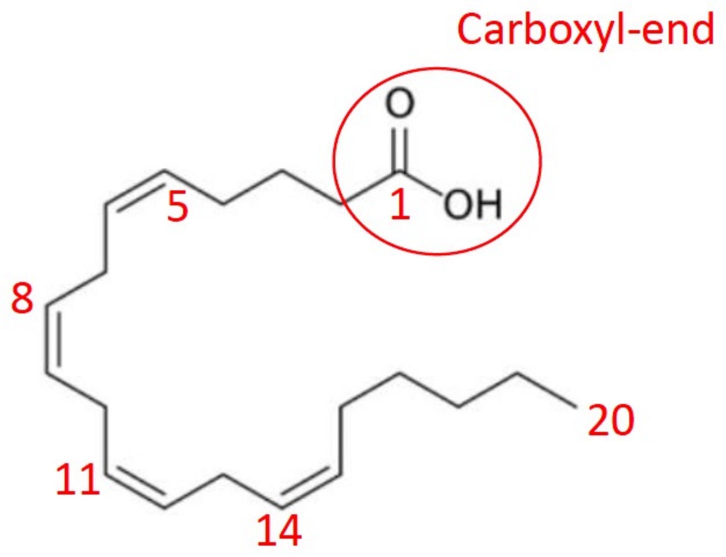
Exercises 7

07.04.2025

1) Animal venoms comprise a complex mixture of components that affect several biological systems. One of the main components of such venoms are secreted enzymes known as secreted phospholipase A2 (sPLA2).
The resulting products upon sPLA2 activity are shown below.

a. Name Product 1 using both the delta and omega systems.



Product 1

20:4 (Delta 5, 8, 11, 14)

Delta system:

- [chain length] : [# double bonds] (Delta [double bond positions])
- Start counting from the carboxyl-end

1) Animal venoms comprise a complex mixture of components that affect several biological systems. One of the main components of such venoms are secreted enzymes known as secreted phospholipase A2 (sPLA2).
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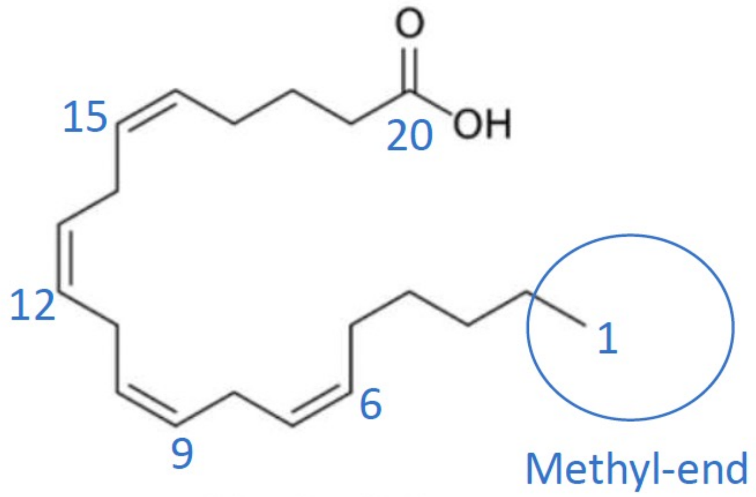


Product 1

20:4 (ω-6)

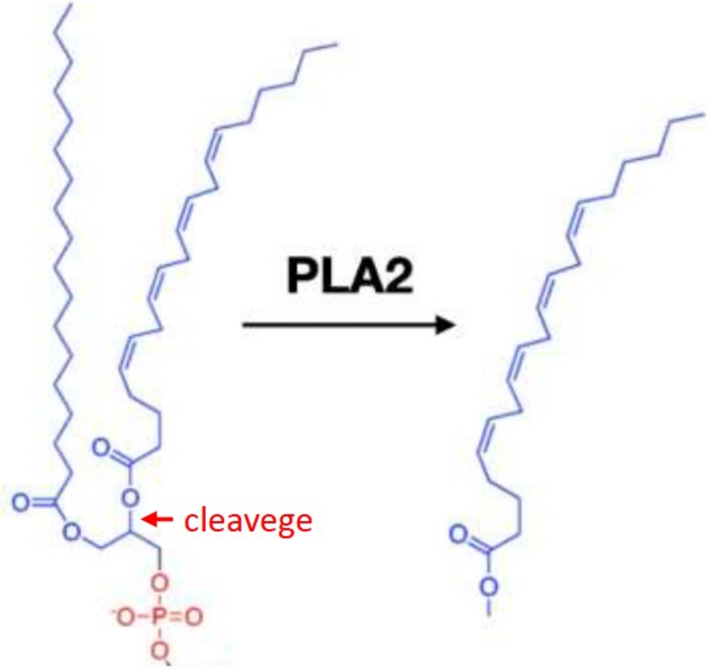
Omega system:

- chain length : # double bonds (Omega [position of first double bond])
- Start counting from methyl-end.
- Double bonds are always separated by 3 carbons

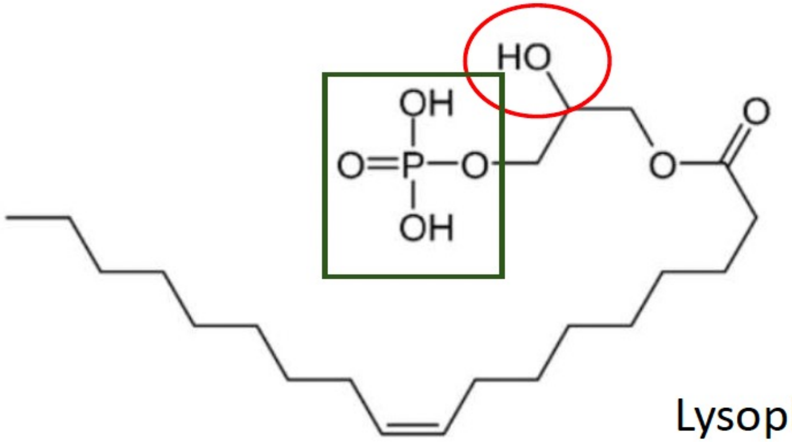
1) Animal venoms comprise a complex mixture of components that affect several biological systems. One of the main components of such venoms are secreted enzymes known as secreted phospholipase A2 (sPLA2).
The resulting products upon sPLA2 activity are shown below.

b. On the picture of product 2, circle the likely site of cleavage/ action by sPLA2.

Which class of lipid does the substrate belong to?



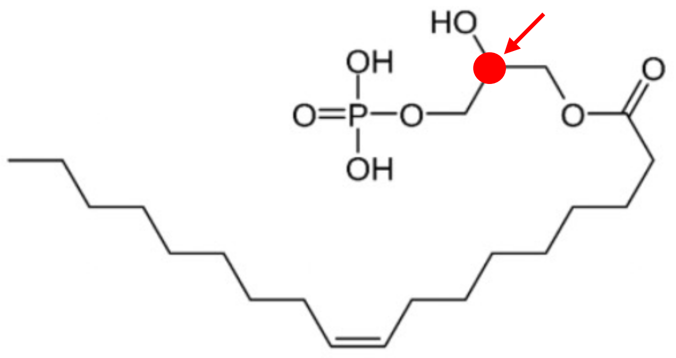
Phospholipase A2 (PLA2) hydrolyzes phospholipids, yielding a lysophospholipid and a fatty acid.



Lysophosphatidic acid is a phospholipid

Product 2

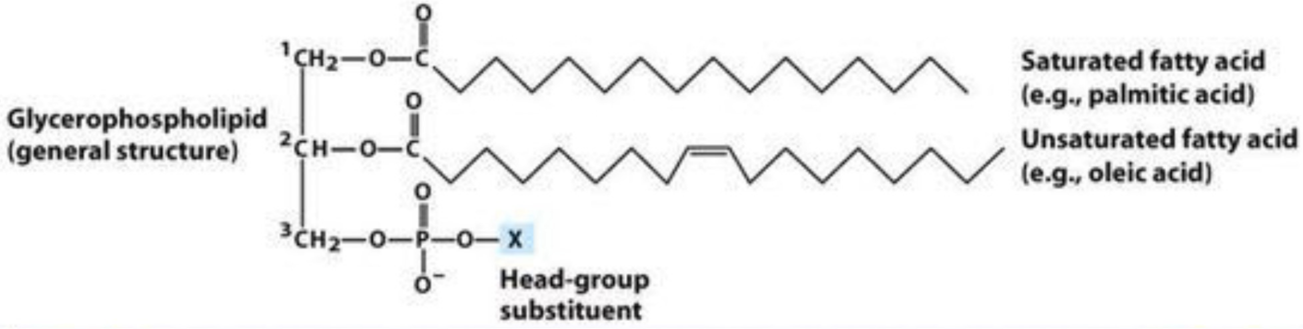
1) Animal venoms comprise a complex mixture of components that affect several biological systems. One of the main components of such venoms are secreted enzymes known as secreted phospholipase A2 (sPLA2).
The resulting products upon sPLA2 activity are shown below.



Product 2

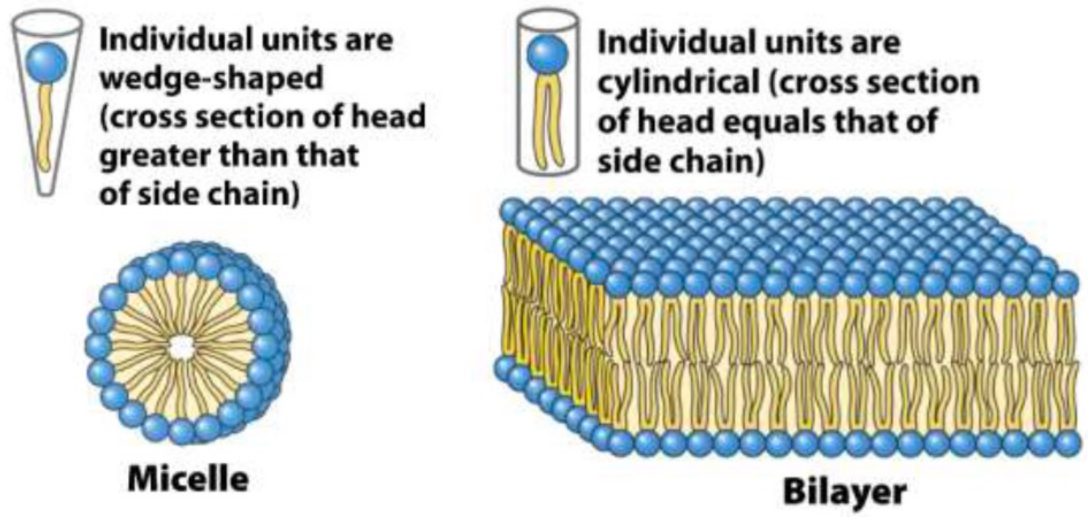
The substrate is a **glycerophospholipid** (phospholipid) because it consists of:
- a glycerol backbone esterified to two fatty acids
- and a third carbon linked to a phosphate group

Reminder - slide 17 from the course:



1) Animal venoms comprise a complex mixture of components that affect several biological systems. One of the main components of such venoms are secreted enzymes known as secreted phospholipase A2 (sPLA2).
The resulting products upon sPLA2 activity are shown below.

c. sPLA2 acts by disrupting the membrane of the host. Can you explain this in terms of sPLA2 impact on membrane bilayer structure?



Lysophospholipid

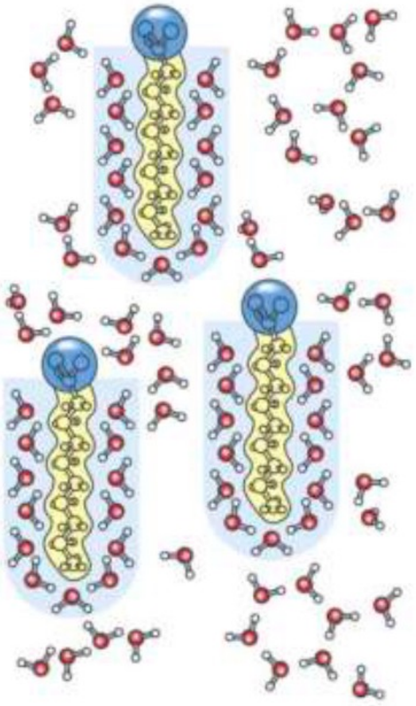
Phospholipid

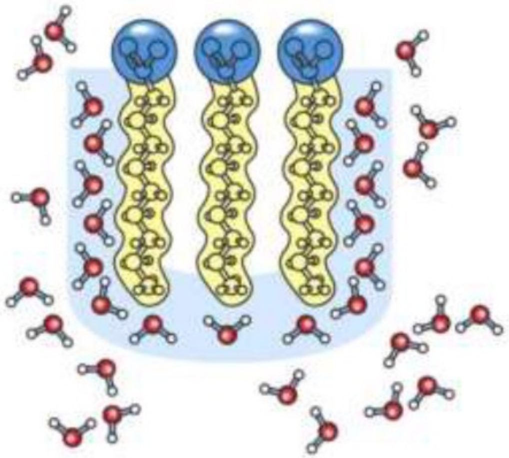
sPLA2 cleaves one acyl chain of the cylinderical fatty acid, yielding a wedge-shaped fatty acid which is incompatible with the membrane structure.

2) Lipid bilayers forming between two water phases have the following important property: they produce bi-dimensional sheets where their edges seal to form liposomes.

a. What lipid-specific properties account for this behaviour?

Membrane lipids are **amphipathic**: one end of the molecule is hydrophobic, the other hydrophilic.

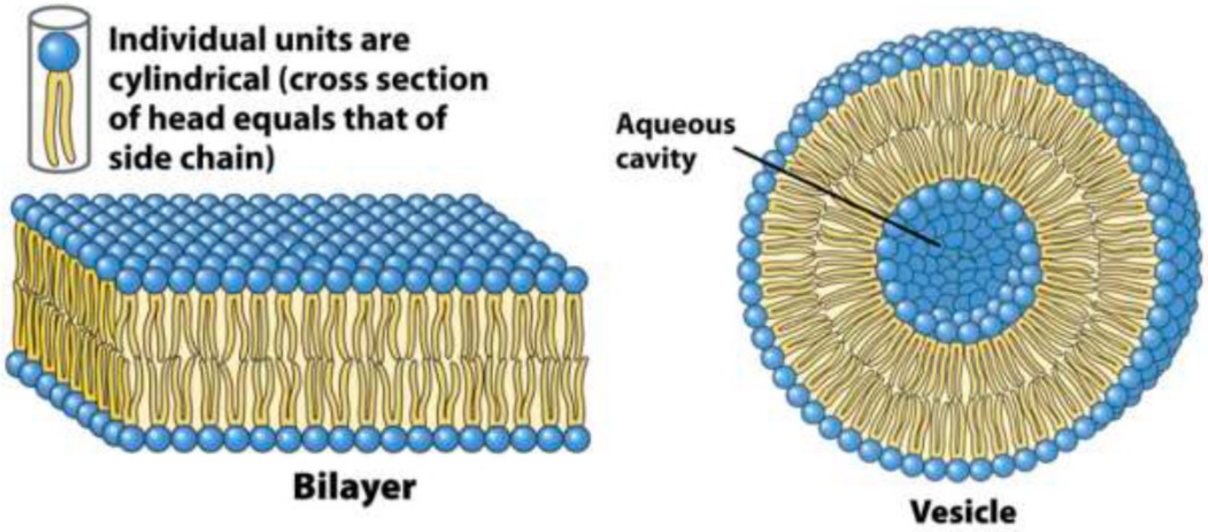




To minimize the interaction of carbon chains with the aqueous environment, amphipathic molecules align side by side.

2) Lipid bilayers forming between two water phases have the following important property: they produce bi-dimensional sheets where their edges seal to form liposomes.

b. What is the consequence of this property on biological membranes?

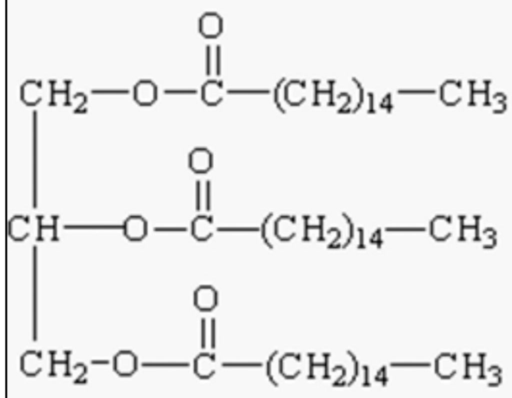


Allows making up the cell membrane and the membrane of sub-cellular compartments:

- Interface between the cell and the environment
- Compartmentalization of the cell

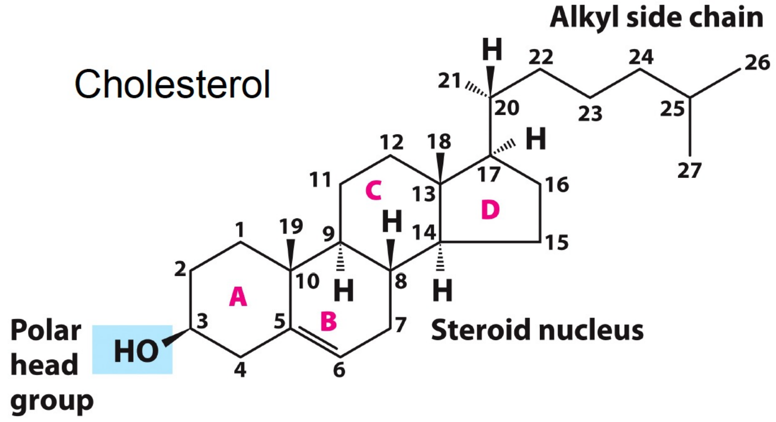
3) A mixture composed by the following lipids is placed on a silica column and eluted with increasingly polar solvents.

In which order are these lipids eluted from the column (explain the rationale)?



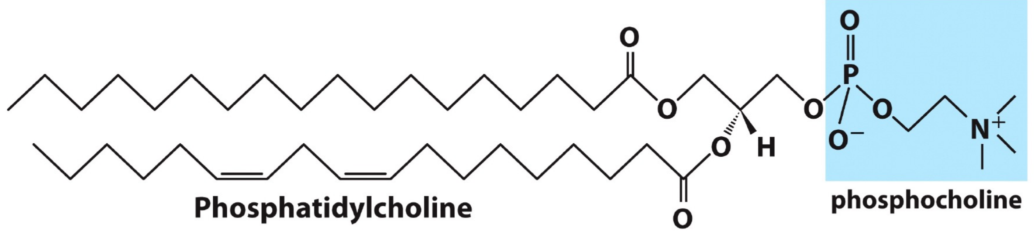
Triglyceride

Cholesterol



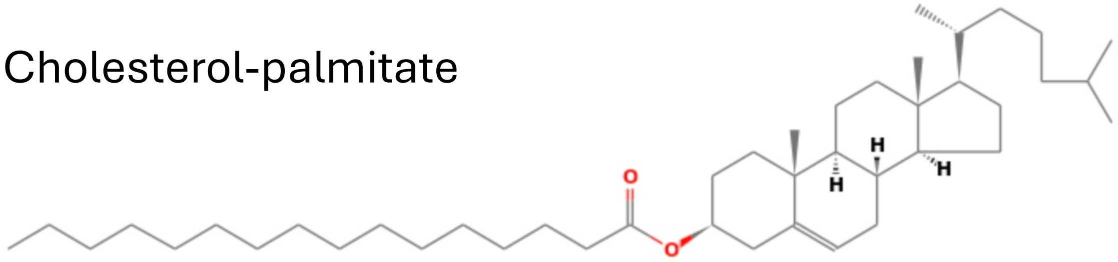
$CH_3(CH_2)_{14}COOH$

Palmitic acid
(Latin *palma*, "palm tree")



Phosphatidylcholine

Cholesterol-palmitate



Not all lipids are equally hydrophobic !

3) A mixture composed by the following lipids is placed on a silica column and eluted with increasingly polar solvents.

In which order are these lipids eluted from the column (explain the rationale)?

On a polar silica column, the less polar molecules are eluted first using nonpolar solvents, while more polar molecules remain adsorbed longer.

1. **Triglyceride:**
– Very nonpolar (all fatty acid chains are esterified with no free polar group).
2. **Cholesterol-palmitate (cholesterol esterified with a fatty acid):**
– Generally nonpolar; the ester function slightly increases polarity, but overall remains low.
3. **Cholesterol:**
– Mainly hydrophobic with one hydroxyl group, making it slightly more polar than its ester.
4. **Palmitic acid:**
– Contains a free carboxyl group (acid), which increases its polarity.
5. **Phosphatidylcholine:**
– Contains a phosphate group and a charged head (zwitterionic), making it the most polar molecule of the mixture.

Summary (from first eluted to last):
Triglyceride < Cholesterol-palmitate < Cholesterol < Palmitic acid < Phosphatidylcholine

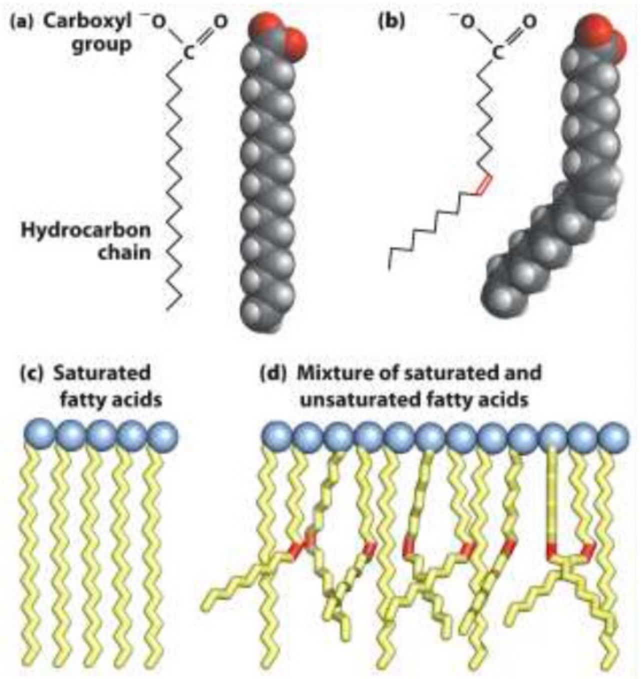
4) The melting points of a series of 18-carbon fatty acids are:

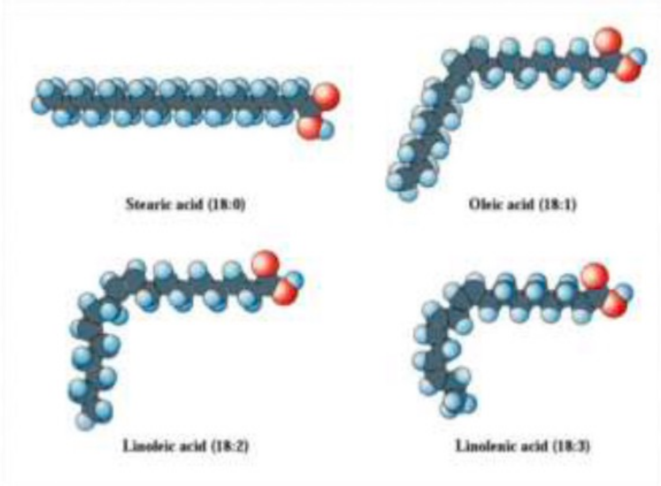
stearic acid, 69.6 C; oleic acid, 13.4 C; linoleic acid, -5 C; and linolenic acid - 11C.

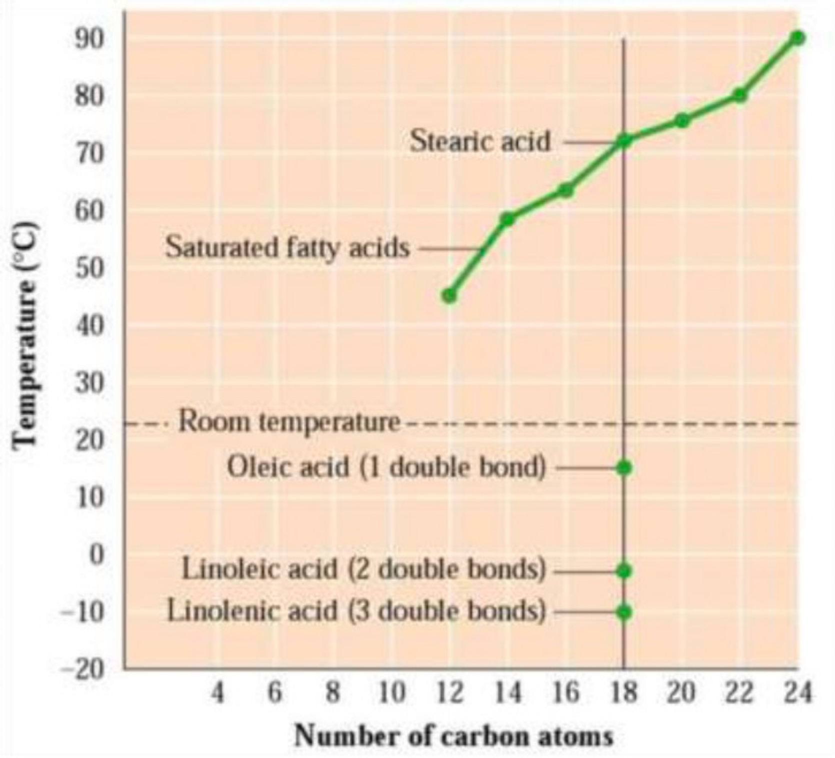
a. What structural aspect of these 18-carbon fatty acids can be correlated with the melting point?

Number of *cis* double bonds

- Decrease packing of the hydrocarbon chains
- Lower packing = lower melting temperature







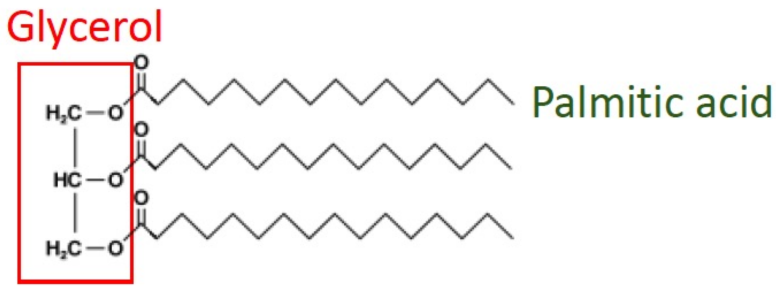
4) The melting points of a series of 18-carbon fatty acids are:
stearic acid, 69.6 C; oleic acid, 13.4 C; linoleic acid, -5 C; and linolenic acid - 11C.

b. List all possible triacylglycerols that can be constructed from glycerol, palmitic acid, and oleic acid. Rank them in order of increasing melting point.

↑ Content of fatty acid = ↑ Melting point

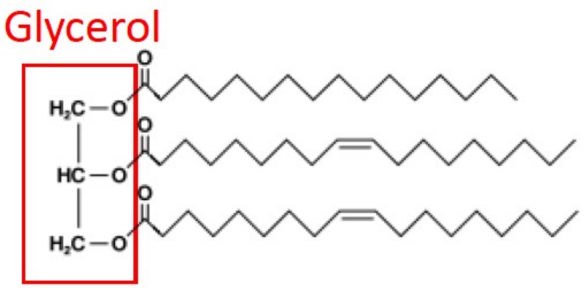
18:1(Δ^9)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	*cis*-9-Octadecenoic acid	Oleic acid (Latin *oleum*, "oil")
16:0	$CH_3(CH_2)_{14}COOH$	*n*-Hexadecanoic acid	Palmitic acid (Latin *palma*, "palm tree")

1. PPP

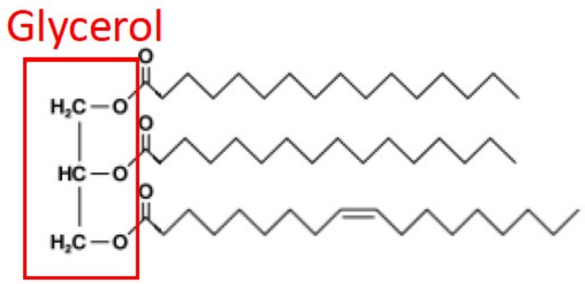


2. OOO

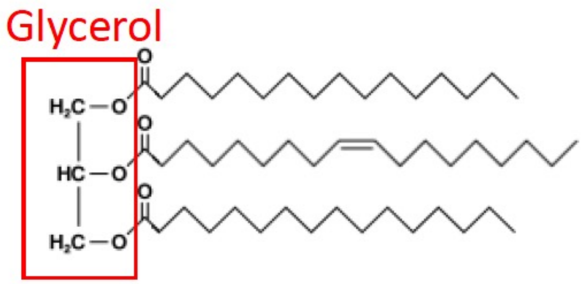
3. POO



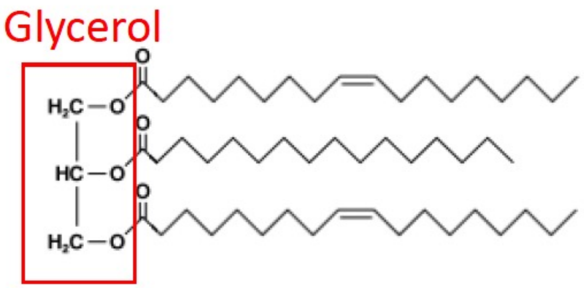
4. PPO



5. POP



6. OPO



Course – Slide5-6-9

4) The melting points of a series of 18-carbon fatty acids are: stearic acid, 69.6 C; oleic acid, 13.4 C; linoleic acid, -5 C; and linolenic acid - 11C.

A triacylglycerol is formed when three fatty acids are esterified to the hydroxyl groups (C1, C2, and C3) of a glycerol molecule.

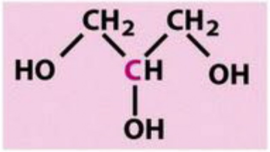
→ Possible combinations (using P for palmitic acid and O for oleic acid):
- **PPP:** All three positions are occupied by palmitic acid.
- **PPO:** Two palmitic acids and one oleic acid.
- **POO:** One palmitic acid and two oleic acids.
- **OOO:** All three positions are occupied by oleic acid.

Although the positions might be interchanged (e.g., PPO, OPO, OOP), they generally lead to the same molecule)

→ Effect on melting point and ranking:
- The more unsaturated chains present, the lower the melting point because the cis double bonds introduce kinks that prevent tight packing.
- **Ranking (from lowest to highest melting point):**

1. **OOO** – Most unsaturated, lowest melting point.
2. **POO** – One saturated chain among two unsaturated chains.
3. **PPO** – Two saturated chains and one unsaturated chain.
4. **PPP** – Fully saturated, highest melting point.

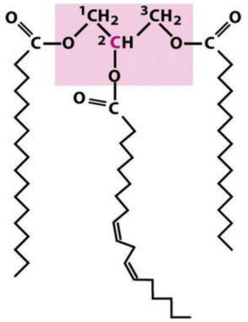
Course – Slide9

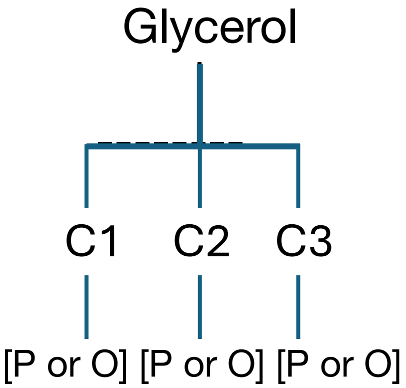


Glycerol

Course – Slide10

Triacylglycerols

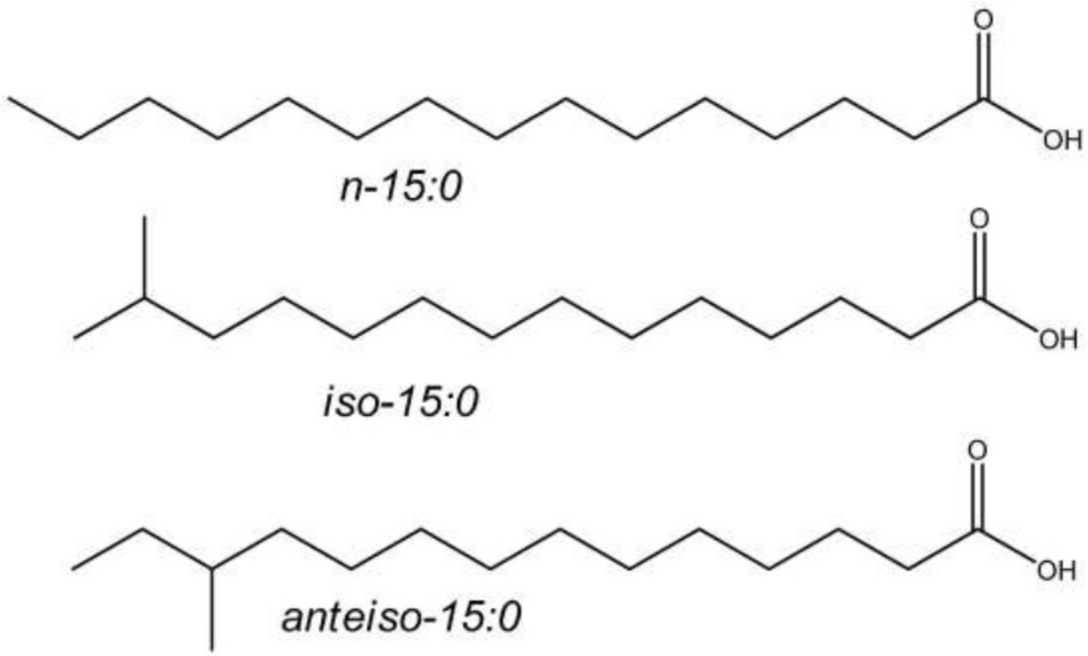




4) The melting points of a series of 18-carbon fatty acids are:

stearic acid, 69.6 C; oleic acid, 13.4 C; linoleic acid, -5 C; and linolenic acid - 11C.

c. Branched-chain fatty acids are found in some bacterial membrane lipids. Would their presence increase or decrease the fluidity of the membrane (that is, give them a lower or higher melting point)? Why?



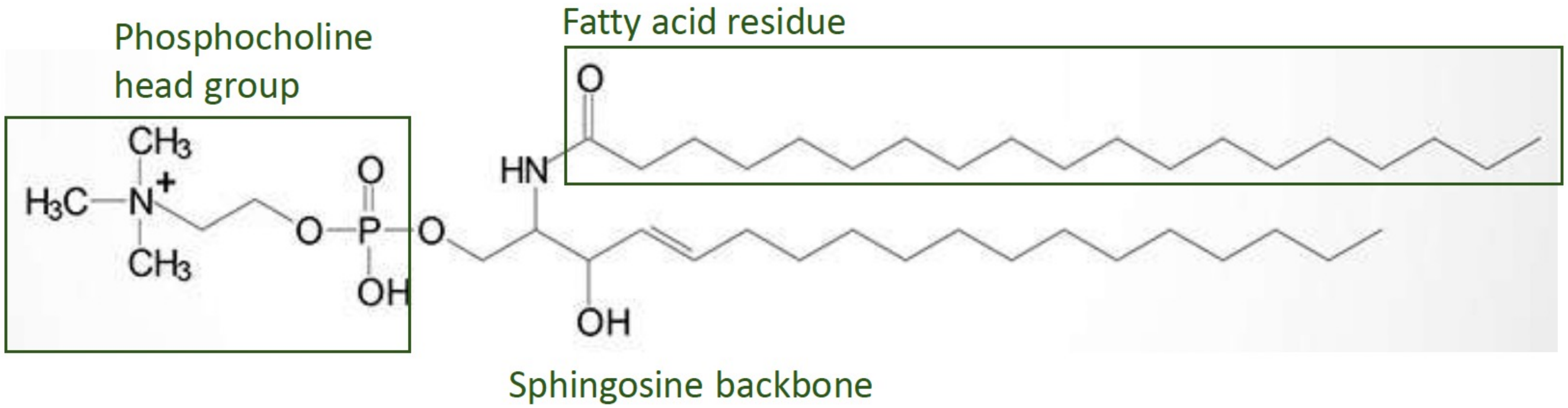
Branching leads to:

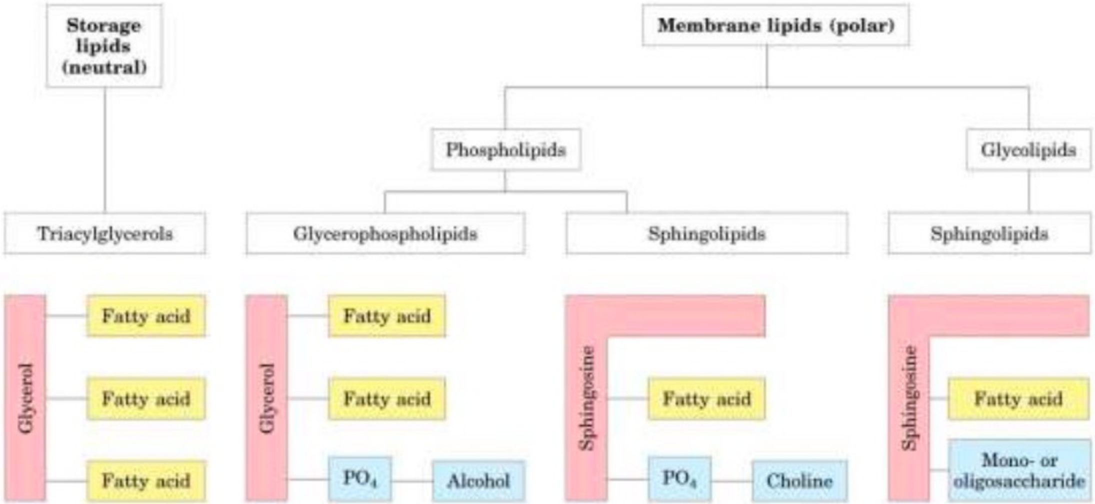
- Increased membrane fluidity
- Decreased packing
- Decreased melting point

➢ Its effect is similar to that of bends caused by double bonds

5) Examine the membrane lipid pictured below and answer the following questions.

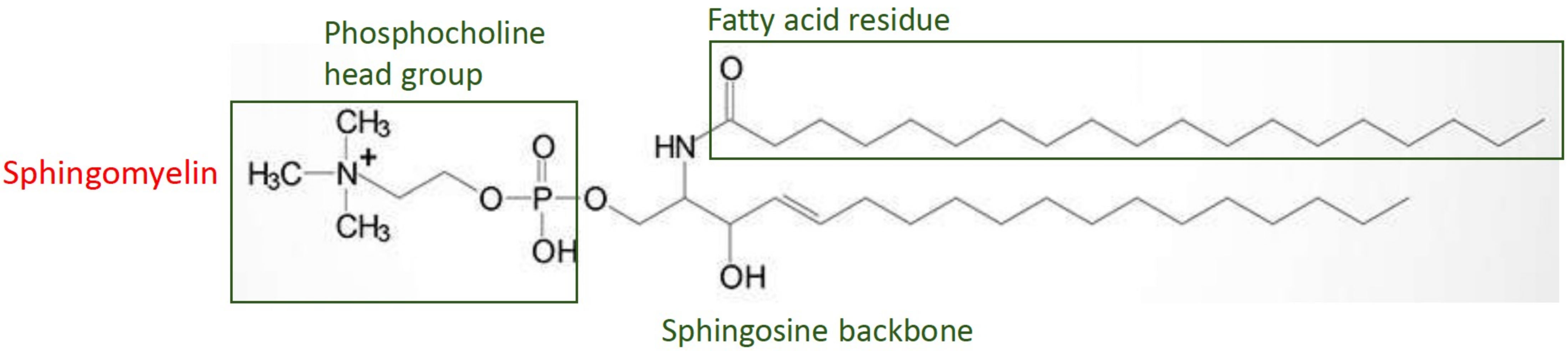
a. Is this lipid classified as a phospholipid or a glycolipid? How can you tell?

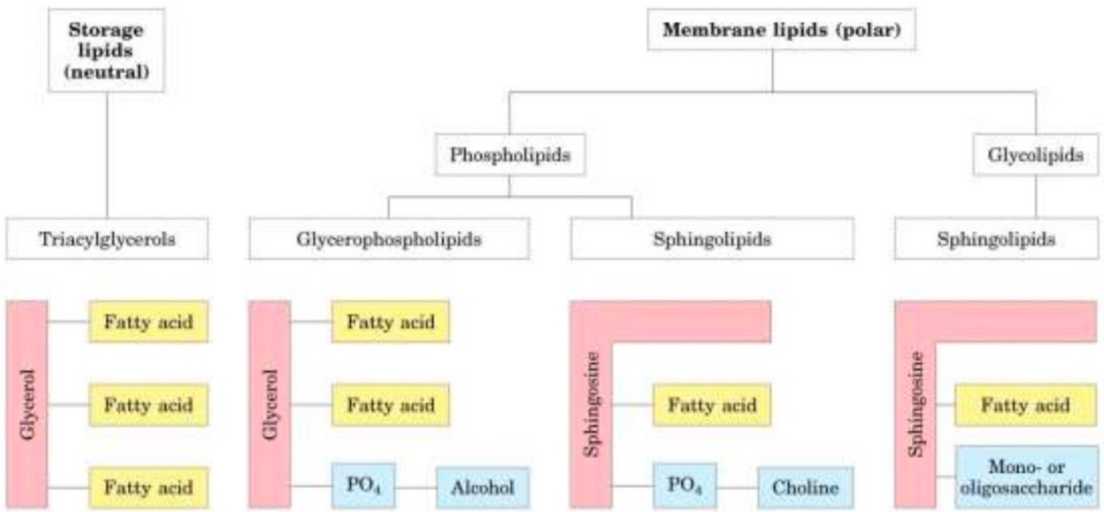




5) Examine the membrane lipid pictured below and answer the following questions.

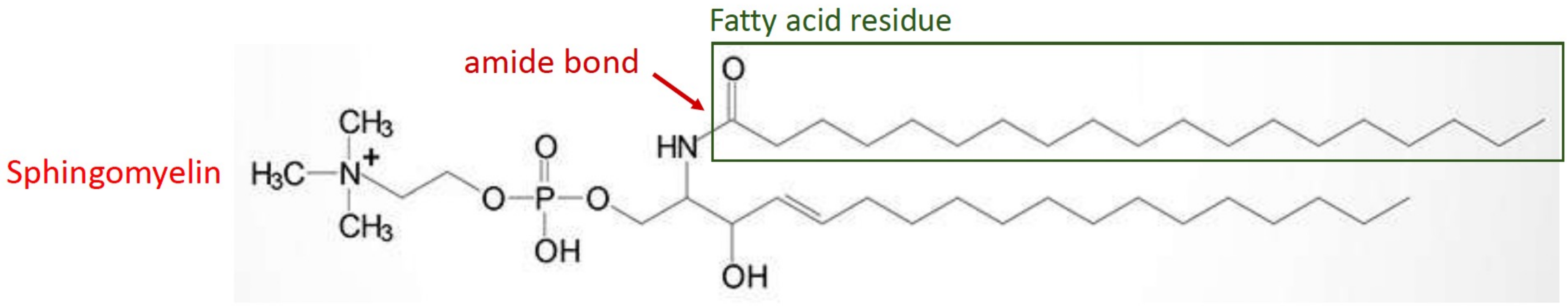
b. Is this lipid considered a sphingolipid or a glycerophospholipid? How can you tell?





5) Examine the membrane lipid pictured below and answer the following questions.

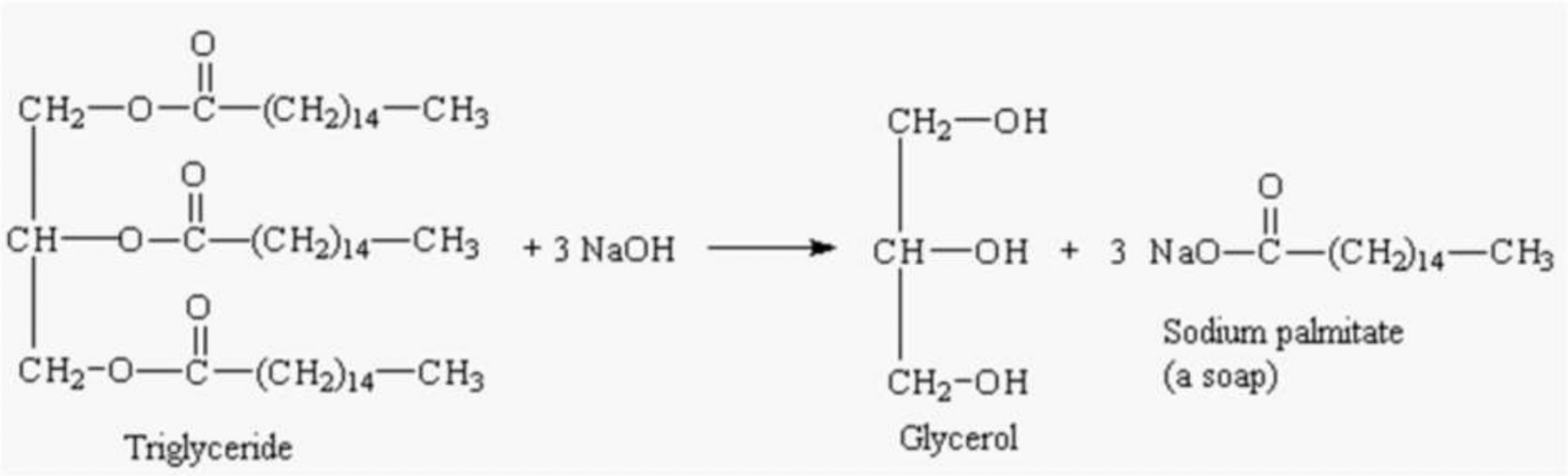
c. What fatty acid chains are used in this lipid? Are they saturated or unsaturated? What kind of bond links the fatty acids to the headgroup?



- 1 fatty acid chain
- No double bonds = saturated

6) A common procedure to clean filters from fats is to use products containing sodium hydroxide. Can you explain how these products work (please draw the involved reaction)?

Saponification



Hydrolysis of triglycerides in alkali environment → glycerol + salt of fatty acid

The hydroxide ion (OH^-) attacks the electrophilic carbonyl carbon in the ester bond of the triglyceride, breaking the ester linkage. This reaction releases a fatty acid as its sodium salt (soap), which is water-soluble, along with glycerol. This process transforms insoluble fats into soluble compounds that can be rinsed away.