



BIOCHEMISTRY

CHEM 123

PRELIMS – PROFESSOR: NIÑO ADONIS CABATINGAN

W1: CELL ULTRASTRUCTURE AND BIOMOLECULES

A HISTORY OF CELL THEORY

ROBERT HOOKE (1665)

- ❖ *Micrographia* was published, Birth of the term Cell after his observations of cork tissue

ANTON VAN LEEUWENHOEK (1670s)

- ❖ The discovery of single celled organism animalcules and the microscopic world

MATTHIAS SCHLEIDEN (1830s)

- ❖ Plants are made up of cells

THEODOR SCHWANN (1830s)

- ❖ Animals are made up of cells too

RUDOLF VIRCHOW (1855)

- ❖ *Omnis cellula e cellula*

A1 FUNDAMENTAL PRINCIPLES OF CELL THEORY

1. All organisms are made up of one or more cells
2. The cell is the basic unit of structure and function in living organism
3. Cells arise from pre-existing cells through division

Expanded concepts:

4. Cells carry genetic materials (DNA) during division
5. All cells share similar chemical composition and metabolic activities
6. Energy flows occurs within cells (metabolism)

A2 CELL

- ❖ basic unit of life
- ❖ smallest known world that perform life's functions

Major structures:

- Cell membrane
- Chromosome
- Cytoplasm

LIFE PROCESSES

- Maintaining boundaries
- Movement
- Responsiveness
- Homeostasis
- Metabolism
- Digestion & Excretion
- Reproduction
- Growth and Develop

Prokaryotes lack a nucleus and membrane-bound organelles, that are present in Eukaryotes

B METHODS USE BY BIOCHEMISTS TO STUDY CELL STRUCTURE

LIGHT MICROSCOPY

- ❖ Visualizes cell shape and basic structures

ELECTRON MICROSCOPY

- ❖ High-resolution imaging of cell ultrastructure

HISTOCHEMISTRY AND CYTOCHEMISTRY

- ❖ Stains and markers to study cell components

AUTORADIOGRAPHY

- ❖ Tracks molecules using radioactive labels

ULTRACENTRIFUGATION

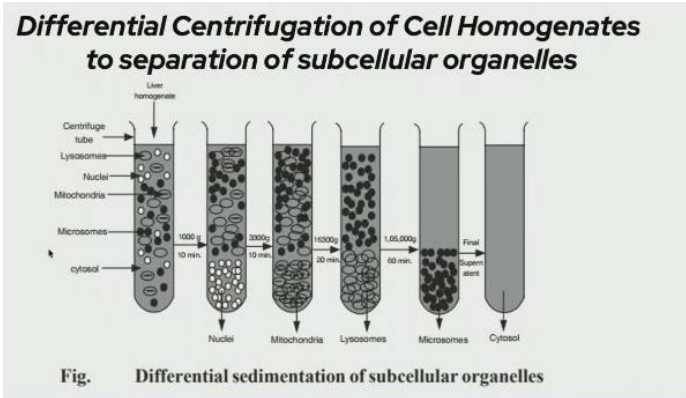
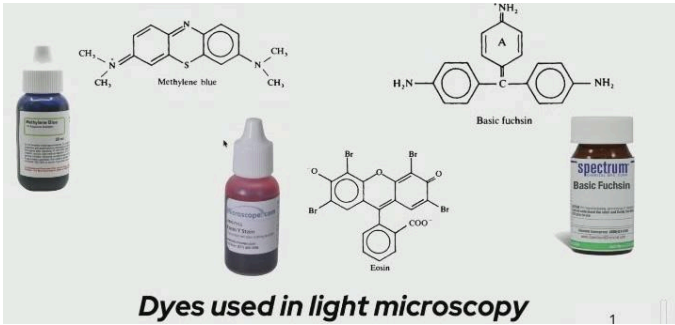
- ❖ Isolates organelles by size and density



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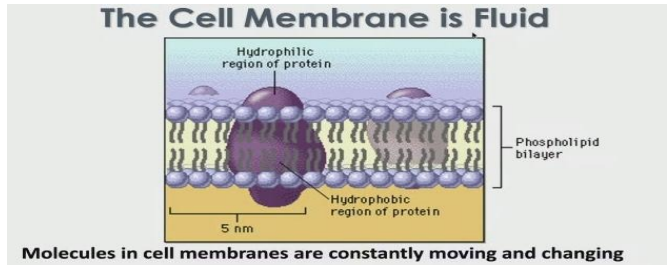


- ❖ Composed of double layer of phospholipids and proteins
- ❖ Surrounds outside of ALL cells
- ❖ Controls what enters or leaves the cell
- ❖ Living layer

→ cell membrane

C2 PHOSPHOLIPID BILAYER

- ❖ **Heads** - glycerol & phosphate, hydrophilic (attract water)
- ❖ **Tails** - fatty acids, hydrophobic (repel water)
- ❖ Make up a bilayer where tails point inward toward each other
- ❖ can move laterally to allow small molecules (O₂, CO₂, & H₂O to enter)



C CELL ULTRASTRUCTURE

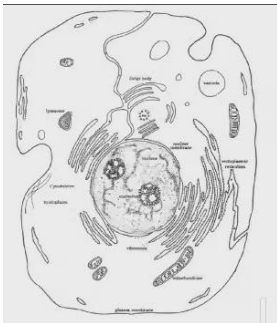


Diagram of mammalian cell

- ❖ The organelles are approximately the correct relative sizes

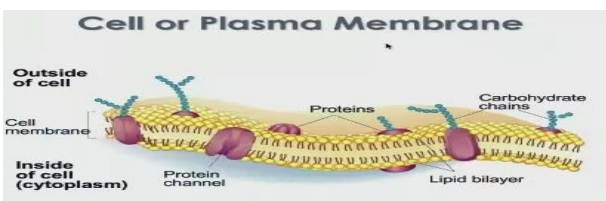
C3 CELL WALL

- ❖ Found outside of the cell membrane
- ❖ nonliving layer
- ❖ supports and protects cell
- ❖ found in plants, fungi, & bacteria

C4 CYTOPLASM OF A CELL

- ❖ Jelly-like substance enclosed by cell membrane
- ❖ Provides a medium for chemical reactions to take place

C1 CELL MEMBRANE



C5 NUCLEUS → largest organelles

- ❖ The control organelle
- ❖ Controls the normal activities of the cell
- ❖ Contains the DNA in chromosomes
- ❖ Bounded by a nuclear envelope (membrane) with pores
- ❖ Usually the largest organelle



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C5.1 INSIDE THE NUCLEUS

- ❖ The genetic material (DNA) is found
- ❖ DNA is spread out and appears as CHROMATIN in non-dividing cells
 - Interphase
- ❖ DNA is condensed & wrapped around proteins forming as CHROMOSOMES in dividing cells
 - Cell Division

C5.2 WHAT DOES DNA DO?

- ❖ DNA is the hereditary material of the cell
- ❖ Genes that make up the DNA molecule code for different proteins

C5.3 NUCLEOLUS → inside nucleus

- ❖ Inside nucleus
- ❖ Disappears when cell divides
- ❖ Makes ribosomes that make proteins

C6 MITOCHONDRION

- ❖ Plural = mitochondria
- ❖ "Powerhouse" of the cell
- ❖ Generate cellular energy (ATP)
- ❖ More active cells like muscle cells have MORE mitochondria
- ❖ Both plants & animal cells have mitochondria
- ❖ Site of CELLULAR RESPIRATION (burning glucose)

C6.1 ENZYME DISTRIBUTION IN MITOCHONDRIA

Location	Characteristics or cross-reference to distribution
Outer Membrane • Monoamine oxidase • Rote none-insensitive NADHS-cytochrome c reductase • Kynurenine hydroxylase • Fatty acid-CoA ligase	Neurotransmitter; catabolism Tryptophan catabolism
Spaces between Inner & Outer membrane • Adenylate kinase • Nucleoside diphosphokinase	AMP + ATP 2 ADP XDP + YTP XTP+ YTP Where X and Y are any of the several Ribonucleosides

Inner Membrane • Respiratory chain enzymes • ATP synthase • Succinate dehydrogenase • Beta-hydroxybutyrate dehydrogenase • Carnitine-fatty acid acetyltransferase	Oxidative phosphorylation Oxidative phosphorylation Lipid Metabolism Lipid Metabolism
Matrix • Malate and isocitrate dehydrogenase • Fumarase and aconitase • Citric synthase • 2-oxoacid dehydrogenase • Beta-oxidative enzyme for fatty acids • Carbomoyl phosphate synthetase I • Ornithine carbamoyl transferase	Citric Acid Cycle Citric Acid Cycle Citric Acid Cycle Citric Acid Cycle Lipid Metabolism Nitrogen Metabolism Nitrogen Metabolism

Additional:

- ❖ Mitochondria come from cytoplasm in the EGG cell during fertilization. Therefore, you inherit your mitochondria from your mother

C7 ENDOPLASMIC RETICULUM

- ❖ Network of hollow membrane tubules
- ❖ Connects to nuclear envelope & cell membrane
- ❖ Functions in Synthesis of cell products & Transport
- ❖ Synthesizes proteins and lipids

C7.1 ROUGH ENDOPLASMIC RETICULUM

- ❖ Has ribosomes on its surface
 - Made of proteins and rRNA.
 - “Proteins factories” for cell
- ❖ Makes membrane proteins and proteins for export out of cell

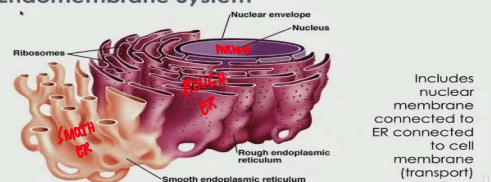
RIBOSOMES

- ❖ Can be attached to Rough ER
- ❖ Be free (unattached) in the cytoplasm

C7.2 SMOOTH ENDOPLASMIC RETICULUM

- ❖ Makes membrane lipids (steroids)
- ❖ Regulates calcium (muscle cells)
- ❖ Destroys toxic substances (liver)

Endomembrane System





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C11

VACUOLES

- ❖ Fluid filled sacks for storage
- ❖ Small or absent in animal cells
- ❖ Plant cells have a large Central Vacuole

C12

CHLOROPLAST

uses sunlight to produce food

- ❖ Found only in prokaryotes (organisms containing chlorophyll)
- ❖ Use energy from sunlight to make own food (glucose)
- ❖ Energy from the sun stored in the Chemical Bonds of Sugars
- ❖ Surrounded by DOUBLE membrane
- ❖ Outer membrane smooth
- ❖ THYLAKOIDS - Inner membrane modified into sacs
- ❖ GRANA - Interconnected Thylakoids in stacks
- ❖ STROMA - Gel like material surrounding thylakoids

C13

CELL DIVISION

- ❖ In order to reproduce, most cells will divide at some point in their lifespan

SOMATIC → mitosis

- ❖ Non-reproductive cells undergo mitosis

GAMETIC → mitosis — meiosis

- ❖ Reproductive cells undergo mitosis then utilize a second process called meiosis

D

BIOMOLECULE

D1

CARBOHYDRATES

saccharides

- ❖ Chemically defined as polyhydroxy aldehydes or ketones or compounds which produce them on hydrolysis
- ❖ sugars or substances that taste sweet
- ❖ Collectively called as saccharides (Greek: sakcharon = sugar)
- ❖ Provide energy (e.g. glucose, starch)

- ❖ Depending on the number of constituting sugar units obtained upon hydrolysis

- Monosaccharides = 1 unit
- Oligosaccharides = 2-10 units
- Polysaccharides = more than 10 units

- ❖ Have multiple functions
- ❖ Most abundant dietary source of energy
- ❖ structurally very important for many living organisms as they form a major structural component
 - e.g. cellulose is an important structural fibre for plants

D2

PROTEINS

- ❖ Make up around 50% of the cellular dry weight
- ❖ Polymers of amino acids arranged in the form of polypeptide chains
- ❖ Perform structural and enzymatic roles (e.g. myosin, enzymes)
- ❖ The structure of proteins is classified as primary, secondary, tertiary and quaternary
 - These structures are based on the level of complexity of the folding of a polypeptide chain
- ❖ Play both structural and dynamic roles
- ❖ **MYOSIN** Protein that allows movement by contraction of muscles
- ❖ Most enzymes are proteinaceous in nature

D3

NUCLEIC ACIDS

DNA
RNA

- ❖ Refer to the genetic material found in the cell that carries all the hereditary information from parents to progeny
- ❖ Two types of nucleic acids
 - Deoxyribonucleic acid (DNA)
 - Ribonucleic acid (RNA)
- ❖ Main function of nucleic acid is the transfer of genetic information and synthesis of proteins by processes known as translation and transcription
- ❖ **NUCLEOTIDE**
 - Monomeric unit of nucleic acids



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- Composed of a nitrogenous base, pentose sugar, and phosphate
- Linked by a 3' and 5' phosphodiester bond

❖ NUCLEOTIDE

- Double-helix or double-helical structure which is formed by hydrogen bonding between the bases of two antiparallel polynucleotide chains
- DNA structure looks similar to a twisted ladder



D4

LIPIDS

- ❖ Organic substances that are insoluble in water, soluble in organic solvents, are related to fatty acids and are utilized by the living cell
- ❖ Form cell membranes and store energy
- ❖ Include fats, waxes, sterols, fat-soluble vitamins, mono-, di-, or triglycerides, phospholipids, etc
- ❖ Unlike carbohydrates, proteins, and nucleic acids, lipids are not polymeric molecules
- ❖ Play great role in the cellular structure and are the chief source of energy

Biomolecule	Elements/Chemical Formula	Function	Monomer/Polymer	Examples	Other
Carbohydrates -end in -ose	Carbon, Hydrogen, Oxygen $C_6H_{12}O_6$ = glucose	Main source of energy	Monomer = sugar or monosaccharide Polymer = starch or polysaccharide	Glucose, fructose, galactose Sugar, starch (potatoes, pasta, etc.)	
Proteins *one of the most important Biomolecules *Nitrogen makes it different	Carbon, Hydrogen, Oxygen and Nitrogen	*control rate of chemical reactions through ENZYMES *Bones and muscles *transport things in and out of cells	Monomer = amino acids Polymer = protein/polypeptide chain	Meat, poultry, eggs, beans, soy, nuts, peanut butter, enzymes	
Nucleic Acids *phosphorus makes it different	Carbon, Hydrogen, Oxygen, Nitrogen and Phosphorus	*stores and transmits genetic information	Monomer = nucleotide Polymer = nucleic acid (DNA)	DNA = deoxyribonucleic acid RNA = ribonucleic acid	
Lipids *no true polymers *DO NOT DISSOLVE IN WATER	Primarily Carbon and Hydrogen	*stores energy and make up biological membranes and waterproof coverings	Made up of 3 Fatty Acids and 1 glycerol	Fats, oils, waxes, membranes	



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W2: HYDROCARBONS AND THEIR DERIVATIVES

A ORGANIC CHEMISTRY & CARBON ATOM

BIOCHEMISTRY

- ❖ Study of chemical substances found in living organisms and the chemical reactions of these substances with each other

ORGANIC CHEMISTRY

- ❖ Study of carbon compounds, all of which have covalent bonds
- ❖ Formerly, it was the study of compounds obtained from living organisms

BIOCHEMICAL SUBSTANCES

- ❖ Chemical substances found in a living organism

➤ BIOINORGANIC SUBSTANCES

- Without carbon
- ex. water, inorganic salts, O₂, CO₂

➤ BIOORGANIC SUBSTANCES

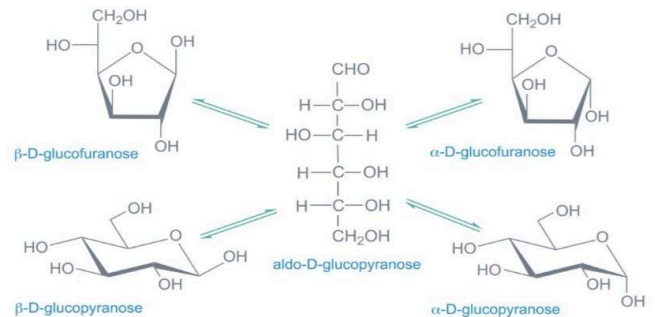
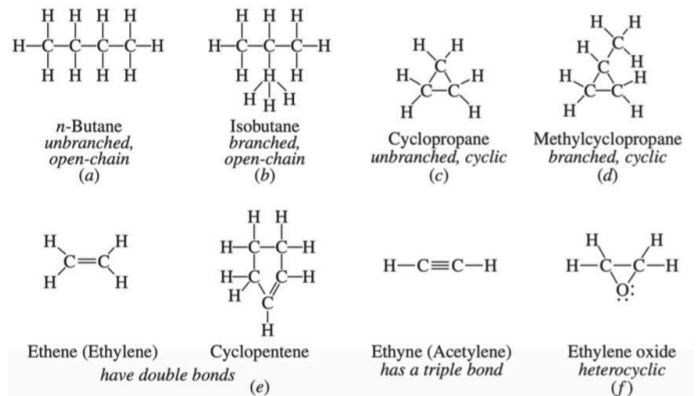
- With carbon
- ex. proteins, lipids, carbohydrates, nucleic acids
- Most abundant

A1 WHY ARE THERE SO MANY COMPOUNDS THAT CONTAIN CARBON?

CARBON ATOM IS UNIQUE

- ❖ Bond with itself, and create Allotropes
 - Graphite
 - Diamond
 - BC8
 - Fullerene
 - Nanotube
 - Graphene

- ❖ Maximum of 4 chemical bonds
 - Four bands may be single, double or triple bonds
 - An organic compound may contain all single bonds or combinations of double or triple bonds
- ❖ Branch or cyclic compounds
 - Carbon can bond not only in straight chains but it can also form branching and cyclic compounds



- ❖ Bonds between C's are covalent and strong, so that C's can form long chains and rings
- ❖ C's can bond to almost every element in the periodic table
- ❖ Numbers of isomers increases as the organic molecules become more complex



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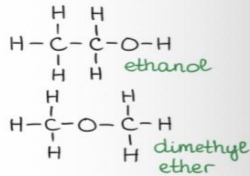
A2

ISOMERS

- Organic compounds with the same molecular formula, but with different bond orders

Molecular formula: C_2H_6O

Possible structures:

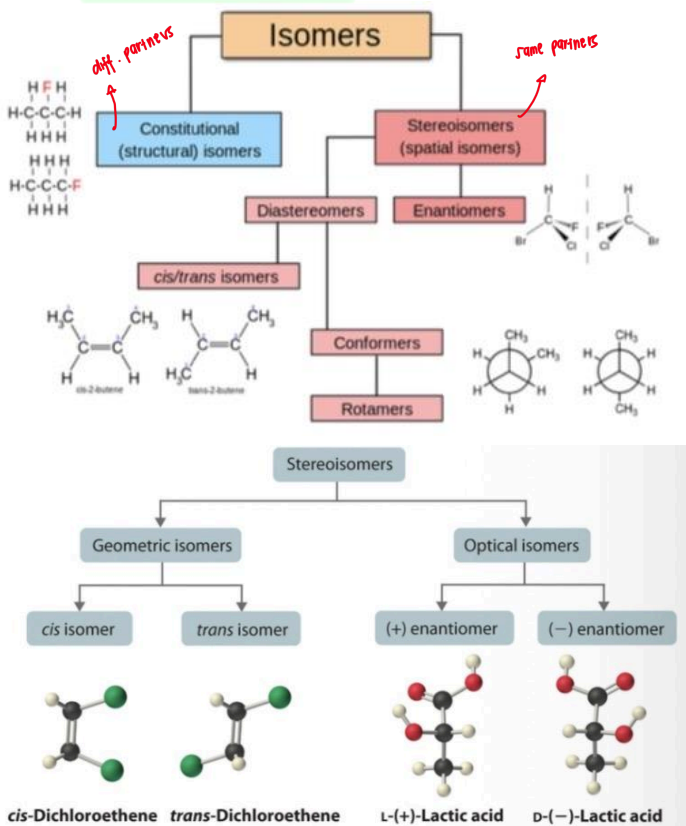


STRUCTURAL ISOMERS

- Atoms have different partners

STEREISOMERS

- Atoms have the same partners but are arranged in space



- Carbon is capable of forming simple to complex compounds
- It can form very long and highly branched carbon chains such as carbohydrates & proteins

B

LEWIS STRUCTURAL FORMULA

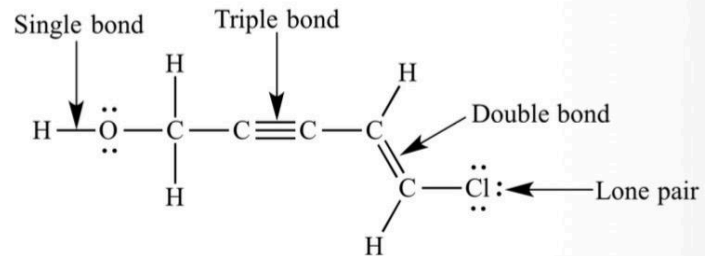


TABLE 1.1 Covalences of H and Second-Period Elements in Groups 2 through 7

Group	1	2	3	4	5	6	7
Lewis Symbol	H·	·Be·	·B·	·C·	·N·	·O·	·F·
Covalence	1	2	3	4	3	2	1
Compounds with H	H-H Hydrogen	H-Be-H Beryllium hydride	H-B-H Boron hydride*	H-C-H Methane	H-N-H Ammonia	H-O-H Water	H-F Hydrogen fluoride

* Exists as B_2H_6 .

TABLE 1.2 Normal Covalent Bonding

BONDING FOR C				BONDING FOR N			BONDING FOR O	
$-\text{C}-$	$-\text{C}=\text{}$	$=\text{C}=\text{}$	$-\text{C}\equiv$	$-\text{N}-$	$-\text{N}=\text{}$	$\text{N}\equiv$	$-\text{O}-$	$\text{O}=\text{}$
as in	as in	as in	as in	as in	as in	as in	as in	as in
$\text{H}-\text{C}-\text{H}$	$\text{H}_2\text{C}=\text{CH}_2$	$\text{O}=\text{C}=\text{O}$	$\text{H}-\text{C}\equiv\text{C}-\text{H}$	$\text{H}-\text{N}-\text{H}$	$\text{H}-\text{O}-\text{N}=\text{O}$	$\text{N}\equiv\text{C}-\text{H}$	$\text{H}-\text{O}-\text{H}$	$\text{O}=\text{C}-\text{H}$
Methane	Ethene (Ethylene)	Carbon dioxide	Ethyne (Acetylene)	Ammonia	Nitrous acid	Hydrogen cyanide	Water	Formaldehyde

C

HYDROCARBONS

- Simplest organic compounds composed of carbon and hydrogen
- serve as foundation of biochemical molecules and energy sources



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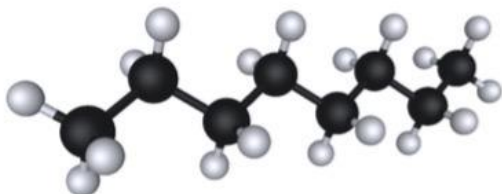
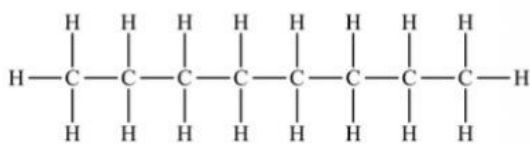
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C1 ALIPHATIC

- ❖ With straight or branched chains

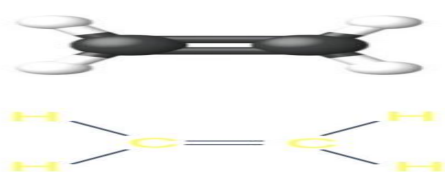
ALKANES → ane → single

- ❖ Single bond
- ❖ Saturated - contains single bonded carbon atoms (C-C)
- ❖ Release energy when burned (ex. Fuels)
- ❖ Non-polar, insoluble in water
- ❖ Most fundamental class of organic compounds known as alkane family, also called the paraffins or saturated hydrocarbons
- ❖ $C_nH_{(2n+2)}$
- ❖ Prefix = no. of carbons
- ❖ Suffix = ane
- ❖ Methane, propane, butane, and octane



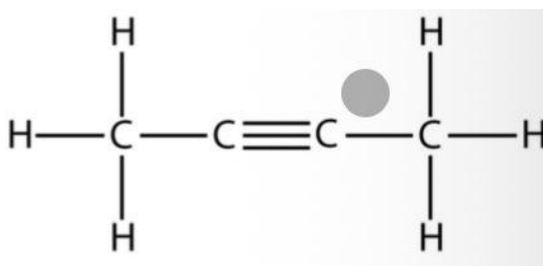
ALKENES → ene → double

- ❖ Double bond
- ❖ Unsaturated - containing at least 1 double or triple carbon-carbon bond
- ❖ Contain a C=C double bond in the continuous carbon-atom chain
- ❖ C_nH_{2n}
- ❖ also called olefins
- ❖ Prefix = no. of carbon
- ❖ Suffix = ene
- ❖ Number in front may give location of double bond



ALKYNES → yne → triple

- ❖ Triple bond
- ❖ Unsaturated
- ❖ C_nH_{2n-2}
- ❖ Prefix = depends on number of carbon atoms in longest continuous chain
- ❖ Suffix = yne
- ❖ Number in front gives location of triple bond



C1.2 AROMATIC

- ❖ Most common aromatic hydrocarbons contain a benzene ring
- ❖ Term 'aromatic' came up because earlier compounds found with a ring structure had pleasant fragrances
- ❖ Some aromatics, like aspirins, are odorless
- ❖ **BENZENE** - most important examples of aromatic hydrocarbons
- ❖ **MICHAEL FARADAY** - first isolated benzene
- ❖ **FRIEDRICH AUGUST KEKULE** - proposed the benzene structure in 1865

C2 CHEMICAL OR MOLECULAR FORMULAS

- ❖ Tell the kind & number of atoms in a molecule

Name	Molecular Formula	Structural Formula
cyclopropane	C_3H_6	or
cyclobutane	C_4H_8	or
cyclopentane	C_5H_{10}	or
cyclohexane	C_6H_{12}	or



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C3 HOMOLOGOUS SERIES

- ❖ Group of related compounds in which each member differs from the one before it by the same additional unit
- ❖ Properties vary in a predictable way

ALKANE	CARBON NUMBER	FORMULA	STRUCTURE
METHANE	1	CH ₄	
ETHANE	2	C ₂ H ₆	
PROPANE	3	C ₃ H ₈	
BUTANE	4	C ₄ H ₁₀	
PENTANE	5	C ₅ H ₁₂	

C4 CYCLOALKANES

- ❖ Has a cyclic or ring structure; the smallest ring contains three carbon atoms
- ❖ C_nH_{2n}
- ❖ IUPAC names are consistent with those of the alkane
- ❖ Used in fuels and the synthesis of other important organic compounds

D HYDROCARBON DERIVATIVES

- ❖ Organic compounds that are based on hydrocarbons with the addition of specific functional groups

FUNCTIONAL GROUPS

- ❖ Specific groups of atoms within molecules that have their own characteristic properties, regardless of the other atoms present in a molecule

D1 ALCOHOLS

- ❖ Organic compound containing the hydroxyl, -OH
- ❖ Functional group formula : R-OH

PRIMARY ALCOHOL (1°)

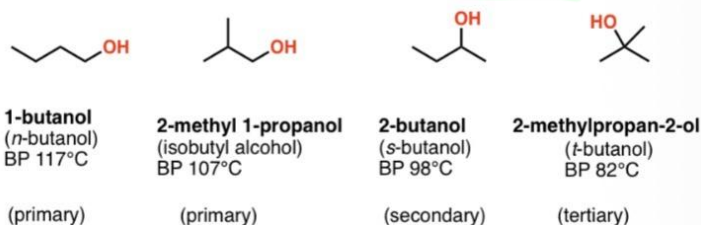
- ❖ OH group is bonded to a carbon that is only bonded to one other carbon

SECONDARY ALCOHOL (2°)

- ❖ OH group is bonded to a carbon that is bonded to two other carbon atoms

TERTIARY ALCOHOL (3°)

- ❖ OH group is bonded to a carbon that is bonded to three other carbon atoms



NOMENCLATURE

1. Locate the longest carbon chain (must contain the carbon attached to the -OH group)
2. Replace the -e at the end of the alkane name with -ol
3. Number the chain so that the -OH group has the lowest number
4. Add a position number before the name of the root to indicate the position of the -OH group
5. Name and number any branches (as you would for alkanes)
6. Put it all together: branches + root

PHYSICAL PROPERTIES OF ALCOHOL METHANOL, ETHANOL, AND GLYCEROL

- ❖ **Color:** colorless
- ❖ **Odor:** have faint odor (alcoholic odor) except glycerol which is odorless
- ❖ **Solubility:** completely miscible with water
- ❖ **Flammability:** flammable with blue, non smoky flame
- ❖ **State:** liquid except glycerol which is viscous liquid
- ❖ **Acid-base properties:** neutral



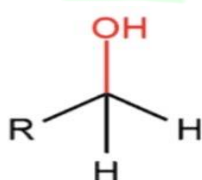
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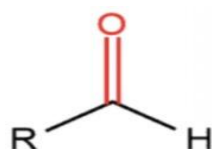
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ALDEHYDE

- ❖ “Alcohol Dehydrogenate”
 - removal of hydrogen from an alcohol
- ❖ contain carbonyl functional group C=O bonded to a hydrogen (H) atom
- ❖ $R-CH=O$



Primary alcohol

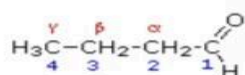


Aldehyde

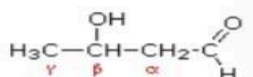
NAMING ALDEHYDE

7. Carbonyl group will always be on a terminal carbon, thus there is no need to give a position number
8. Simply name the carbon chain; drop the -e from the end and add -al; give the C=O position 1
9. Add branches (if any) as you have for all others

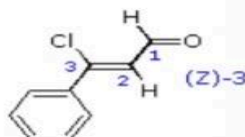
Aldehydes



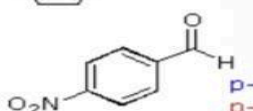
butanal
butyraldehyde



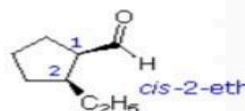
3-hydroxybutanal
 β -hydroxybutyraldehyde
or aldol



(Z)-3-chloro-3-phenyl-2-propenal



p-nitrobenzenecarbaldehyde
p-nitrobenzaldehyde



cis-2-ethylcyclopentanecarbaldehyde



pentanedial
glutaraldehyde

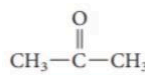
PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

10. Carbonyl group is polar, aldehydes and ketones have higher boiling points than hydrocarbons
11. They have no H attached to the O, so do not have hydrogen bonding, and have lower boiling points than alcohols
12. Like ethers, aldehydes and ketones can hydrogen bond with water, so those with less than 5 carbons are generally soluble in water
13. Aldehydes and ketones can be flammable and/or toxic, though generally not highly so
14. They usually have strong odors, and are often used as flavorings or scents

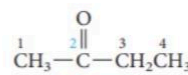
D2

KETONE

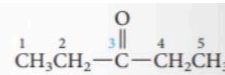
- ❖ Contain the carbonyl group C=O
- ❖ Has an alkyl group on either side of the C=O
- ❖ $R-CO-R$



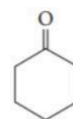
propanone
(acetone)



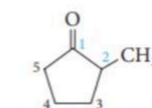
2-butanone
(ethyl methyl ketone)



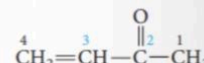
3-pentanone
(diethyl ketone)



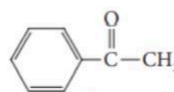
cyclohexanone



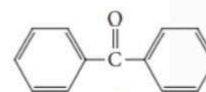
2-methylcyclopentanone



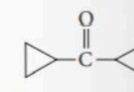
3-buten-2-one
(methyl vinyl ketone)



acetophenone
(methyl phenyl ketone)



benzophenone
(diphenyl ketone)



dicyclopropyl ketone



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TYPES of KETONE BODIES

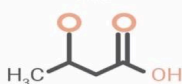
There are three types of ketones produced when the body goes into ketosis:

ACETOACETATE



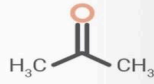
- Created from the breakdown of **fatty acids**.
- Either converted into **BHB** or turned into **acetone**.

BETA-HYDROXYBUTYRIC ACID



- Formed from acetoacetate.
- Not technically a ketone because of its structure, but we consider it as one within the keto diet.

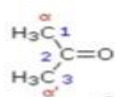
ACETONE



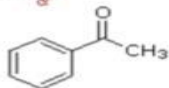
- Created as a **side product** of acetoacetate.
- Breaks down quickly.
- Is **removed** from the body through the waste or the breath

NAMING KETONES

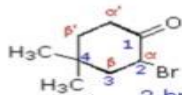
- Find the longest carbon chain containing C=O
- Number the chain so that C=O has lowest number
- Drop the final -e from the alkane name and add -one
- Name and add branches as you would for alkanes



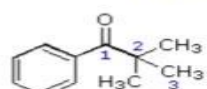
propanone
acetone



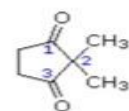
phenylethanone
acetophenone
methyl phenyl ketone



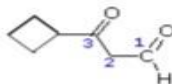
2-bromo-4,4-dimethylcyclohexanone



2,2-dimethyl-1-phenylpropanone
t-butyl phenyl ketone



2,2-dimethyl-1,3-cyclopentanedione



3-cyclobutyl-3-oxopropanal

PHYSICAL PROPERTIES OF KETONES

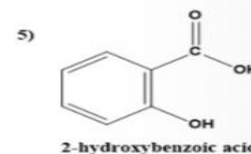
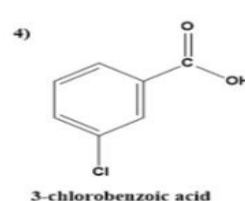
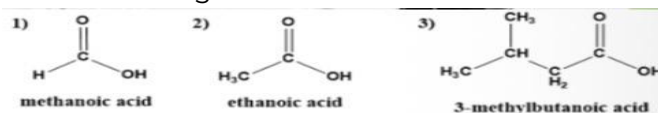
- Ketones are liquids, with boiling points rising as the molecules get bigger
- Van der Waals dispersion forces in ketones get stronger as the molecules get longer and have more electrons

- Small ketones are freely soluble in water but solubility falls with chain length
- Ketones also do not have hydrogen bonding but can make hydrogen bonds with water

D3

CARBOXYLIC ACID

- Contain **carboxyl group**
- R-COOH
- Polar molecules
- Soluble in water
- Have high MP and BP



NAMING CARBOXYLIC ACIDS

- Name the parent alkane: drop the -e at the end of the alkane name and add -oic acid
- Carboxyl group is always given position one (no need to state this)
- Name any branches as we do for alkanes

PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

- Very polar due to both the carbonyl group and the hydroxyl group
- Can H-bond with each other, and in fact exist primarily of dimers (two molecules held together by H-bonding)
- Have high boiling points (higher than corresponding alcohols)
- Those with less than 5 carbons are soluble in water



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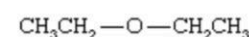
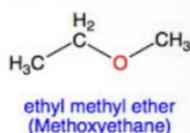
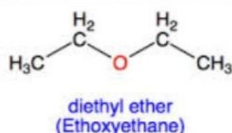
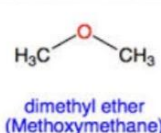
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- those with more than 5 C's can be soluble when ionized

D4

ETHERS

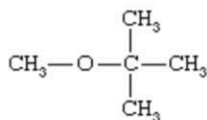
- ❖ Organic compound that has two alkyl groups joined by an oxygen atom
- ❖ R-O-R
- ❖ R and R indicate two alkyl groups
 - can be the same or different
- ❖ Like alcohols, ethers are extremely flammable and should be used with caution



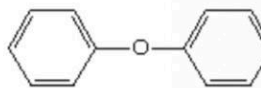
common name: diethyl ether
(ethyl ether or "ether")
IUPAC name: ethoxyethane



methyl ethyl ether
or ethyl methyl ether
methoxyethane



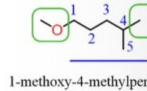
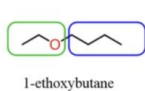
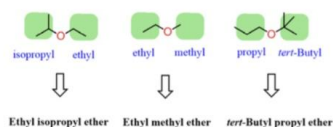
common name: methyl-*t*-butyl ether
(MTBE)
IUPAC name: 2-methoxy-2-methylpropane



diphenyl ether
or phenyl ether
phenoxybenzene

NOMENCLATURE

1. List the alkyl groups that are attached to the oxygen atom, in order of increasing length
2. Place the suffix -ether at the end of the name (no numbers are needed to show the location of the oxygen atom)



Physical properties of ethers

name	structure	mp (°C)	bp (°C)	density (grams per millilitre)
dimethyl ether	$\text{CH}_3-\text{O}-\text{CH}_3$	-140	-25	0.66
ethyl methyl ether	$\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_3$		8	0.72
diethyl ether	$\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$	-116	35	0.71
dipropyl ether	$\text{CH}_3\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3$	-122	91	0.74
diisopropyl ether	$(\text{CH}_3)_2\text{CH}-\text{O}-\text{CH}(\text{CH}_3)_2$	-86	68	0.74
divinyl ether	$\text{CH}_2=\text{CH}-\text{O}-\text{CH}=\text{CH}_2$	-101	28	0.77
1,2-dimethoxyethane (DME)	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$	-58	83	0.86
methyl phenyl ether (anisole)	$\text{CH}_3-\text{O}-\text{C}_6\text{H}_5$	-37	154	0.99
cyclopropyl methyl ether		-119	45	0.81
diphenyl ether		27	259	1.07
furan		-86	32	0.94
tetrahydrofuran (THF)		-108	65	0.89
1,4-dioxane		11	101	1.03

PHYSICAL PROPERTIES OF ETHERS

POLARITY OF FUNCTIONAL GROUP

- ❖ The bent shape around the oxygen atom in an ether means the two C-O dipoles do not counteract each other
- ❖ Because a C-O bond is less polar than an O-H bond, an ether is less polar than an alcohol

HYDROGEN BONDING

- ❖ Because there is no O-H bond in an ether, hydrogen bonding does not occur between ether molecules
- ❖ Ethers can accept hydrogen bonding from water molecules

SOLUBILITY IN WATER

- ❖ Ethers are usually soluble in water
- ❖ The solubility of an ether decreases as the size of the alkyl groups increases

MELTING AND BOILING POINT

- ❖ The boiling points of ethers are much lower than the boiling points of alcohols with the same number of carbon atoms



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W3: CARBOHYDRATES – THE BUILDING BLOCK

A OCCURRENCE, FUNCTION, & CLASSIFICATION OF CARBOHYDRATES

CARBOHYDRATES

- ❖ Most abundant class of bioorganic molecules on the planet
- ❖ Polyhydroxy ketones and polyhydroxy aldehyde, which are created through photosynthesis
- ❖ They have variety of functions in the body and taken through diet

PHOTOSYNTHESIS

- ❖ Allows green plants to produce carbohydrates by converting carbon dioxide from the air, water from the soil as reactants, and sunlight absorbed by chlorophyll as energy source

PLANTS USE CARBOHYDRATES

- ❖ As structural elements in a form of cellulose as energy reserves like starch, and immediate energy source in a form of simple carbohydrates

DIETARY INTAKE

- ❖ Of fruits and veggies from plants is the major carbohydrate source for humans and animals

A1 FUNCTIONS OF CARBOHYDRATES IN HUMANS

- ❖ Its oxidation provides energy
- ❖ Act as storage to provide short-term energy reserve (e.g. Glycogen)
- ❖ It can supply carbon atoms for the synthesis of other biomolecules
- ❖ It forms the framework of DNA and RNA

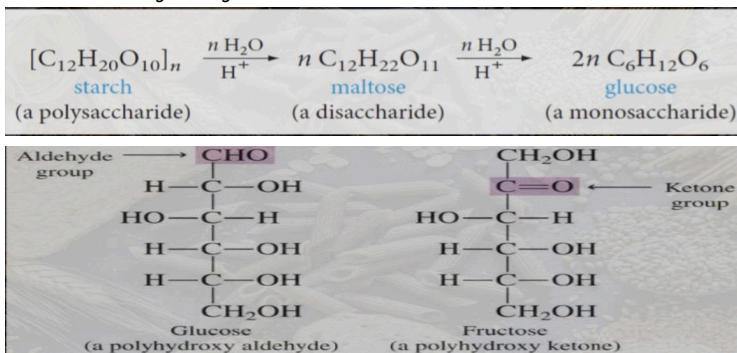
PAGE 14

BSN 1-Y2-20

- ❖ It can be linked to lipids and proteins for cell recognition process

A2 CARBOHYDRATES – THAT IS, “HYDRATES OF CARBON”

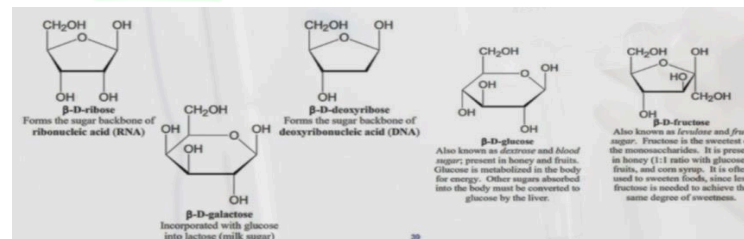
- ❖ The simplest carbohydrates have general formulas of $C_nH_{2n}O_n$ or $C_n(H_2O)_n$
- ❖ Carbohydrates are polyhydroxy aldehydes, polyhydroxy ketones, or substances that give such compounds on hydrolysis



A3 CLASSIFICATION OF CARBOHYDRATES

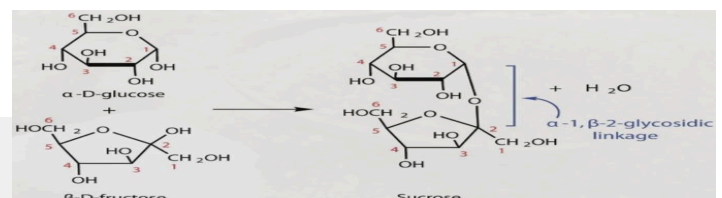
MONOSACCHARIDE

- ❖ Building block of all carbohydrates
- ❖ Contains single unit of polyhydroxy aldehydes, polyhydroxy ketones that cannot be broken down by hydrolysis reaction



DISACCHARIDE

- ❖ Contains two units of monosaccharides covalently bonded with one another through glycosidic bond





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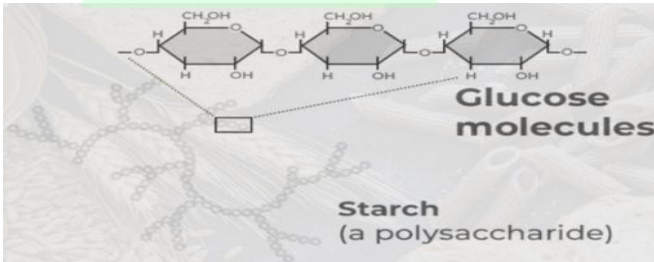
OLIGOSACCHARIDE

- Contains 3 to 10 monosaccharide units covalently bonded with one another, and usually associated with proteins and lipids



POLYSACCHARIDE

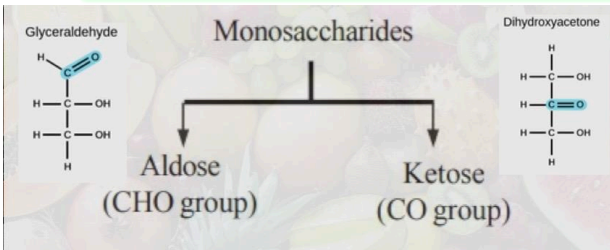
- A polymeric carbohydrate that contains many units of monosaccharides covalently bonded with one another through glycosidic bond



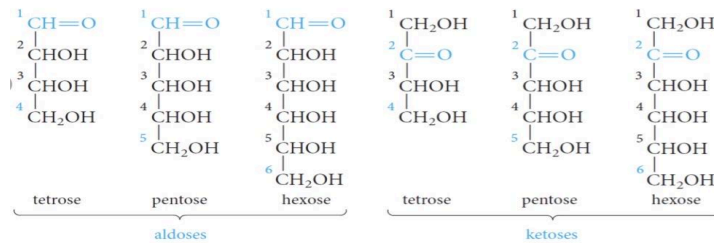
B CLASSIFICATION OF BIOCHEMICALLY IMPORTANT MONOSACCHARIDES

B1 CLASSIFICATION OF MONOSACCHARIDES

- Based on type of functional group (carbonyl)
- Based on the number of carbon atoms

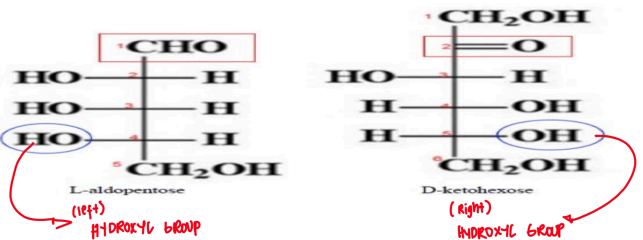


Number of Carbon Atoms (n)	Name	Examples
3	Triose	Glyceraldehyde Dihydroxyacetone
4	Tetrose	Erythrose Threose
5	Pentose	Arabinose
6	Hexose	Glucose
7	Heptose	Sedoheptulose Mannoheptulose



B2 HOW TO NAME ACYCLIC MONOSACCHARIDE

- Acyclic monosaccharides have three different characteristics:
 - The number of carbon atoms it contains
 - Its D or L configuration
 - The placement of its carbonyl group (aldehyde or ketone)



B3 GLYCERALDEHYDE AND DIHYDROXYACETONE

- Each is related to glycerol in that each has a carbonyl group in place of one of the hydroxyl groups

GLYCERALDEHYDE

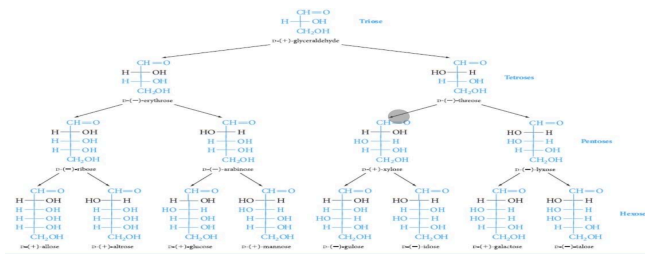
- Simplest aldose
- Other aldoses can be derived from glyceraldehyde by adding carbon atoms, each with a hydroxyl group
- In aldoses, the chain is numbered from the aldehyde carbon



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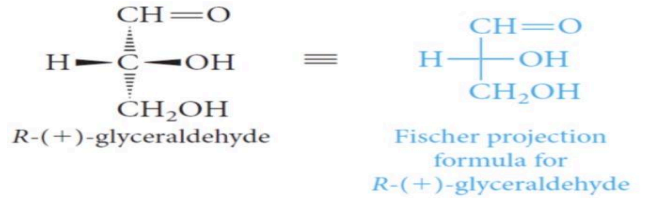
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EMIL FISCHER

- ❖ Invented his system of projection formulas for his studies on carbohydrates stereochemistry that

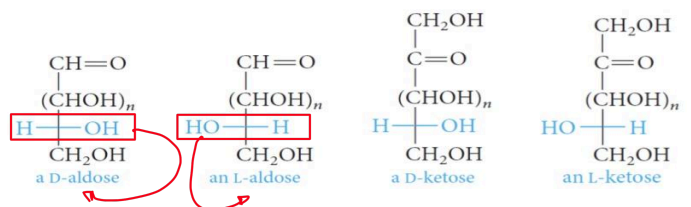


- ❖ Fischer also introduced a stereochemical nomenclature that preceded the R,S system and that is still in common use for monosaccharides and amino acids

- D - represent the configuration of (1)-glyceraldehyde, with the hydroxyl group on right; its enantiomer
- L - (2)-glyceraldehyde with the hydroxyl group on the left
- CHO - most oxidized carbon was placed on the top

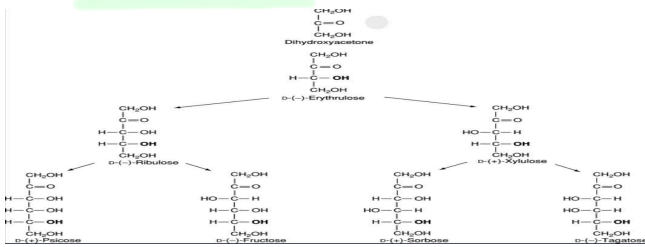


- ❖ Fischer extended his system to other monosaccharides in the following way
 - **D-monosaccharide**
 - if the stereogenic carbon farthest from the aldehyde
 - ketone group had same configuration as D-glyceraldehyde (hydroxyl on the right)
 - **L-monosaccharide**
 - if the configuration at the remote carbon had the same configuration as L-glyceraldehyde (hydroxyl on the left)



DIHYDROXYACETONE

- ❖ Simplest ketose
- ❖ Other ketoses can be derived from dihydroxyacetone by adding carbon atoms, each with a hydroxyl group
- ❖ In most ketoses, the carbonyl group is located at C-2



C

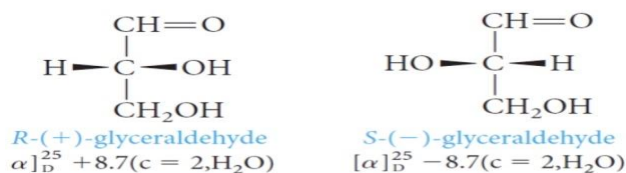
CYCLIC FORMS OF MONOSACCHARIDES

CYCLIC MONOSACCHARIDES

- ❖ Form through an intramolecular reaction between the carbonyl group and alcohol group of the open-chain monosaccharide

C1 FISCHER PROJECTION FORMULA & D, L-MONOSACCHARIDE

- ❖ Glyceraldehyde has one stereogenic carbon atom (C-2) and hence can exist in two enantiomeric forms



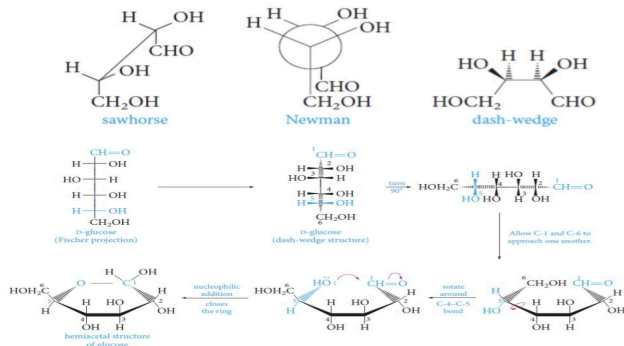


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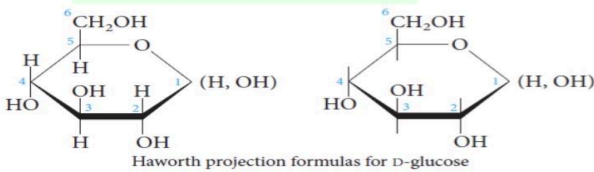
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We can also write the structure as



C2 HAWORTH PROJECTION FORMULAS FOR D-GLUCOSE

- ❖ In a Haworth projection, the ring is represented as if it were planar and viewed edge on, with the oxygen at the upper right
- ❖ The carbons are arranged clockwise numerically, with C-1 at the right
- ❖ Substituents attached to the ring lie above or below the plane



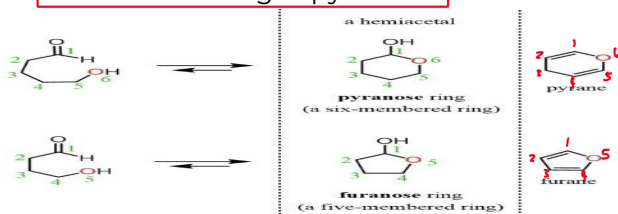
W.N. HAWORTH

- ❖ Introduced a useful way of representing the cyclic forms of monosaccharides

C3 HOW TO NAME CYCLIC MONOSACCHARIDE

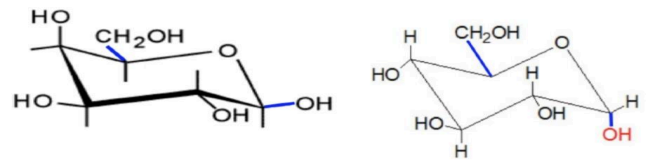
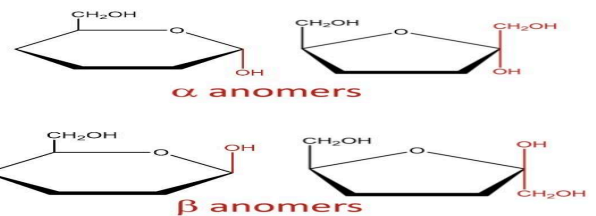
RULE 1

- ❖ 5 carbon rings - furanose
- ❖ 6 carbon rings - pyranose



RULE 2

- ❖ When acyclic molecules are turned into cyclic molecules, it creates a chiral center at the anomeric carbon and this gives rise to a and b anomers
 - a) anomeric OH and CH₂OH groups are trans → receiving side
 - b) anomeric OH and CH₂OH are cis → shipping side
- ❖ These anomers are placed in the beginning in naming cyclic carbohydrates



This is β because OH and CH₂OH are cis.
This sugar is β-galactopyranose because there are 6 carbons, which gives it the suffix pyranose and since the molecule is galactose, it has the prefix galacto.

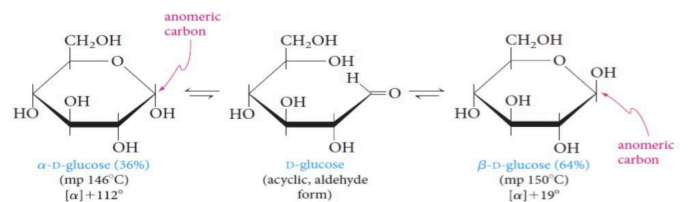
This is α because OH and CH₂OH are trans.
This sugar is α-glucopyranose because there are 6 carbons, which gives it the suffix pyranose and since the molecule is glucose, it has the prefix gluco.



trans-D-glucopyranose

cis-D-glucopyranose

Anomeric carbons: Mutarotation



- ❖ In the cyclic, aldehyde form of glucose, C-1 is achiral, but in the cyclic structures, this carbon becomes chiral
- ❖ Consequently, two hemiacetal structures are possible, depending on the configuration at the new chiral center



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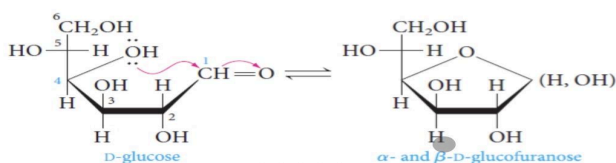
C4 PYRANOSE AND FURANOSE STRUCTURES

PYRANOSE (6)

- ❖ Six-membered cyclic form of most monosaccharides is the preferred structure
- ❖ formed by reaction of the hydroxyl group at C-5, with the carbonyl group
- ❖ After the six-membered oxygen heterocycle pyran

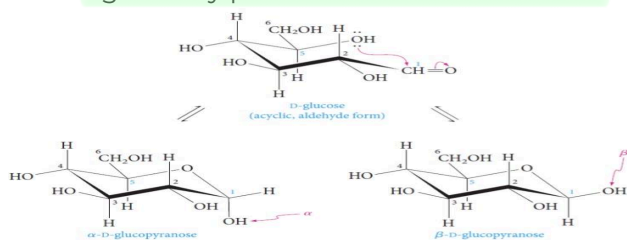
FURANOSE (5)

- ❖ Hydroxyl group at C-4 reacts
- ❖ Five-membered ring
- ❖ After the parent five-membered oxygen heterocycle furan



FORMATION OF PYRANOSSES

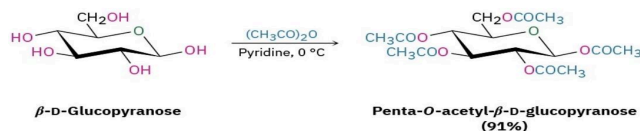
- ❖ Haworth projections depict pyranose rings as planar
- ❖ However, as with cyclohexane, the rings generally prefer a chair conformation



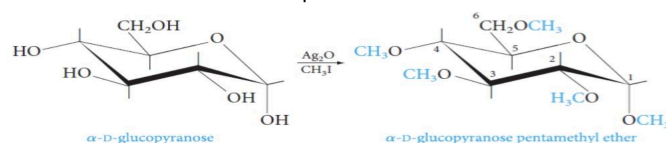
D REACTIONS OF MONOSACCHARIDES

D1 ESTERS AND ETHERS OF MONOSACCHARIDES

- ❖ Monosaccharides contains hydroxyl groups
 - It is not surprising that they undergo reactions typical of alcohols
- ❖ They can be converted to esters by reactions with acid halides or anhydrides

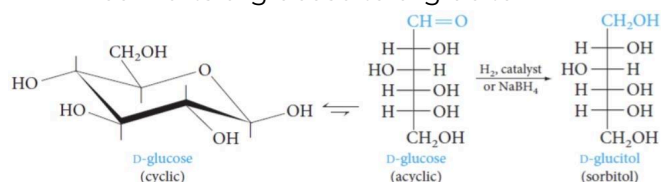


- ❖ The hydroxyl group can also be converted to ethers by treatment with an alkyl halide and a base
 - Because sugars are sensitive to strong bases, the mild base silver oxide is preferred



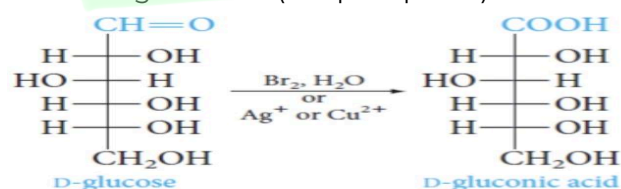
D2 REDUCTION OF MONOSACCHARIDES

- ❖ The carbonyl group of aldoses and ketose can be reduced by various reagents
- ❖ The products are polyols, called alditols
- ❖ ex. catalytic hydrogenation or reduction with sodium borohydride (NaBH_4) converts d-glucose to d-glucitol



D3 OXIDATION OF MONOSACCHARIDES

- ❖ Benedict's reagent reacts with an aldose to give Cu_2O (red precipitate)





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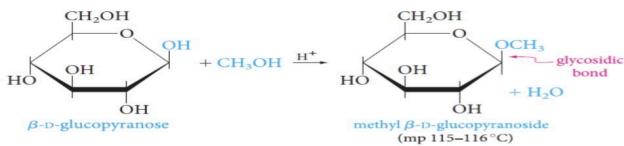
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D4

GLYCOSIDES FROM MONOSACCHARIDES

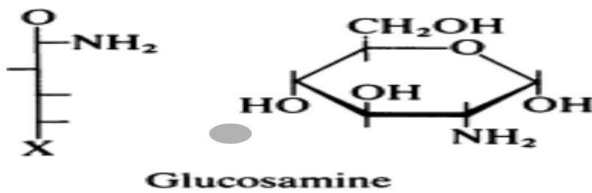
- ❖ Because monosaccharides exist as cyclic hemiacetals, they can react with one equivalent of an alcohol to form acetals
- ❖ ex. reaction of β -D-glucose with methanol



D5

AMINO SUGAR FORMATION

- ❖ Glucosamine is a natural compound found in cartilage
 - Cartilage - tough tissue that cushions joints



IMPORTANT MONOSACCHARIDES

- ❖ Includes glucose, galactose, fructose, and ribose
- ❖ Glucose and galactose
 - Aldohexoses
- ❖ Fructose
 - ketohexose
- ❖ Ribose
 - Aldopentose

CLASSIFICATION OF MONOSACCHARIDES

- ❖ Aldoses & Ketoses
- ❖ Triose, Tetrose, Pentose, and Hexose



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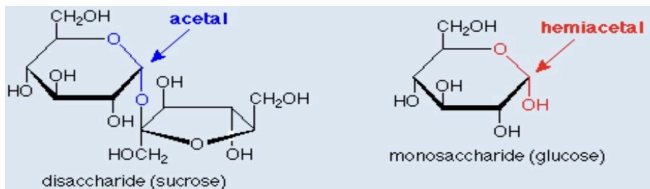
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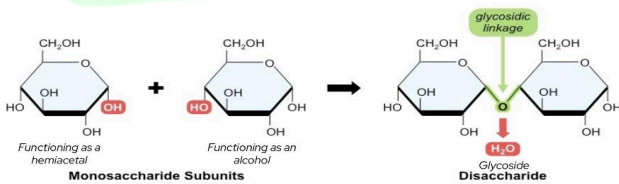
W4: COMPLEX CARBOHYDRATES FROM DISACCHARIDES TO POLYSACCHARIDES

A DISACCHARIDES

- ❖ Produced by the same reaction how cyclic monosaccharide (hemiacetal form) can react with an alcohol to form glycoside (acetal)
- ❖ Glycosides formed from the linkage of two monosaccharides



- ❖ In disaccharide formation, one of the monosaccharide reactants functions as a hemiacetal, and the other functions as an alcohol



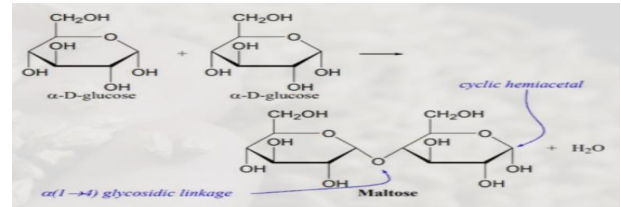
GLYCOSIDIC LINKAGE

- ❖ Bond between two monosaccharides resulting from the reaction between the hemiacetal carbon atom -OH group of one monosaccharide and an -OH group of the other monosaccharide

A1 BIOCHEMICALLY IMPORTANT DISACCHARIDES

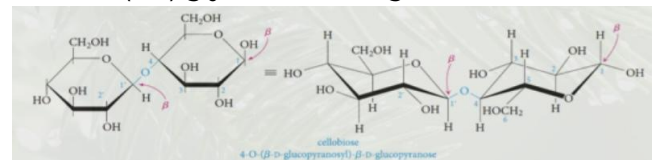
MALTOSE (MALT SUGAR)

- ❖ Often called as malt sugar
- ❖ produced whenever the polysaccharide starch breakdown
- ❖ happens in plants when seeds germinate and in human beings during starch digestion
- ❖ α(1-4) glycosidic linkage



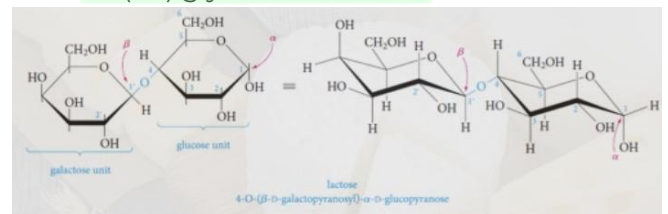
CELLOBIOSE

- ❖ Produced as an intermediate in the hydrolysis of polysaccharide cellulose
- ❖ Contains two D-glucose monosaccharides but differs in that β(1-4) glycosidic linkage



LACTOSE

- ❖ Hydrolysis of lactose gives D-galactose and d-glucose
- ❖ The anomeric carbon of the galactose unit has the β configuration at C-1 and is linked at the hydroxyl group at C-4 of the glucose unit
- ❖ β(1-3) glycosidic bond



SUCROSE (TABLE SUGAR)

- ❖ Known as table sugar
- ❖ Most abundant of all disaccharides and occurs throughout plant kingdom
- ❖ made up of α-D-glucose and β-D-glucose connected at α,β(1-2) glycosidic bond



BIOCHEMISTRY

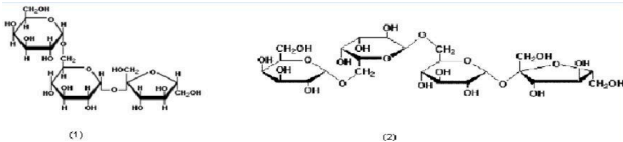
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B

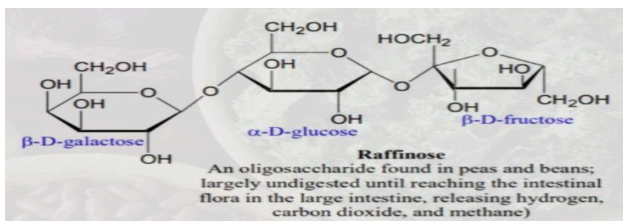
OLIGOSACCHARIDES

- ❖ Contain 3 to 10 monosaccharide units bonded to each other via glycosidic linkages
- ❖ ex. Raffinose and Stachyose



RAFFINOSE

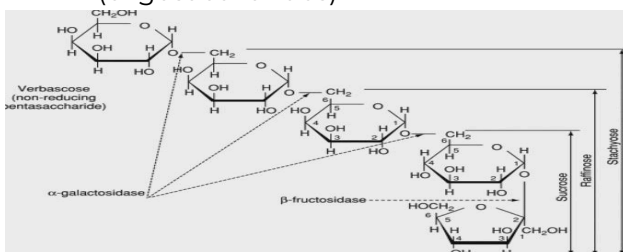
- ❖ Oligosaccharide found in peas and beans
- ❖ Largely undigested until reaching the intestinal flora in the large intestine, releasing hydrogen, carbon dioxide, and methane



B1

COMPARISON

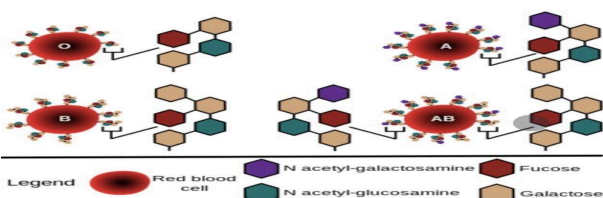
- ❖ Comparison of Sucrose (disaccharide) to Raffinose, Stachyose and Verbascose (oligosaccharides)



B2

HUMAN BLOOD

- ❖ Classified into four types (A, B, AB and O)
- ❖ The biochemical basis for various blood involved oligosaccharides



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C

STORAGE, STRUCTURAL & ACIDIC POLYSACCHARIDES

POLYSACCHARIDES

- ❖ Contain many linked monosaccharides
- ❖ Vary in chain length and molecular weight
- ❖ Polymers in which monosaccharides are monomers
- ❖ Most give a single monosaccharide on complete hydrolysis
- ❖ The monosaccharide units may be linked linearly, or the chains may be branched

- Storage Polysaccharides
- Structural Polysaccharides
- Acidic Polysaccharides

C1

STORAGE POLYSACCHARIDES

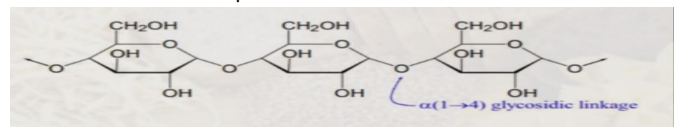
STARCH

- ❖ Polymer consisting of D-glucose units
- ❖ Usually insoluble in water because of high molecular weight, but they can form thick colloidal suspensions with water

Two types:

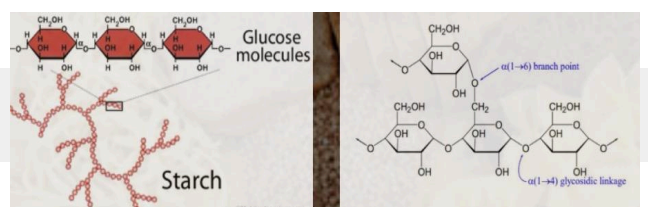
AMYLOSE

- Consisting of long, unbranched chains of glucose (from 1000 to 2000 molecules)
- Connected by a(1-4) glycosidic linkage
- Forms helices (coils) which can trap molecules of iodine



AMYOPECTIN

- Consisting of long, branched chains of glucose (from 105 molecules)
- Connected by a(1-4) glycosidic linkage main chain
- a(1-6) glycosidic linkage for the branch
- 80-90% of starch in plants is in this form





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GLYCOGEN

- ❖ Energy-storing carbohydrate of animals
- ❖ Made of a 1,4- and 1,6-linked glucose units
- ❖ Glycogen carbohydrates provides short-term energy storage
- ❖ Excess simple sugars not immediately used for energy or cell structures are bonded together in branching chain called glycogen
- ❖ Stored short-term in muscle and liver tissue
- ❖ Stores approximately 4 calories per gram and is a quick source of energy when food molecules are unavailable in the bloodstream
- ❖ Has a higher molecular weight than starch (perhaps 100,000 glucose units)
- ❖ Its structure is even more branched than that of amylopectin, with a branch every 8 to 12 glucose units

C2

STRUCTURAL POLYSACCHARIDES

CELLULOSE

- ❖ Cellulase is an unbranched glucose polymer
- ❖ Monosaccharides are connected at b(1-4) glycosidic linkage
- ❖ Type of dietary fiber found naturally in fruits, vegetables, and cereals

- ❖ Humans cannot digest cellulose whereas cows can do so because their gut contains certain bacteria capable of digesting cellulose

CHITIN

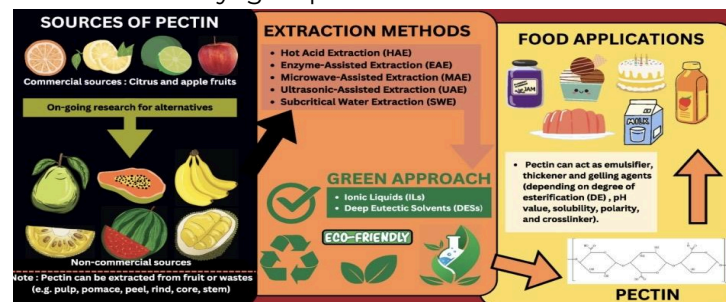
- ❖ Nitrogen-containing polysaccharide that forms the shells of crustaceans and the exoskeleton of insects
- ❖ Similar to cellulose, except that the hydroxyl group at C-2 of each glucose units is replaced by an acetylamino group
 - $\text{CH}_3\text{CONH-}$

AMINO SUGAR

- ❖ One of the sugar hydroxyl groups is replaced by an amino group
- ❖ Usually the $-\text{NH}_2$ group is also acetylated
- ❖ d-glucosamine is one of the more abundant amino sugars

PECTIN

- ❖ Obtained from fruits and berries
- ❖ Used in making jellies
- ❖ They are linear polymers of d-galacturonic acid, linked with 1,4-aglycosidic bonds
- ❖ d-galacturonic acid has the same structure as d-galactose, except that the C-6 primary alcohol group is replaced by a carboxyl group



SUGAR PHOSPHATE

- ❖ Phosphate esters of monosaccharides are found in all living cells, where they are intermediates in carbohydrate metabolism
- ❖ Phosphates of the five-carbon sugar ribose and its 2-deoxy analog are important in nucleic acid structures (DNA and RNA) and in other key biological compound
- ❖ **Deoxyribose** - double-stranded sugar phosphate

DEOXY SUGAR

- ❖ One or more of the hydroxyl groups is replaced by a hydrogen atom
- ❖ The most important example is 2-deoxyribose, the sugar component of DNA
 - It lacks the hydroxyl group a C-2 and occurs in DNA in the furanose form



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C3 ACIDIC POLYSACCHARIDES

HYALURONIC ACID

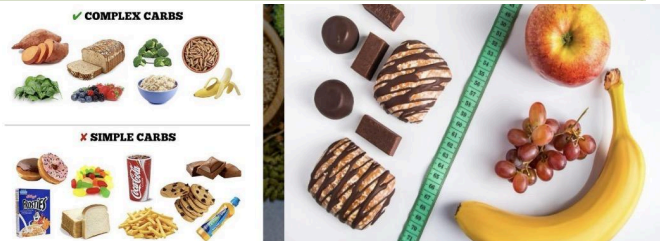
- ❖ Polymer of disaccharides
- ❖ Composed of D-glucuronic acid and N-acetyl-D-glucosamine, linked via alternating β -(1-4) and β -(1-3) glycosidic bonds

HEPARIN

- ❖ Unfractionated mixture of partially sulfated polymers of several carbohydrates
- ❖ Including
 - D-glucosamine
 - 2-deoxy-2-sulfamino-D-glucose
 - 2-acetamido-2-deoxy-D-glucose
 - D-glucuronic acid
 - L-iduronic acid

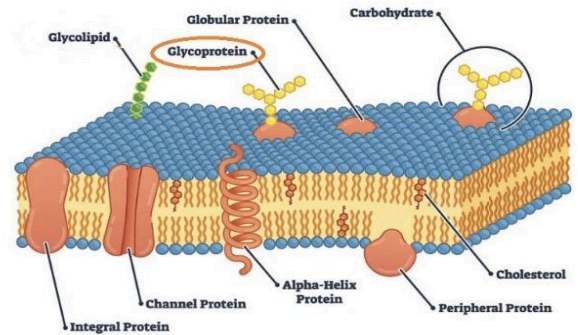
D DIETARY CONSIDERATIONS, & THE GLYCOCONJUGATES

D1 DIETARY CONSIDERATIONS



D2 GLYCOLIPIDS AND GLYCOPROTEINS

- ❖ Molecules in which oligosaccharides are attached to lipids/proteins



Glycoproteins Vs. Glycolipids

