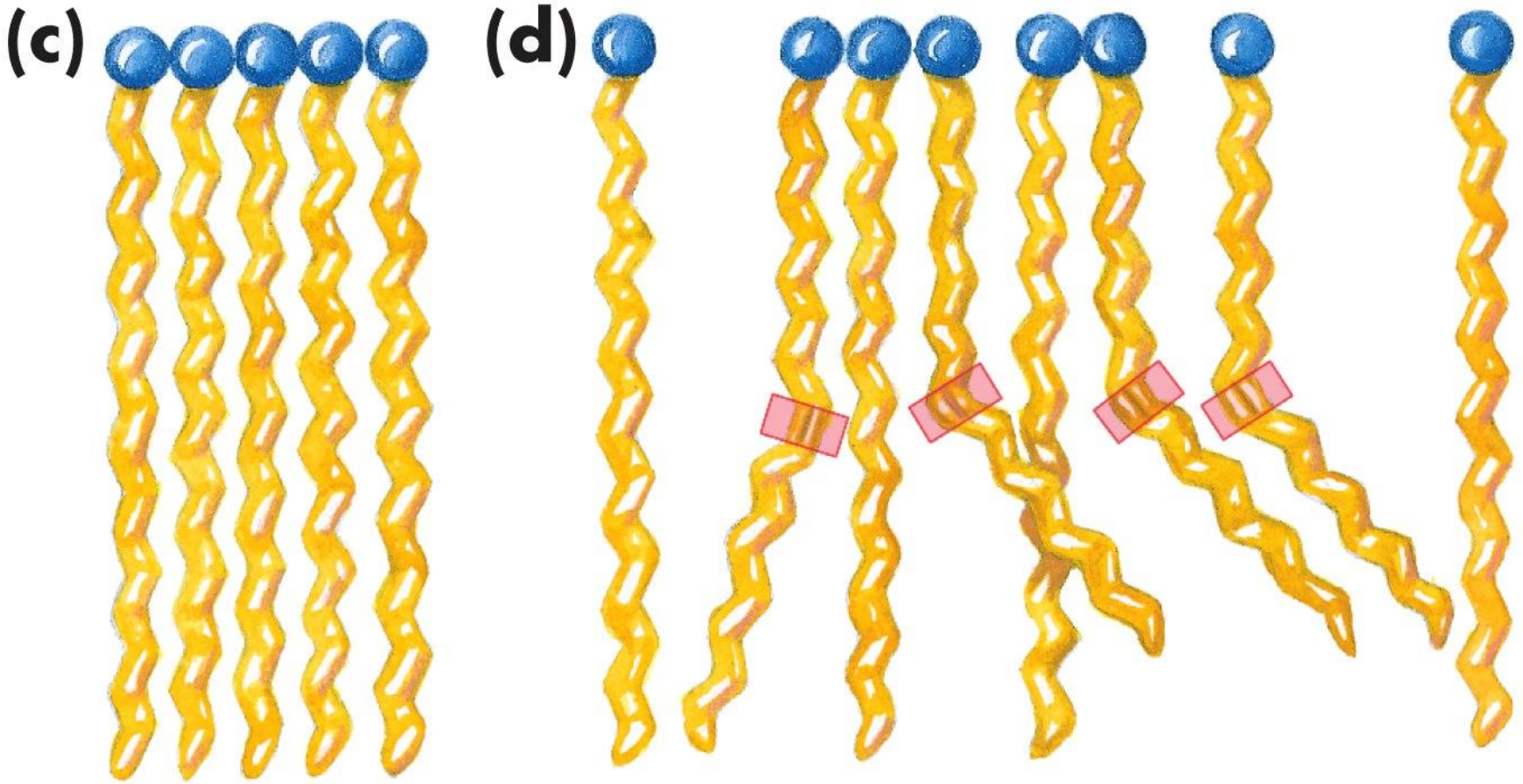
Carbon skeleton	Structure*	Systematic name†	Common name (derivation)	Melting point (°C)	Solubility at 30 °C (mg/g solvent)	
					Water	Benzene
12:0	$CH_3(CH_2)_{10}COOH$	*n*-Dodecanoic acid	Lauric acid (Latin *laurus*, "laurel plant")	44.2	0.063	2,600
14:0	$CH_3(CH_2)_{12}COOH$	*n*-Tetradecanoic acid	Myristic acid (Latin *Myristica*, nutmeg genus)	53.9	0.024	874
16:0	$CH_3(CH_2)_{14}COOH$	*n*-Hexadecanoic acid	Palmitic acid (Latin *palma*, "palm tree")	63.1	0.0083	348
18:0	$CH_3(CH_2)_{16}COOH$	*n*-Octadecanoic acid	Stearic acid (Greek *stear*, "hard fat")	69.6	0.0034	124
20:0	$CH_3(CH_2)_{18}COOH$	*n*-Eicosanoic acid	Arachidic acid (Latin *Arachis*, legume genus)	76.5		
24:0	$CH_3(CH_2)_{22}COOH$	*n*-Tetracosanoic acid	Lignoceric acid (Latin *lignum*, "wood" + *cera*, "wax")	86.0		
16:1(Δ^9)	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	*cis*-9-Hexadecenoic acid	Palmitoleic acid	1–0.5		
18:1(Δ^9)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	*cis*-9-Octadecenoic acid	Oleic acid (Latin *oleum*, "oil")	13.4		
18:2($\Delta^{9,12}$)	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	*cis*-,*cis*-9,12-Octadecadienoic acid	Linoleic acid (Greek *linon*, "flax")	1–5		
18:3($\Delta^{9,12,15}$)	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	*cis*-,*cis*-,*cis*-9,12,15-Octadecatrienoic acid	α-Linolenic acid	−11		
20:4($\Delta^{5,8,11,14}$)	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3COOH$	*cis*-,*cis*-,*cis*-,*cis*-5,8,11,14-Icosatetraenoic acid	Arachidonic acid	−49.5		

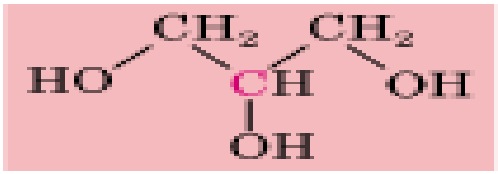
*All acids are shown in their nonionized form. At pH 7, all free fatty acids have an ionized carboxylate. Note that numbering of carbon atoms begins at the carboxyl carbon.

†The prefix *n*- indicates the "normal" unbranched structure. For instance, "dodecanoic" simply indicates 12 carbon atoms, which could be arranged in a variety of branched forms; "*n*-dodecanoic" specifies the linear, unbranched form. For unsaturated fatty acids, the configuration of each double bond is indicated; in biological fatty acids the configuration is almost always cis.

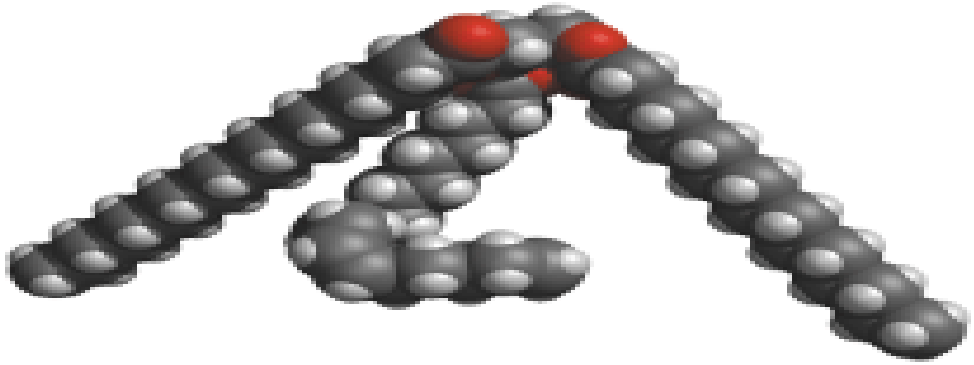
	Carbon Atoms/ Double Bonds	Common Name	mp (°C)
Saturated	12:0	lauric acid	44
	14:0	myristic acid	58
	16:0	palmitic acid	63
	18:0	stearic acid	71
	20:0	arachidic acid	77
Unsaturated	16:1	palmitoleic acid	-0.5
	18:1	oleic acid	16
	18:2	linoleic acid	-5
	18:3	linolenic acid	-11
	20:4	arachidonic acid	-49

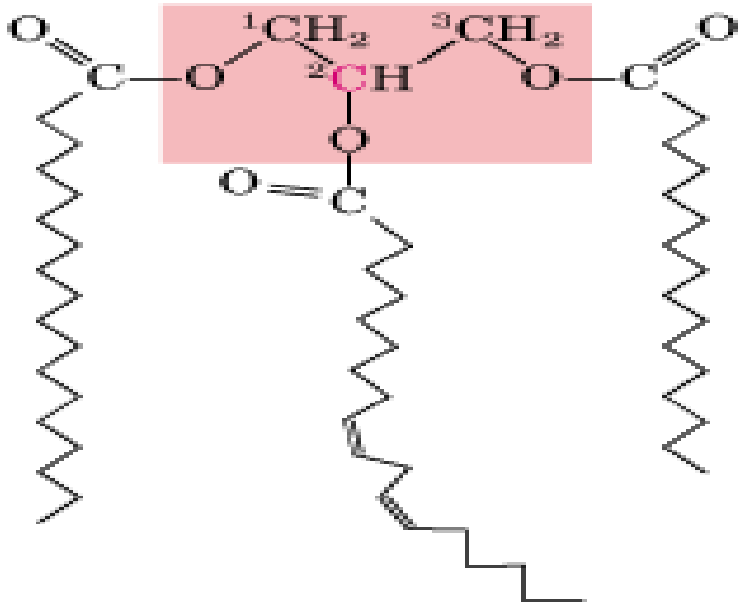
Physical Properties of Fatty Acids





Glycerol

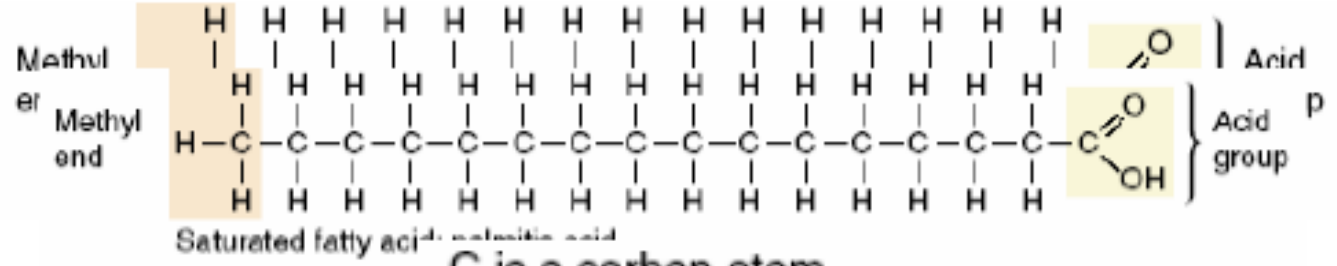




1-Stearoyl, 2-linoleoyl, 3-palmitoyl glycerol,
a mixed triacylglycerol

- **Nomenclature:** three forms are used; common names, systematic names, and abbreviations
  - palmitic acid (common name), hexadecanoic (systematic name), 16:0 (abbreviation, means 16 carbons and no double bonds)
  - oleic acid; octadecanoic; 18:1(D9) (means 18 carbons, one double bond between C9 and C10. C1 is the carboxyl carbon)
  - linoleic acid; cis-,cis-9-12-octadecanoic; 18:2(D9,12) (18 carbons, double bonds between C9 and C10 and between C12 and C13)

The Types of Fatty Acids



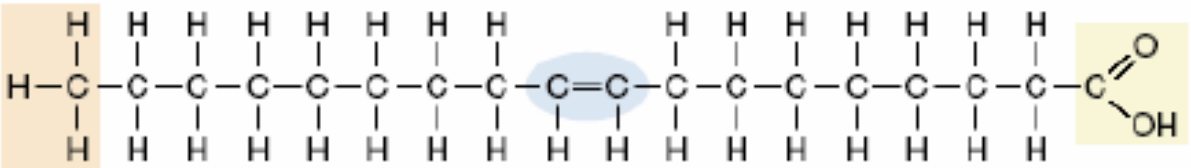
C is a carbon atom.
H is a hydrogen atom.
— is a single bond.
= is a double bond.

- **Saturated fatty acid**: a fatty acid carrying the maximum possible number of hydrogen atoms (having no points of unsaturation). Saturated fats are found in animal foods like meat, poultry, and full-fat dairy products, and in tropical oils such as palm and coconut.

Storage of Fat

- 5-6 times more efficient to store than carbohydrate or protein
  - More energy dense
  - Has less water per gram
- Most triglycerides stored in adipose tissue
  - Some in muscle tissue, quite a bit in liver, little in blood

The Types of Fatty Acids

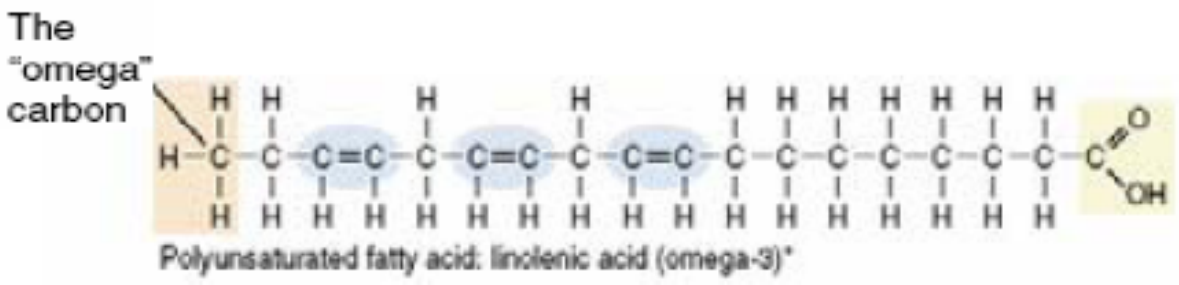


Monounsaturated fatty acid: oleic acid (omega-9)*

C=C is a point of unsaturation.

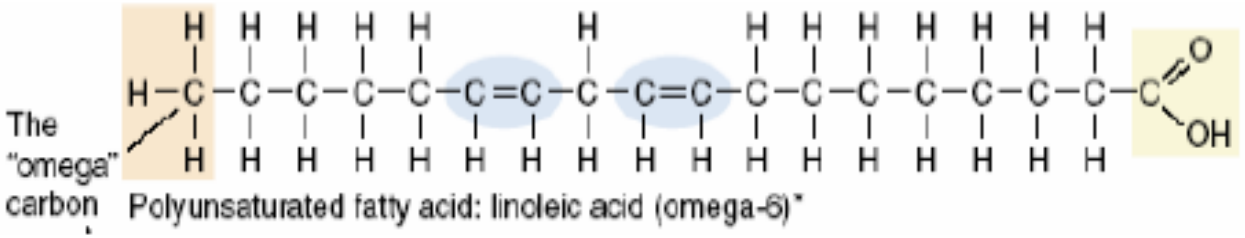
- **Unsaturated fatty acid:** a fatty acid with one or more points of unsaturation. Unsaturated fats are found in foods from both plant and animal sources. Unsaturated fatty acids are further divided into monounsaturated fatty acids and polyunsaturated fatty acids.
- **Monounsaturated fatty acid:** a fatty acid containing one point of unsaturation, found mostly in vegetable oils such as olive, canola, and peanut.

The Types of Fatty Acids



- **Polyunsaturated fatty acid:** (sometimes abbreviated PUFA) a fatty acid in which two or more points of unsaturation occur, found in nuts and vegetable oils such as safflower, sunflower, and soybean, and in fatty fish.

Polyunsaturated Fatty Acids

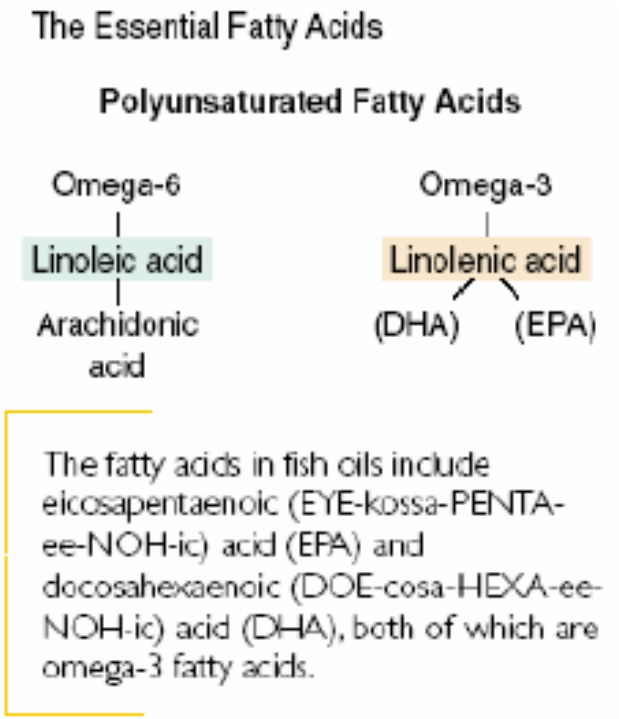


Polyunsaturated fatty acid: lincleic acid (omega-6)*

- **Linoleic (lin-oh-LAY-ic) acid**, **linolenic (lin-oh-LEN-ic) acid:** polyunsaturated fatty acids, essential for human beings.
- **Essential fatty acid:** a fatty acid that cannot be synthesized in the body in amounts sufficient to meet physiological need.

- arachidonic acid; 20:4(D5,8,11,14)
- Most commonly-occurring fatty acids have even number of carbons.
- This is because the biosynthetic pathway builds chains in 2-carbon units.
- There is a general pattern of double bonds: the 1st is between C9 and C10, then others are usually spaced three carbons apart.
- The double bonds are almost never conjugated (they would be if they were two carbons apart).
- In naturally occurring fatty acids, almost all double bonds are in cis conformation.

Essential Fatty Acids



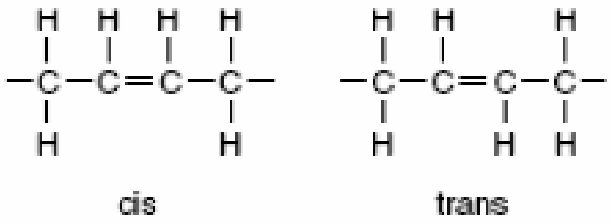
- Omega-3 fatty acids, found in fish oils, offer a protective effect on health.
  - Interest in fish oils was first kindled when someone thought to ask why the Eskimos of Greenland, who eat a diet very high in fat, have such a low rate of heart disease.
  - Blood clot formation, inflammation (e.g. arthritis, asthma), irregular heart rhythm and cancer also seem to be beneficially affected by DHA and/ or EPA.

The Trans Fatty Acid Controversy

- **Trans fatty acid:** a type of fatty acid created when an unsaturated fat is hydrogenated.
  - Hydrogenation is performed in order to increase shelf-life of food
  - Found primarily in margarines, shortenings, commercial frying fats, and baked goods.
  - Trans fatty acids have been implicated in research as culprits in heart disease.

TYPES OF UNSATURATED FATTY ACIDS: *CIS* VERSUS *TRANS*

Unsaturated fatty acids are either in *cis* form or in *trans* form, depending on the way in which the hydrogen atoms are attached to the points of unsaturation in the carbon chain. If the hydrogen atoms are attached to the same side of the points of unsaturation, the arrangement is called *cis*. If the hydrogen atoms are attached to different sides, the arrangement is called *trans*.

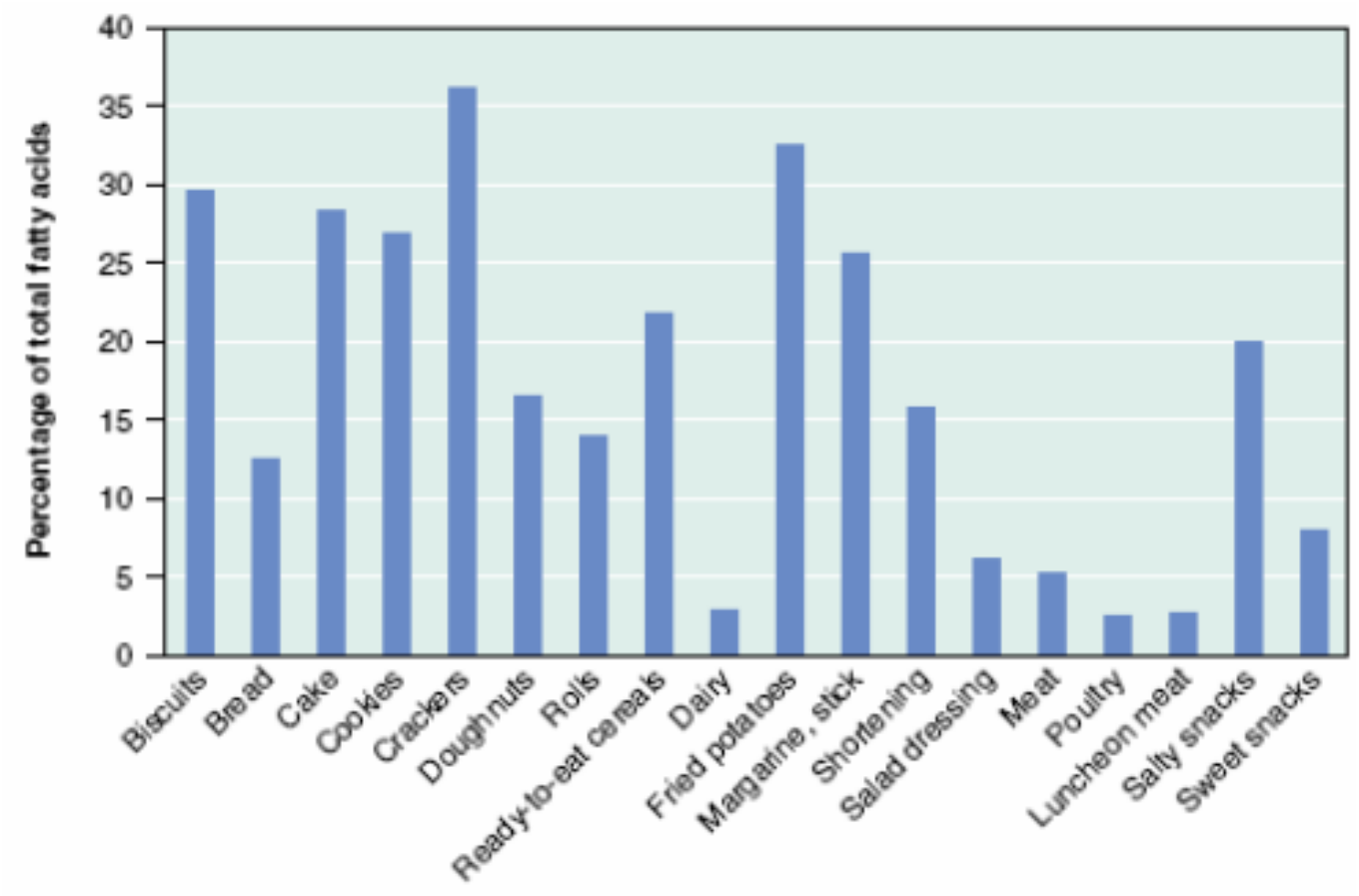


cis trans

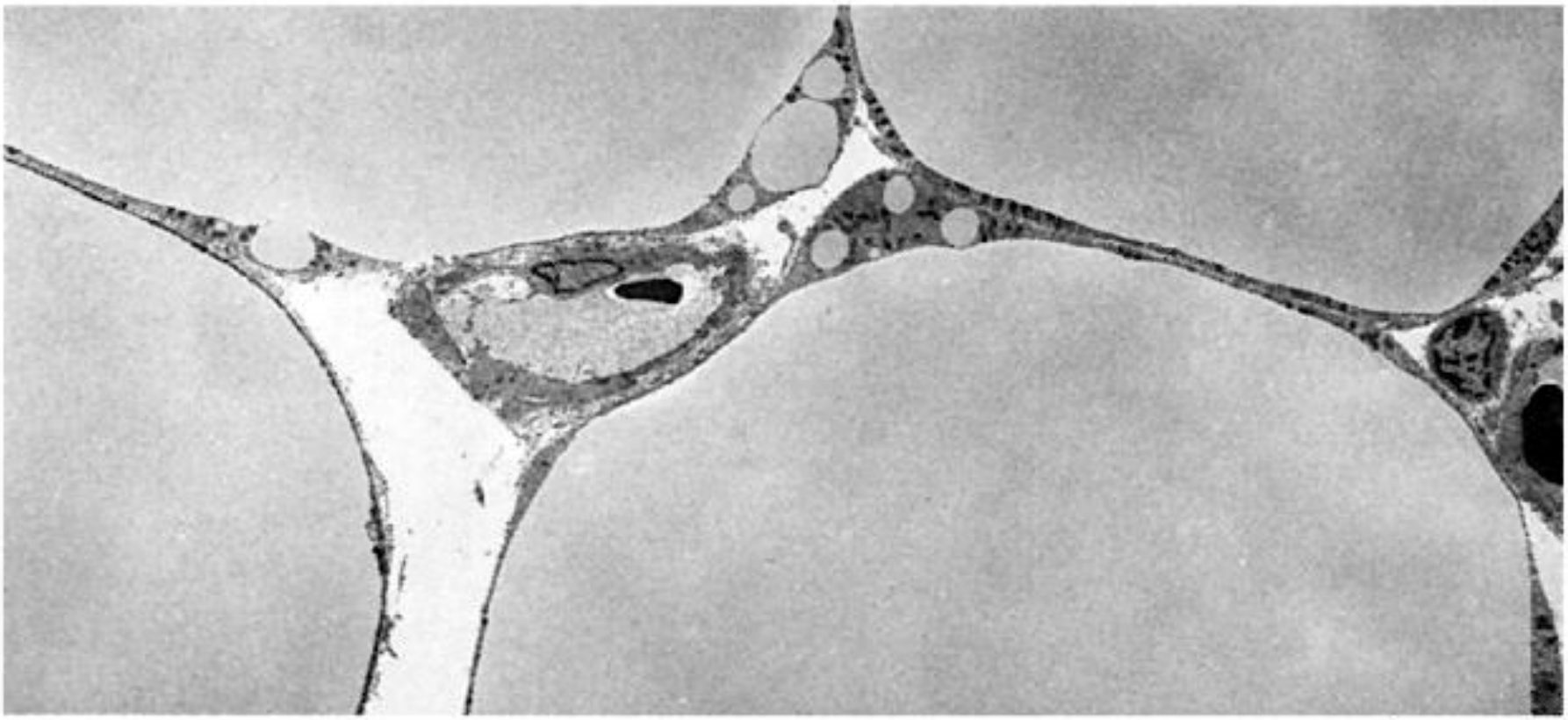
cis = same

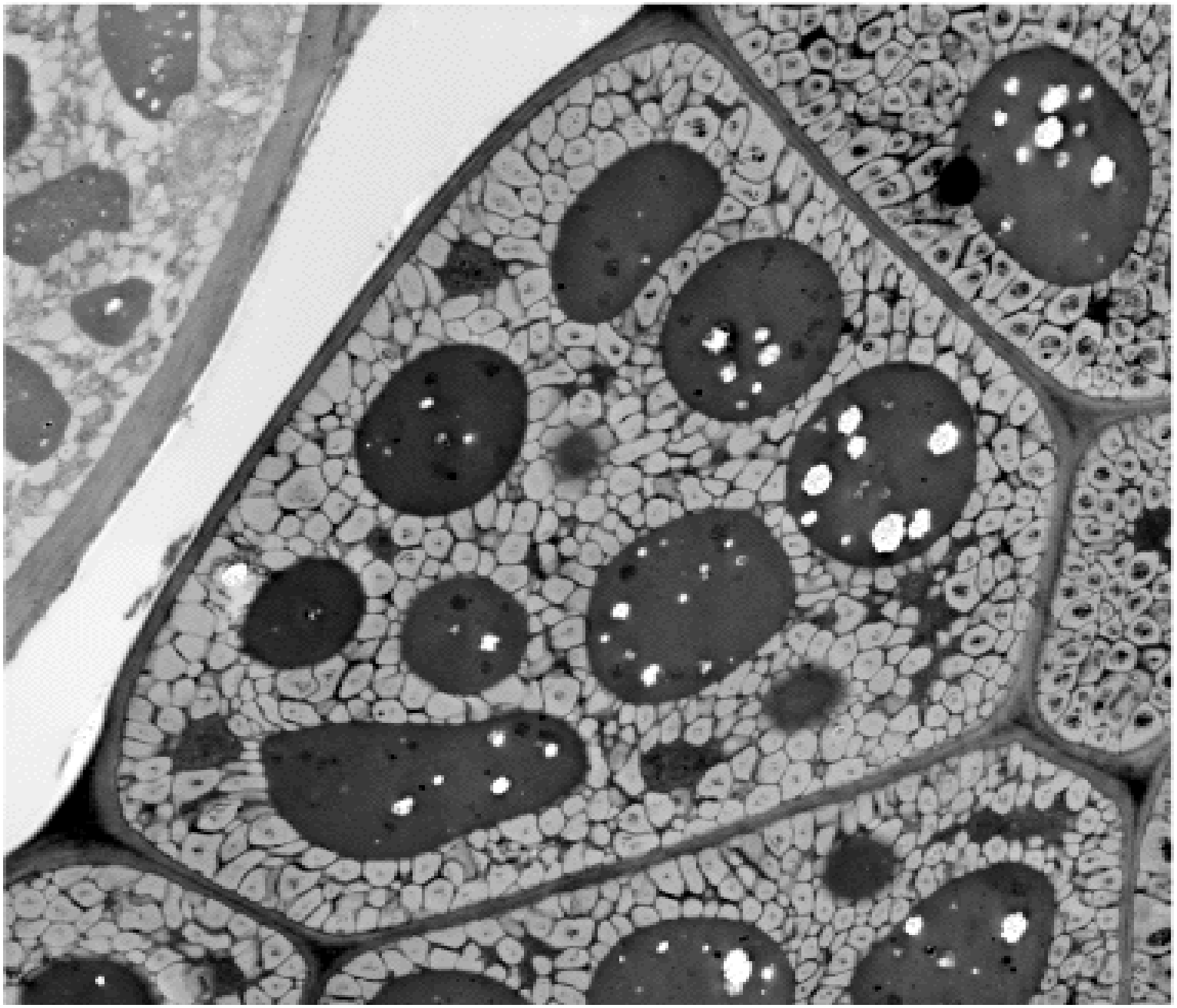
trans = across

Food Sources of Trans Fats



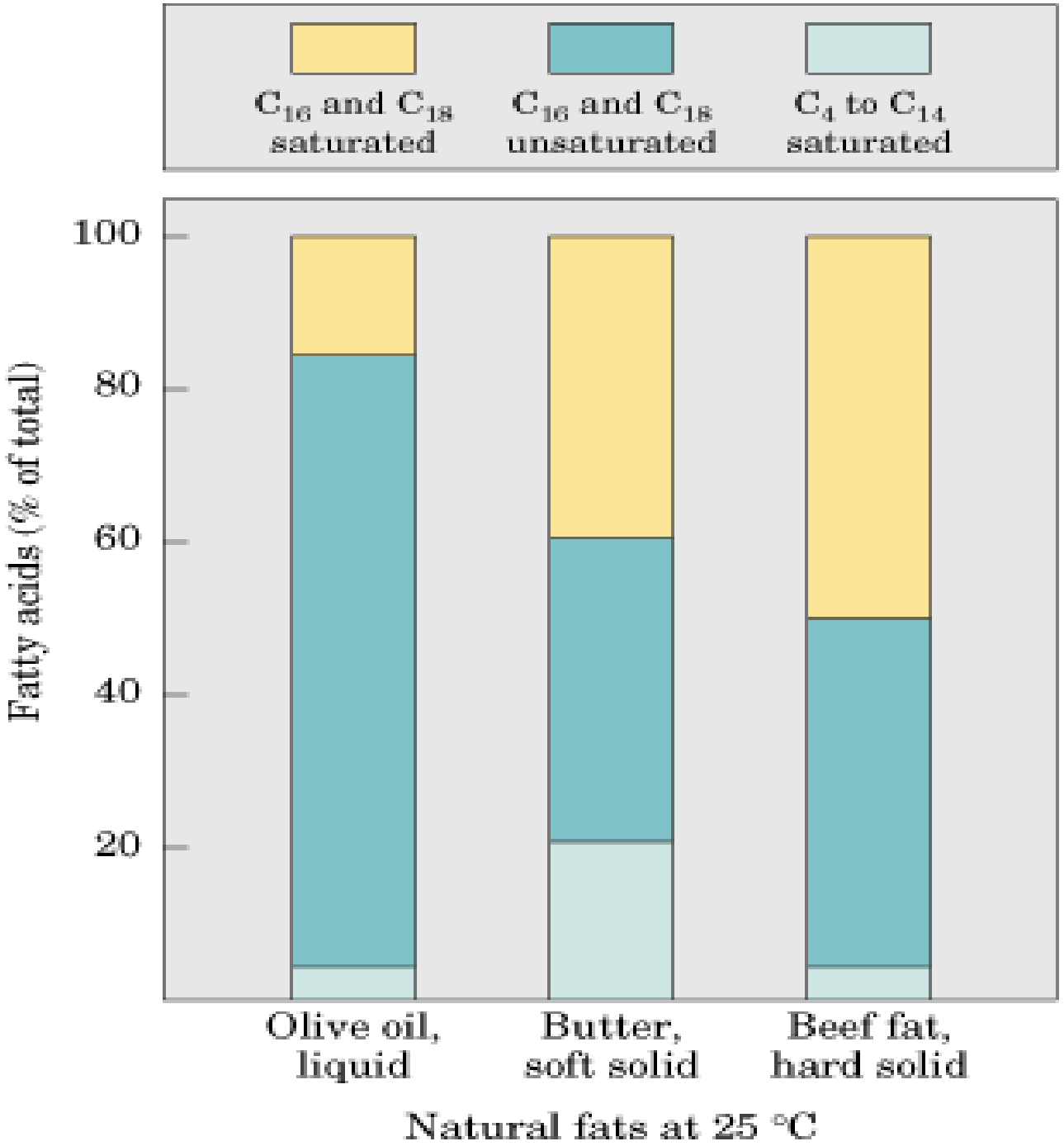
Fat Storage Cells are Fat-filled




(b)
3 μm

Chemical and physical properties of fatty acids:

- largely determined by the length and degree of unsaturation of the hydrocarbon chain. These properties affect the melting point.
- At 25 °C, saturated fatty acids with 12-24 carbons have waxy consistency, whereas unsaturated fatty acids of the same length are oily liquids.
- The longer the chain, the higher the melting point (compare lauric acid, 44 °C with stearic acid, 70 °C)

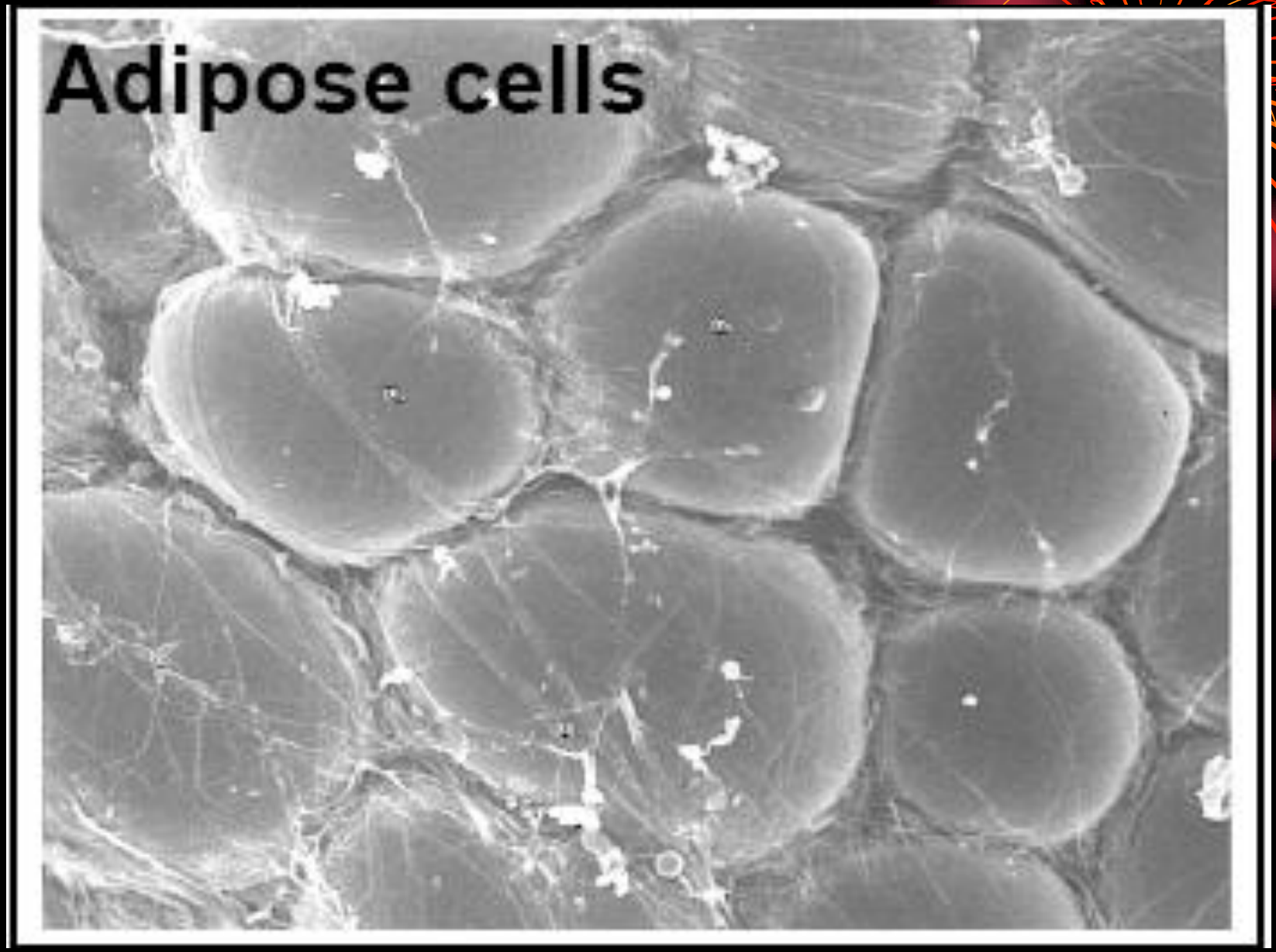

C_{16} and C_{18} saturated
C_{16} and C_{18} unsaturated
C_4 to C_{14} saturated
100
80
60
40
20
Fatty acids (% of total)
Olive oil, liquid
Butter, soft solid
Beef fat, hard solid
Natural fats at 25 °C

- Double bonds lower the melting temperature (compare stearic acid, 70 °C with oleic, 13 °C). Cis double bonds bend the chains, preventing tight packing and favoring the liquid form .
- These factors are important in determining membrane fluidity, which is critical to proper membrane function.
- Many cells can change the fatty acid content of their membranes in response to temperature changes to keep membranes fluid at lower temperatures.

- The nonpolar hydrocarbon chain is very hydrophobic.
- This accounts for the insolubility in water. However, the p*K*a of the carboxyl group is about 4.7.
- Therefore, at neutral pH fatty acids will be anionic.
- Actually, fatty acids are usually not found in the body as free acids, but instead are esterified to some backbone molecule (glycerol or sphingosine)

Triacylglycerols: fatty acid esters of glycerol .

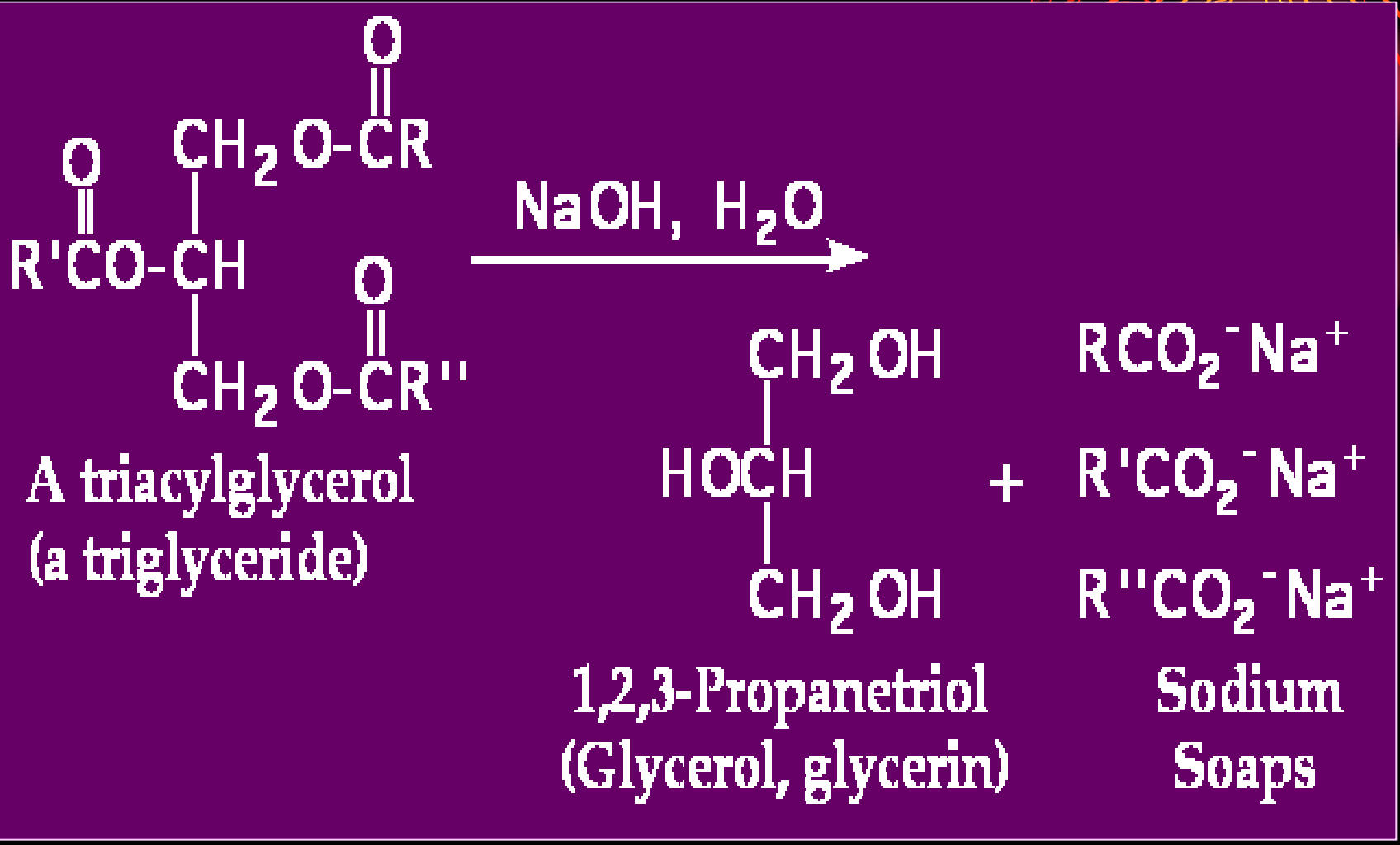
- 3 fatty acids in ester linkages with the 3 OH groups of glycerol:
- The three fatty acids can be identical, but more commonly there are three different chains.
- Triacylglycerols are non-polar because the polar groups are bound up in ester bonds.
- Therefore they are insoluble in water.
- This is a major storage form of fatty acids.


Adipose cells

- They are stored primarily in adipose tissue as lipid vacuoles in the cytoplasm of adipocytes.
- This is a much more efficient way to store energy than glycogen:

fatty acids are very reduced (lots of electrons) and stored with virtually no water, saving weight.

- Most natural fats, such as those in vegetable oil, dairy products, and animal fat, are complex mixtures of simple and mixed triacylglycerols.
- When food becomes rancid, this is due to oxidative cleavage of the double bonds in unsaturated fatty acids, which produces aldehydes and carboxylic acids of shorter chain length and therefore higher volatility.


NaOH, H2O
A triacylglycerol
(a triglyceride)
1,2,3-Propanetriol
(Glycerol, glycerin)
Sodium
Soaps