Lecture 5

BT 203 Biochemistry 3-0-0-6

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Key Concepts

- What are Lipids?
- What are the different types of lipids?
- What are fatty acids?
- What are the different types of fatty acids?
- What are diseases associated with glycoconjugates?

LIPIDS

General Information

- > A lipid is an organic substance found in living systems that is insoluble in water but is soluble in organic solvents
- ➤ May contain phosphoric acid, nitrogenous base and carbohydrates
- Lipids vary widely in their structures. They have mostly carbon, hydrogen and some have a few polar atoms/ functional groups

Bloor's Criteria

- Insoluble in water and soluble in organic solvents such as chloroform, benzene, acetone
- Esters of fatty acids
- Possibility of utilization by living organisms

Biomedical Importance

- Important dietary constituents and acts as a fuel
- > Can be stored in the body-in almost unlimited amount
- > Insulation
- Building materials
- > Essential for neurons and membranes

LIPIDS AS PIGMENTS

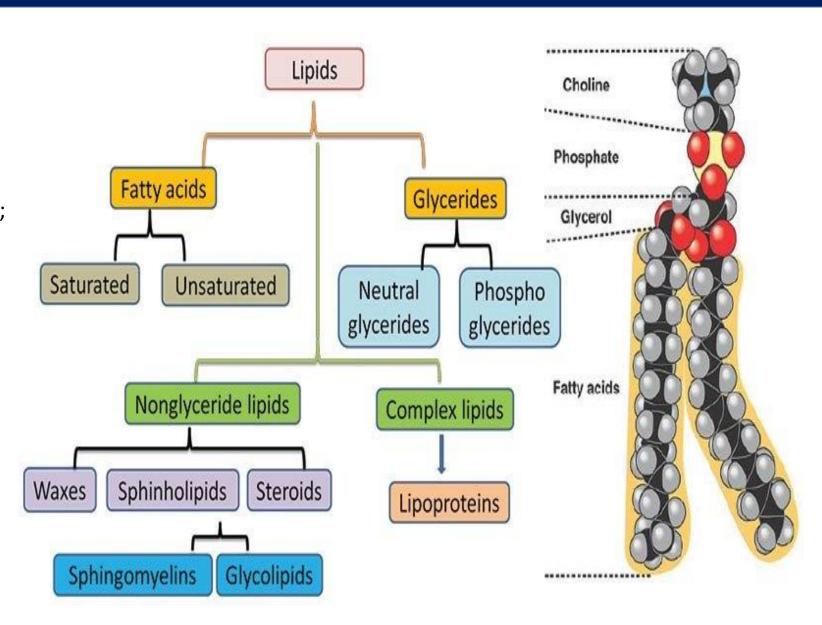




LIPIDS- CLASSIFICATION

Classification of lipids

- I. Simple Lipids –Esters of fatty acids with various alcohols
- a. Neutral fats- tri-esters of fatty acids and glycerol
- b. Waxes-mono-hydroxy aliphatic alcohols;
 Vitamin A and D are palmitic or stearic acids esters
- II. Compound Lipids- Esters of fatty acids
- a. Phospholipids
- b. Glycolipids
- c. Sulpholipids
- d. Aminolipids
- e. Lipoproteins
- **III. Derived Lipids**
- a. Fatty acids
- b. Mono- and di-acylglycerides
- c. Alcohols



Derived Lipids

Fatty Acids (FA)

- Organic acid found in triglycerides
- Obtained from the hydrolysis of fats
- Mono-carboxylic acid ranging in chain length from C4 to C24 carbon atoms
- Amphipathic molecule

Types of FA

- Depending on Number of carbon atoms Odd chain Even chain
- Depending on length of hydrocarbon chains- Short chain

Medium chain

Long chain

Very long chain

Depending on nature of hydrocarbon chain-

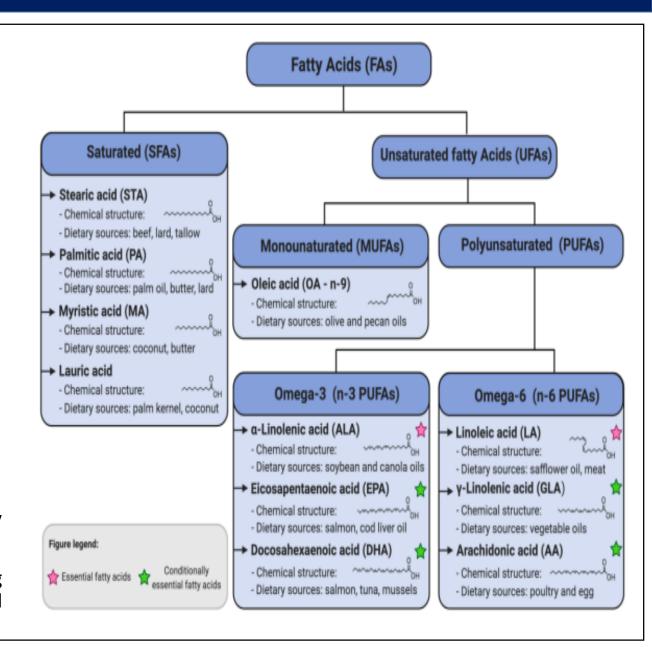
Saturated

Unsaturated

Branched

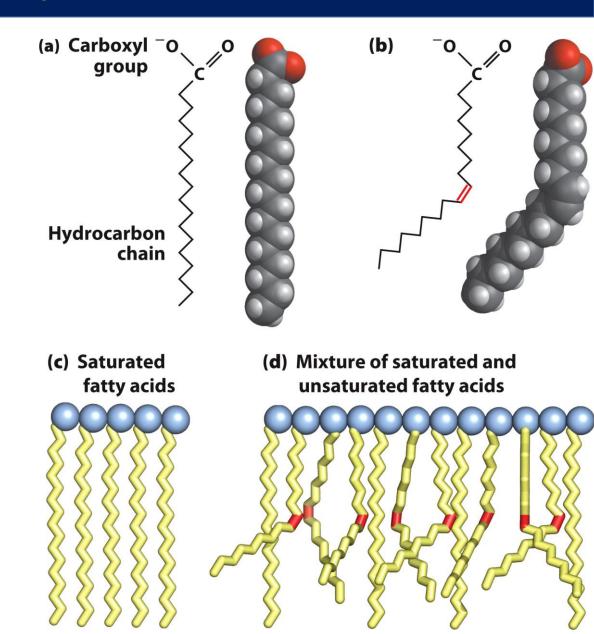
Hydroxy

- Almost all natural unsaturated fatty acids have cis stereochemistry in C=C's.
- Small amounts of trans are produced in stomachs of ruminating animals by partial enzymatic hydrogenation of polyunsaturated fats, and thus are present in small amounts in milk and butter



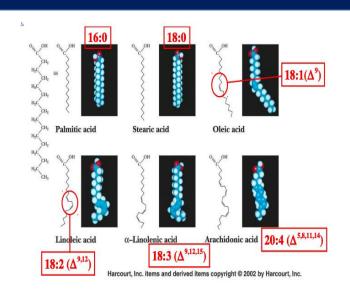
Properties of fatty acids

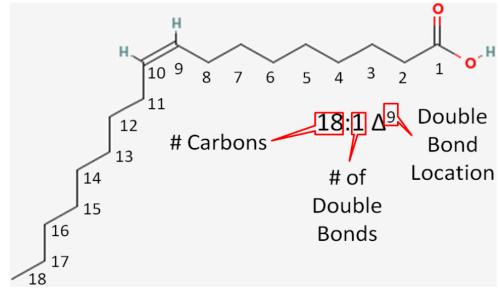
- ➤ Saturated fatty acids pack tightly and form more rigid, organized aggregates
- ➤ Unsaturated chains bend and pack in a less ordered way, with greater potential for motion
- Membrane fluidity determined by temperature and the degree of fatty acid unsaturation of phospholipids
- ➤ Certain bacteria can modulate fatty acid unsaturation in response to temperature



Nomenclature of fatty acids

- Number of carbon atoms
- "Oic" being the substitute
- ✓ Saturated fatty acids end in "anoic" e.g. octanoic acid
- ✓ Unsaturated fatty acids end in "enoic" e.g. octadecenoic acid





	common name	IUPAC name	melting point (C°)	
16:0	palmitate	hexadeconoate	63	
16:1 Δ ⁹	palmitoleate	cis-∆9-hexadeconoate	-0.5	
18:0	stearate	octadeconoate	70	
18:1 ∆ ⁹	oleate	cis-∆9- octadeconoate	13	
18:2 $\Delta^{9,12}$	linoleate	cis- $\Delta^{9,12}$ - octadeconoate	-9	
18:3 $\Delta^{9,12,15}$	linolenate	cis- $\Delta^{9,12,15}$ - octadeconoate	-17	
20:0	arachidate	eicosanoate	75	
20:4 $\Delta^{5,8,11,14}$	arachindonate	cis- $\Delta^{5,8,11,14}$ -eicosatetraenoate	-49	

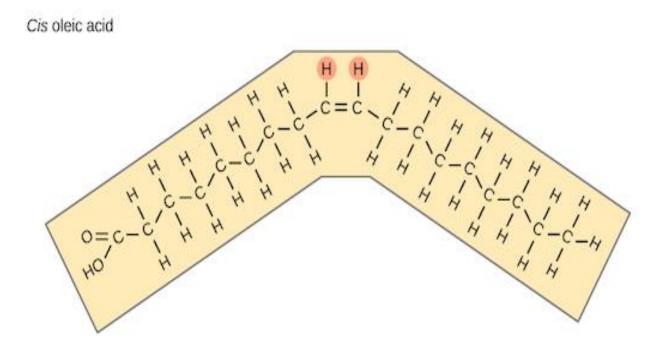
Number of carbon atoms	18
Number of double bonds	1
Number of carbons from the carboxylic acid end to the first double bond	9
Name: 18:9() cis-9-	

octadecenoic acid

Configuration of Unsaturated fatty acids

✓ Unsaturated fatty acids contain double bonds

- ✓ Exists in either cis- or transconfiguration
- ✓ Cis-configuration: The two hydrogen atoms associated with the double bond are present on the same side causing the kink
- ✓ Trans-configuration: The two hydrogen atoms associated with the double bond are present on the different side



Trans oleic acid

Food is tasty???

- Trans fatty acids form by partial dehydrogenation of unsaturated fatty acids
 - Done to increase shelf life or stability at high temperature of oils used in cooking (especially deep frying)
- A trans double bond allows a given fatty acid to adopt an extended conformation
- Trans fatty acids can pack more regularly and show higher melting points than cis forms
- Consuming trans fats increases risk of cardiovascular disease
 - Avoid deep-frying partially hydrogenated vegetable oils
 - Current trend: reduce trans fats in foods (Wendy's, KFC).

TABLE 10-2

Trans Fatty Acids in Some Typical Fast Foods and Snacks

	Trans fatty acid content		
	In a typical serving (g)	As % of total fatty acids	
French fries	4.7-6.1	28-36	
Breaded fish burger	5.6	28	
Breaded chicken			
nuggets	5.0	25	
Pizza	1.1	9	
Corn tortilla chips	1.6	22	
Doughnut	2.7	25	
Muffin	0.7	14	
Chocolate bar	0.2	2	

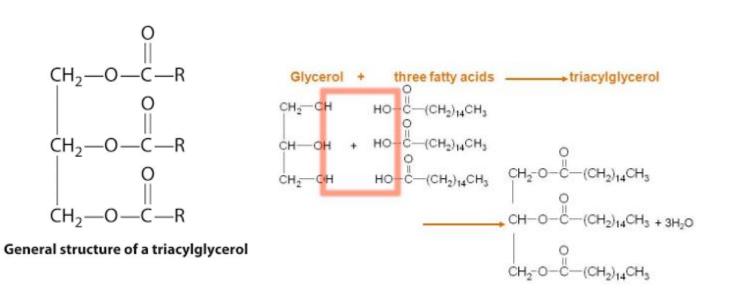
Source: Adapted from Table 1 in Mozaffarian, D., Katan, M.B., Ascherio, P.H., Stampfer, M.J., & Willet, W.C. (2006). Trans fatty acids and cardiovascular disease. *N. Engl. J. Med.* 354, 1604–1605.

Note: All data for foods prepared with partially hydrogenated vegetable oil in the United States in 2002.

Simple Lipids

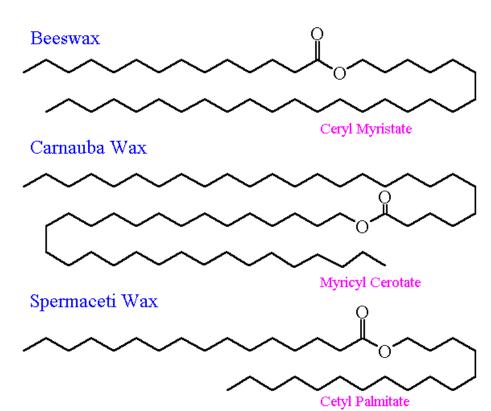
Simple lipids are esters of fatty acids with alcohol

- 1. Fats and oils: esters of fatty acid with glycerol
- 2. Waxes: esters of fatty acids with high molecular weight monohydric alcohol

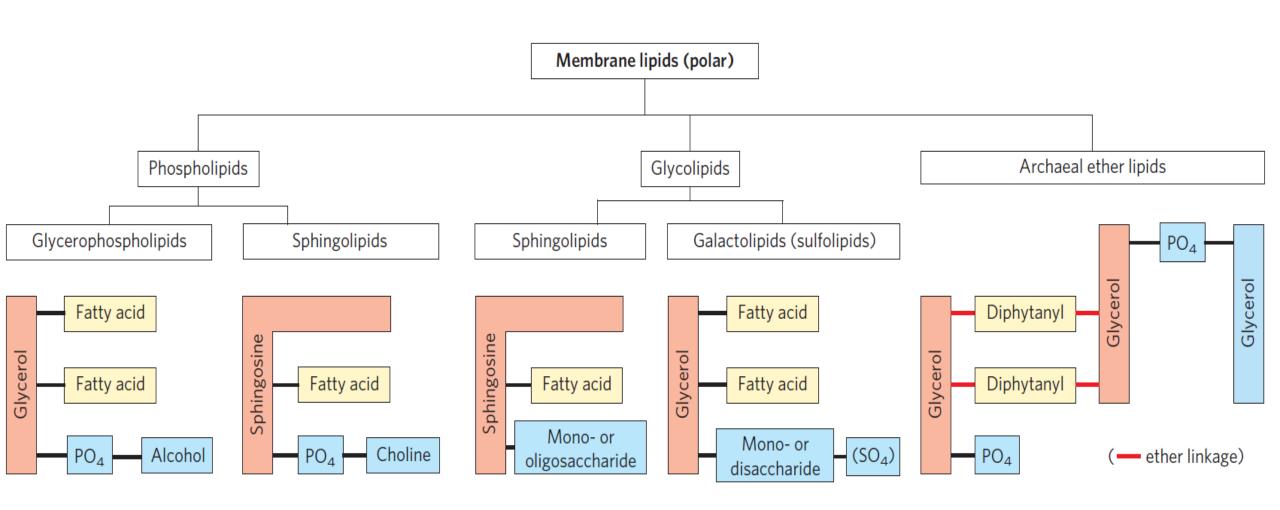








Compounds Lipids (Membrane Lipids)

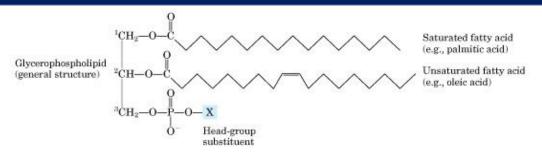


Glycerophospholipids

- ✓ Phosphatidic acid derivatives
- ✓ Structure- Two fatty acids are attached in ester linkage to the first and second carbons of glycerol, and a highly polar or charged group is attached through a phosphodiester linkage to the third carbon
- ✓ Diacylglycerols linked to a polar alcohol by a phosphodiester bond
- ✓ The fatty acids vary within each group, but usually are sat'd C16/18 at C1, and unsat'd C18/20 at C2
- ✓ Note: the charge on the alcohol may be positive, negative, or neutral

$$^{1}CH_{2}OH$$
 $^{1}EH_{2}OH$
 $^{1}EH_{2}OH$
 $^{1}OH_{2}OH$
 $^{1}OH_{2}OH$
 $^{1}OH_{2}OH$
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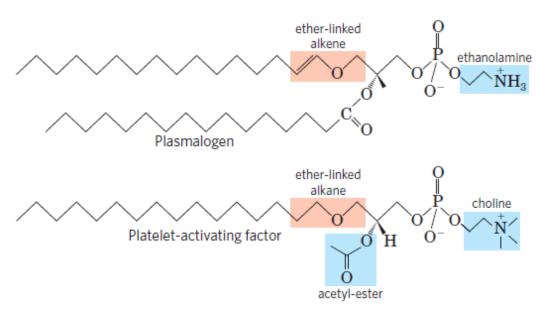
L-Glycerol 3-phosphate (sn-glycerol 3-phosphate)



Name of glycerophospholipid	Name of X	Formula of X	Net charge (at pH 7)
Phosphatidic acid	-	— н	-1
Phosphatidylethanolamine	Ethanolamine	$-$ CH ₂ —CH ₂ — $\overset{+}{\mathrm{N}}\mathrm{H}_3$	0
Phosphatidylcholine	Choline	$- \mathrm{CH_2-\!CH_2-} \!$	0
Phosphatidylserine	Serine	$- \begin{array}{c} - \begin{array}{c} - \\ \text{CH}_2 - \\ \text{COO}^- \end{array} \end{array}$	-1
Phosphatidylglycerol	Glycerol	$-$ СН $_2$ —СН $_2$ —ОН	-1
Phosphatidylinositol 4,5-bisphosphate	myo-Inositol 4,5- bisphosphate	H O—P OH H OH HO OH HO O—P	-4
Cardiolipin	Phosphatidyl- glycerol	- CH ₂ CHOH O CH ₂ -O-P-O-CH ₂ CH-O-C-R ¹ O CH ₂ -O-C-R ²	-2

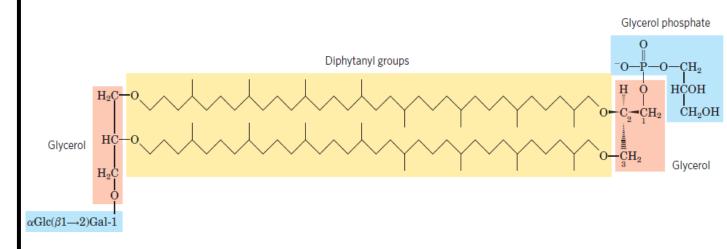
Unique Glycerophospholipids

Ether Glycerophospholipids



- ✓ One of the two acyl chains is attached to glycerol in ether
- ✓ Plasmalogens- Heart lipids (double bond between C-1 and C-2 linkage)
- ✓ Platelet activating factor

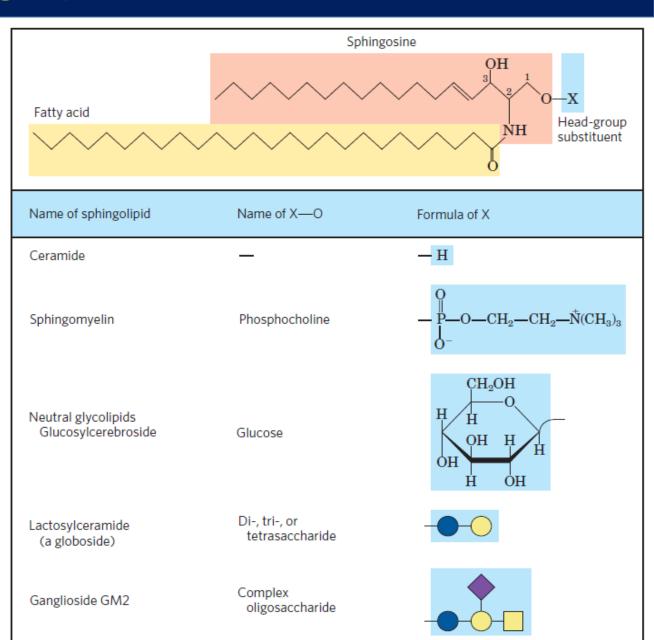
Archaea Membranes



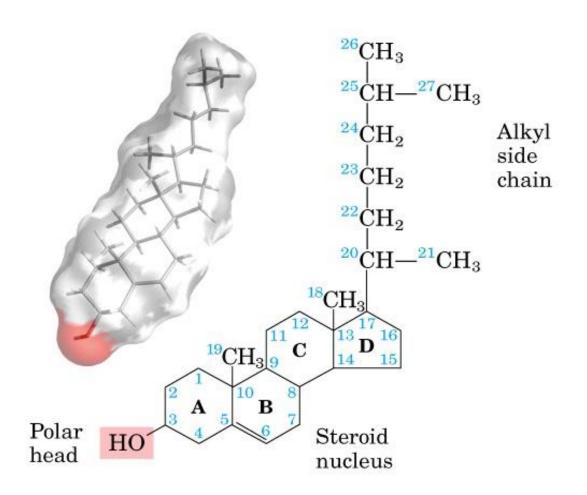
- ✓ Archaea live in ecological niches with extreme conditions
- ✓ Membrane lipids containing long-chain (32 carbons) branched hydrocarbons linked at each end to glycerol
- ✓ Linkages are through ether bonds, which are much more stable to hydrolysis at low pH and high temperature
- ✓ Glycerol dialkyl glycerol tetraethers (GDGTs)

Sphingolipids

- ✓ Derivatives of long-chain amino alcohol sphingosine
- Ceramide (headgroup = H) is the parent of all sphingolipids
- ✓ Sphingomyelins polar headgroup (phospholipids)
 - phosphocholine
 - phosphoethanolamine
- ✓ Glycosphingolipids sugars, no phosphate (Neutral)
 - cerebrosides (1 sugar + ceramide)
 - globosides (2 sugars or more + ceramide)
- ✓ Gangliosides- oligosaccharide headgroups (Charged)
 - with one or more sialic acid residues



Sterols: Structural Lipids, Hormone Precursors, and Detergents



- ✓ Structural lipids present in the membranes of most eukaryotic cells
- ✓ Structure- Steroid nucleus, consisting of four fused rings, three with six carbons and one with five.

Cholesterol

- The most fundamental and famous steroid is cholesterol
- Have a structural role in most eukaryotic membranes
- Hormone derivatives regulate gene expression
- Sterols in other species: stigmasterol in plants and ergosterol in fungi

Important steroids in body

- Androgens These are "male sex hormones" that regulate the development of the male reproductive system and the secondary sexual characteristics in males.
- Progesterone, estrone, and estradiol These are "female sex hormones" that regulate the development of the female reproductive system and are responsible for the maintenance of secondary sexual characteristics in females.
- Aldosterone This steroid controls water and electrolyte balances.
- Cortisone This compound is involved in metabolism and in controlling inflammation.
- Bile salts Facilitates the digestion of certain lipids and the absorption of fat-soluble vitamins.
- Vitamin D An important steroid that controls calcium absorption and deposition in the bone. Recent research also suggests that vitamin D plays a fundamental role in the prevention of many cancers. High consumption of vitamin D and sun exposure appear to reduce cancer risk.

Important steroids in body

VITAMINS

THE CHEMICAL STRUCTURES OF VITAMINS

Vitamins are the essential nutrients that our body needs in small amounts. More specifically, an organic compound is defined as a vitamin when it is required by an organism, but not synthesised by that organism in the required amounts (or at all). There are thirteen recognised vitamins.

VITAMIN A

Important for eyesight. Also strengthens immune system and keeps skin and linings of parts of the body healthy.

VITAMIN B6

Helps make some brain chemicals: needed for normal brain function. Also helps make red blood cells and immune system cells.

VITAMIN E

ALPHA-TOCOPHEROL group includes tocopherols & tocotrienols An antioxidant that helps prevent damage to cells and may have a preventative role in

cancer. Also helps make red blood cells.

VITAMIN B1

can also occur in pyrophosphate ester form Used to keep nerves & muscle tissue healthy. Also important for processing of carbohydrates and some proteins.

VITAMIN B7

produced by intestinal bacteria

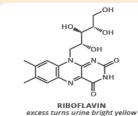
Needed for metabolism of various compounds. Often recommended for strengthening hair, but evidence is variable.

VITAMIN B9

found as tetrahydrofolate in food

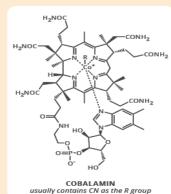
Important for brain function & mental health. Aids production of DNA & RNA. Important when tissues are growing quickly.

VITAMIN B2



Important for body growth, red blood cell production, and keeping the eyes healthy. Also helps processing of carbohydrates.

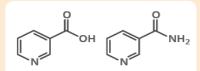
VITAMIN B12



Important for the nervous system, for making red blood cells, and helps in the

production of DNA and RNA

VITAMIN B3



NICOTINIC ACID NICOTINEAMIDE niacin is collective name for these compounds

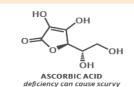
Helps with digestion and digestive system health. Also helps with the processing of carbohydrates.

VITAMIN B5

PANTOTHENIC ACID also occurs in pyrophosphate ester form

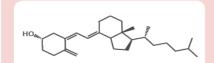
Important for manufacturing red blood cells and maintaining a healthy digestive system. Also helps process carbohydrates.

VITAMIN C



Important for a healthy immune system; helps produce collagen, used to make skin and other tissues. Also helps wound healing.

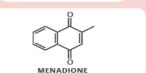
VITAMIN D



CHOLECALCIFEROL natural form; different form used in supplements

Important for bone health and maintaining the immune system function. May also have a preventative role in cancers.

VITAMIN K



all K vitamins are menadione or derivatives

Helps blood clot properly, & plays a key role in bone health. Newborns receive vitamin K injections to prevent bleeding.

Vitamins can be divided broadly into two classes.



These vitamins are not stored in the body. As such, generally, they are required more frequently than the fat-soluble vitamins.

FAT-SOLUBLE VITAMINS

These vitamins are stored in the liver and fatty tissues until required. As such, they can be harmful if too much is taken in.





Summary

- ✓ Lipids- water insoluble compounds, storage and membrane lipids
- √Fatty acids and their classifications
- ✓ Relevance of fatty acids in biological systems
- ✓ Membrane proteins and their classifications
- √ Glycerophospholipids
- **√**Sphingolipids
- √Sterols- Cholesterol and its analogues
- √Biological relevance of different steroids present in human body
- √Vitamins and its significance