Chapter 5

Lipids

Introduction

❑ Definition/classification

- Lipids are a class of biological molecules defined by low solubility in water and high solubility in non-polar solvents.
  - They are waxy, greasy or oily compounds found in plants and animals.

- Typically exist in nonnumeric forms

- The term may include wider range of compounds /structures including
  - ✓ Free fatty acids (FFA's)
  - ✓ Trigycerides (TG's)
  - ✓ Glycerophospolipids (GPL)
  - ✓ Sphigolipids (SL)
  - ✓ Isoprenoids (Steroids, terpenes, carotenes, lipid vitamins)
  - ✓ Eicosanoids
  - ✓ Waxes etc…

Functional role of Lipids

❖ Biological

- Structural components membrane:- Phospholipids, Sphingomyelins, Steroids (sterols)
- Energy storage:- Triacylglycerols
- Lipid solubilization and digestion:- Bile acids
- Moisture barrier :-Waxes
- Chemical messengers/signaling molecules :- Eicosanoids (prostaglandin), phosphatidylinositol
- Vitamin :-Lipid Vitamins (A, D,E, K)
- Photosynthetic accessory pigments:- Carotenoids, Chlorophyll
- Electron carriers (lipid soluble):- Plastoquinone/ubiquinone
- Protection/ aroma:- Essential oils
- Thermal insulation and protection-shock absorbers
- Supply essential fatty acids
- Hold fat soluble substances- fat-soluble vitamins
- Flavor and mouth feel
- Secretes hormones-adipose tissue
- Satiety

Fatty acids

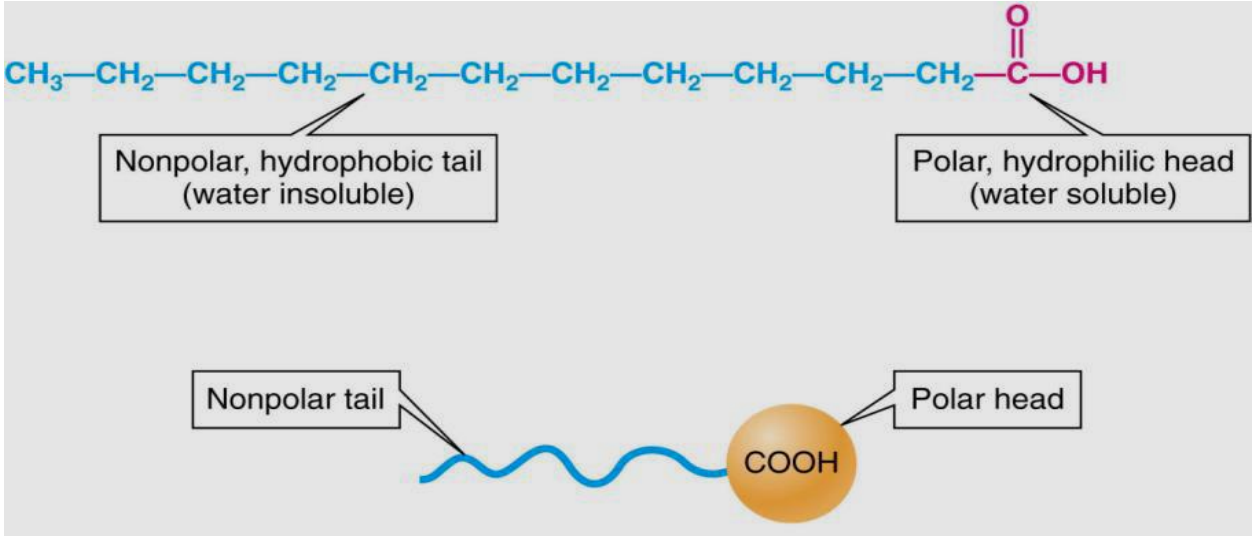
❑ Definition

❖ Fatty acids are long chain of monocarboxylic acids

➢ They are amphipathic molecules containing

✓ Polar **carboxyl group** (-COOH) and

✓ Non-polar **hydrocarbon** (R-) tail



Fatty acids

❑ Classification

i) Based on chain length:- as

- ✓Short (3-6 C), medium (7-11 C), long (12-24 C), and very long (>24 C)

ii) Based on prsence of unsaturation:- as

- ✓ **Saturated** – with no double bonds.
- ✓ **Unsaturated** – with one or more non-conjugated double bonds

iii) Based on dietary sources:- as

- ✓Essential fatty acids and
- ✓ Non-essential fatty acids

Fatty acids

❑ Characteristics

- ❖ Fatty acids always have even number of carbon atoms(10-24)
- ❖ All naturally occurring unsaturated fatty acids have cis-configuration
- ❖ They can be represented in three ways
  - ➢ **Common name**:- derived from their source
  - ➢ **Systematic name** :- just as carboxylic acids
  - ➢ **Short term representation**:- generally represented as A: B (**Δ or ω**)$^{x,y,z,\cdots}$ where
    - – **A** = total no of carbon atoms contained
    - – **B** = total no of unsaturated bonds
    - – **(Δ or n)-Greek letters** :- indicate way of labeling C-atoms
    - – **x, y, z, …** :- numbers used to represent position of unsaturated bonds

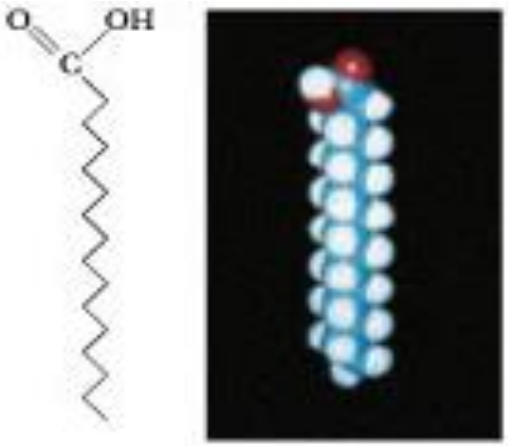
Fatty acids

Common Biological Fatty Acids

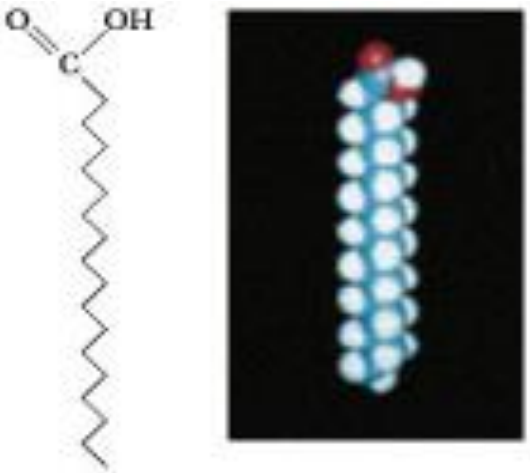
Number of Carbons	Common Name	Systematic Name	Symbol	Structure
Saturated fatty acids				
12	Lauric acid	Dodecanoic acid	12:0	$CH_3(CH_2)_{10}COOH$
14	Myristic acid	Tetradecanoic acid	14:0	$CH_3(CH_2)_{12}COOH$
16	Palmitic acid	Hexadecanoic acid	16:0	$CH_3(CH_2)_{14}COOH$
18	Stearic acid	Octadecanoic acid	18:0	$CH_3(CH_2)_{16}COOH$
20	Arachidic acid	Eicosanoic acid	20:0	$CH_3(CH_2)_{18}COOH$
22	Behenic acid	Docosanoic acid	22:0	$CH_3(CH_2)_{20}COOH$
24	Lignoceric acid	Tetracosanoic acid	24:0	$CH_3(CH_2)_{22}COOH$
Unsaturated fatty acids (all double bonds are *cis*)				
16	Palmitoleic acid	9-Hexadecenoic acid	16:1	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$
18	Oleic acid	9-Octadecenoic acid	18:1	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
18	Linoleic acid	9,12-Octadecadienoic acid	18:2	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$
18	α-Linolenic acid	9,12,15-Octadecatrienoic acid	18:3	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$
18	γ-Linolenic acid	6,9,12-Octadecatrienoic acid	18:3	$CH_3(CH_2)_4(CH{=}CHCH_2)_3(CH_2)_3COOH$
20	Arachidonic acid	5,8,11,14-Eicosatetraenoic acid	20:4	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$
24	Nervonic acid	15-Tetracosenoic acid	24:1	$CH_3(CH_2)_7CH{=}CH(CH_2)_{13}COOH$

Fatty acids

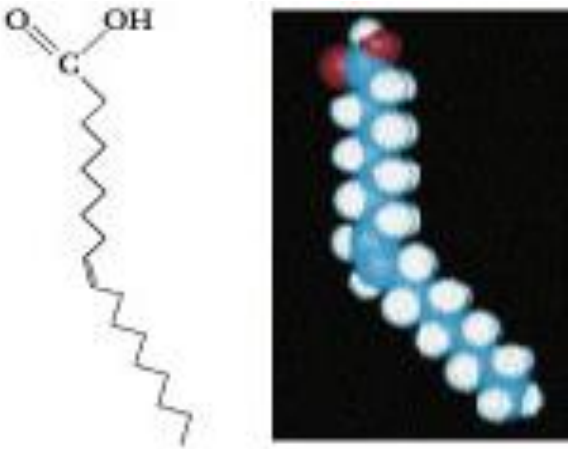
❑ Structure



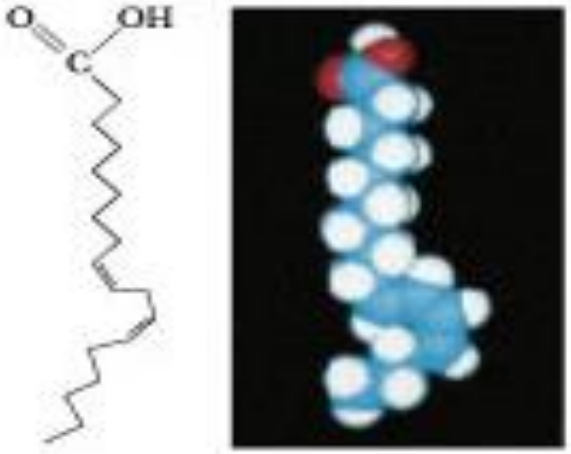
Palmitic acid



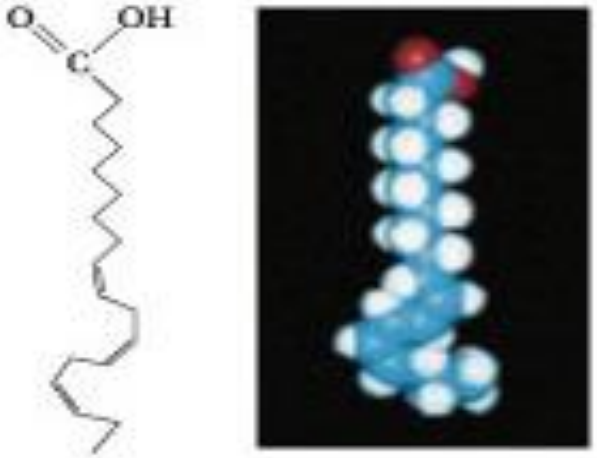
Stearic acid



Oleic acid



Linoleic acid



α–Linolenic acid

Arachidonic acid

Fatty acids

Physical Properties

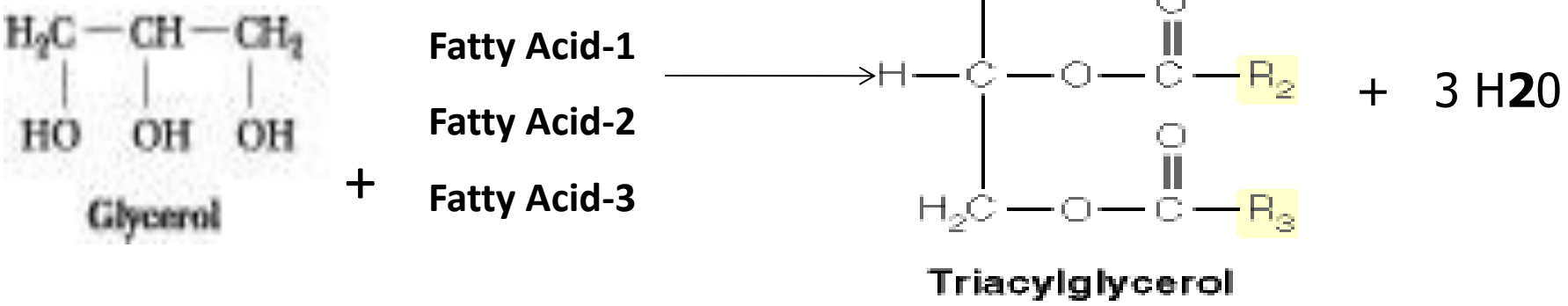
- Physical state
  - With few exceptions all fatty acids exist in solid state at room temprature
- Solubility
  - Longer chains more hydrophobic, less soluble
  - Double bonds increase solubility
- Melting points
  - Depend on chain length and saturation
  - Double bonds lead acyl chain disorder and low melting temps
  - Unsaturated FAs are solids at Room Temp

Triglycerides

❑ Definition/Classification

❖ Are lipids composed of glycerol and three fatty acids attached through ester linkage

❖ Are essential constituents of fats and



❖They can be classified as

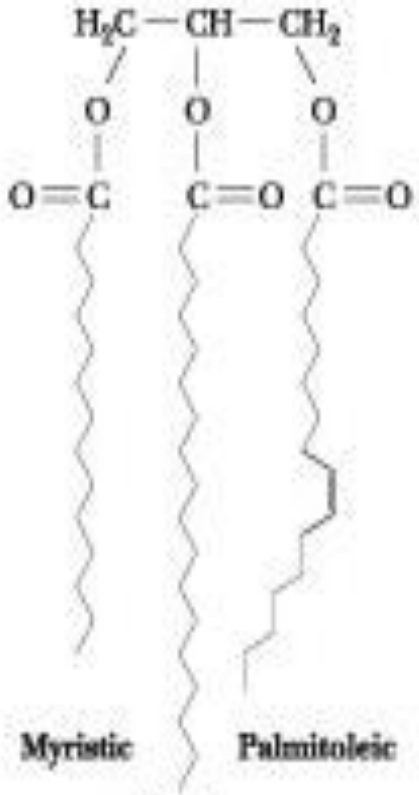
- **Simple esters**:- contain ester formed from similar fatty acids
- **Mixed esters** (most common):- involve esters derived from different fatty acids

Triglycerides

❑ Structure

All are stearic acids

(a simple triacylglycerol)

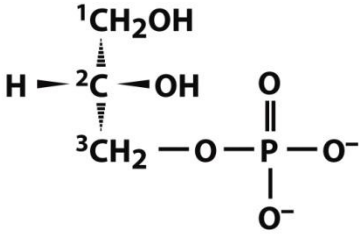


A mixed triacylglycerol

Glycerophospholipid

❑ Definition/structure

- ❖ They are 1,2-diacylglycerol that has a phosphate group attached at C-3 of glycerol backbone

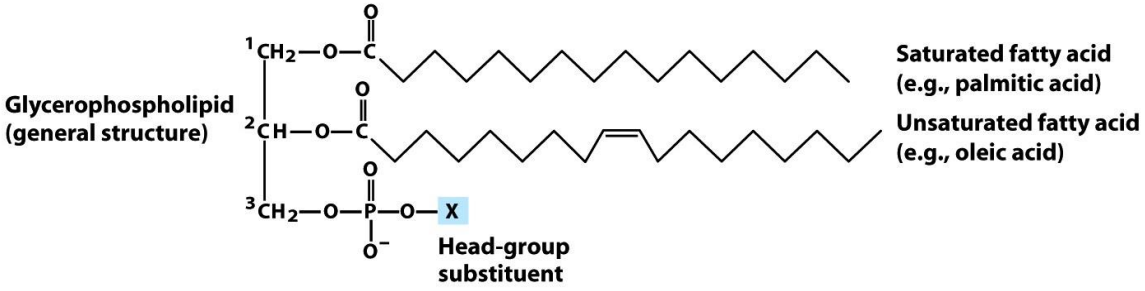


L-Glycerol 3-phosphate

- ❖ They are also known as a ***phosphoglyceride*** or a ***glycerol phosphatide***

- ❖ Generally possess **one** head and **two** tail groups

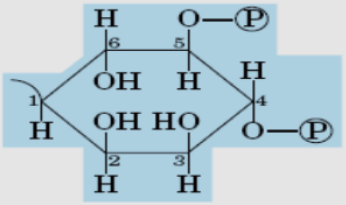
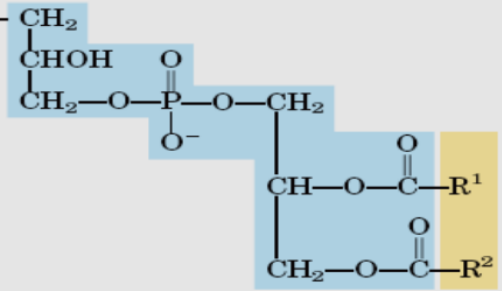
- ❖ The negatively charged phosphate head group can add polar groups linked through phospho diesters with ethanolamine, choline, serine, glycerol, inositol phosphate, phosphatidyl glycerol



Glycerophospholipid

❑ Classification

❖ Based on type of polar groups linked to the phosphate group

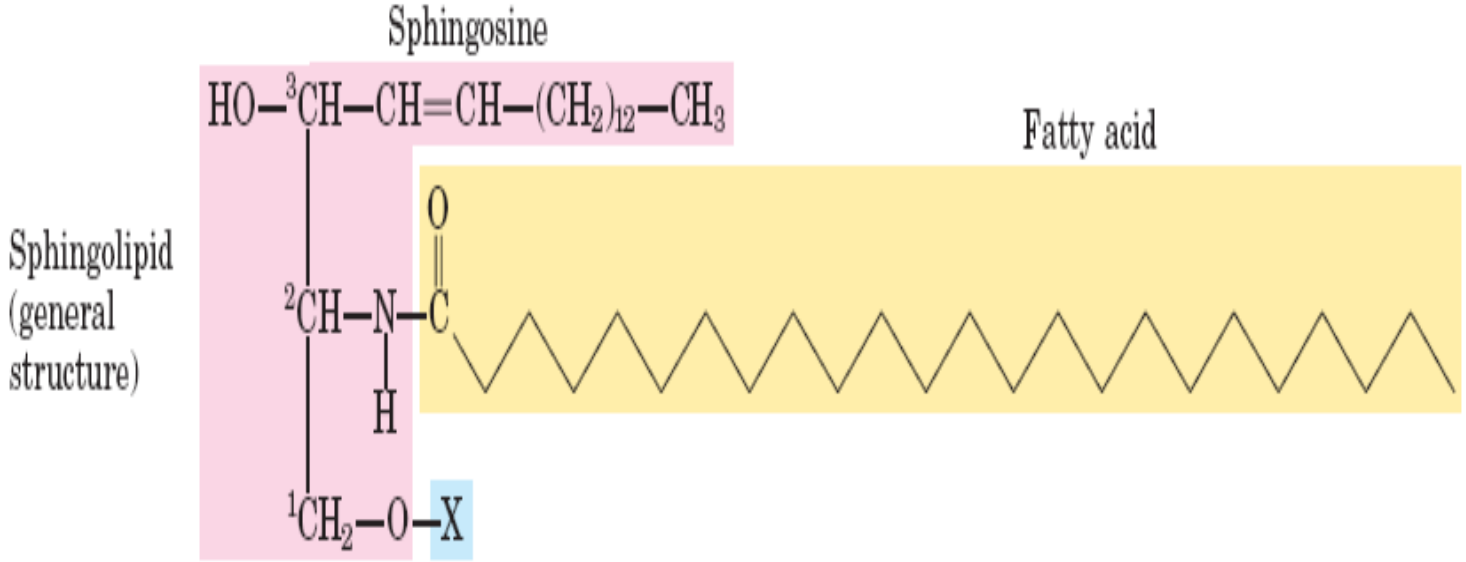
Name of glycerophospholipid	Name of X	Formula of X	Net charge (at pH 7)
Phosphatidic acid	—	— H	−1
Phosphatidylethanolamine	Ethanolamine	— CH_2—CH_2—$\overset{+}{N}H_3$	0
Phosphatidylcholine	Choline	— CH_2—CH_2—$\overset{+}{N}(CH_3)_3$	0
Phosphatidylserine	Serine	— CH_2—$CH(COO^-)$—$\overset{+}{N}H_3$	−1
Phosphatidylglycerol	Glycerol	— CH_2—$CH(OH)$—CH_2—OH	−1
Phosphatidylinositol 4,5-bisphosphate	*myo*-Inositol 4,5-bisphosphate		−4
Cardiolipin	Phosphatidyl-glycerol		−2

Sphingolipids

❑ Definition/structure

❖ Are lipids which are based on long chain of amino alcohol called **sphignosine**

❖ Amino groups at C-2 can be acylated with fatty acids to give the simplest sphingolipid called **ceramide**



Sphingolipids

❑ Classification

❖ Sphingolipids are classified based on various polar groups attached on c-1 into

➢ Glycophosphingolipids

-If sugars are attached to c-1 using glycosidic linkage

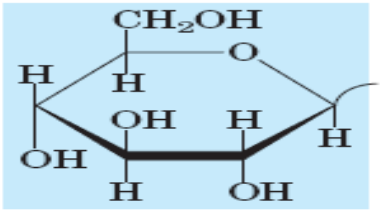
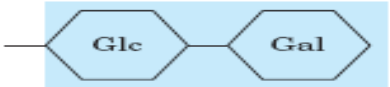
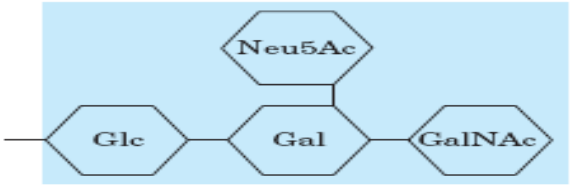
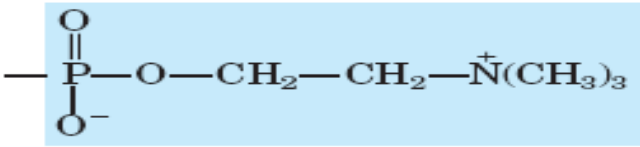
➢ Phosphosphingolipids

-If phosphocholine/phosphoserine is attached to c-1 using phosphodiester linkage

Sphingolipids

❑ Classification

- ❖ Glycosphingolipids and phosphosphingolipids are further classified based on type of sugar attached to C-1 into

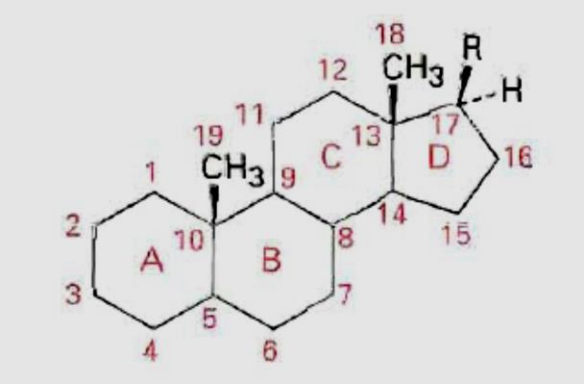
Name of sphingolipid	Name of X	Formula of X
Ceramide	—	— H
Neutral glycolipids Glucosylcerebroside	Glucose	
Lactosylceramide (a globoside)	Di-, tri-, or tetrasaccharide	
Ganglioside GM2	Complex oligosaccharide	
Sphingomyelin	Phosphocholine	

Steroids

❑ Definition/structure

❖ Are compounds based on tetracyclic fused ring system

❖They are mostly derived from triterpenoids (lansterol, squaline, ergosterol etc)



❖Many steroids have methyl groups at the 10^{th} &13^{th} positions(called angular methyl groups)

❖They normally differ by the type of

- Side chains are at C_{17} (usually classified based on this) and
- Functional groups at C_3 (-O or -OH groups) and C_{11} (-O, –OH gives oxygen function)

Steroids

❑ Classification

i) Based on their source

- ❖ Animal steroids:- include
  - ➢ Insects steroids (ecdysteroids)-such as ecdysterone
  - ➢ Steroid hormones:-androgens, estrogens, progestagens, glucocorticoids and mineralocorticoids.
  - ➢ Cholesterol
  - ➢ Bile acids
- ❖ Plant steroids:- Phytosterols, Brassinosteroids
- ❖ Fungus steroids :- Ergosterols

Steroids

❑ Classification

ii) Based on their carbon number

Class	Number of carbon atoms	Examples
Cholestanes	27	Cholesterol
Cholanes	24	Cholic acid
Pregnanes	21	Progesterone
Androstanes	19	Testosterone
Estranes	18	Estradiol

Composition

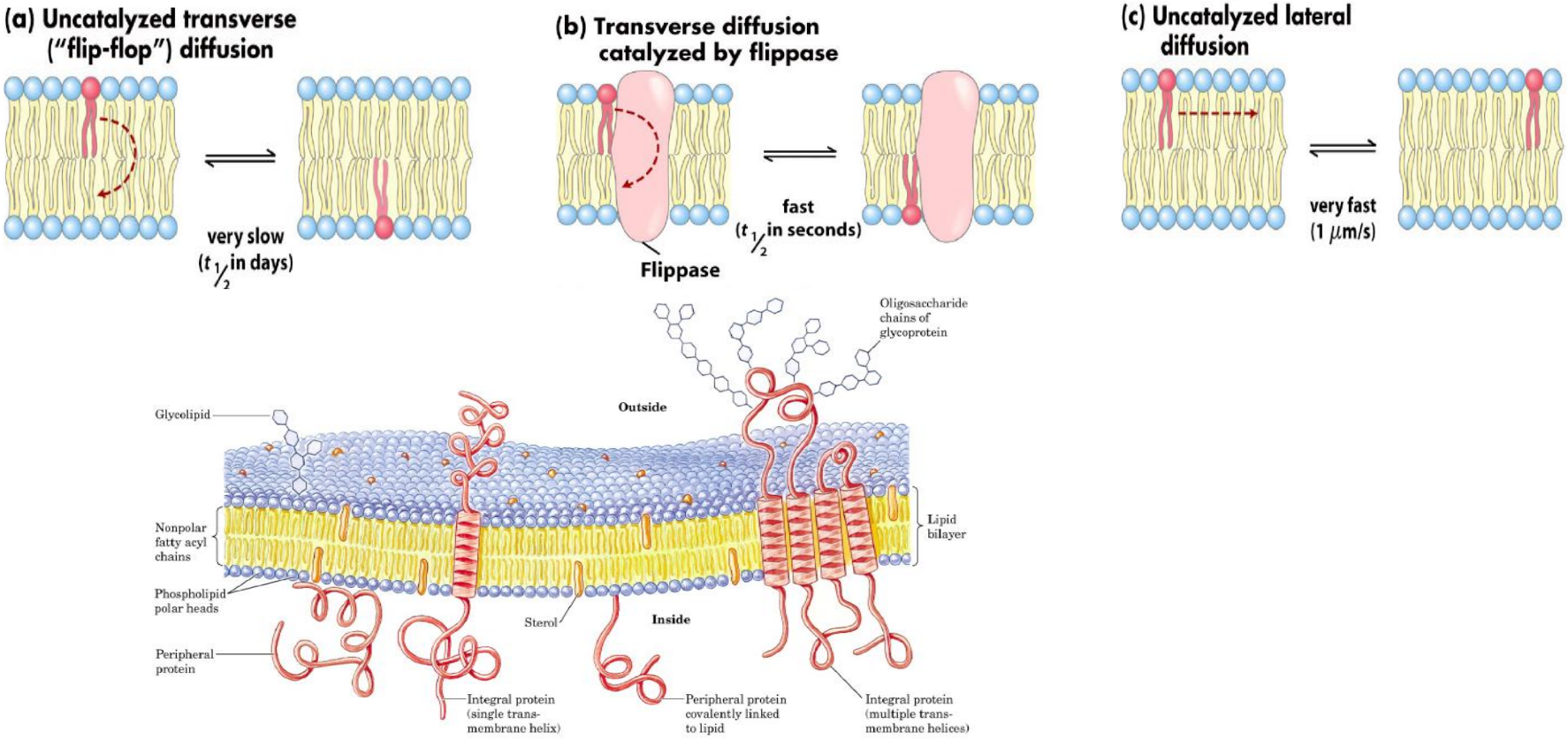
- They are bilayer of phospholipids(flexible)-about 50 Å in width with Other constituents like
  - lipids (e.g Free fatty acids, cholesterol, carbidolipids etc)
  - Conjugate lipids (glycolipids, lipoproteins)
  - Protein

Phospholipid composition of organelle membranes from rat liver

	Percentage of total phospholipids in membranes from different organelles					
	Mitochondria	Microsomes	Lysosomes	Plasma membrane	Nuclear membrane	Golgi membrane
Cardiolipin	18	1	1	1	4	1
Phosphatidylethanolamine	35	22	14	23	13	20
Phosphatidylcholine	40	58	40	39	55	50
Phosphatidylinositol	5	10	5	8	10	12
Phosphatidylserine	1	2	2	9	3	6
Phosphatidic acid	–	1	1	1	2	<1
Sphingomyelin	1	1	20	16	3	8
Phospholipids (mg/mg protein)	0.175	0.374	0.156	0.672	0.500	0.825
Cholesterol (mg/mg protein)	0.003	0.014	0.038	0.128	0.038	0.078

Architecture

- The membrane lipid bilayer is a fluid that is
  - ✓highly mobile in plane (lateral diffusion) is easy
  - ✓flip-flops across layers is very rare (transverse diffusion)



Role

- Create an external boundary to the cell and also form internal compartments (vesicles, organelles)
- Are sites for
  - Selective barrier -exchange of chemical substances (pores, transporters , vesicles etc)
  - Many enzymatic reactions
  - Build up electrochemical potentials for use in signaling & energy production

Membrane Transport

- Biological membranes facilitate selective transport/exchange of chemical substances across a membrane

- Membrane transport is to be carried mainly by proteins that can serve as channels/pores or carrier molecules.

- Transport is mostly to be initiated by
  - concentration gradient
  - electrochemical gradient or
  - other reasons created across the membranes

- The two main types of membrane transport systems include are possible
  - Passive transport /facilitated diffusion and
  - Active transport

Membrane Transport

A) **Passive transport**

- Is carried down the concentration/electrochemical gradient
- Doesn't require energy
- Generally include

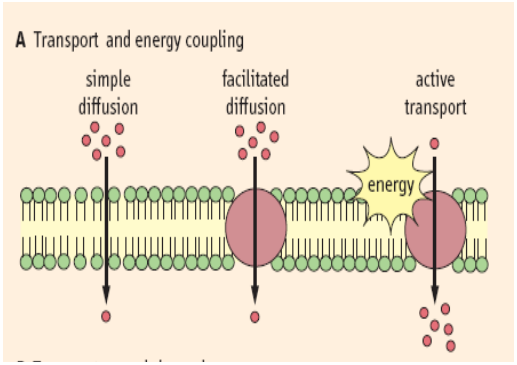
I) Simple diffusion:-Involves transport of

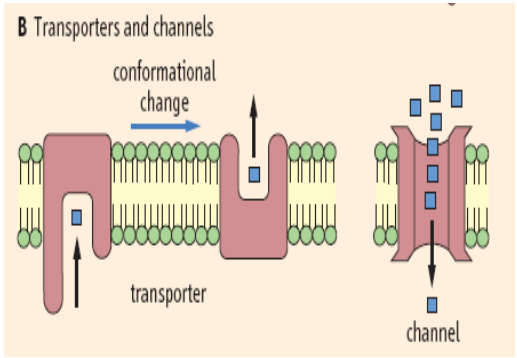
- ✓Small, non-polar molecules (such as O_2, CO_2, N_2) and
- ✓ Small, uncharged polar molecules (such as urea, ethanol, and organic acids) move through membranes

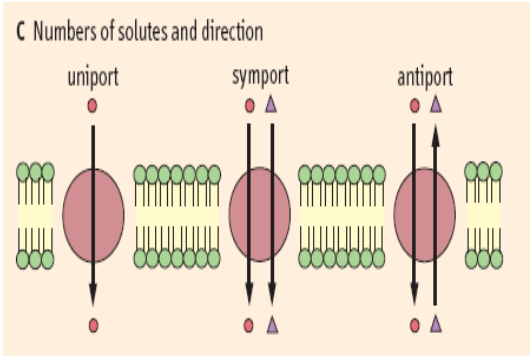
ii) Facilitated diffusion:- Transport of larger, polar molecules, such as amino acids or sugars, into a cell

- Requires the involvement of membrane proteins known as transporters also called porters, permeases, translocases, or carrier proteins.

iii) Ionophore mediated:- involve ionophores (special transporters to carry ions)







B) Active transport

- Is pumping a substance against concentration gradient
- Requires energy

  -Cells spend 30-50% of their ATP on active transport

- Can proceed in two different ways

  - Primary active transport:- do not require secondary species to assist transportation
  - Secondary active transport :- require secondary species to assist transportation