Chemistry of Fats and Oils

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Contents

1. Introduction
2. Common Properties of Fats and Oils
2. Major Constituents of Fats and oils:
   Chemistry of Triglycerides and Fatty Acids
3. Reactions of Fats and Oils
4. Minor Constituents of Fats and Oils
5. Conclusion

Introduction

Fats and oils are biochemical units synthesized by plants and animals and made up of mostly carbon, hydrogen and oxygen elements.

- They are the most calorie-dense of all the nutrients found in foods: ~9kcal/g and contribute roughly 30-50% of our daily calorie intake.
- They improve palatibility of foods by modifying flavour and texture
- They are insoluble in water but soluble in most organic solvents.
- They are greasy to the touch, and have lubricating properties.
- They are not readily volatile.
- When burnt they do not leave any residue.
- They have lower densities than water.
- At normal room temperatures they range in consistency from liquids to solids. When solids, they are referred to as “fats” and when liquid they are called “oils.”

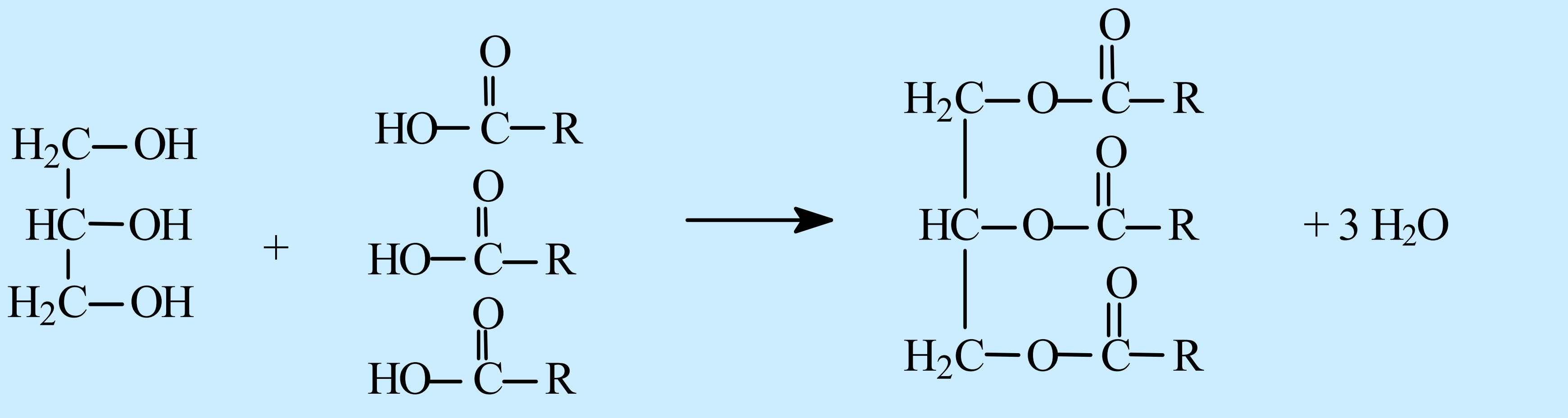
Chemical Properties

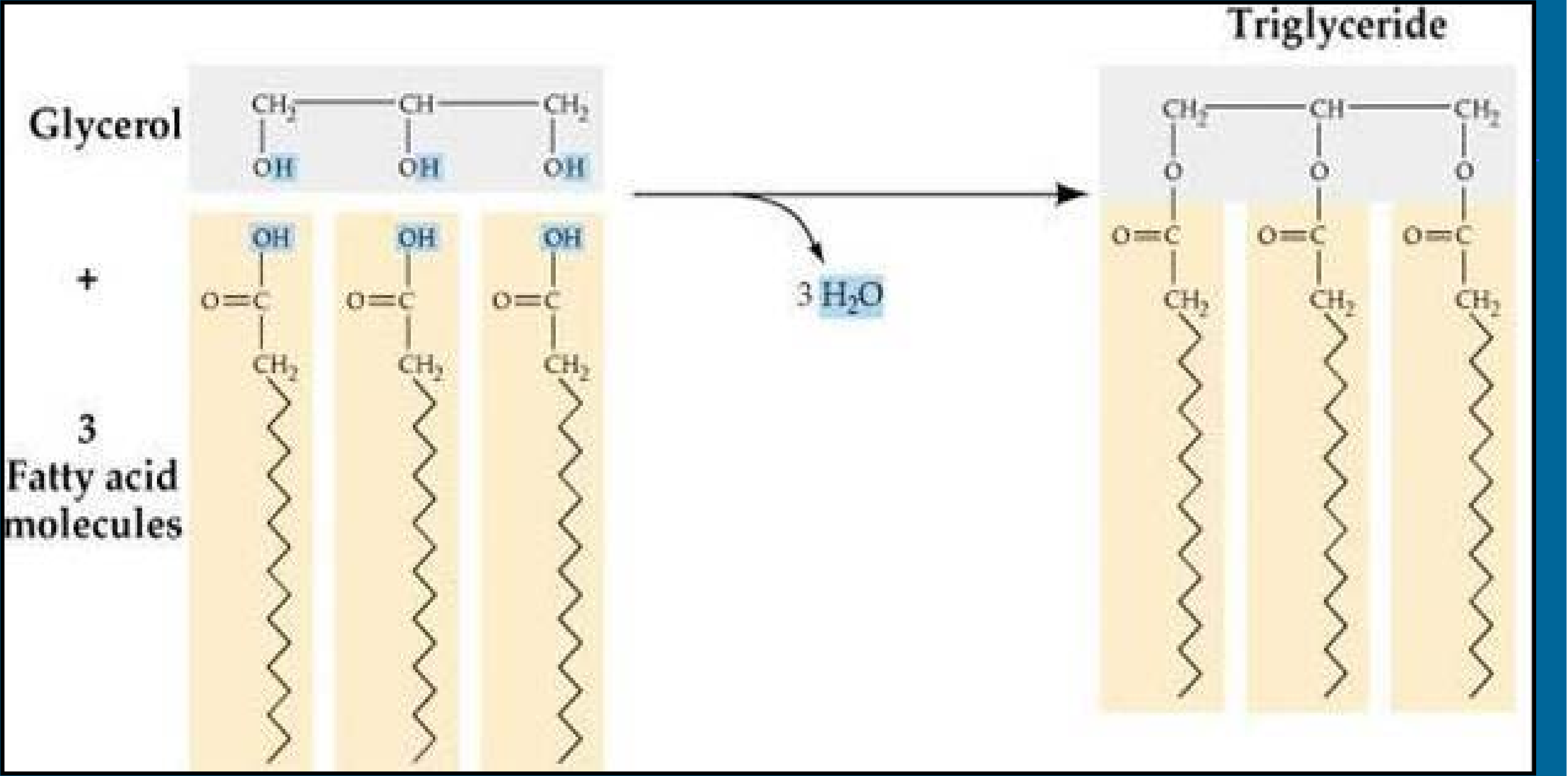
They belong to the upper class of biochemical compounds known as “Lipids”.

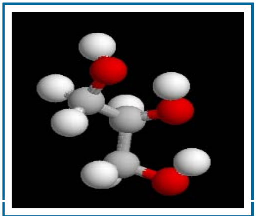
- In addition to fats and oils, the term lipids also include mono- and diglycerides, phosphatides, cerebrosides, sterols, terpenes, fatty alcohols, fatty acids, fat-soluble vitamins, and similar substances that are also found in minor amounts in fats and oils.

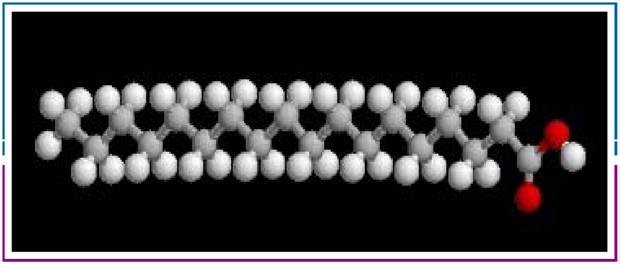
Triglycerides

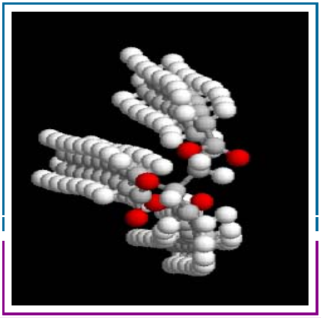
- The major and predominant component of fats and oils are triacylglcerols or ‘triglycerides’.
- A “triglyceride” is an ester of glycerol and three fatty acids.




Glycerol
+
3
Fatty acid
molecules
CH₂ CH CH₂
OH OH OH
O=C
CH₂
3 H₂O
Triglyceride
O
O=C
CH₂



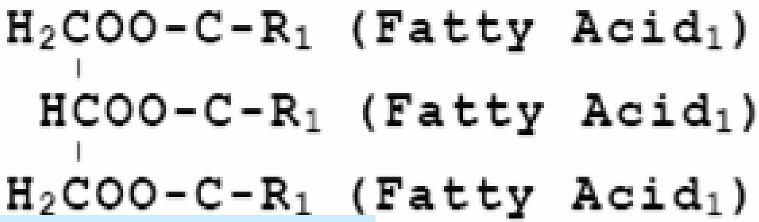




TRIGLYCERIDES

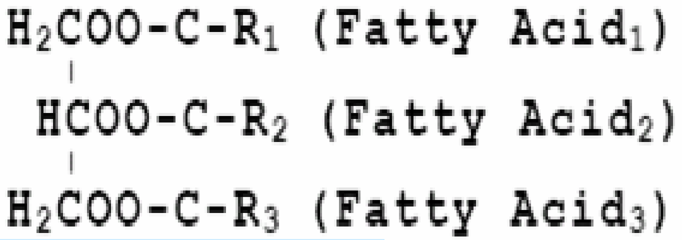
When all of the three fatty acids in a triglyceride are identical, it is termed a “simple” triglyceride.

The more common forms, however, are the “mixed” triglycerides in which two or three kinds of fatty acids are present in the same triglyceride molecule.



$$\begin{array}{l}
H_2COO\text{-}C\text{-}R_1\ (\text{Fatty Acid}_1) \\
\ \ | \\
\ HCOO\text{-}C\text{-}R_1\ (\text{Fatty Acid}_1) \\
\ \ | \\
H_2COO\text{-}C\text{-}R_1\ (\text{Fatty Acid}_1)
\end{array}$$

Simple Triglyseride



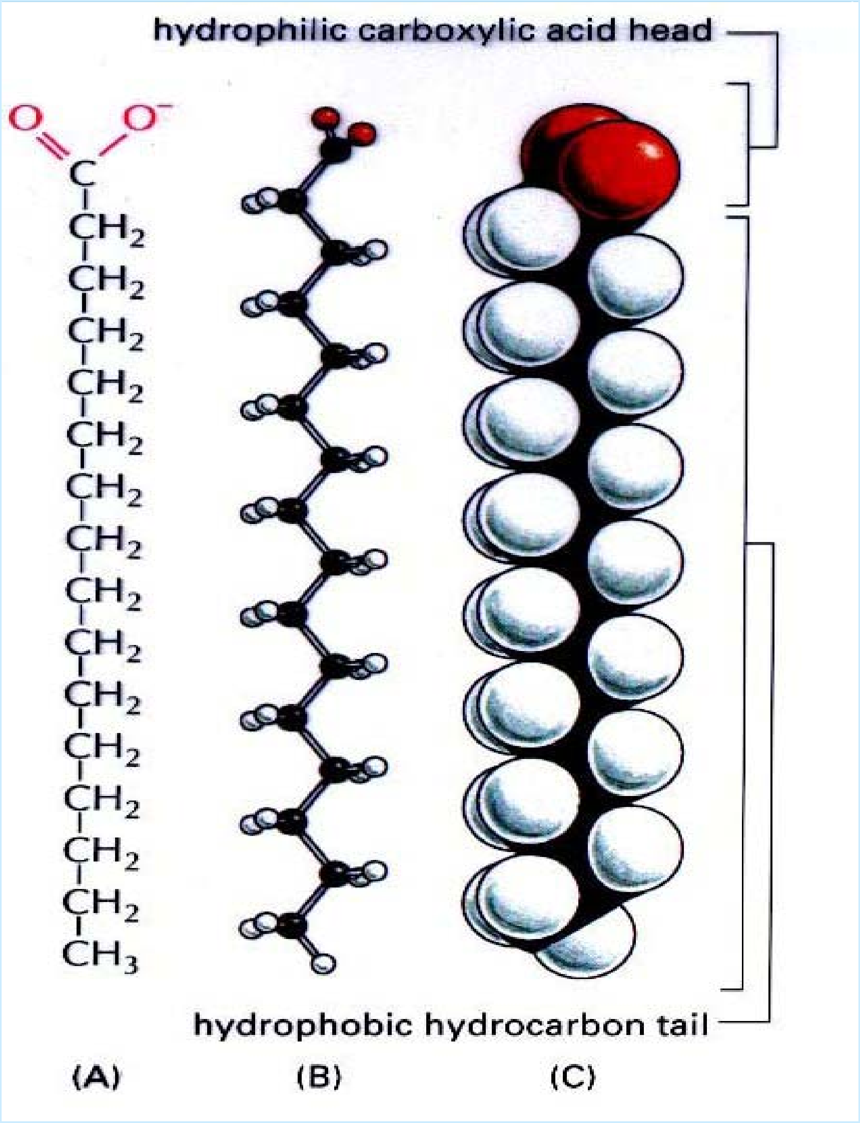
$$\begin{array}{l}
H_2COO\text{-}C\text{-}R_1\ (\text{Fatty Acid}_1) \\
\ \ | \\
\ HCOO\text{-}C\text{-}R_2\ (\text{Fatty Acid}_2) \\
\ \ | \\
H_2COO\text{-}C\text{-}R_3\ (\text{Fatty Acid}_3)
\end{array}$$

Mixed Triglyseride

FATTY ACIDS

The major portion of the triglyceride molecule is made up of fatty acids: One hundred grams of fat or oil contains approximately 95 grams of fatty acids.

Both the physical and chemical characteristics of fats are influenced greatly by the kinds and proportions of the component fatty acids and the way in which these are positioned on the triglyceride molecule.

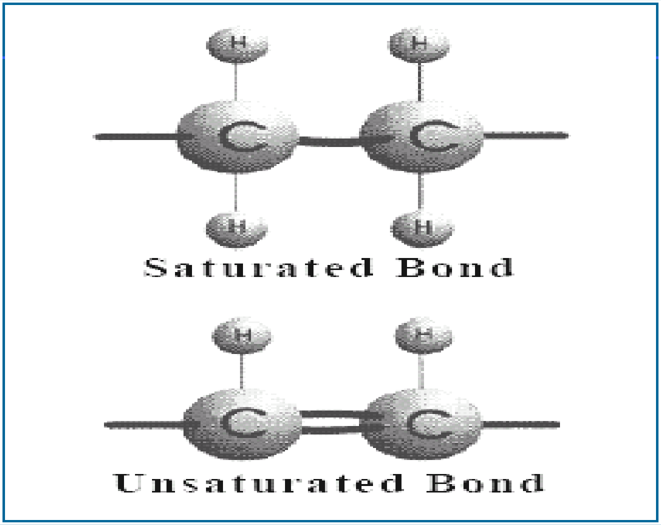


Fatty Acids

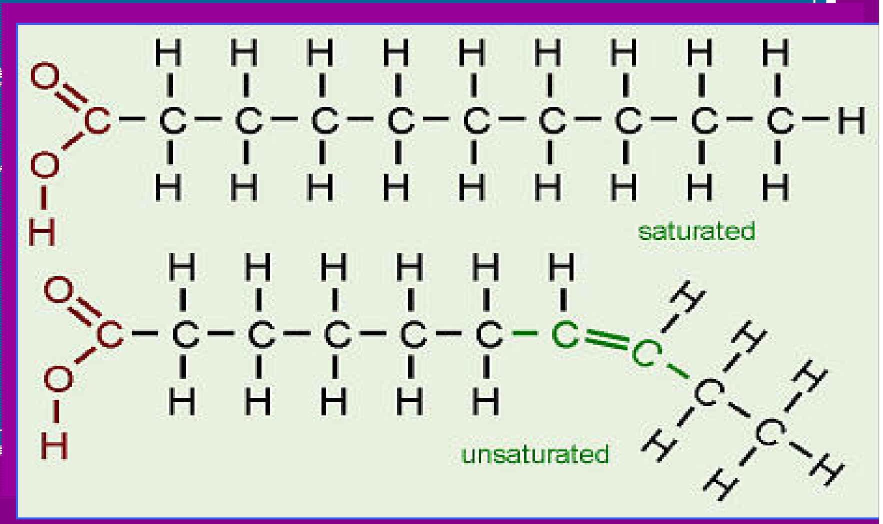
The predominant fatty acids found in most edible oils are saturated and unsaturated carbon chains with an even number of carbon atoms and a single carboxyl group.

Fatty acids can be classified according to their degree of ‘saturation’.

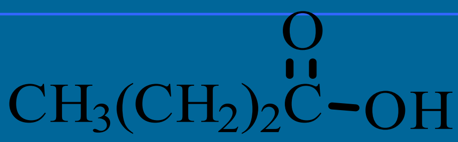
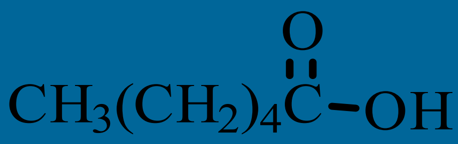
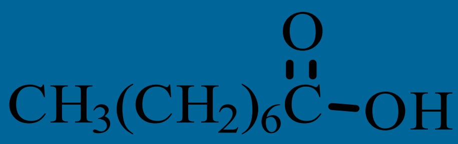
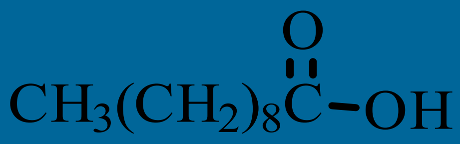
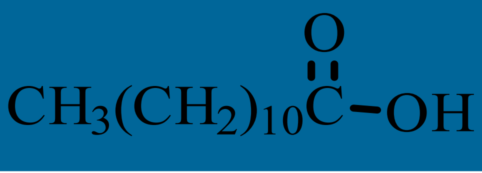
Saturated vs. Unsaturated Fatty Acids

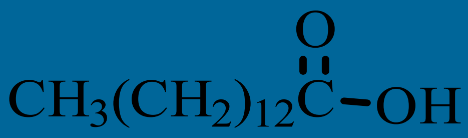
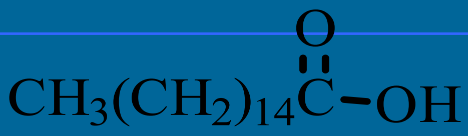
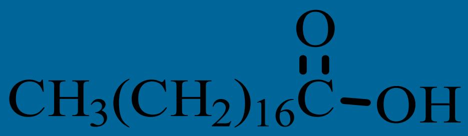
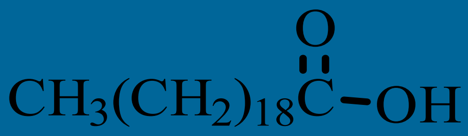
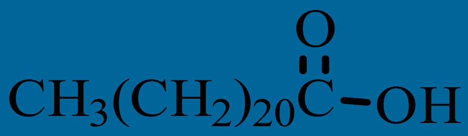
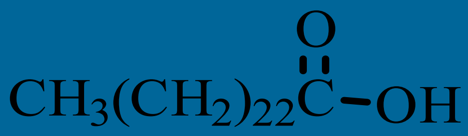


- Fatty acids containing only saturated (single carbon-to-carbon) bonds are called “saturated”.
- Fatty acids containing one or more double carbon-to-carbon bonds are termed “unsaturated.”
- The Iodine number or (Iodine Value) is used to assess the degree of unsaturation of fatty acids in fats and oils since iodine will add to their double bonds in proportion with unsaturation, IV being higher in higher degrees of unsaturation.



Common Saturated Fatty Acids:

Common Name	Systematic Name	Formula
Butyric acid (4C)	n-butanoic	 $CH_3(CH_2)_2\overset{\overset{O}{\parallel}}{C}-OH$
Caproic acid(6C)	n-hexanoic	 $CH_3(CH_2)_4\overset{\overset{O}{\parallel}}{C}-OH$
Caprylic acid (8C)	n-octanoic	 $CH_3(CH_2)_6\overset{\overset{O}{\parallel}}{C}-OH$
Capric acid(10C)	n-decanoic	 $CH_3(CH_2)_8\overset{\overset{O}{\parallel}}{C}-OH$
Lauric acid(12C)	n-dodecanoic	 $CH_3(CH_2)_{10}\overset{\overset{O}{\parallel}}{C}-OH$

Common Name	Systematic Name	Formula
Myristic acid(14C)	n-tetradecanoic	 $CH_3(CH_2)_{12}\overset{\overset{O}{\|}}{C}-OH$
Palmitic acid(16C)	n-hexadecanoic	 $CH_3(CH_2)_{14}\overset{\overset{O}{\|}}{C}-OH$
Stearic acid(18C)	n-octadecanoic	 $CH_3(CH_2)_{16}\overset{\overset{O}{\|}}{C}-OH$
Arachidic acid(20C)	n-eicosanoic	 $CH_3(CH_2)_{18}\overset{\overset{O}{\|}}{C}-OH$
Behenic acid(22C)	n-docosanoic	 $CH_3(CH_2)_{20}\overset{\overset{O}{\|}}{C}-OH$
Lignoceric acid(24C)	n-tetracosanoic	 $CH_3(CH_2)_{22}\overset{\overset{O}{\|}}{C}-OH$

Common Monounsaturated Fatty Acids (Monoenoic-MUFA)

Common Name	Systematic Name *cis*
Myristoleic	9-tetradecenoic acid
Palmitoleic	9-hexadecenoic acid
Oleic	9-octadecenoic acid
Erucic	13-docosenoic acid

Common Polyunsaturated Fatty Acids (Polyenoic-PUFA)

Common Name	Systematic Name
Linoleic:	9,12-octadecadienoic acid(2 double bonds)
Linolenic:	9,12,15-octadecatrienoic acid(3 double bonds)
Arachidonic:	5,8,11,14-eicosatetraenoic acid(4 double bonds)

Linoleic and linolenic acids are called "essential fatty acids" because they cannot be synthesized by the human body and must be supplied in the diet. Arachidonic acid can be synthesized by the body from dietary linoleic acid.

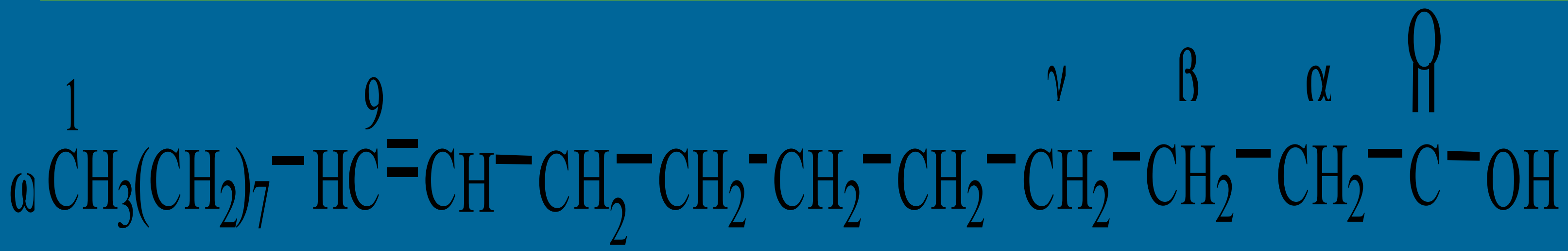
These acids are considered essential because they are either an essential component of membranes or precursor of a group of hormone-like compounds called eicosanoids including prostaglandins, thromboxanes, and prostacyclins which are important in the regulation of widely diverse physiological processes.

Recommended Dietary Allowances for dietary linoleic acid necessary to prevent essential fatty acid deficiency in humans is roughly 1 to 2% of total dietary calories.

“Omega” Fatty Acids

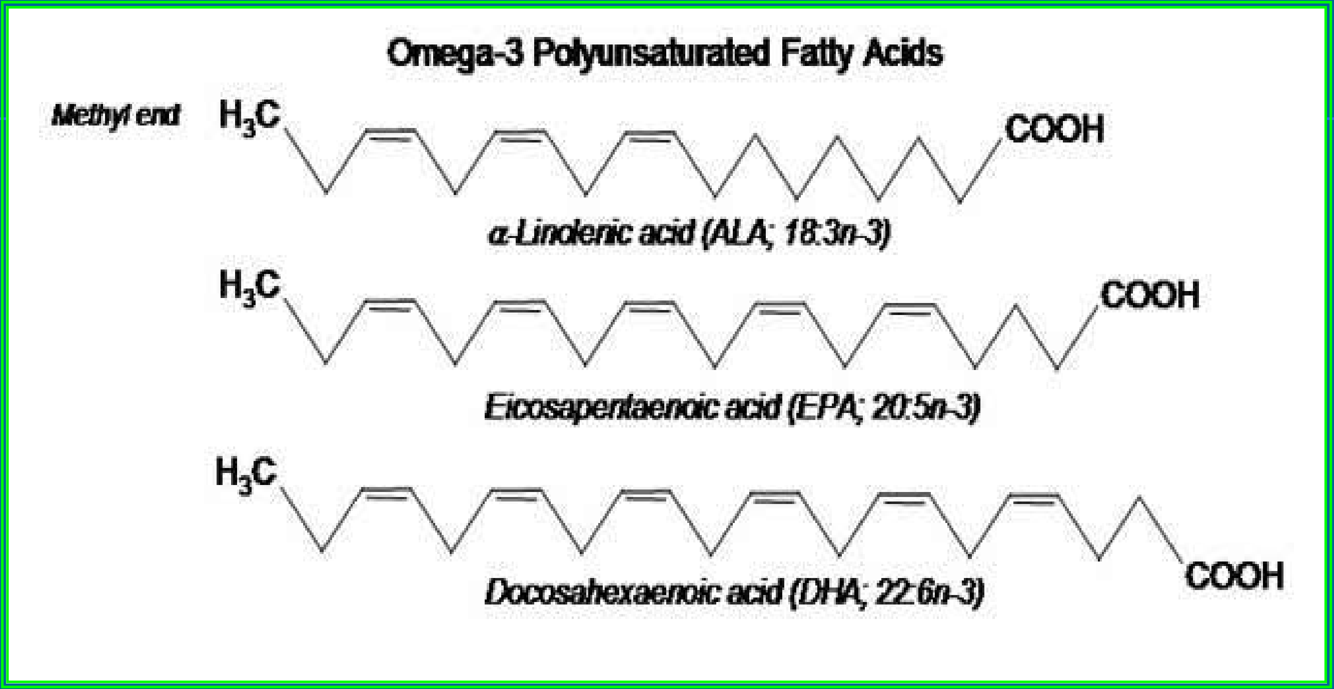
The “omega” or “n-” classification or nomenclature for fatty acids: The terms “omega” or “n-” refer to the position of the double bond of the fatty acid closest to the methyl end of the molecule.

Thus, oleic acid which has its double bond on the 9th carbon from the methyl end is considered an omega-9 (or an n-9) fatty acid.



$$\omega\,\overset{1}{CH_3}(CH_2)_7-\overset{9}{HC}=CH-CH_2-CH_2-CH_2-CH_2-\overset{\gamma}{CH_2}-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-\overset{\overset{O}{\|}}{C}-OH$$

omega 9 - octadecen<u>oic</u> acid


Omega-3 Polyunsaturated Fatty Acids

α-Linolenic acid (ALA; 18:3n-3)

Eicosapentaenoic acid (EPA; 20:5n-3)

Docosahexaenoic acid (DHA; 22:6n-3)

Nutritionally more significant omega fatty acids:

Omega-3 PUFA

Isomerism in Fatty Acids

- Isomers are chemical compounds composed of the same elements combined in the same proportions, thus having the same closed molecular formulae but with a different arrangement of their constituent atoms.
- These differences may result from different carbon skeletons(branched or straight chain), different positions of double bonds, or some other different arrangements of the atoms in space.
- The two important types of isomerism among fatty acids are:
  (1) positional
  (2) geometric

Positional Isomerism

- When two fatty acids are identical except for the position of the double bond, they are referred to as ‘positional isomers’.

- Example: Petroselinic and oleic acids

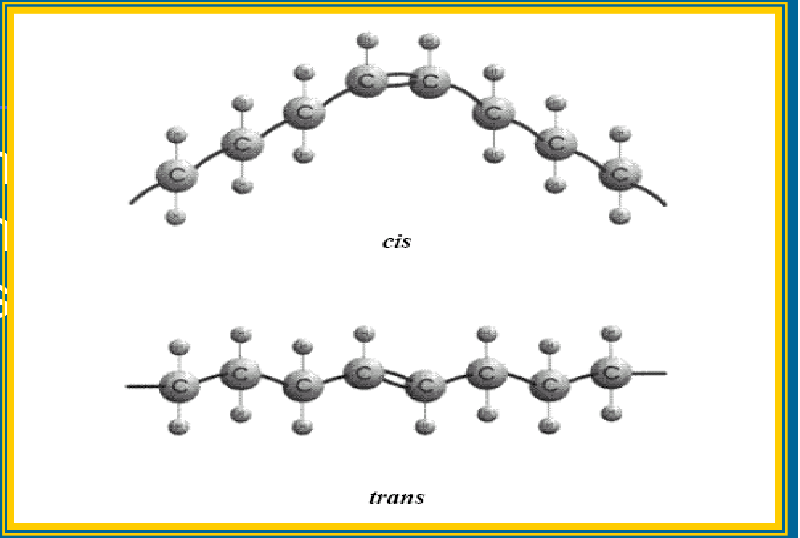
Petroselinic acid is an 18C fatty acid present in parsleyseed oil with a single doublebond at 6th carbon (6-octadecenoic acid) whereas its positional isomer oleic acid is again an 18C monounsaturated acid with its single double bond at the 9th carbon (9-octadecenoic acid).

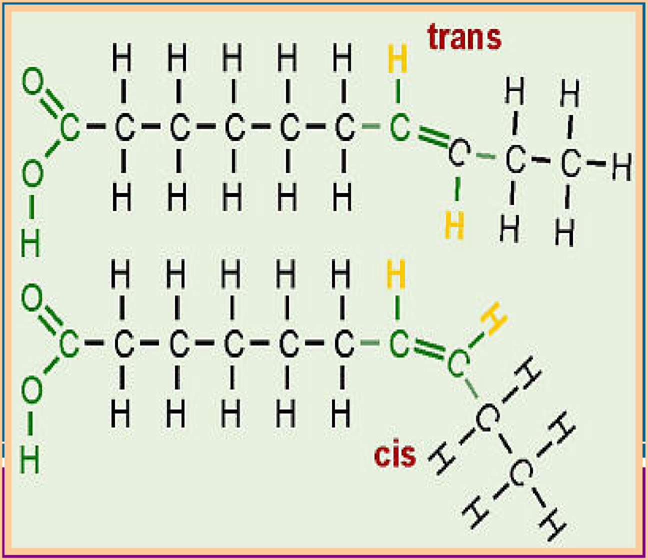
Geometric Isomerism

- Unsaturated fatty acids can exist in either the *cis* or *trans* form dependin on the configuration of the hydrogen atoms attached to the carbon atoms joined by the double bonds.

- If the hydrogen atoms are on the same side of the carbon chain, the arrangement is called *cis*.

- If the hydrogen atoms are on opposite sides of the carbon chain, the arrangement is called *trans*.

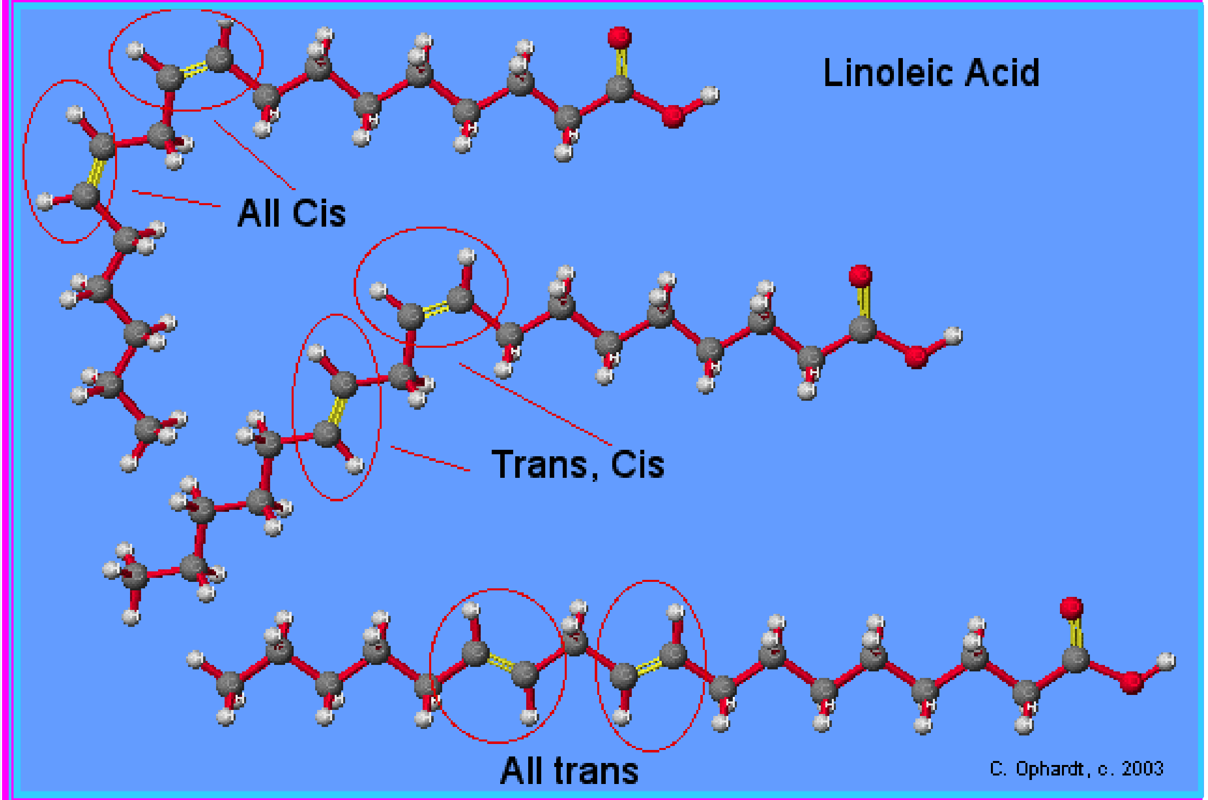




Geometric Isomerism

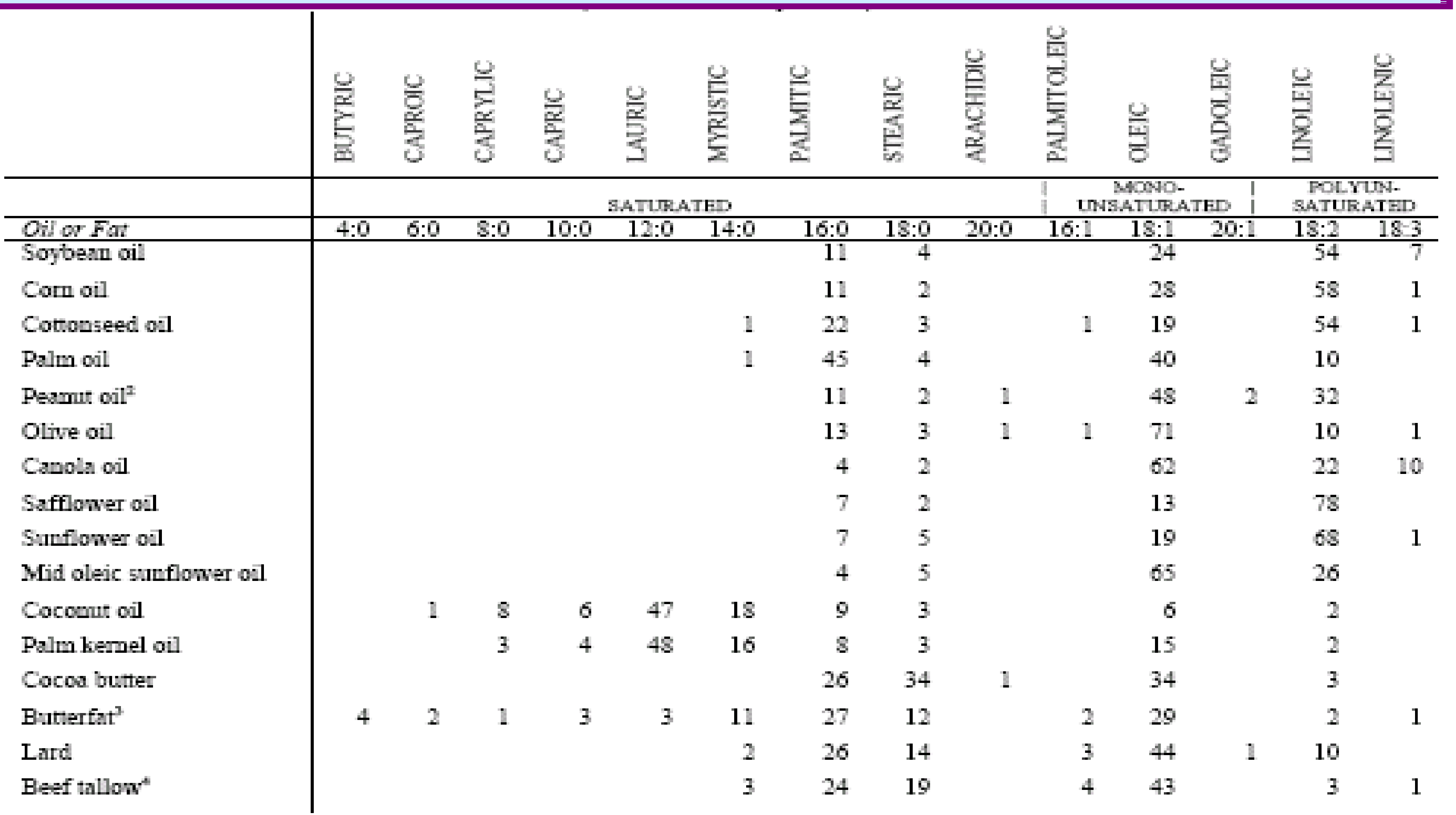
With two double bonds, four geometric isomers are possible:

1. All cis: *cis-cis,*
2. *cis-trans,*
3. *trans-cis,*
4. All trans: *trans-trans*.



C. Ophardt, c. 2003

Fatty Acid Compositions* of Common Fats and Oils

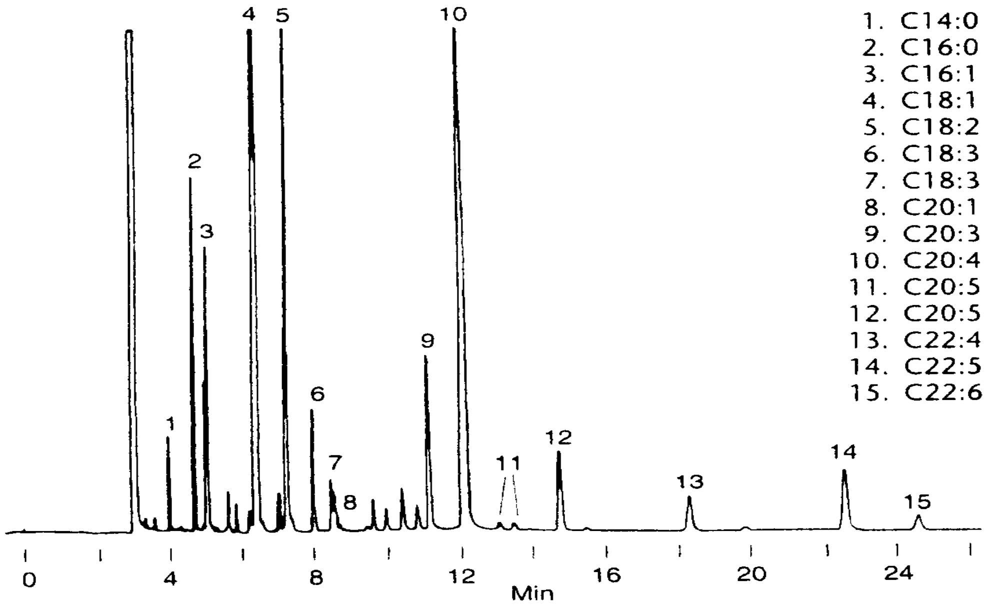


	BUTYRIC	CAPROIC	CAPRYLIC	CAPRIC	LAURIC	MYRISTIC	PALMITIC	STEARIC	ARACHIDIC	PALMITOLEIC	OLEIC	GADOLEIC	LINOLEIC	LINOLENIC
	SATURATED									MONO-UNSATURATED			POLYUN-SATURATED	
Oil or Fat	4:0	6:0	8:0	10:0	12:0	14:0	16:0	18:0	20:0	16:1	18:1	20:1	18:2	18:3
Soybean oil							11	4			24		54	7
Corn oil							11	2			28		58	1
Cottonseed oil						1	22	3		1	19		54	1
Palm oil						1	45	4			40		10	
Peanut oil[2]							11	2	1		48	2	32	
Olive oil							13	3	1	1	71		10	1
Canola oil							4	2			62		22	10
Safflower oil							7	2			13		78	
Sunflower oil							7	5			19		68	1
Mid oleic sunflower oil							4	5			65		26	
Coconut oil		1	8	6	47	18	9	3			6		2	
Palm kernel oil			3	4	48	16	8	3			15		2	
Cocoa butter							26	34	1		34		3	
Butterfat[3]	4	2	1	3	3	11	27	12		2	29		2	1
Lard						2	26	14		3	44	1	10	
Beef tallow[4]						3	24	19		4	43		3	1

* : as % of total fatty acids

Analysis of Fatty Acids (FAME*)

1



Fatty Acid Methyl Esters (GC)

Column: **SP-2330, 30m x 0.25mm ID, 0.20µm film**
Cat. No.: **24019**
Oven: 200°C
Carrier: helium, 20cm/sec (set at 200°C)
Det.: FID, 250°C
Inj.: 0.5µL chloroform containing FAMEs from natural source, split 100:1 (250°C)

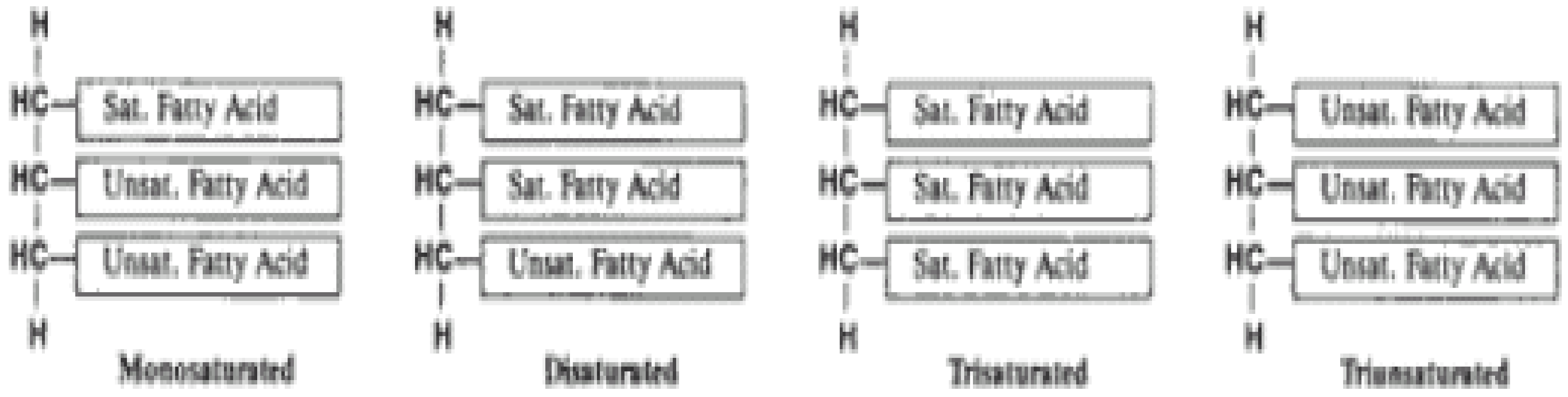
FAME*: Fatty Acid Methyl Esters

Triglycerides

- Fats and oils are practically always mixtures of triglycerides in varying proportions. In some fats one triglyceride predominates, in others several are present in nearly equal amounts. Apparently no natural fat or oil consists solely of a single triglyceride.

- The triglycerides of seven acids (lauric, myristic, palmitic, oleic, linoleic and linolenic) make up the great bulk of the natural fats and oils.

Triglycerides



- Natural triglyceride molecules contain both saturated and unsaturated fatty acids.
- Depending on the type of fatty acids in the molecule, triglycerides can be classified as mono-, di-, and triunsaturated or mono-, di-, and trisaturated. The degree of unsaturation of the triglyceride is thus related to the number of double bonds present in its fatty acid components.

Triglycerides

Physical properties of triglycerides depend very much on their fatty acid components:

Melting point of the fat or oil increases as the number of carbons in the hydrocarbon chains increases and as the number of double bonds decreases. This is why:

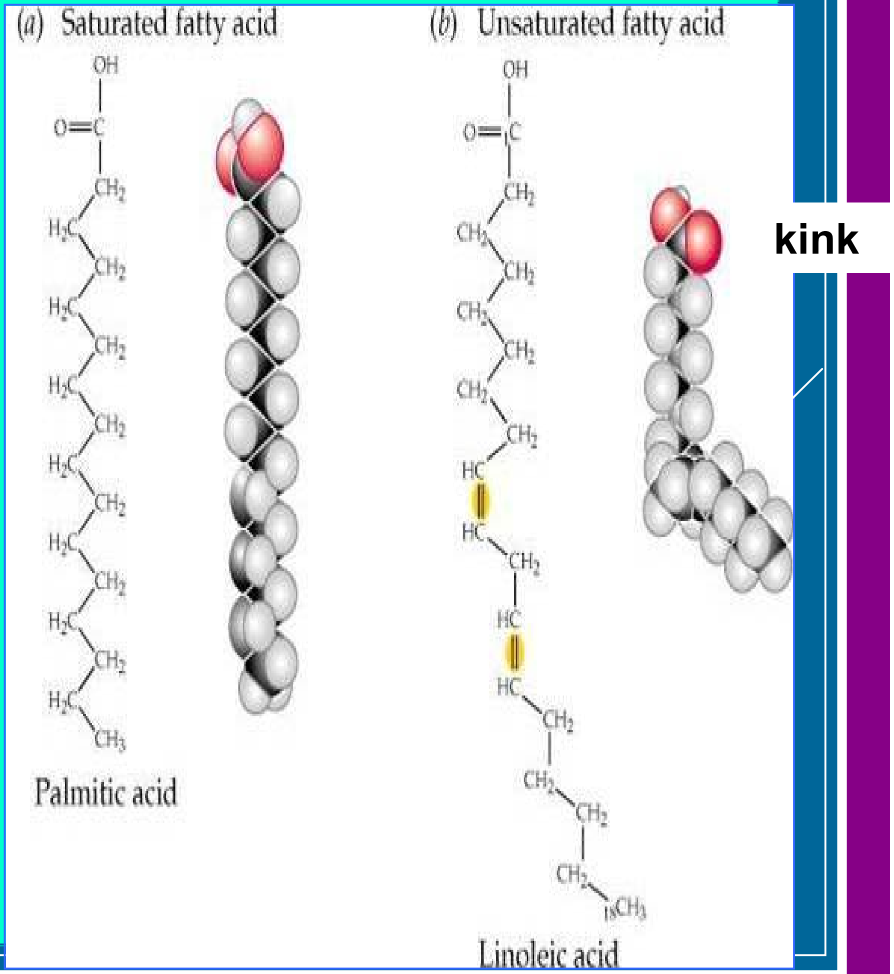
-triglycerides rich in unsaturated fatty acids are generally liquid at room temperature,

-triglycerides rich in saturated fatty acids are generally semisolids or solids at room temperature.

Triglycerides

- In triglycerides rich in saturated fatty acids:
  - saturated hydrocarbon chains can lie parallel and pack into well-ordered, compact crystalline forms.
  - there are strong dispersion forces between their chains; therefore they have melting points above room temperature(solid)

- In triglycerides rich in unsaturated fatty acids:
  - the hydrocarbon chains have a less ordered structure because of the kinky configuration of the double bonds,
  - dispersion forces between unsaturated hydrocarbon chains are weaker; these triglycerides therefore have melting points below room temperature(liquid)


(a) Saturated fatty acid

Palmitic acid

(b) Unsaturated fatty acid

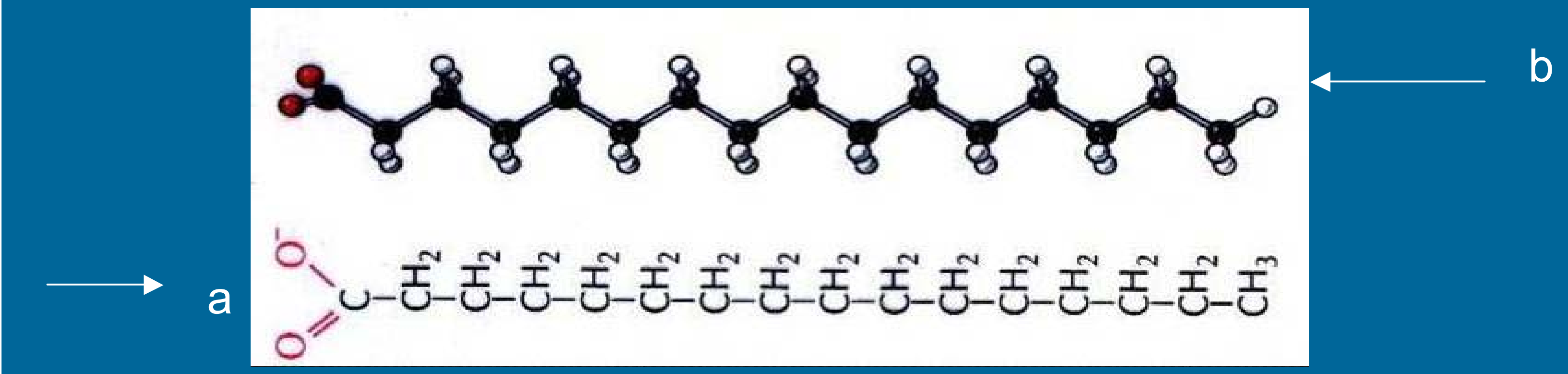
Linoleic acid

kink

Reactions of Fats and Oils

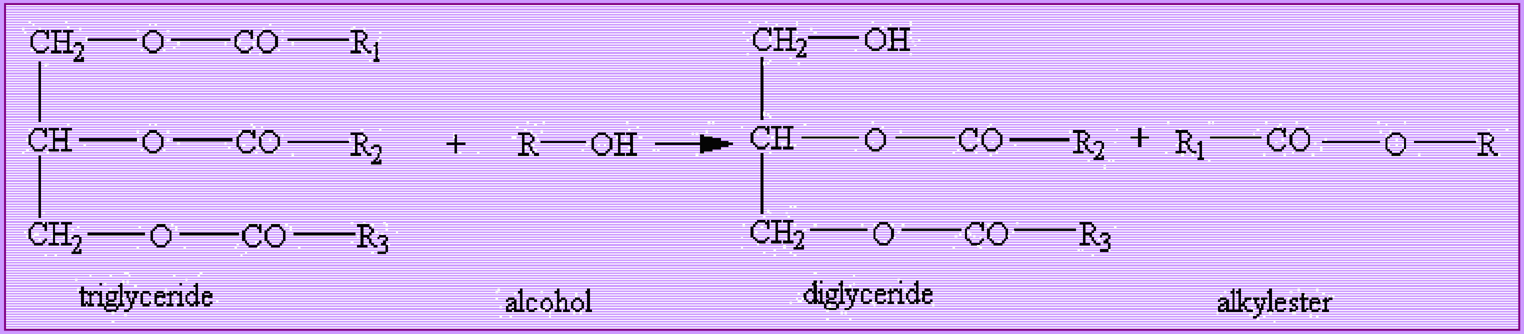
a. Reactions in the carboxylic group

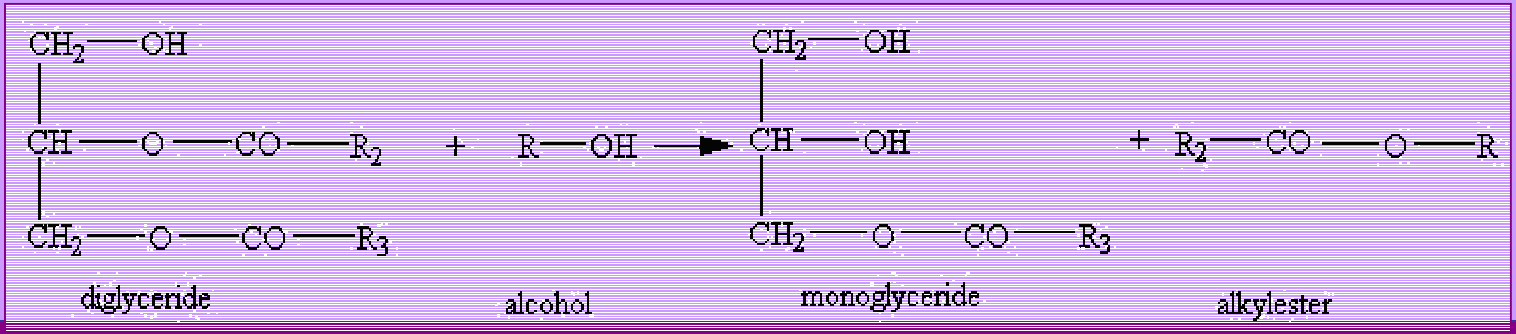
b. Reactions in the fatty acid chain



a.1.Hydrolysis

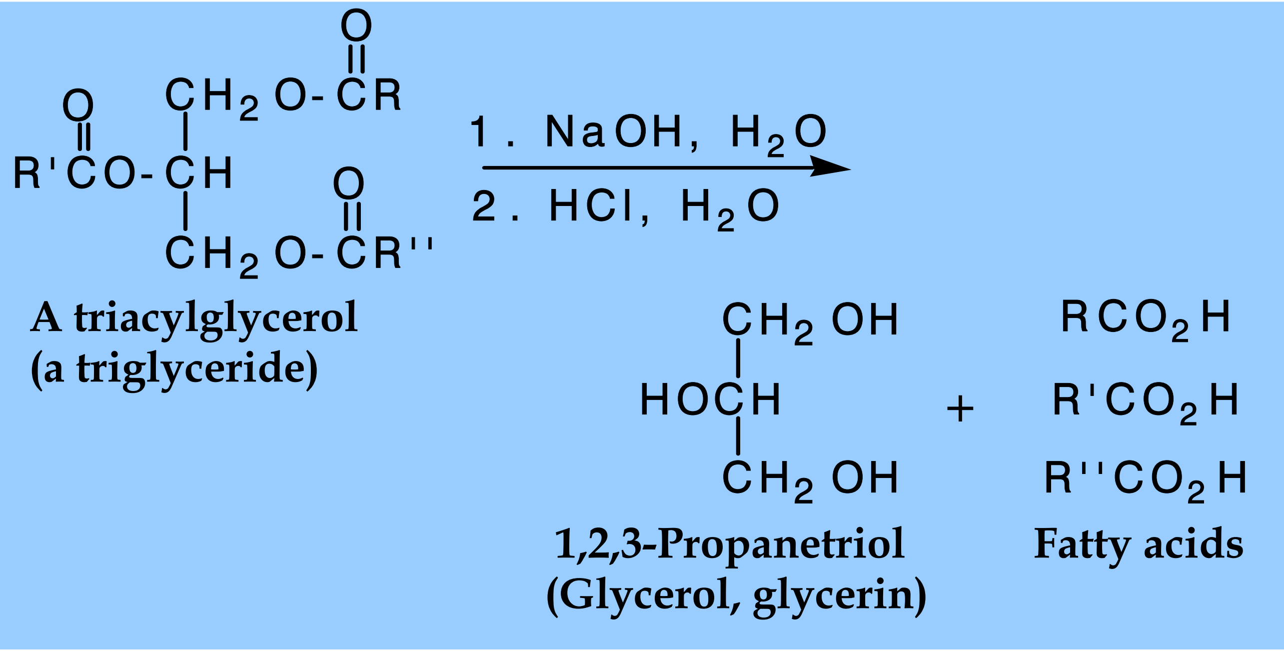
Triglycerides can be broken down to their constituents by chemical agents (or by enzymes-lipases- as in the digestive tracts of humans and animals). Partial hydrolysis of triglycerides will yield mono- and diglycerides and fatty acids.





Hydrolysis

When the hydrolysis of a triglyceride is carried to completion with water in the presence of an acid or base catalyst, the mono-, di-, and triglycerides will hydrolyze to yield glycerol and fatty acids.



A triacylglycerol (a triglyceride)

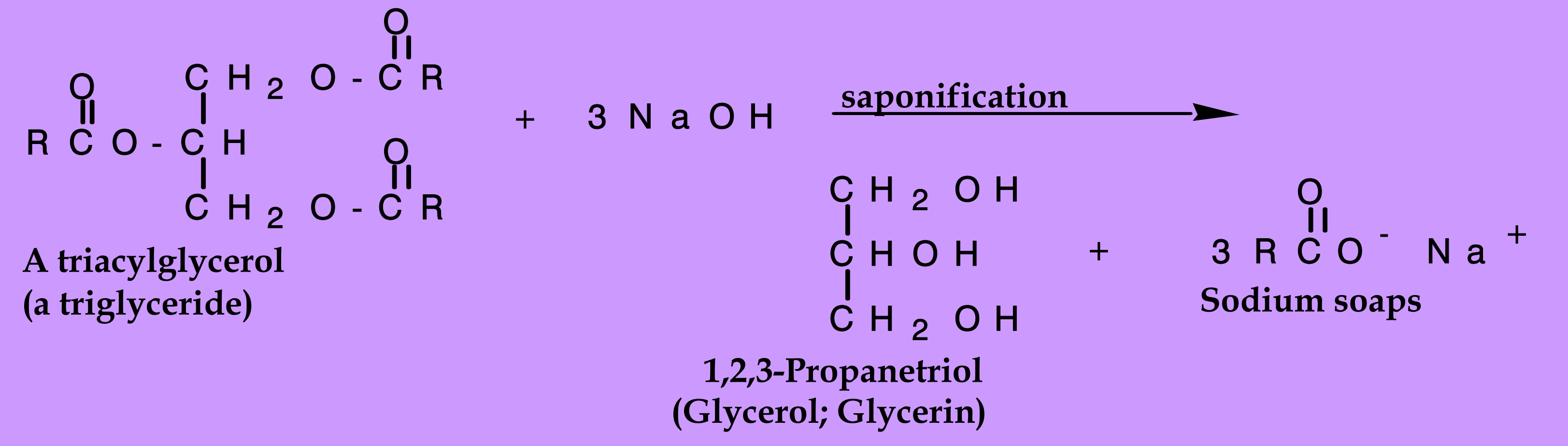
1,2,3-Propanetriol (Glycerol, glycerin)

Fatty acids

a.2.Saponification

- Natural soaps are prepared by boiling fats (i.e. lard or other animal fats) with NaOH, in a reaction called saponification

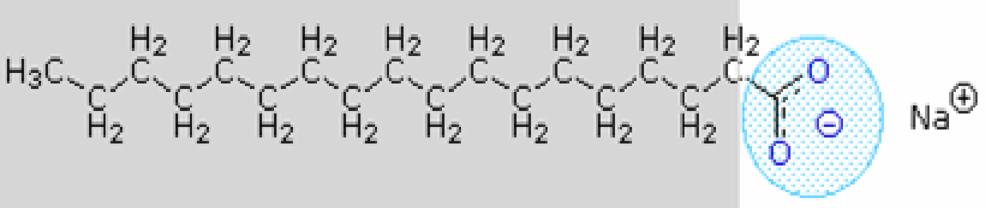
(*sapo:* soap in Latin)



A triacylglycerol
(a triglyceride)

1,2,3-Propanetriol
(Glycerol; Glycerin)

Sodium soaps



a soap
sodium stearate

Soaps

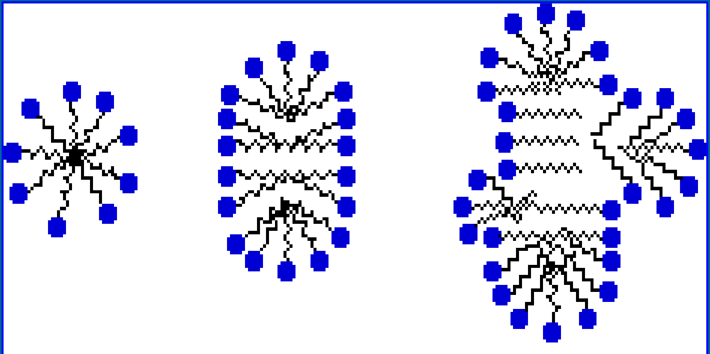
Soaps clean by acting as emulsifying agents:

the long hydrophobic hydrocarbon chains of soaps are insoluble in water and tend to cluster in such a way as to minimize their contact with water

the polar hydrophilic carboxylate groups tend to remain in contact with the surrounding water molecules

driven by these two forces, soap molecules spontaneously cluster into “micelles”

- When soap is mixed with water-insoluble grease, oil, and fat stains, the nonpolar parts of the soap micelles “dissolve” nonpolar dirt molecules and they are carried away in the polar wash water that dissolves the polar carboxylate parts.



micelle assemblies of amphiphiles

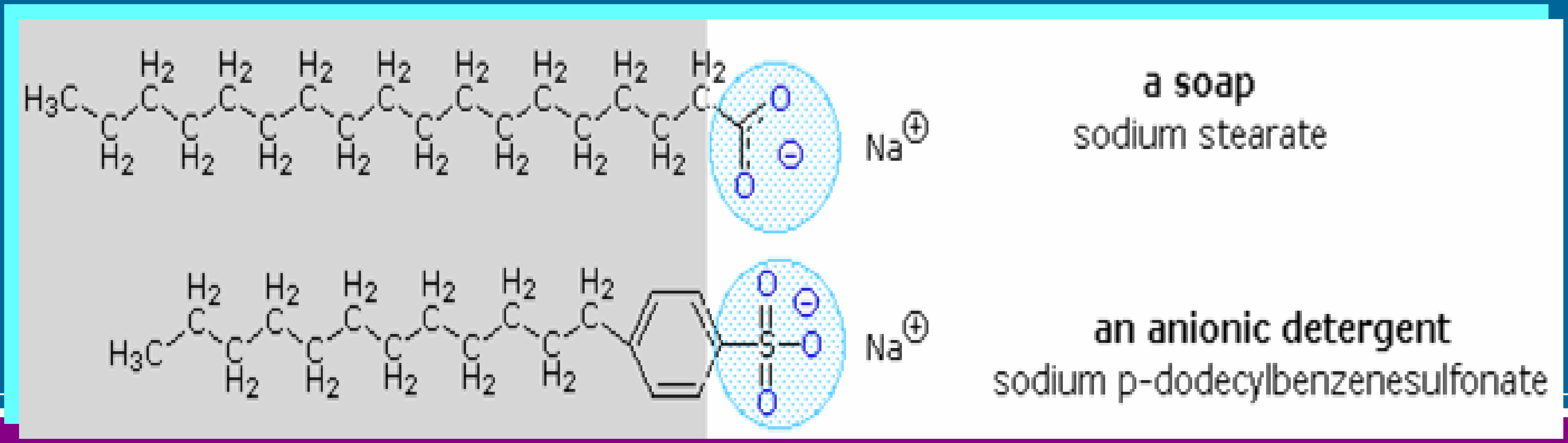
Synthetic Detergents

The design criteria for a good detergent are

- a long hydrocarbon tail of 12 to 20 carbons
- and a polar head group,just like soaps.

The most widely used synthetic detergents are the linear alkylbenzene sulfonates

(i.e. Sodium dodecylbenzene sulfonate)



a soap
sodium stearate

an anionic detergent
sodium p-dodecylbenzenesulfonate

a.3.Esterifications

Esterification is the reverse of hydrolysis: a process where an alcohol (i.e. glycerol) is reacted with an acid (i.e. fatty acid) to form an ester (i.e. mono-, di-, and triglycerides).

There are many different types of esterification reactions: Example: Alcoholysis: An alcohol such as glycerol is reacted with fat or oil to produce esters such as mono- and diglycerides.

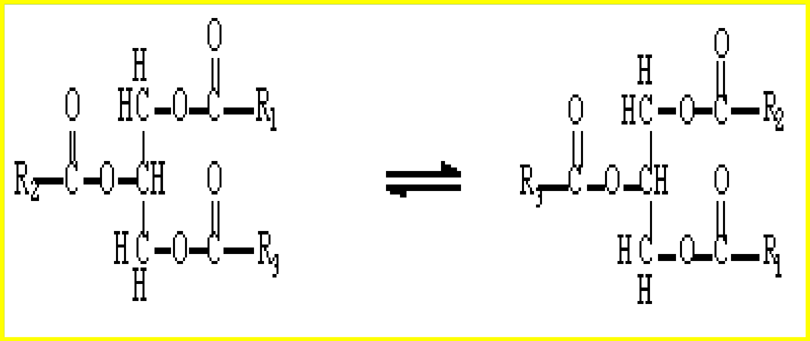
Using the esterification processes, edible acids, fats, and oils can be reacted with edible alcohols to produce useful edible ingredients (i.e.emulsifiers) and also biodiesel fuels as will later be explained in much greater detail during the course.

Interesterification

- Interesterification, which is the rearrangement or a redistribution of the fatty acids on the triglyceride, is accomplished by catalytic methods at relatively low temperatures.
- The predominant commercial application for interesterification is the production of specialty fats for the confectionery and margarine industries. This process permits further tailoring of triglyceride properties to achieve the required steep melting curves.

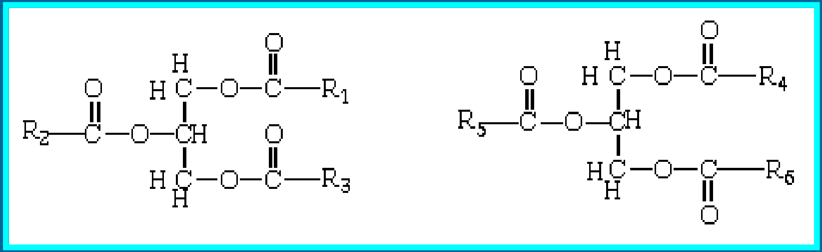
Interesterifications within a single triglyceride or between triglycerides

Within a single triglyceride:

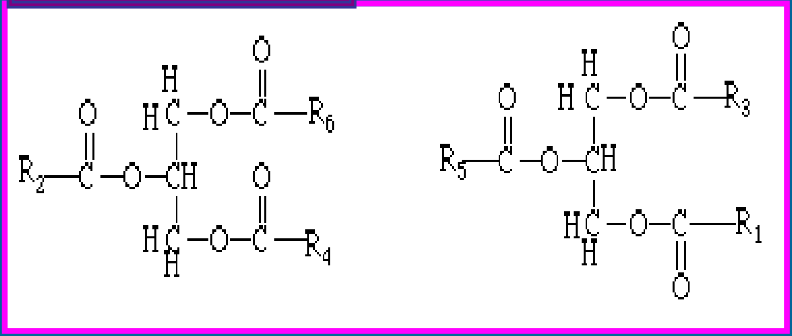


Between 2 triglycerides;

Start with:



End with:



Enzymatic Interesterifications

- By utilizing enzymes in place of chemicals, the oils are subjected to less severe processing conditions.

- Enzyme interesterification is economical, increases processing flexibility, friendly for the environment, and also provides numerous desired functional characteristics.

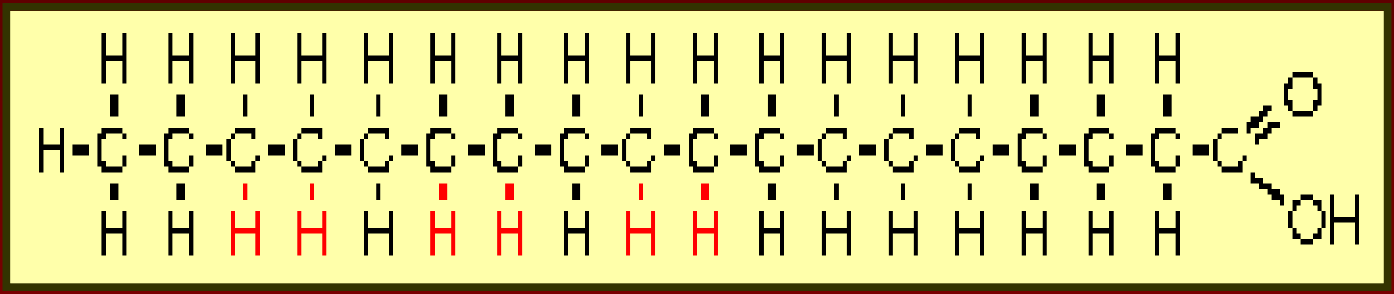
Transesterification

- The transesterification process converts triglyceride esters into alkyl esters by means of a catalyst (lye) and an alcohol reagent, usually methanol, which yields methyl esters (biodiesel), the methanol replacing the glycerine.

  In transesterification, the lye catalyst first breaks the bonds holding the fatty acid chains to the glycerine; the glycerine falls away, the fatty acid chains then bond with the methanol. The triglyceride molecule is turned into three separate methyl ester molecules plus glycerine as a by-product.

b.1.Hydrogenation

- Hydrogenation is the process by which hydrogen is added directly to points of unsaturation in the fatty acid chainness (of triglycerides).

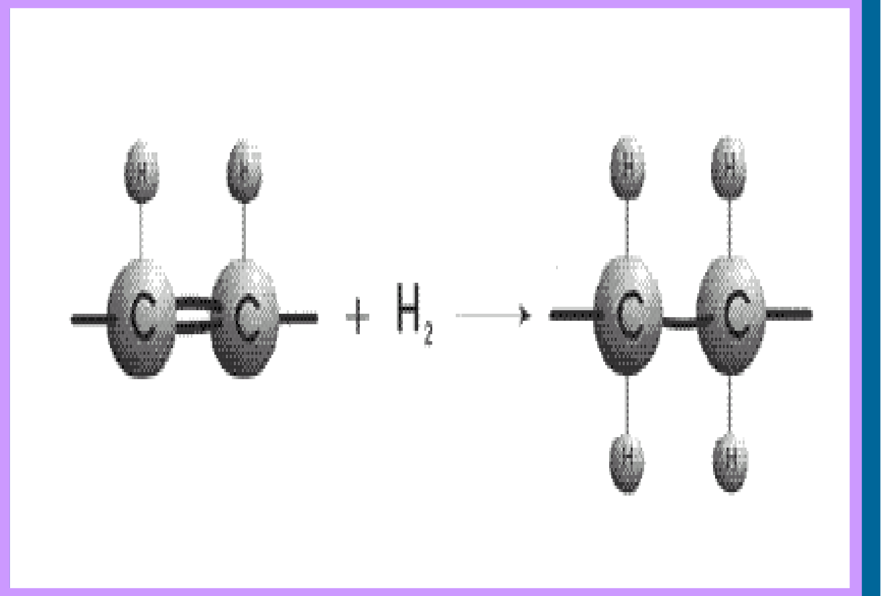


Why hydrogenate?

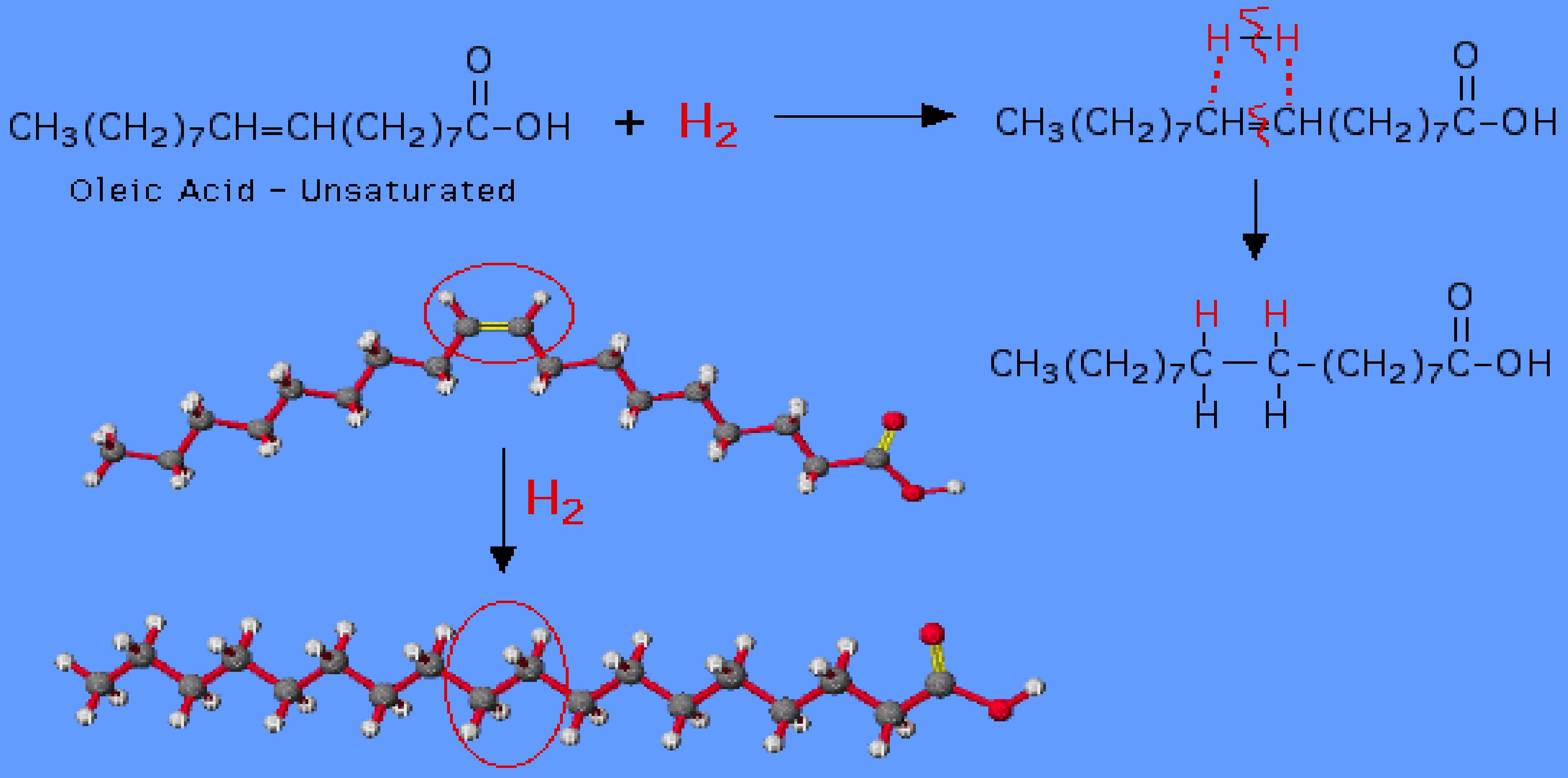
- Imparts plasticity
- Improves texture (crystal structure)
- Increases versatility in food applications
- Increases stability of oils
- Increases melting range
- Improves flavour stability

Hydrogenation

- Hydrogen gas is reacted with the double bonds of the unsaturated fatty acids of oils at elevated temperatures and pressure in the presence of a catalyst (i.e.nickel).



Hydrogenation of Oleic Acid



$$\mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7\overset{\overset{O}{\|}}{C}{-}OH} + \mathrm{H_2} \longrightarrow \mathrm{CH_3(CH_2)_7\overset{\overset{H}{\vdots}}{C}H{=}\overset{\overset{H}{\vdots}}{C}H(CH_2)_7\overset{\overset{O}{\|}}{C}{-}OH}$$

$$\downarrow$$

$$\mathrm{CH_3(CH_2)_7\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}(CH_2)_7\overset{\overset{O}{\|}}{C}{-}OH}$$

Oleic Acid - Unsaturated

Stearic Acid - Saturated

C. Ophardt, c. 2003

Hydrogenation

- Hydrogenation conditions can be varied by the manufacturer to meet certain physical and chemical characteristics desired in the finished product.
- This is achieved through selection of the proper temperature, pressure, time, catalyst, and starting oils.
- Both positional and geometric (*trans*) isomers are formed to some extent during hydrogenation, the amounts depending on the conditions employed.

b.2.Oxidation

- Oxidation of fats and oils that is induced by air at room temperature is referred to as “autoxidation.”
- This is a slow process in which oxygen reacts with unsaturated fatty acids and where initially peroxides are formed as “primary oxidation products” which in turn break down to hydrocarbons, ketones, aldehydes, as well as epoxides and alcohols as “secondry oxidation products”.
- The result of the autoxidation of fats and oils is the development of objectionable flavors and odors characteristic of the condition known as “oxidative rancidity.”

Rancidity

- Definition: Formation of off flavors and odors from breakdown of fats
- Rancidity of fats and oils are of two types:
    - Hydrolytic or enzymatic rancidity:Resulting mostly in hydrolysed short chain fatty acids (i.e.most common in butter and chocolate)
    - Oxidative rancidity: addition of oxygen to double bonds of oils, resulting in small chain oxygenated compounds like peroxides, aldehydes, ketones (i.e. Most common in polyunsaturated oils).

Accelerating Factors: degree of unsaturation, heat, light and presence of metals

Stability of Fats and Oils

- **Stability** is defined as the resistance of a fat or oil to rancidity.
- Oxidative stability may be assessed by determining **peroxide value**, **anisidine value**, or **induction period** of oils or oil-bearing materials.
- Hydrolytic stability is assessed by determination of **free fatty acids(FFA) or acid value** in the oil or fat.

How to Prevent/Control Rancidity

- Deactivation as to heat, light and moisture in handling and storage

- Antioxidant additives
  - BHA, BHT
  - Tocopherols

- Hydrogenation
  - Remove unsaturation

b.3.Polymerisation

- All commonly used fats and oils, particularly those high in polyunsaturated fatty acids, tend to form some larger molecules known broadly as polymers when heated under extreme conditions of temperature(250-275°C) and time.
- Polymers in fats and oils arise by formation of either carbon bridges(carbon to carbon bonds) or oxygen bridges between molecules. These can occur particularly during deep fat frying. The fat or oil first polymerizes to dimers and trimers, and then to higher polymers.

Production Technology for Oils and Fats

After obtaining the crude oil or fat from the plant or animal raw materials, most crude fats and oils are not in a state that will allow them to be directly consumed since they also contain many undesirable impurities.

Refining: Treatments applied to crude oils or fats to make them acceptable for human consumption.

It may consist of a simple alkaline washing(neutralisation) followed by drying and filtration, or it may involve some other stages like bleaching, winterisation and deodorization before marketing for human consumption.

Minor Constituents in Fats and Oils

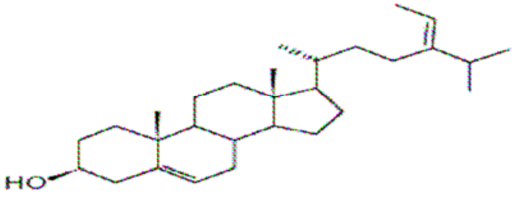
In addition to triglycerides, all fats and oils contain some nonglycerides, the major ones being sterols, phosphatides, vitamins and pigments.

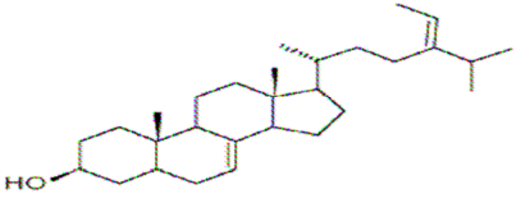
These non-triglyceride components are found in various trace amounts in the unsaponifiable portion of the fat or oil and are quite characteristic for each source.

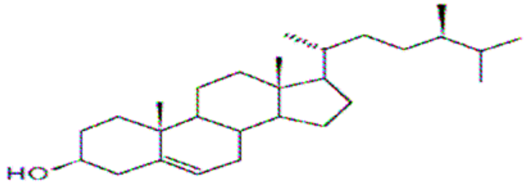
Sterols

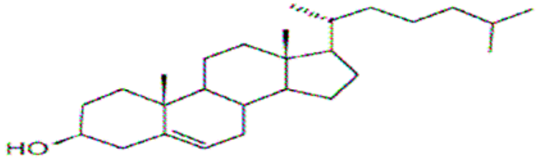
Sterols, or steroid alcohols, are a class of substances that contain the common steroid nucleus plus an 8 to 10 carbon side chain and an alcohol group.

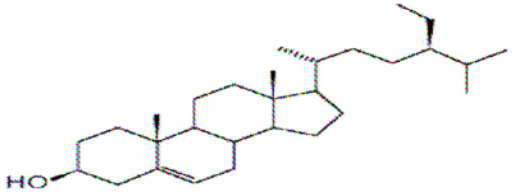
In animal fats "cholesterol" is the only sterol, whereas in vegetable oils they are quite numerous and are called under the general name of "phytosterols".

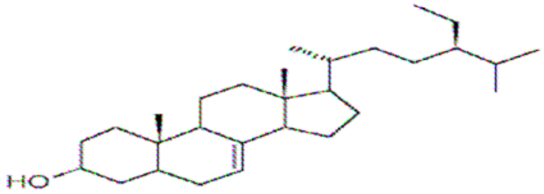

Δ^5-Avenasterol

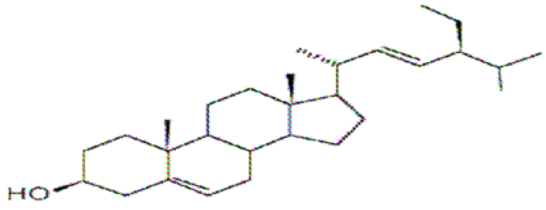

Δ^7-Avenasterol


Campesterol


Cholesterol

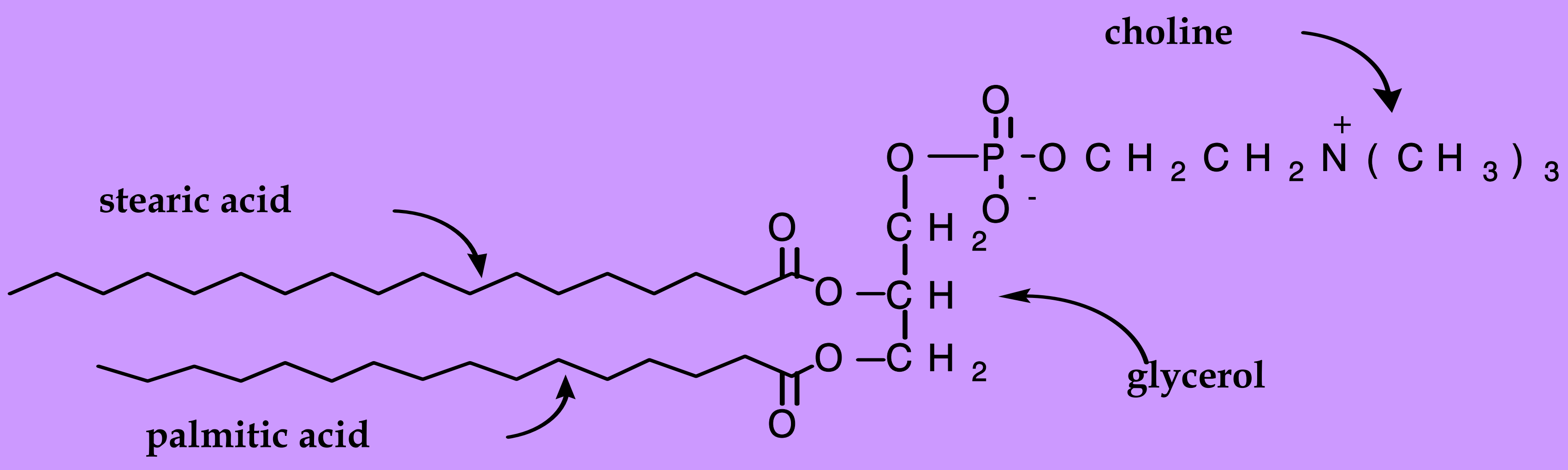

β-Sitosterol


Δ^7-Stigmastenol


Stigmasterol

Phosphatides

- Phosphatides consist of alcohols (usually glycerol), combined with fatty acids, phosphoric acid, and a nitrogen-containing compound(like choline).
- Lecithin and cephalin are most common phosphatides found in edible fats.
- Refining removes almost all the phosphatides from the fat or oil.

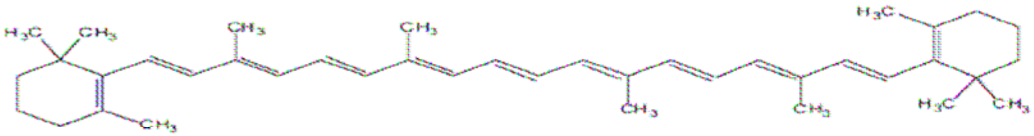


Lecithin

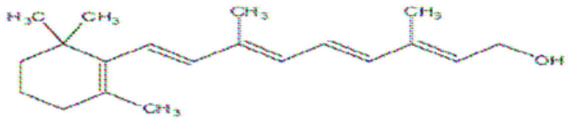
Oil-soluble Vitamins

Though generally not a rich source for vitamins, vegetable oils contain significant amounts of tocopherols (with Vitamin E activity) and β-carotenes (Vitamin A precursor) as pigments.

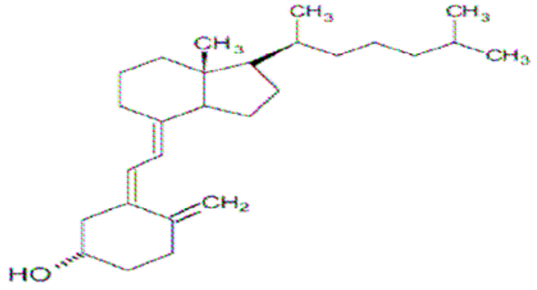
Fats from land and marine animals contain substantial amounts of Vitamins D and A.



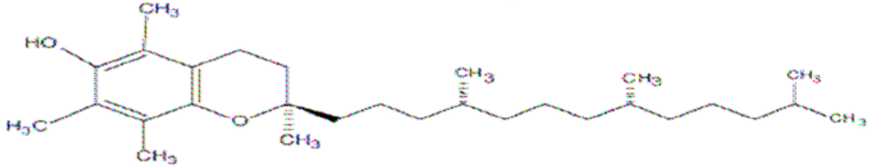
β-Carotene



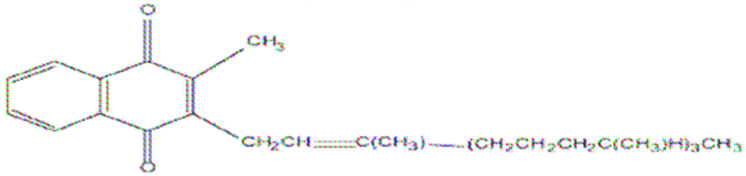
Vitamin A (retinol)



Vitamin D₃



Vitamin E



Vitamin K₁

Future Prospects and Conclusion

- Agricultural biotechnology has been successfully applied to achieve modifications in the chemistry of fats and oils: The typical oils derived from biotechnological means are high and midoleic sunflower, low linolenic/low saturate soybeans, high linoleic flaxseed oil, low linolenic canola, high laurate canola, high oleic canola, and high stearate canola.

- Genetically modified oils of the future will likely have customized fatty acid compositions to achieve improved nutrient profiles: reduction in saturated fatty acid content, improved oxidative stability resulting in a reduced need for hydrogenation, reduced calories or bioavailability, creation of specific fatty acid profiles for particular food applications, and creative “functional” foods for the population as well as for specific medical and industrial purposes.

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3. *Food Chemistry* by O. Fennema, Marcel Dekker, Inc. New York, NY.1998

4. *Food Fats and Oils* by Institute of Shortening and Edible Oils, 8th Edition, 1999.