Biochem-703 (old) / Biochem-603 (new)

3(3-0)

Biochemistry of Lipids

Teaching Strategies		Lectures, Assignment presentations by the students, Question-answer session			
Assessment	Marks (%)	Sessional	Mid	Final	Total 100%
	Criteria	Assignments	Paper	Paper	-
		6 marks (10%)	18	36	60
	Result	60 marks (100%)			

- **Learning objectives**

To impart basic and advanced knowledge of lipids, and fundamental chemistry of these bio-macromolecule and in depth metabolism.

- **Theory**

Introduction and functions of lipids; Classification, structures, physical and chemical properties of fatty acids; Fatty acids present in special sources, ϖ_3 and ϖ_6 fatty acids; Triglycerides, phospholipids, glycolipids, sphingoglycolipids, sulpholipids and gangliosides; Lipids as signals, cofactors and pigments; Structure and physiological significance of cholesterol and its esters, bile acids and bile salts; Prostaglandins, Thromboxanes and Leukotriene and their role in biological system; Lipoprotein system and lipid distribution, lipid monolayers, bilayers and micelles; Composition and architecture of biological membranes; Biosynthesis and degradation of triglycerides, saturated and unsaturated fatty acids, phospholipids and cholesterol; Regulation of lipid metabolism; Inborn errors of lipid metabolism; Biosynthesis and utilization of ketone bodies.

Suggested Readings

- Chatterjea, M. N. and R. Shinde. 2012. Textbook of Medical Biochemistry. 8th ed (Indian edition). Jaypee Brothers, Medical Publishers (P) Ltd, New Delhi, India.
- Ferrier, D. R. 2013. Biochemistry: Lippincott's Illustrated Reviews. 6th ed. Lippincott Williams and Wilkins. U.S.A.
- Murray, R.K., D.A. Bender, K. M. Botham, P.J. Kennelly, V.W. Rodwell and P.A.Weil. 2012. Harper's Illustrated Biochemistry. 29th ed. McGraw Hill. New York, NY, USA.
- Nelson, D.L and M.M. Cox. 2013. Lehninger Principles of Biochemistry. 6th ed. WH Freeman & Company, New York, NY, USA.
- Rodwell, V and D. Bender. 2015. Harpers Illustrated Biochemistry. 30th Ed. McGraw Hill. New York, NY, USA.
- Voet, D., Voet, J.G and C.W. Pratt. 2013. Fundamentals of Biochemistry, Life at the Molecular Level. 4th ed. John Wiley & Sons. Inc. New York, NY, USA.

Lipids

- Organic, heterogenous substances in plants & animal
- Insoluble in water (hydrophobic) but soluble in non-polar solvents
- Building blocks - fatty acids, glycerol, sphingosine (sphingol) & sterols

Classification of Lipids

A] Simple Lipids: consist of following subgroups:

- **Fats (**Esters of fatty acids with glycerol)
- **Waxes (**Esters of fatty acids with alcohols other than glycerol (high mol.wt. monohydric alcohols)

B] Compound or Complex Lipids

Esters of fatty acids containing groups in addition to an alcohol & a fatty acid

- **Phospholipids:** contain an alcohol, fatty acid (s) & a phosphoric acid residue
- **Glycolipids**: contain sphingosine, a fatty acid & carbohydrate
- **Sulpholipids**: contain sphingosine; a fatty acid, a sugar & a sulfate group
- **Lipoproteins:** These are complexes of lipids with proteins.

C] Derived, Precursor or Associated Lipids

- Hydrolytic products of **above-mentioned** compounds
- include diglycerides, fatty acids, alcohols including glycerol, sterols, vitamins D, E, K

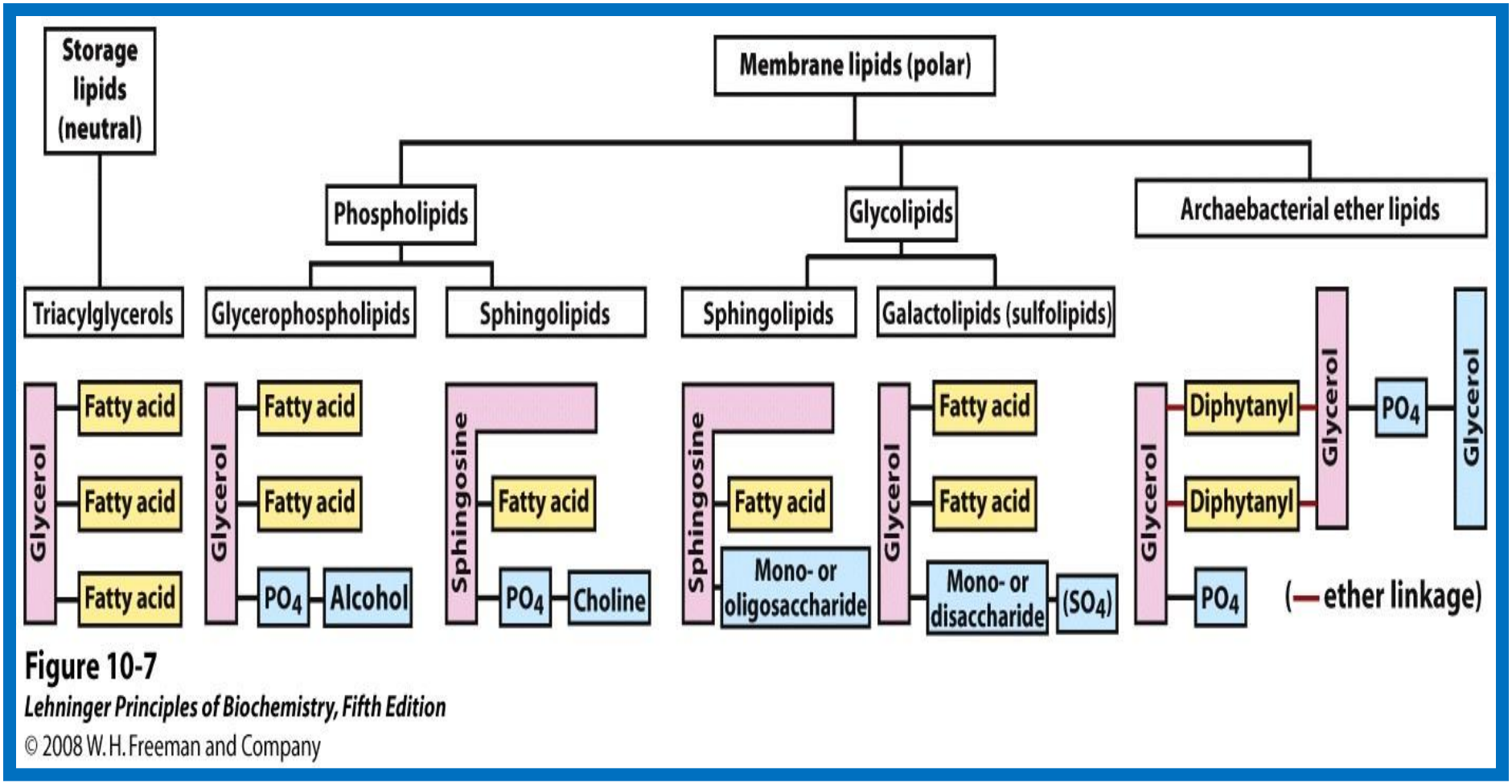

Figure 10-7

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FATTY ACIDS (FA)

- Acids occurring in natural triglycerides (FATs)
- Monocarboxylic acids, (a single carboxylic group at the end of a hydrocarbon chain which makes them acids)
- Most contain even number of C atoms, 4 to 24 carbon atoms, Majority of FA have 16 & 18 C atoms
- Naturally occurring saturated FA < 8 C - liquid at room temperature
- Waxes, FA have 34 C atoms, Some bacterial waxes - complex fatty acids that may contain as many as 90 C atoms

Nutritionally Essential Fatty Acids

Certain FA must be taken in food by man because these FA cannot be synthesized in the body (example: Polyunsaturated FA)

Saturated Fatty Acids (SFA)

Symbols of SFA have two numbers;

1. First no. represents no. of C atoms
2. Second no. denotes no. of double bonds which is zero in SFA

Common name	Systemic name	Formula	Symbol
Butyric acid	(butanoic acid):	$CH_3(CH_2)_2COOH$	C4:0
Palmitic acid	(hexadecanoic acid):	$CH_3(CH_2)_{14}COOH$	C16:0
Stearic acid	(octadecanoic acid):	$CH_3(CH_2)_{16}COOH$	C18:0
Arachidic acid	(icosanoic acid):	$CH_3(CH_2)_{18}COOH$	C20:0

Palmitic acid & Stearic acid are the most abundant SFA in humans

Unsaturated Fatty Acids (USFA)

More reactive than SFA

- 1 double bond = monounsaturated (or monoenoic) fatty acids (MUFA)
- > than 1 double bond= Polyunsaturated, i.e. polyenoic fatty acids (PUFA)

Common name	Formula	Symbol
Palmitoleic acid	$C_{15}H_{29}COOH$	$16{:}1\Delta^{9}$
Oleic acid	$C_{17}H_{33}COOH$	$18{:}1\Delta^{9}$
Linoleic acid	$C_{17}H_{33}COOH$	$18{:}2\Delta^{9,12}$
Linolenic acid	$C_{17}H_{29}COOH$	$18{:}3\Delta^{9,12,15}$
Arachidonic acid	$C_{19}H_{31}COOH$	$20{:}4\Delta^{5,8,11,14}$

Oleic acid & palmitoleic acid are the most abundant MUFA in humans

Unsaturated Fatty Acids (USFA)

Symbol of **USFA**

- First no. represents no. of *C* atoms
- Second no. represents no. of double bonds
- Δ is Greek letter, delta; it signifies double bond
- No. following delta is the no. of the first carbon atom of the double bonds, counting carbon atoms from carboxyl-containing terminal side

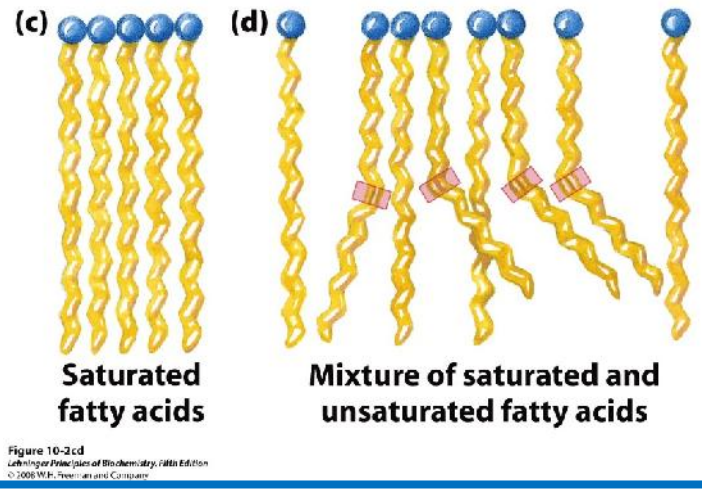
For example, the symbol of arachidonic acid means that it has 20 carbon atoms and 4 double bonds which are present at carbon atoms No. 5, 8, 11 and 14.

The packing of fatty acids into stable aggregates

The extent of packing depends on the degree of saturation.

(c) Fully saturated fatty acids in the extended form pack into nearly crystalline arrays, stabilized by many hydrophobic interactions.

(d) The presence of one or more fatty acids with cis double bonds interferes with this tight packing and results in less stable aggregates



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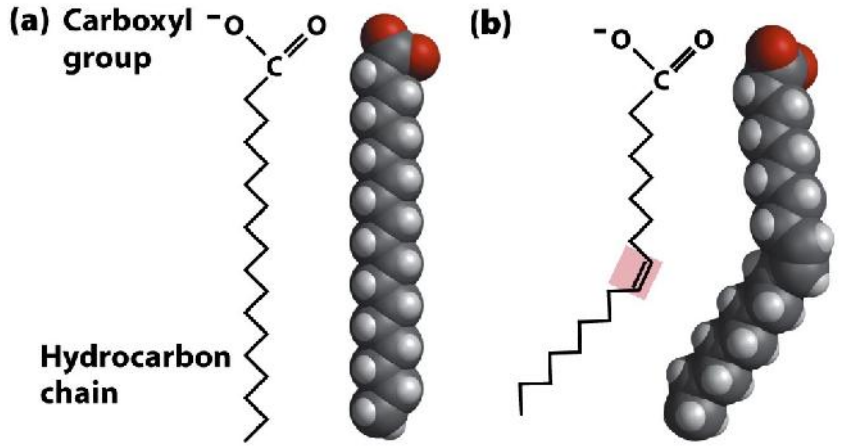
The packing of fatty acids into stable aggregates

The extent of packing depends on the degree of saturation.

(a) Two representations of the fully saturated acid stearic acid, 18:0.

(b) The cis double bond (shaded) in oleic acid, 18:1(Δ^9), restricts rotation and introduces a rigid bend in the hydrocarbon tail. All other bonds in the chain are free to rotate



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Properties of Fatty Acids (FA)

1. Melting point

- M.P. of SFA- increase with an increase in their chain length

Example: M.P. is 8°C for butyric acid (4C), 62°C for palmitic acid (16C) and 70°C for stearic acid (18C)

- M.P. of USFA decrease with increasing unsaturation
- Higher the saturation & higher chain length, higher will be M.P.
- Vegetable oils like cottonseed oil, corn oil, soyabean oil, etc. have an excess of unsaturated fatty acids & are liquid at room temperature

Fatty acid	No. of double bonds	Melting point
Oleic	1	14 °C
Linoleic	2	- 5 °C
Linolenic	3	- 10 °C
Arachidonic	4	- 50 °C

2. Solubility

- Terminal carboxyl group provides hydrophilic property to FA making them water soluble
- Non-polar hydrocarbon chain being hydrophobic tends to make FA hydrophobic, i.e. water insoluble
- **Thus** the water solubility of FA is determined in part by the ratio of the polar hydrophilic carboxyl group to the non-polar hydrophobic residues

Example:

FA	CH_3:COOH ratio
Butyric acid	3:1
Palimitic acid	15:1
Stearic acid	17:1
Acetic acid	1:1

Acetic acid is completely miscible with water because it contains only one hydrophobic, i.e. methyl group CH_3COOH

- As the chain length increases, the solubility of FA decreases due to the increased number of methylene groups
- With the same chain length, the presence of double bonds increases the solubility;
- **Thus** palmito-oleic acid is more soluble than palmitic acid

Special Reactions of Unsaturated Fatty Acids

Hydrogenation

This result in the production of SFA by adding H at double bond

Halogenation

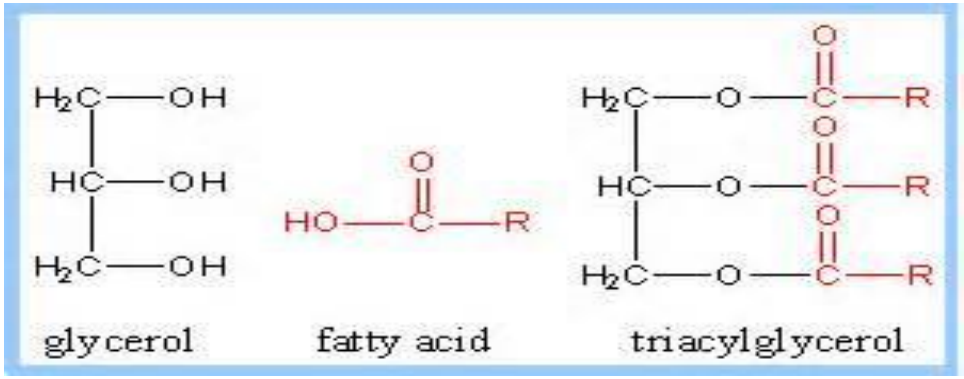
Halogens are added to double bonds & degree of halogenation is a good index of the degree of unsaturation of FA.

Oxidation

It is a complicated process & the products of oxidation are manifold

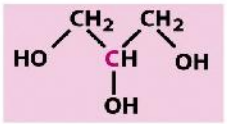
Neutral Fats or Triglycerides or Triacylglycerols

- Neutral fats (fats) are FA esters of glycerol, i.e. triglycerides (triacylglycerols; TAGs)
- .Most common & widespread class of lipids in nature being specially abundant in nuts, seeds, fat depots of animals
- Triglycerides (TAGs) represent the storage form of lipids

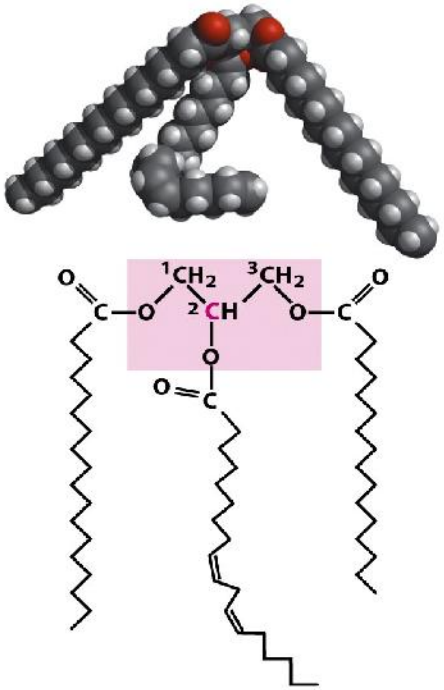


TAGs - Classification

- **Simple Fats**: If three fatty acids present are same, e.g. palmitic acid (tripalmitin)
- **Mixed Fats**: If three fatty acids present are different, e.g. palmitic acid, stearic acid, oleic acid



Glycerol



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

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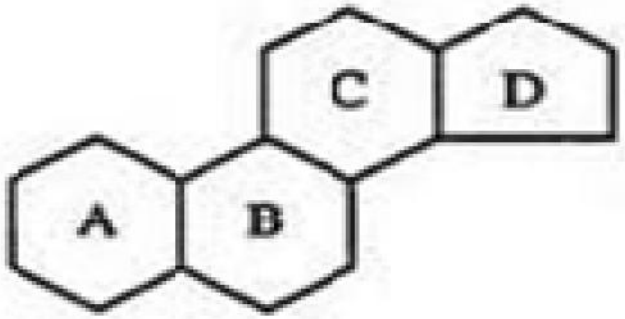
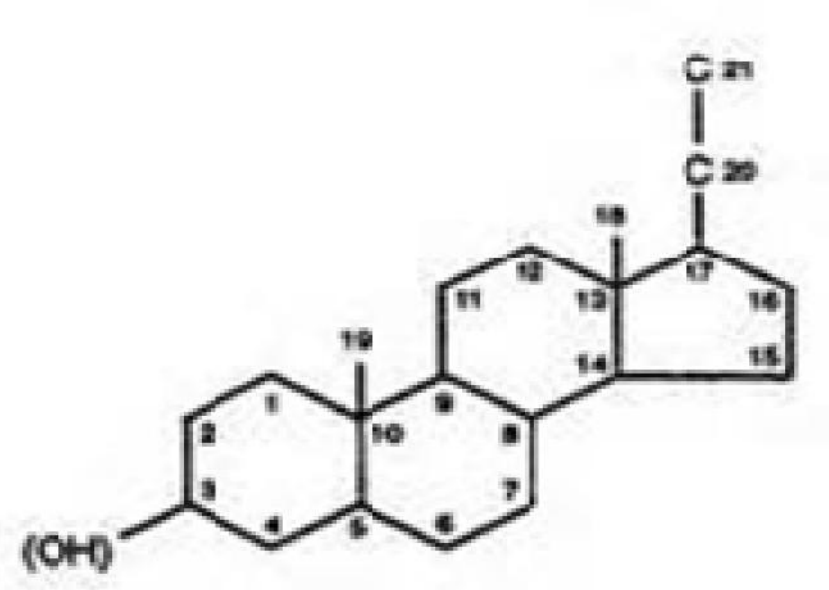
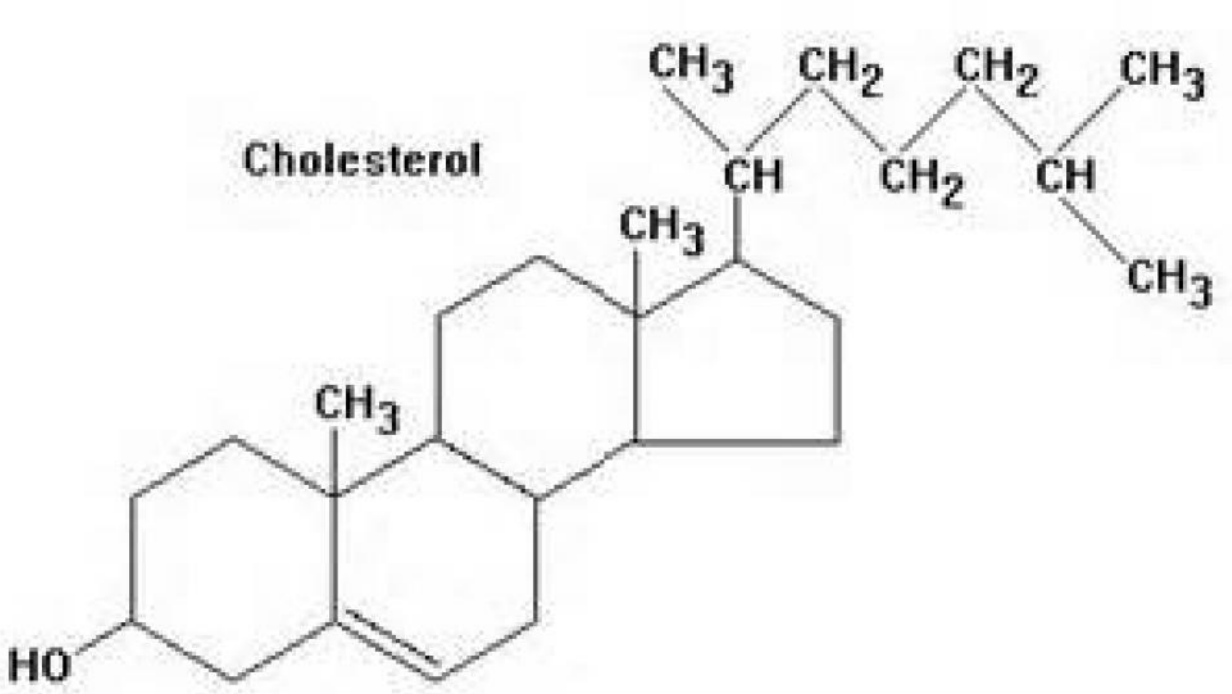
STEROIDS & STEROLS

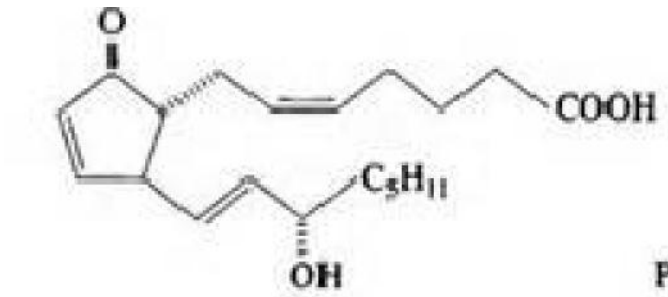




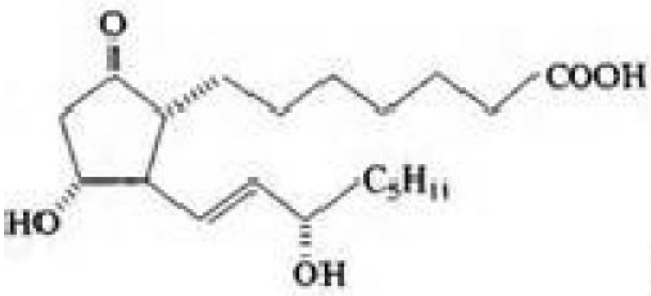
CHOLESTEROL



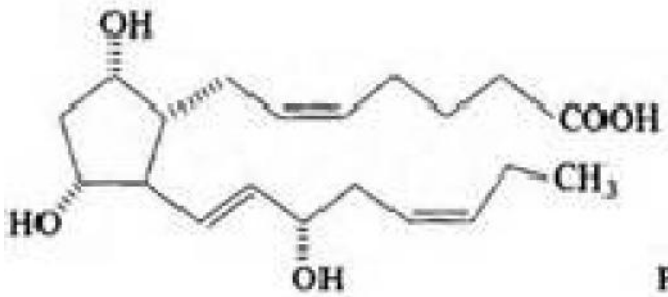
PROSTAGLANDINS



Prostaglandin A_2



Prostaglandin E_1



Prostaglandin $F_{3\alpha}$