BIOCHEMISTRY

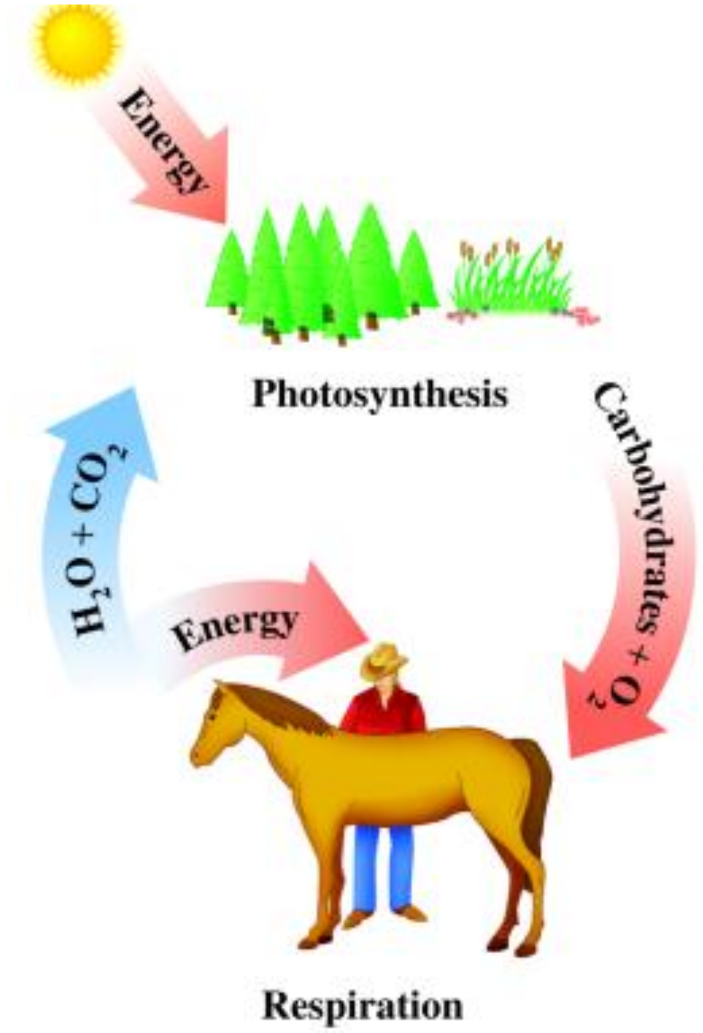
3rd Chemistry Students

Dr. Aboubakr H. Hegap

Lecture 1

Carbohydrates

Carbohydrates



- Produced by photosynthesis in plants.
- The major source of energy from our diet.
- Composed of the elements C, H, and O.

$C_n(H_2O)_n$

$$6CO_2 + 6H_2O + \text{energy} \underset{\text{Respiration}}{\overset{\text{Photosynthesis}}{\rightleftarrows}} C_6H_{12}O_6 + 6O_2$$

glucose

Carbohydrates

- The most abundant organic compounds in nature (50% of the earth’s biomass).

- 3/4 of the weight of plants.

- 1% of the weight of animals and humans (they do not store).

- 65% of the foods in our diet.

Carbohydrates

1. Monosaccharide + H_2O $\xrightarrow{H^+ \text{ or enzyme}}$ no hydrolysis

2. Disaccharide + H_2O $\xrightarrow{H^+ \text{ or enzyme}}$ two monosaccharide units

3. Polysaccharide + many H_2O $\xrightarrow{H^+ \text{ or enzyme}}$ many monosaccharide units

Monosaccharides (Simple Sugar)

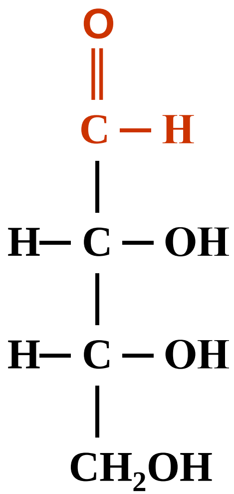
A carbohydrate that cannot be split or hydrolyzed into smaller carbohydrates.

Monosaccharides are carbohydrates with:

- The simplest carbohydrates
- 3-9 carbon atoms
- A carbonyl group (aldehyde or ketone)
- Several hydroxyl groups

$C_n(H_2O)_n$

$C_nH_{2n}O_n$



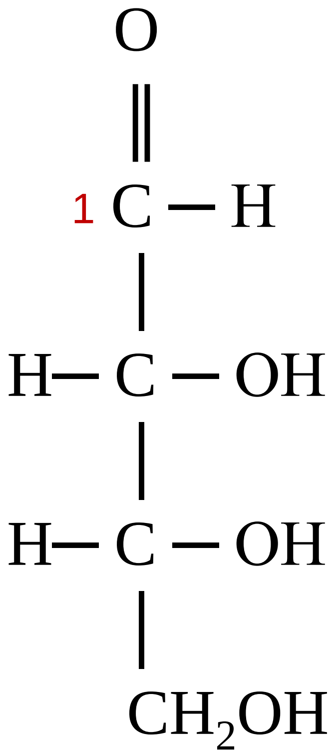
Monosaccharides - Aldose

Aldose is monosaccharide:

- With an aldehyde group and many hydroxyl (-OH) groups.

- *triose* (3C atoms)
- *tetrose* (4C atoms)
- *pentose* (5 C atoms)
- *hexose* (6 C atoms)

“Aldo-” + suffix



aldose

an aldotetrose

(Erythose)

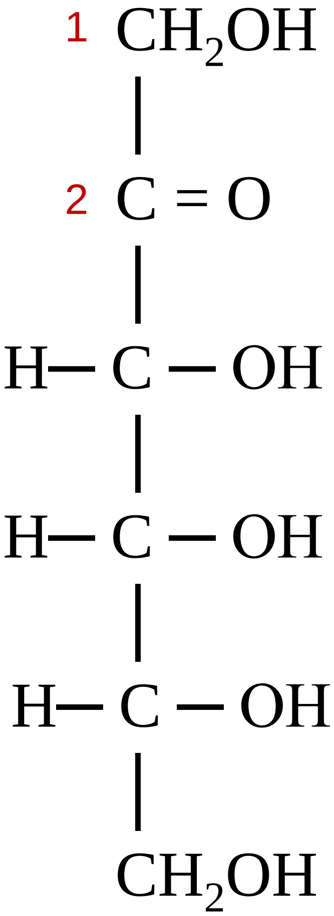
Monosaccharides - Ketose

Ketose is monosaccharide:

- With a ketone group and many hydroxyl (-OH) groups.

- *triose* (3C atoms)
- *tetrose* (4C atoms)
- *pentose* (5 C atoms)
- *hexose* (6 C atoms)

“Keto-” + suffix



$$\begin{array}{rc} 1 & \mathrm{CH_2OH} \\ & | \\ 2 & \mathrm{C=O} \\ & | \\ & \mathrm{H-C-OH} \\ & | \\ & \mathrm{H-C-OH} \\ & | \\ & \mathrm{H-C-OH} \\ & | \\ & \mathrm{CH_2OH} \end{array}$$

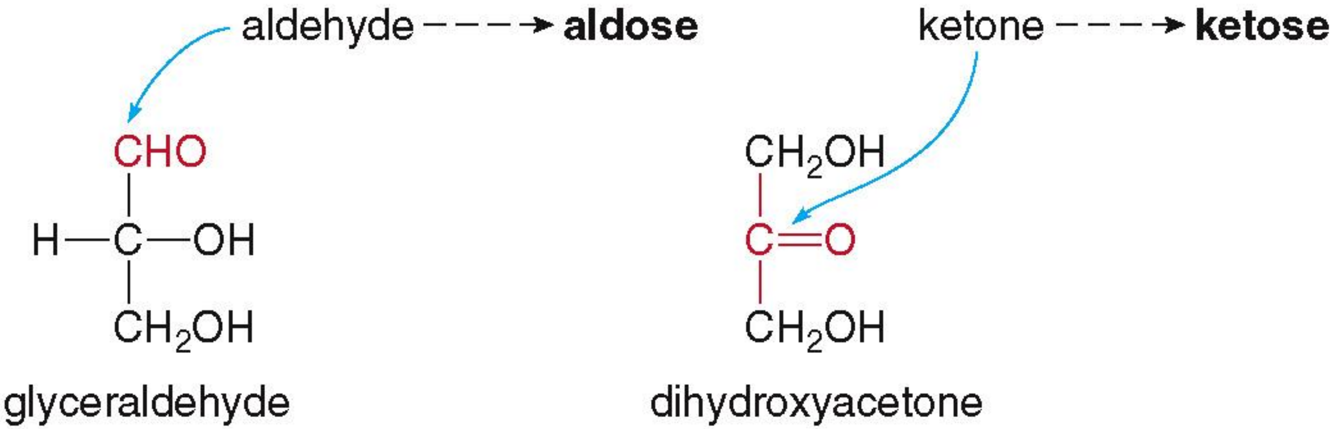
ketose

a ketohexose

(Fructose)

Monosaccharides (Simple Sugar)

- The simplest aldose is glyceraldehyde.
- The simplest ketose is dihydroxyacetone.



$C_3H_6O_3$

$C_3H_6O_3$

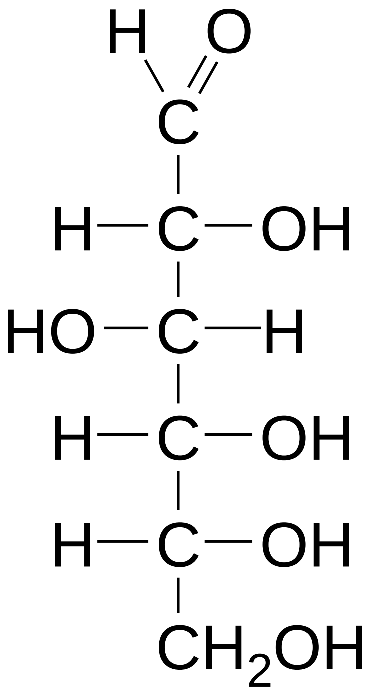
Constitutional Isomers

Some important Monosaccharides

Glucose (Dextrose)

($C_6H_{12}O_6$, aldohexose) – Blood sugar

- The most abundant monosaccharide
- Is found in fruits, vegetables,
  corn syrup, and honey.
- Is found in disaccharides such as sucrose, lactose, and maltose.
- Makes up polysaccharides such as starch, cellulose, and glycogen.



Some important Monosaccharides

Glucose (Dextrose)

- Normal blood glucose levels are 70-110 mg/dL.

- Excess glucose is stored as the polysaccharide glycogen or as fat.

- Insulin (a protein produced in the pancreas) regulates blood glucose levels by stimulating the uptake of glucose into tissues or the formation of glycogen.

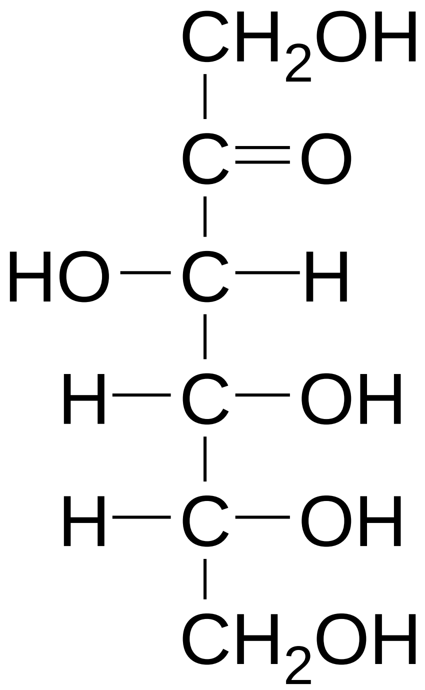
- Patients with diabetes produce insufficient insulin to adequately regulate blood sugar levels, so they must monitor their diet and/or inject insulin daily.

Some important Monosaccharides

Fructose

($C_6H_{12}O_6$, ketohexose),

- Is the sweetest of the carbohydrates.
- Is found in fruit juices and honey **(fruit sugar).**
- In bloodstream, it is converted to its isomer, glucose.
- Is bonded to glucose in sucrose (a disaccharide known as table sugar).



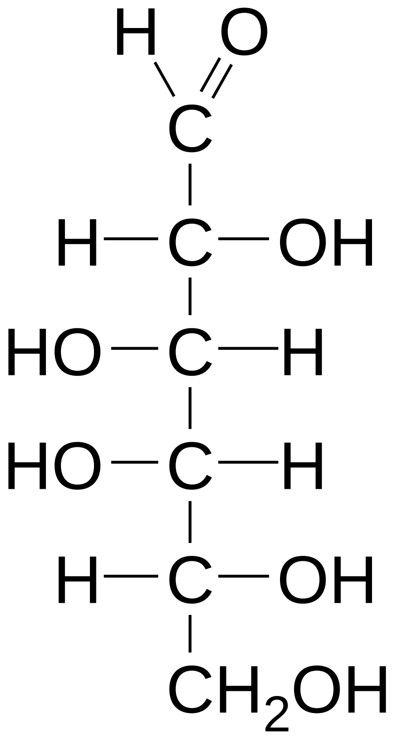
Carbohydrates
Lecturer 2

Some important Monosaccharides

Galactose

($C_6H_{12}O_6$, aldohexose),

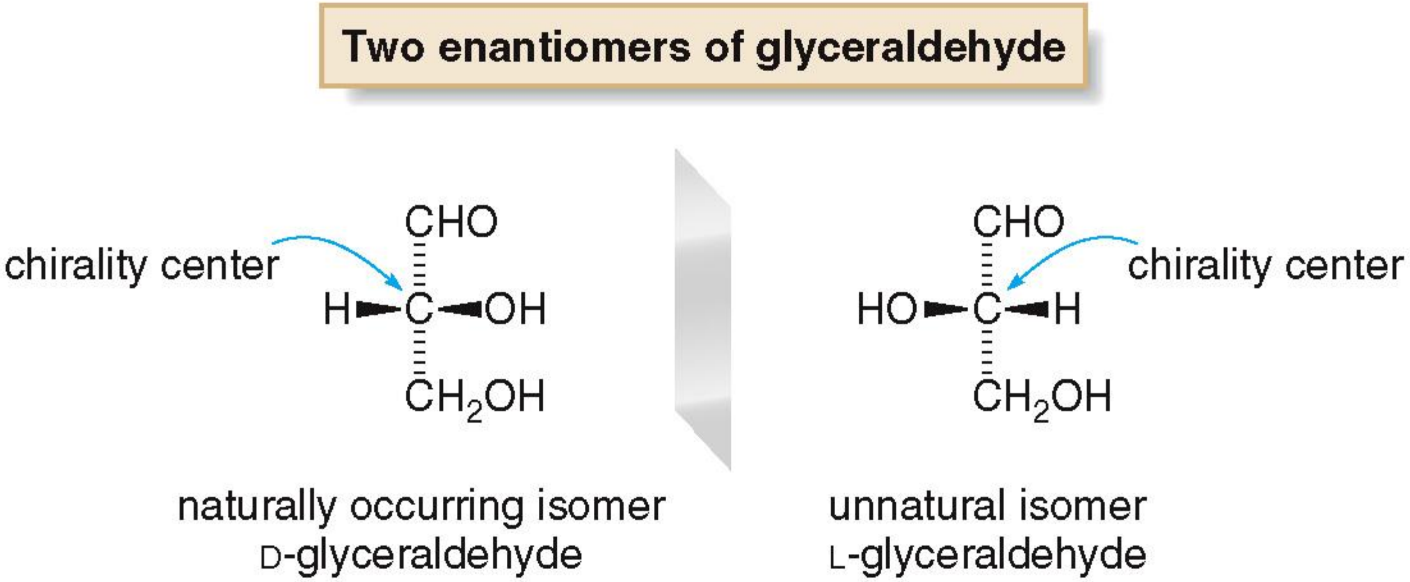
- Has a similar structure to glucose except for the –OH on Carbon 4.
- Cannot find in the free form in nature.
- Exist in the cellular membranes of the brain and nervous system.
- Combines with glucose in lactose (a disaccharide and a sugar in milk).



Chirality

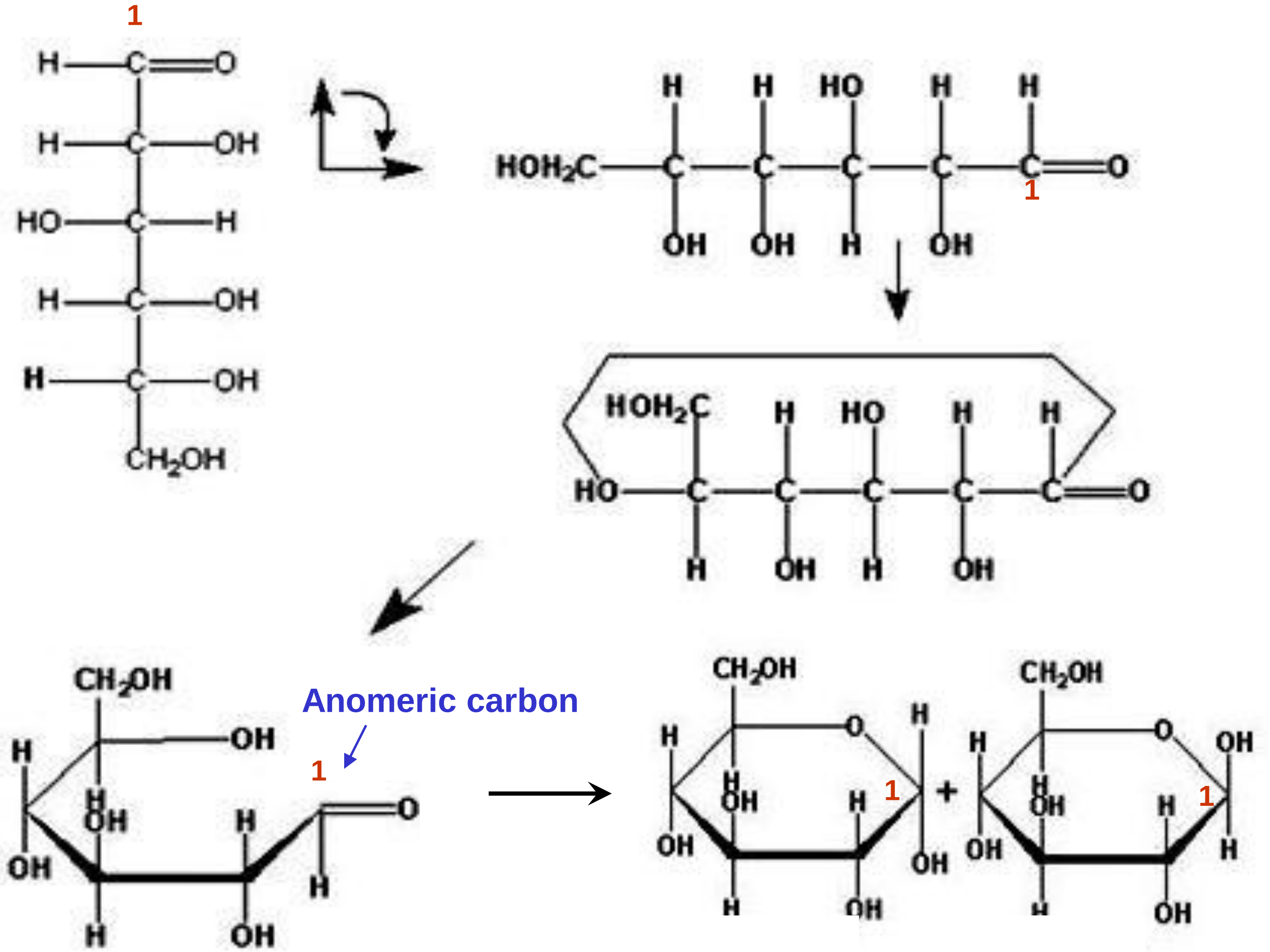
All carbohydrates have 1 or more chirality centers.

Glyceraldehyde, the simplest aldose, has one chirality center, and has two possible enantiomers.



Cyclic Structure – 1- Haworth Structure

Which represents the cyclic form of sugar.



1

1

Anomeric carbon

1

1

1

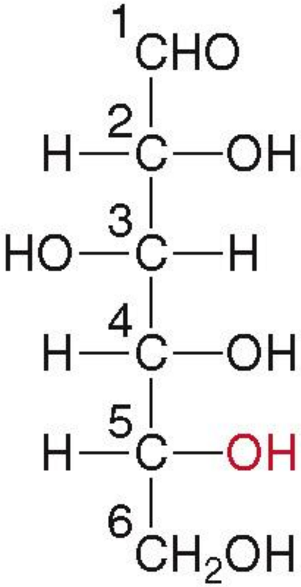
Alpha (α)

Beta (β)

More stable form

Anomers

Cyclic Structure – Haworth Structure

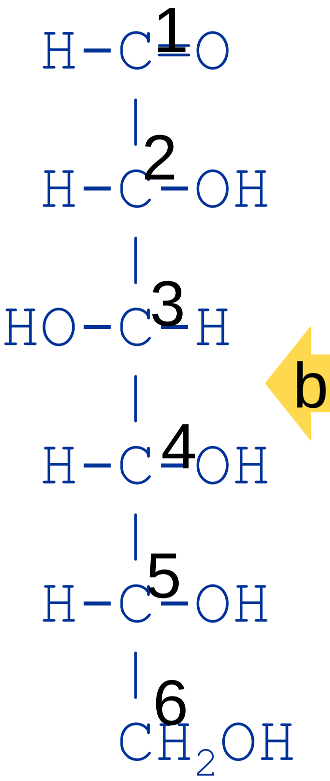


D-glucose

This OH group is the right distance away from the carbonyl for cyclization to a six-membered ring.

Glucose

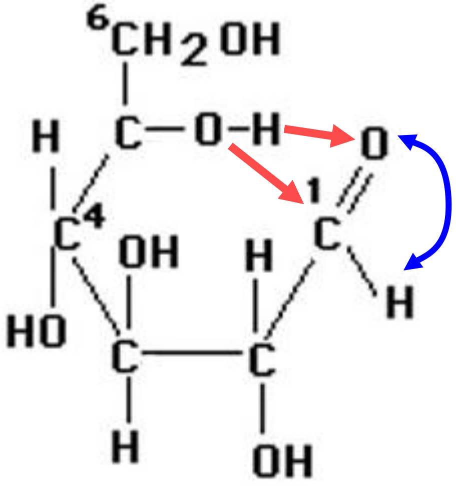
Structural formula.
Straight chain
glucose



bends

Glucose

glucose bending

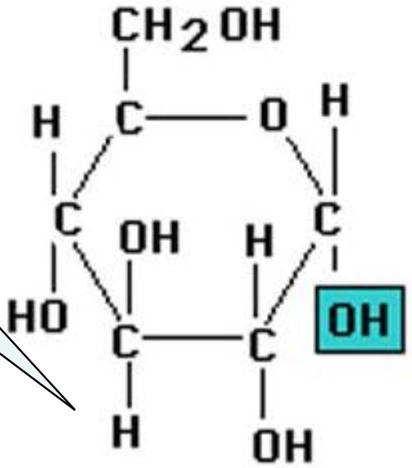


flips
either
way

Glucose

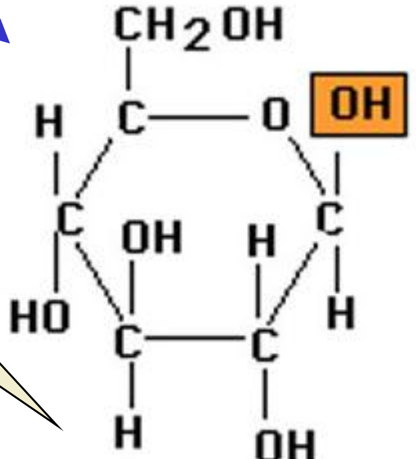
Two ring-shape
versions

Used in
making
starch



alpha-
glucose

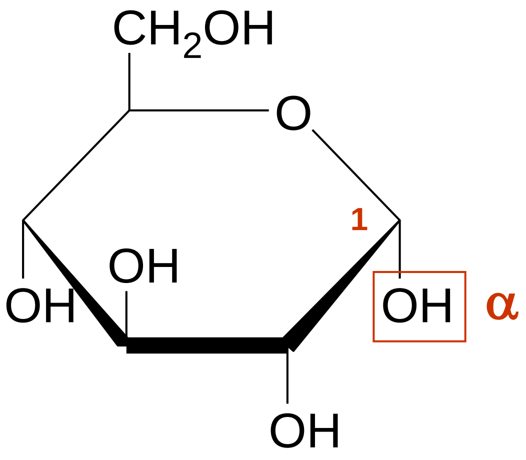
Used in
making
cellulose



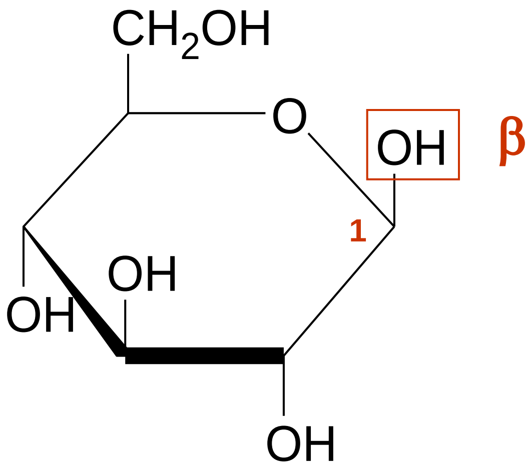
beta-glucose

Glucose bends itself into 4 different shapes **millions** of times a second

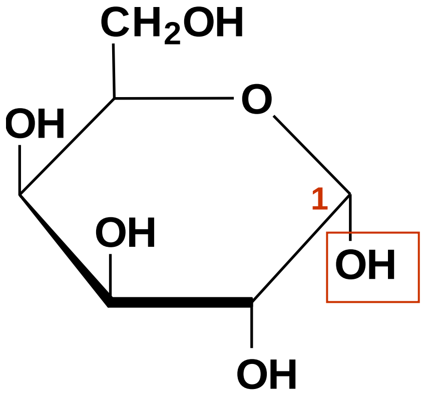
Cyclic Structure – Haworth Structure



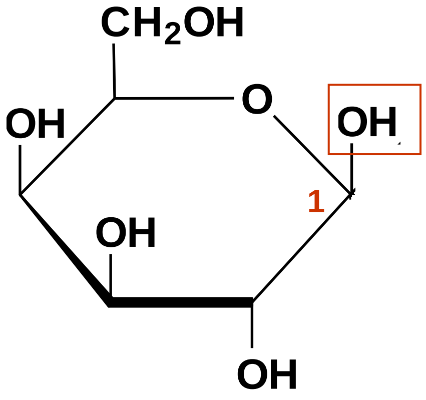
α-D-Glucose



β-D-Glucose

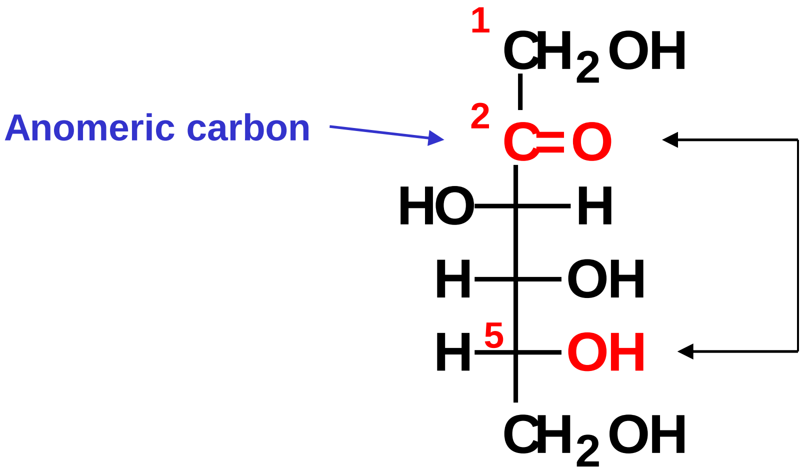


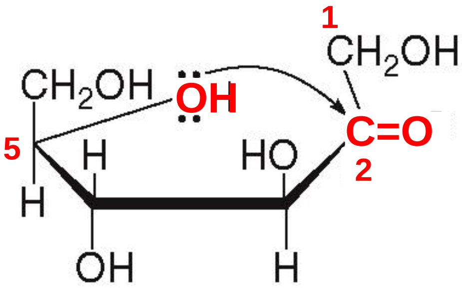
α-D-Galactose

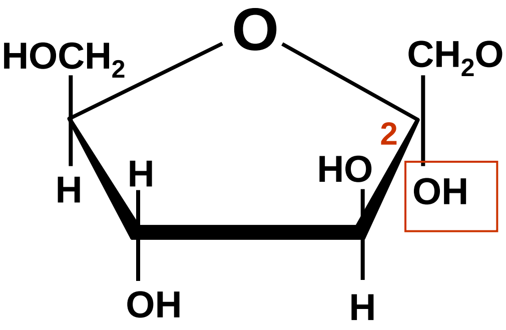


β-D-Galactose

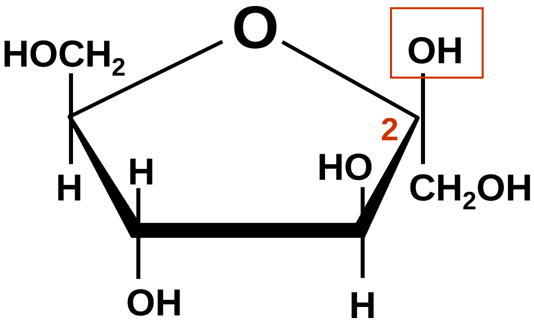
Cyclic Structure – Haworth Structure





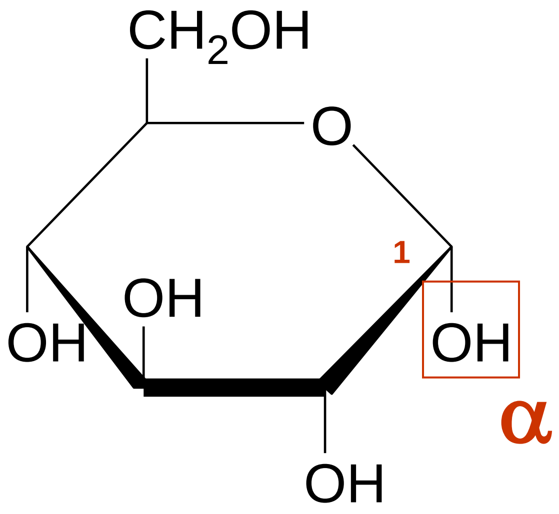


α-D-fructose

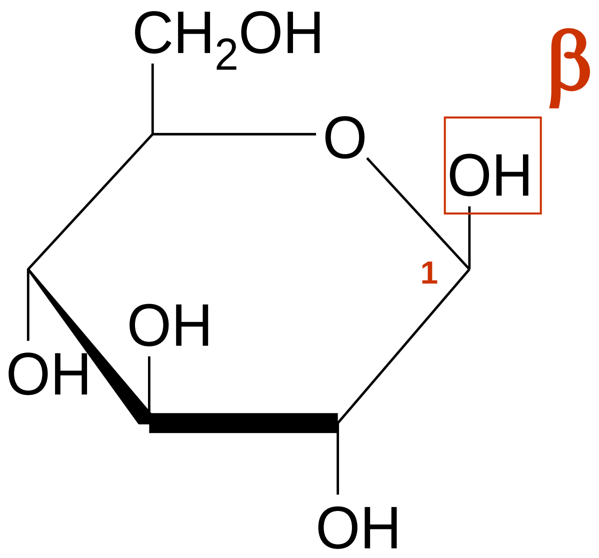


β-D-fructose

Cyclic Structure – Haworth Structure



α-D-Glucose

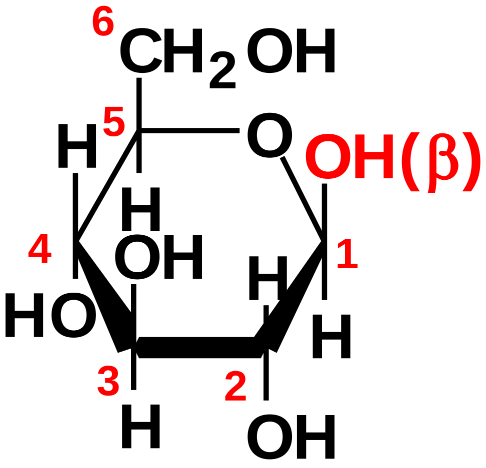


β-D-Glucose

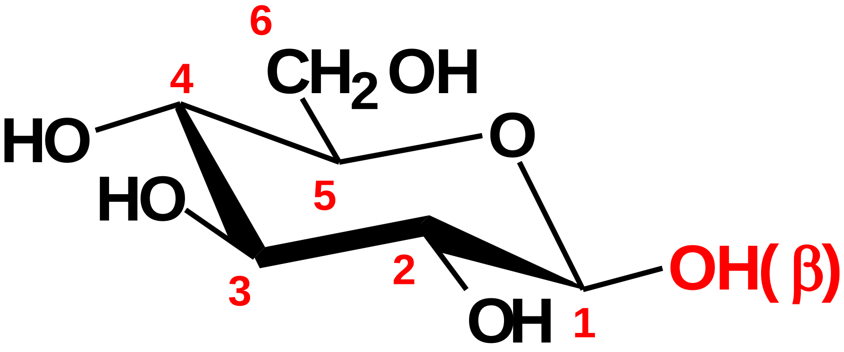
Humans have α-amylase (an enzyme) and they can digest starch products such as pasta (contain α-glucose)

Humans do not have β-amylase (an enzyme) and they cannot digest cellulose such as wood or paper (contain β-glucose)

2- Chair Conformation



β-D-Glucose
(Haworth projection)



β-D-Glucose
(Chair conformation)

Equatorial

Cyclic Structure 3- Fischer Projections

- Horizontal lines represent bonds projecting forward from the stereocenter.

- Vertical lines represent bonds projecting to the rear.

- Only the stereocenter (tetrahedral carbon) is in the plane.

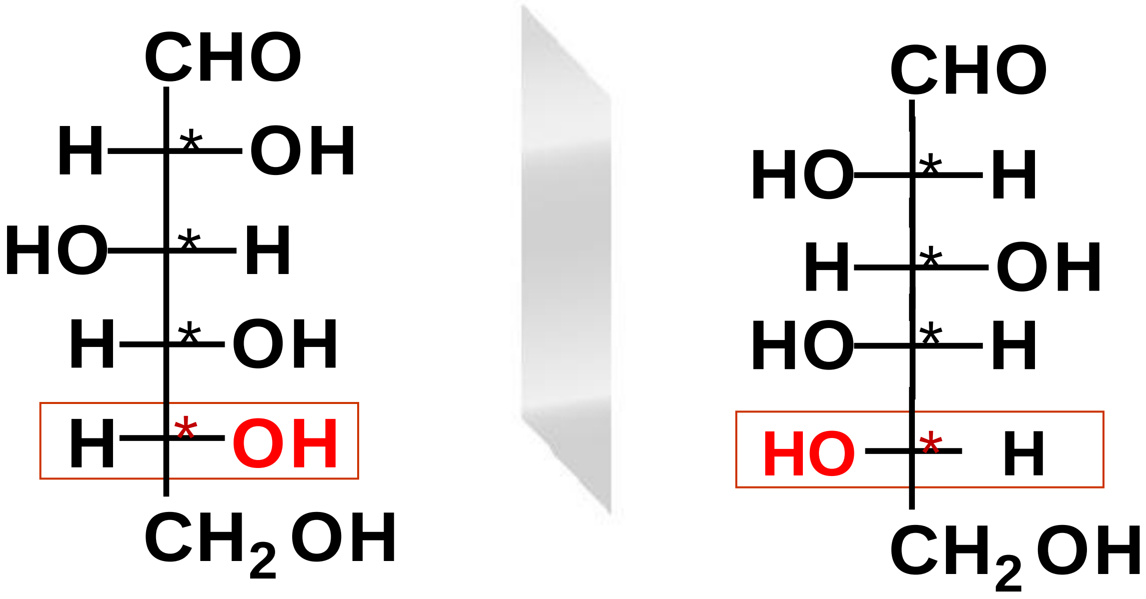
3D

2D

3- Fischer Projections

1. Carbon with four different groups bonded to it.

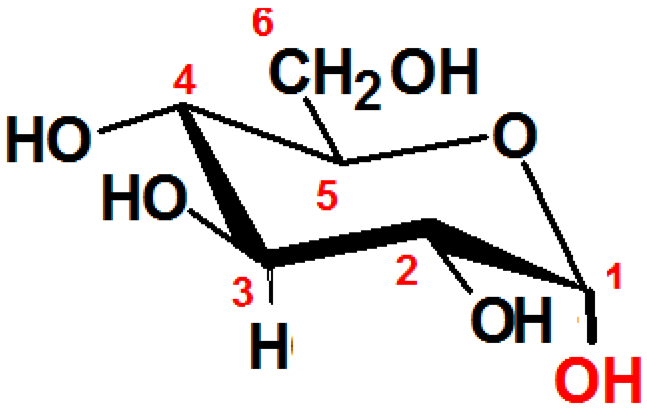
2. The chiral carbon furthest from the carbonyl group (-CHO).

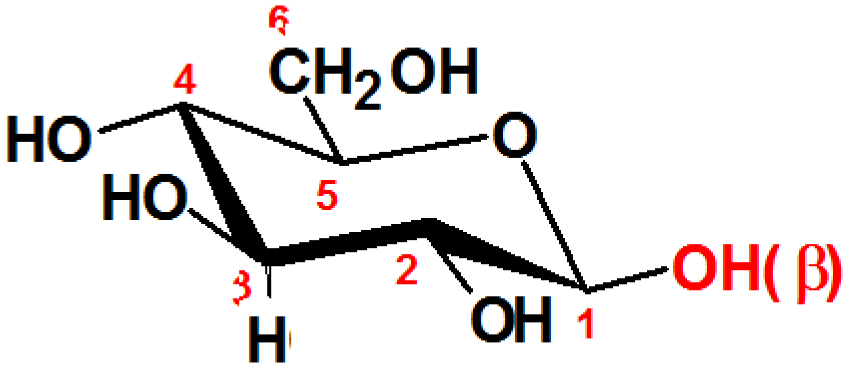


D - glucose

L - glucose

Naturally occurring enantiomer

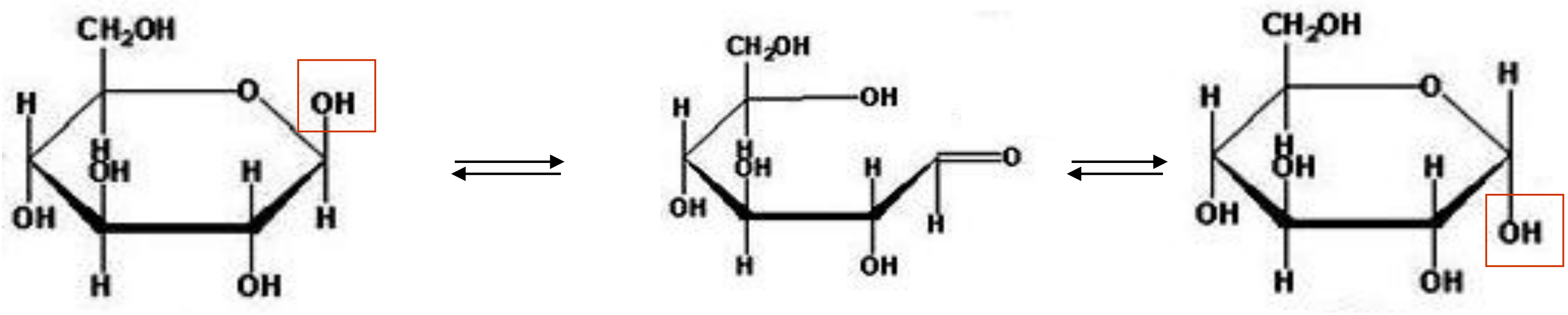




Alpha anomer presents is less in solution due to the repulsion Between OH on C-1 and hydrogens on 1 and 3 , but not presents in beta anomer so it is more stable.

Mutarotation

Change in specific rotation that accompanies the equilibration of α and β anomers in aqueous solution.



β-D-glucose

Open-chain form
(acyclic)

α-D-glucose

64%

< 0.02%

36%

β-D-glucose in aquas soln. 19°-----52.7°

α-D-glucose in aquas soln. 112°-----52.7°

Physical properties of Monosaccharides

- Colorless

- Sweet Tasting

- Crystalline solids

- Polar with high melting points (because of OH groups)

- Soluble in water and insoluble in nonpolar solvents
  (H-bond because of OH groups)

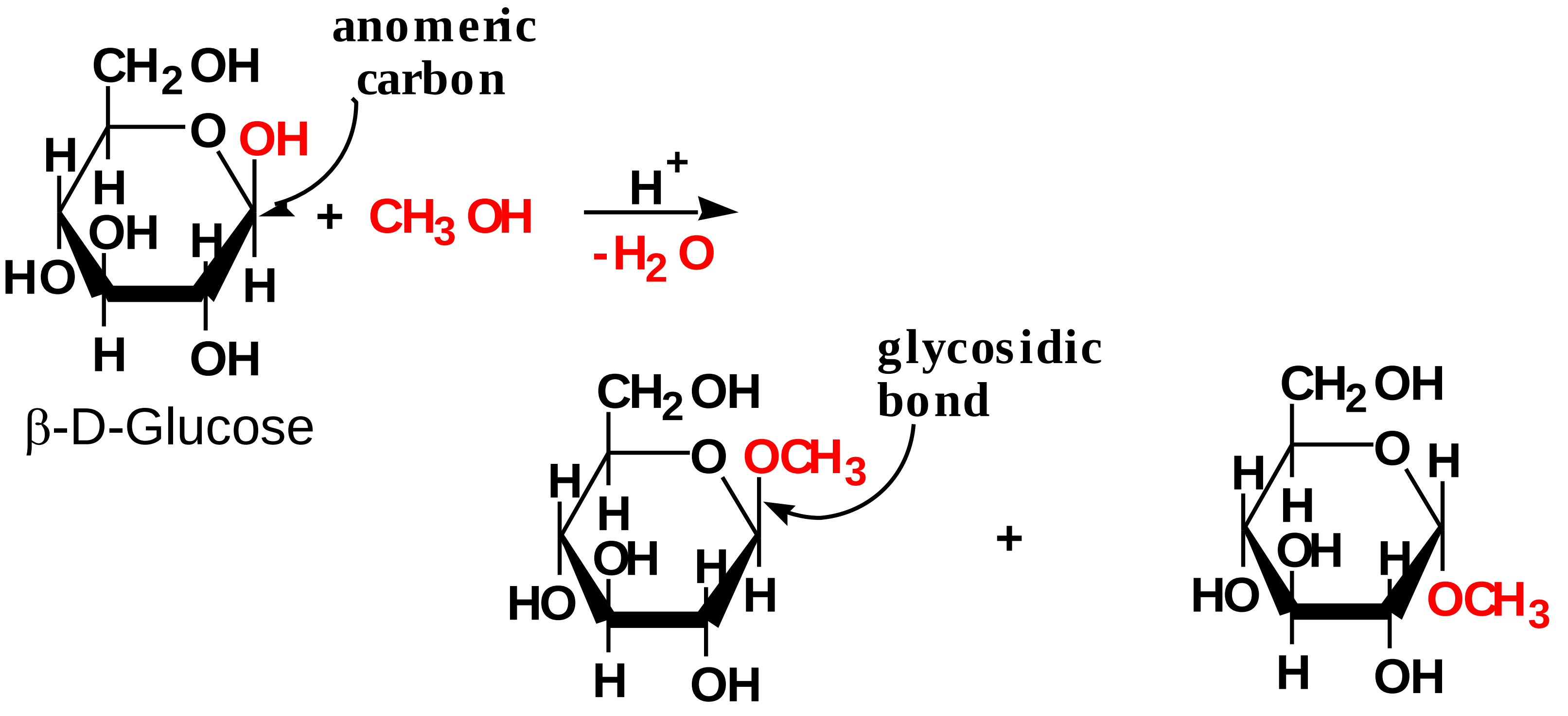
Lecture 3

Chemical properties of Monosaccharides

1. Formation of Glycosides (Acetals)
2. Oxidation
3. Reduction

1- Formation of Glycosides (Acetals)

- Exist almost exclusively in cyclic hemiacetal forms.
- They react with an alcohol to give acetals.
- Acetals are stable in water and bases but they are hydrolyzed in acids.



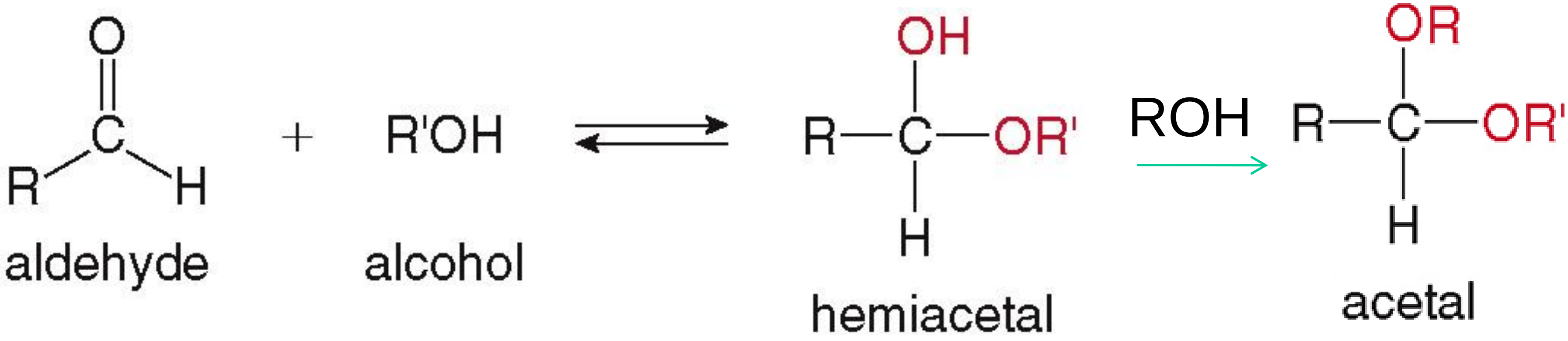
β-D-Glucose

Methyl β-D-Glucoside

Methyl α-D-Glucoside

Difference between glucose and aldhyde

Aldehydes and ketones react with alcohols to form hemiacetals.



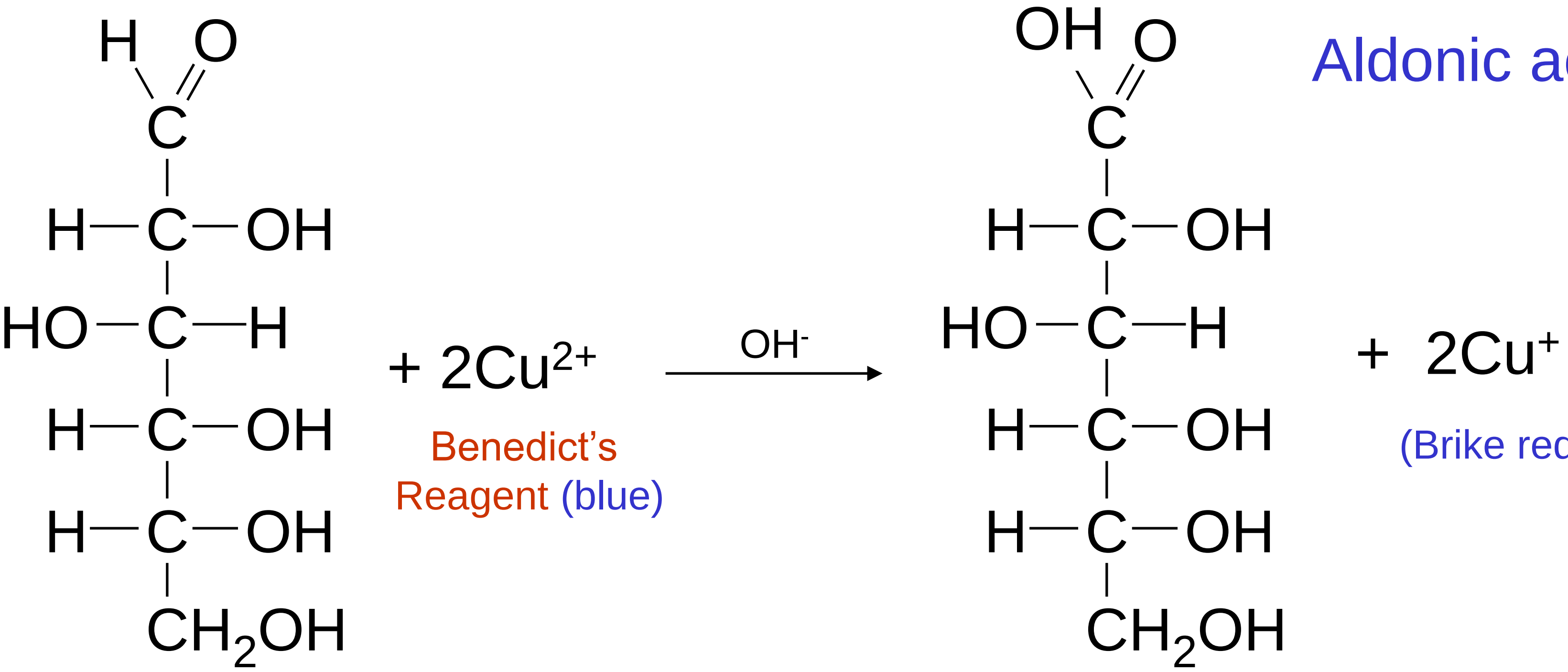
Unstable

A hemiacetal contains a hydroxyl group (OH) and an alkoxy group (OR) on the same carbon.

But glucose reacts with one ROH to form acetal.

2- Oxidation of Monosaccharides

Aldonic acids



Benedict's Reagent (blue)

(Brike red)

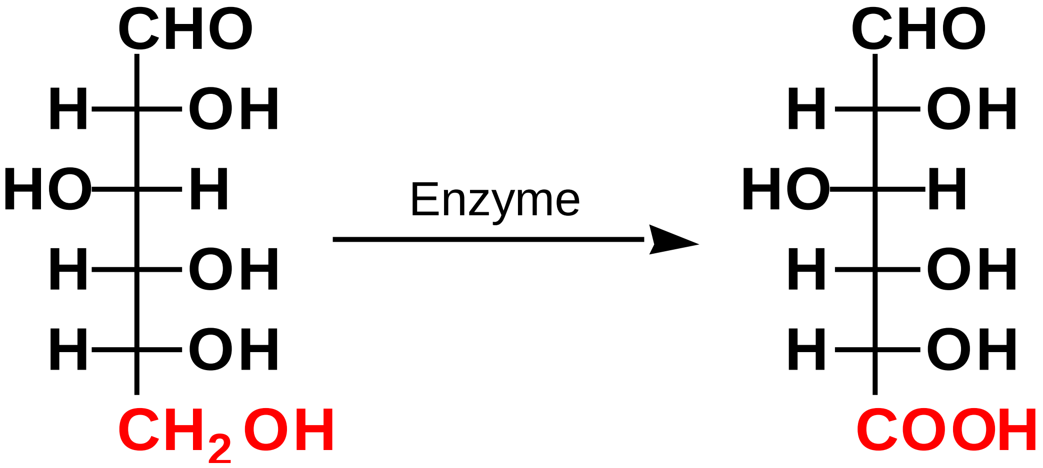
D - glucose

D – gluconic acid

Reducing sugars: reduce another substance.

Oxidation of Monosaccharides

primary alcohol at C-6 of a hexose is oxidized to uronic acid by an enzyme (catalyst).



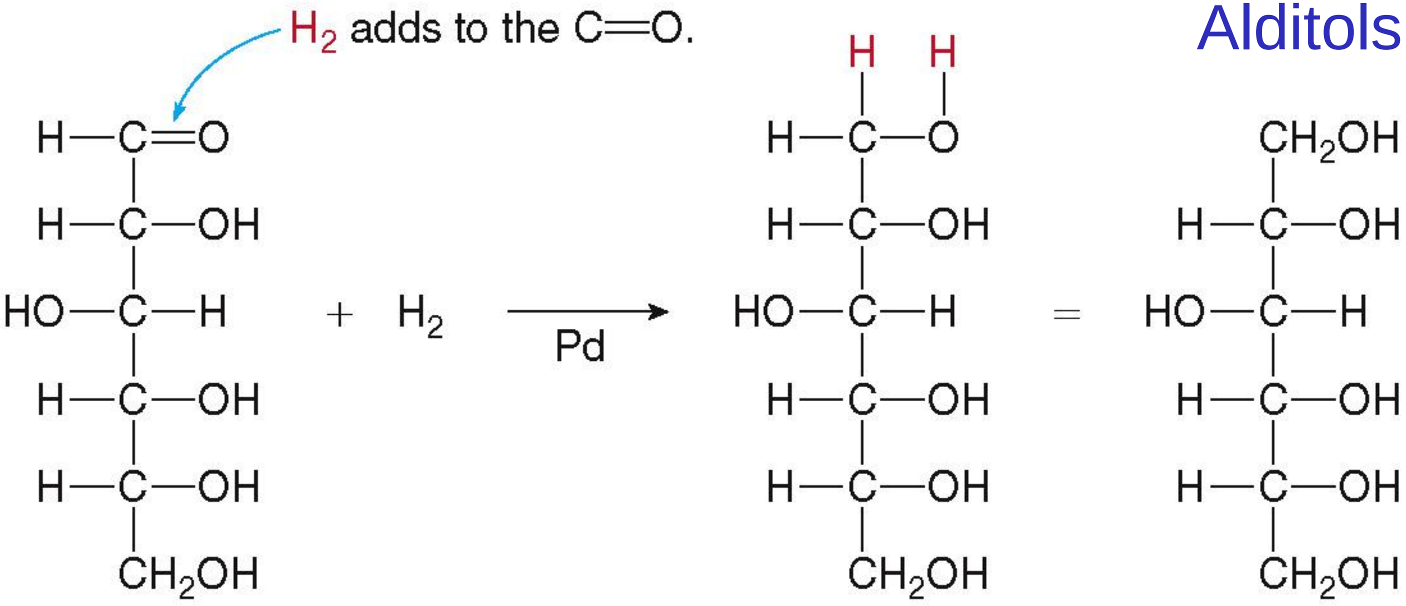
D-glucose

D-glucuronic acid
(a uronic acid)

Exist in connective tissue
Detoxifies foreign phenols and alcohols

3- Reduction of Monosaccharides

Alditols


H_2 adds to the C=O.

D-glucose
(D-sorbose)

glucitol
(sorbitol)

The alditol contains an OH group on every C.

Sugars alcohols: sweetners in many sugar-free (diet drinks & sugarless gum).

Problem: diarrhea and cataract

Disaccharides

A disaccharide:

- Consists of two monosaccharides linked by a *glycosidic bond* (when one –OH group reacts with another –OH group).

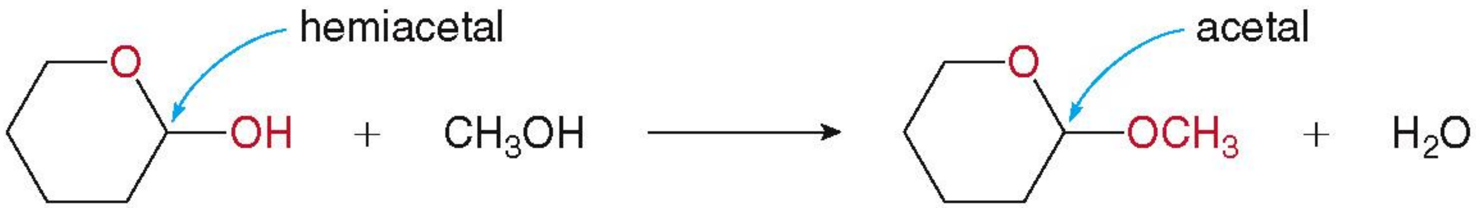
Glucose + Glucose → Maltose + H_2O

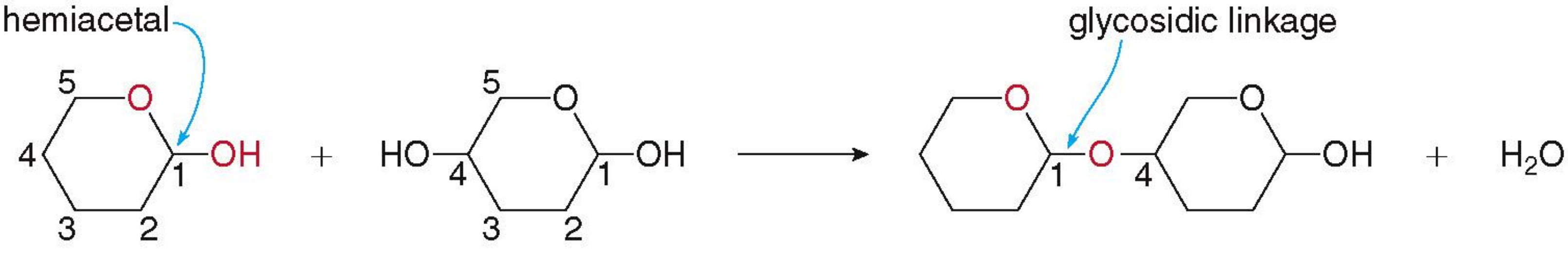
Glucose + Galactose → Lactose + H_2O

Glucose + Fructose → Sucrose + H_2O

Disaccharides

Disaccharides have at least one acetal carbon (a carbon atom singly bonded to two OR (alkoxy) groups.

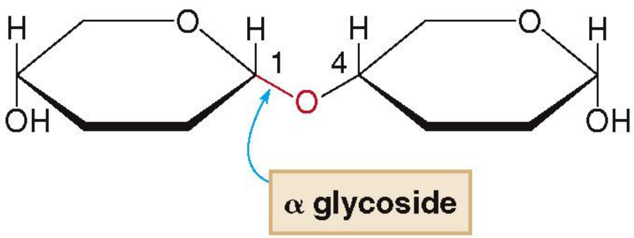




general structure
of a disaccharide

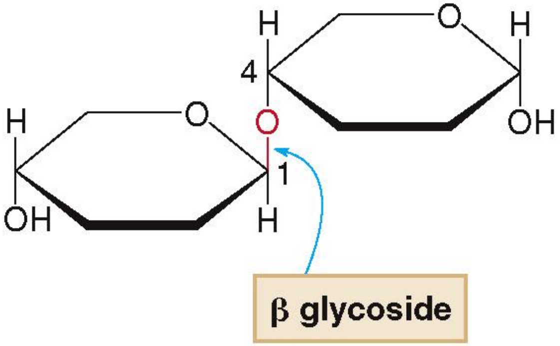
Disaccharides

The glycosidic bond joining the two rings can be alpha (α) or beta (β).



The glycoside bond is **down.**

1→4-α-glycosidic linkage



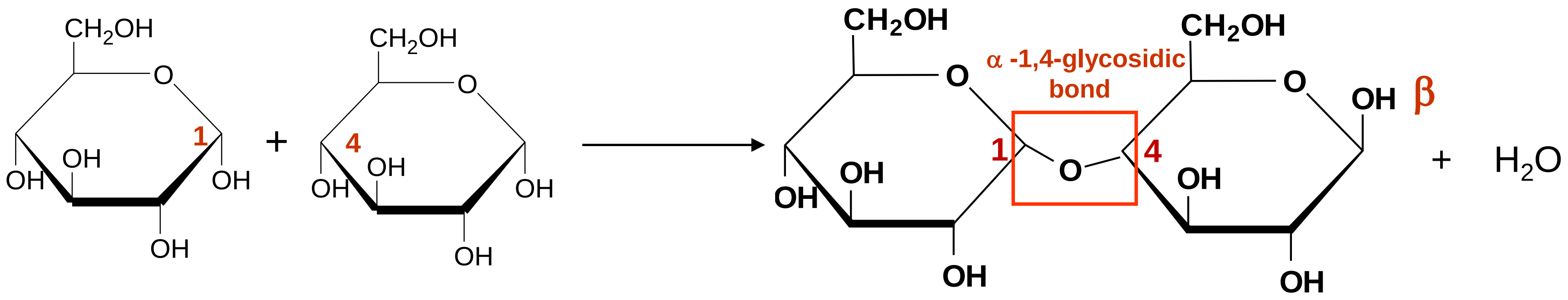
The glycoside bond is **up.**

1→4-β-glycosidic linkage

Disaccharides

Maltose:

- Is a disaccharide of two glucose molecules.
- Has a *α* -1,4-glycosidic bond (between two α-glucoses).
- Is obtained from the breakdown of starches.
- Is a reducing sugar (carbon 1 can open to give a free aldehyde to oxidize).



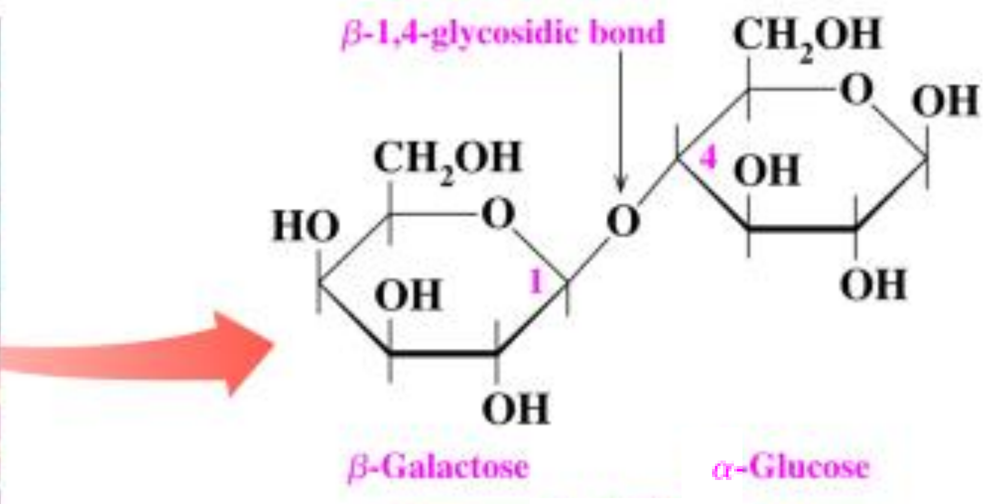
α-glucose α-glucose

maltose

Disaccharides

Lactose:

- Is a disaccharide of galactose and glucose.
- Has a *β* -1,4-glycosidic bond (between *β*-galactose and α-gulcose).
- Is found in milk and milk products (almost no sweet).
- Is a reducing sugar (carbon 1 can open to give a free aldehyde to oxidize).

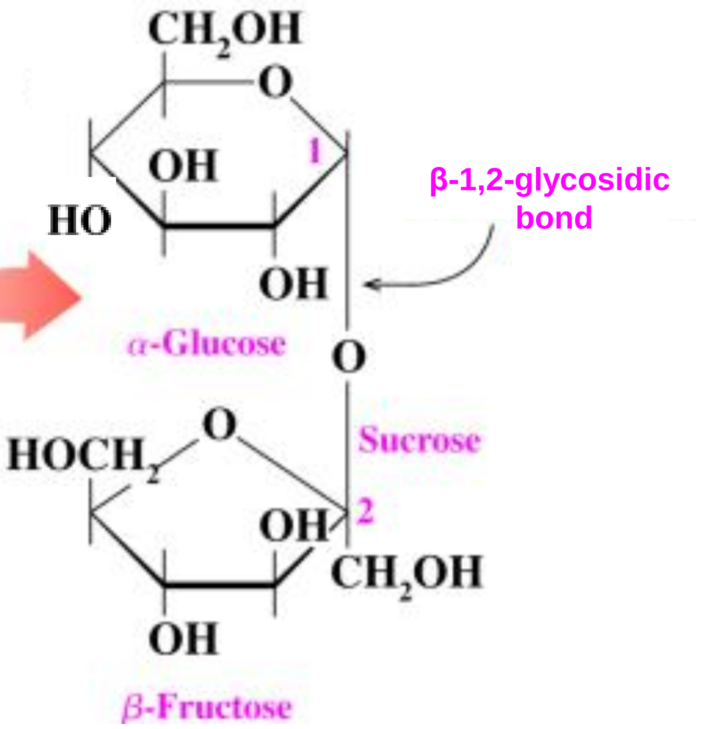


lactose

Disaccharides

Sucrose:

- Is found in table sugar (obtained from sugar cane and sugar beets).
- Consists of glucose and fructose.
- Has an *α,β*-1,2-glycosidic bond (between α-glucose and β-fructose).
- Is not a reducing sugar (carbon 1 cannot open to give a free aldehyde to oxidize).

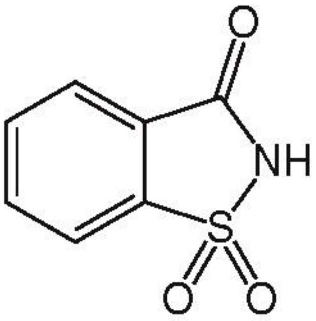


Artificial sweeteners

Saccharine:

It (sold at Sweet’n Low) was used extensively during World War I.

There were concerns in the 1970s that saccharin causes cancer.



saccharin
(Trade name: Sweet’n Low)

Polysaccharides

- Polymers of many monosaccharides units.
- Starch
  - Amylose (20%)
  - Amylopectin (80%)

(starch that stores glucose in plants such as rice, potatoes, beans, and wheat - energy storage).

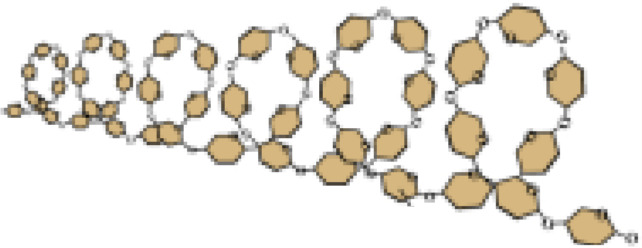
- Glycogen (an energy storage in animals & humans)
- Cellulose (plant and wood structures).

Polysaccharides

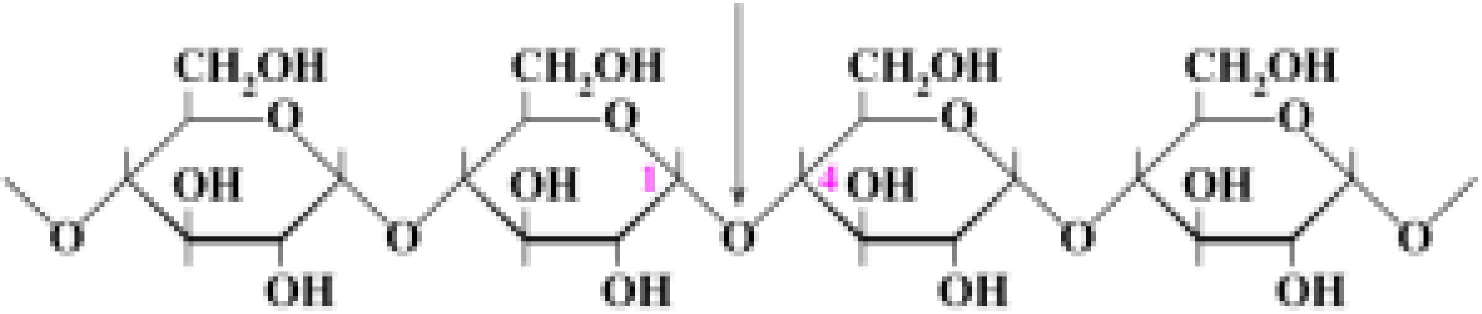
Amylose:

- Is a polysaccharide of *α*-glucose in a continuous (unbranched) chain (helical or coil form).

- Has α-1,4-glycosidic bonds between the *α*-glucose units (250 to 4000 units).



α-1,4-glycosidic bond

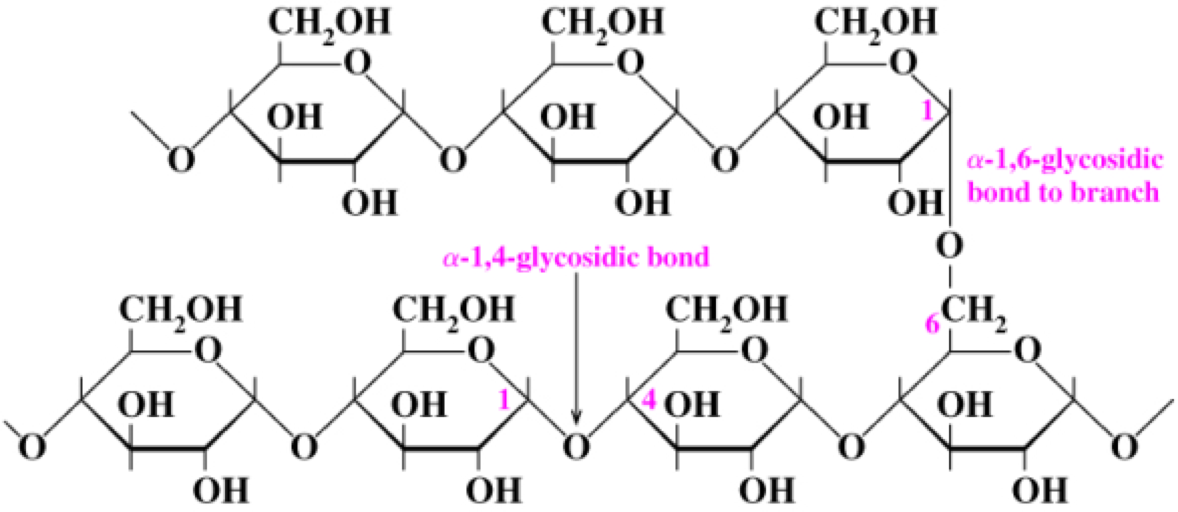


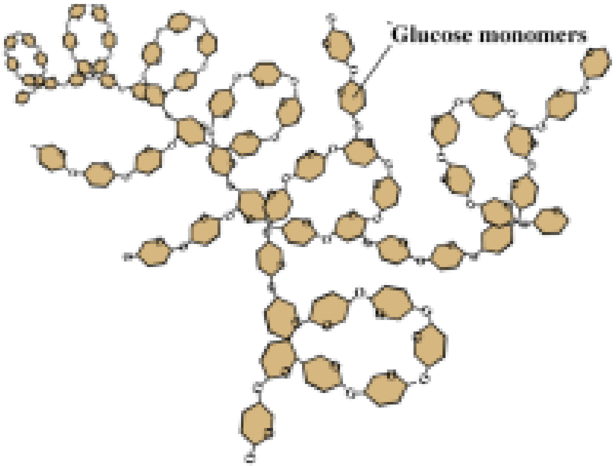
Polysaccharides

Amylopectin:

- Is a polysaccharide of glucose units in branched chains.
- Has α-1,4-glycosidic bonds between the *α*-glucose units.
- Has *α*-1,6 bonds to branches of glucose units.

  (at about every 25 glucose units, there is a branch).
- Both forms of starch are water soluble.





Polysaccharides

Amylose, Amylopectin (starch)

↓ H^+ or α-amylase (enzyme in saliva)

Dextrins (6-8 glucose units)

Digestion process

↓ H^+ or α-amylase (enzyme in pancreas)

Maltose (2 glucose units)

↓ H^+ or α-maltase (enzyme)

Many *α*-D-glucose units

Respiration

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{energy}$$

glucose

Fermentation

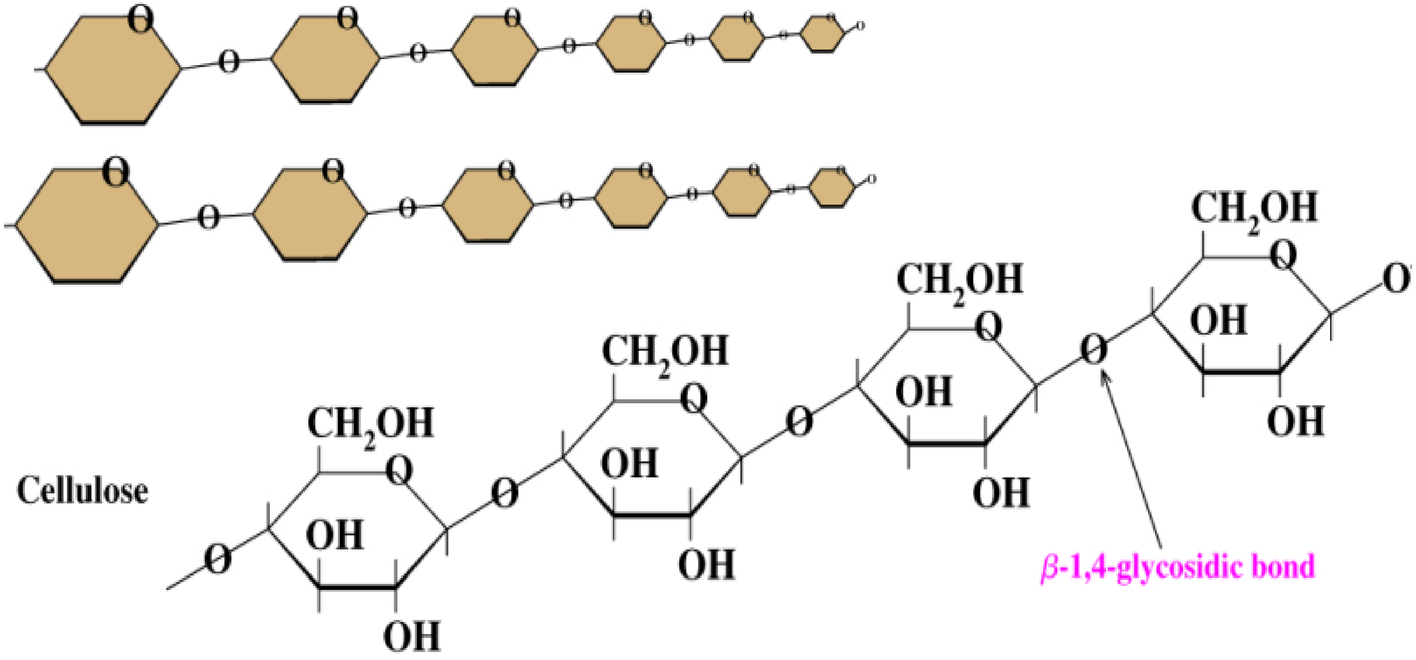
$$C_6H_{12}O_6 \xrightarrow{\text{Yeast}} 2C_2H_5OH + CO_2 + \text{energy}$$

Ethanol

Polysaccharides

Cellulose:

- Is a polysaccharide of glucose units in unbranched chains with β-1,4-glycosidic bonds (2200 glucose units).
- Has rigid structure (H-bond) and insoluble in water.
- Is the major structural material of wood & plants (cotton: 100%).
- Cannot be digested by humans because of the β-1,4-glycosidic bonds (needs an enzyme: β-glycosidase).



Polysaccharides

Cellulose:

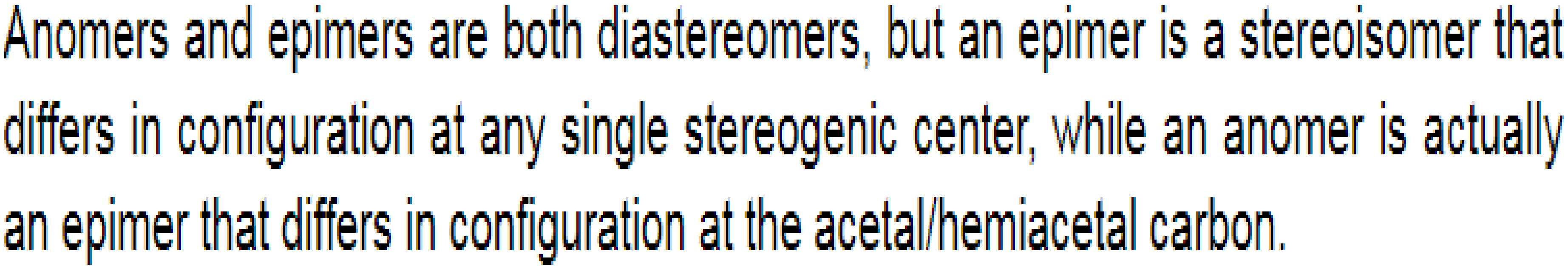
- Cellulose makes up the insoluble fiber in our diets.

- It passes through the digestive system without being metabolized.

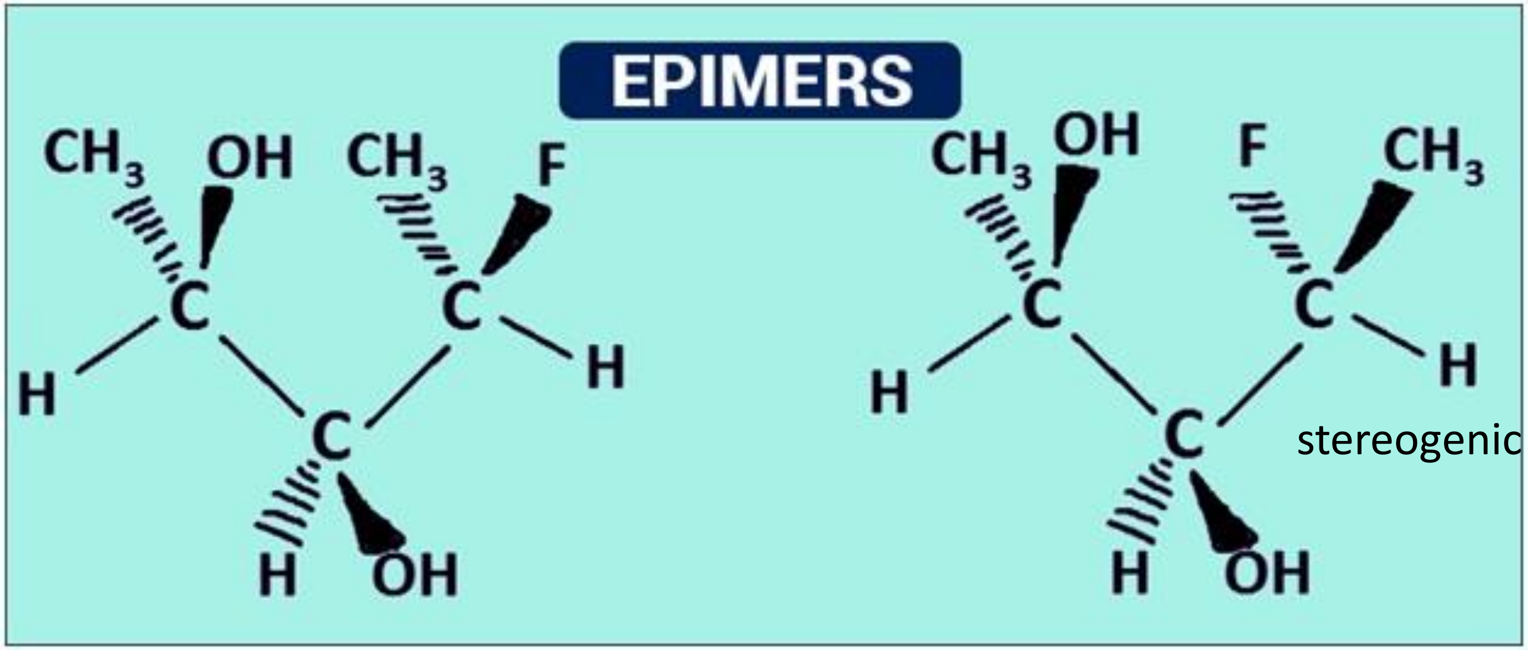
- Fiber is important in adding bulk to waste to help eliminate it more easily (even though it gives us no nutrition).

Epimers and Anomers

are both optical isomers that differ in the configuration at single carbon atom.



Anomers and epimers are both diastereomers, but an epimer is a stereoisomer that differs in configuration at any single stereogenic center, while an anomer is actually an epimer that differs in configuration at the acetal/hemiacetal carbon.

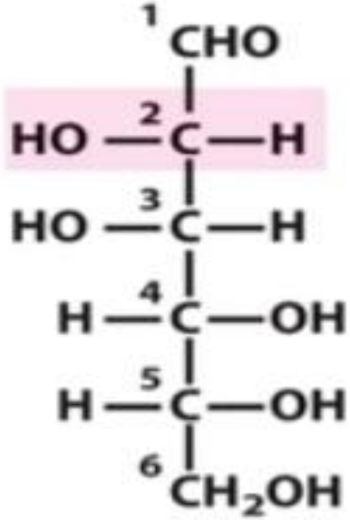


stereogenic center

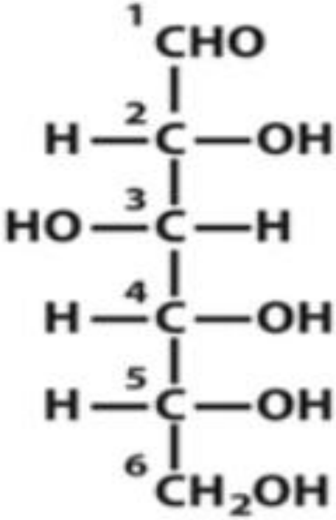
Epimers

Epimers are optical isomers that differ in the configuration of a single carbon atom

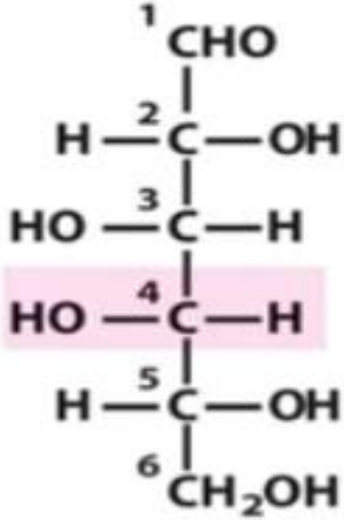
For example, D-galactose and D-mannose are epimers of D-glucose.



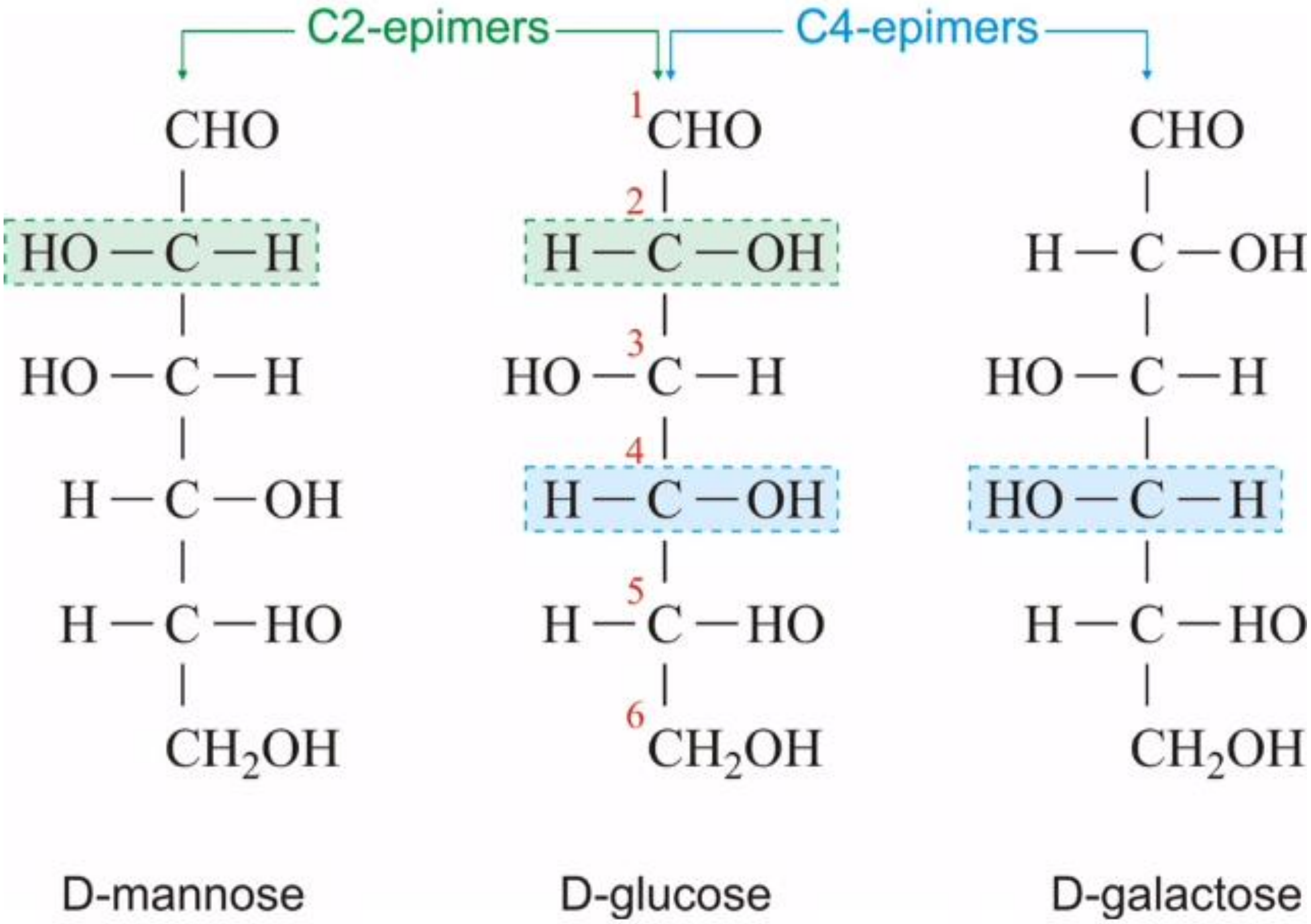
D-Mannose
(epimer at C-2)



D-Glucose

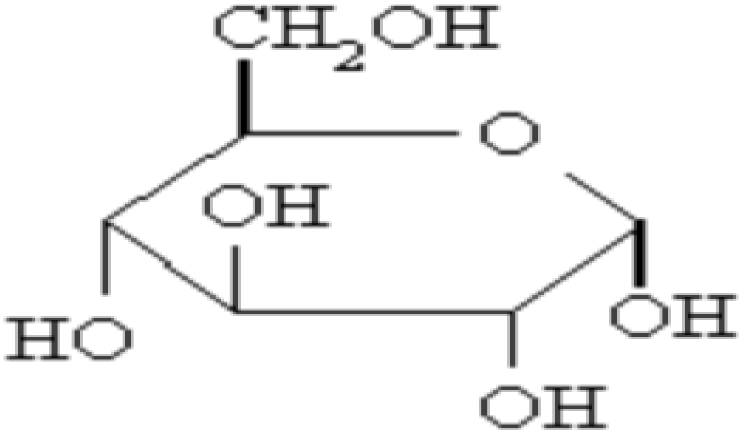


D-Galactose
(epimer at C-4)

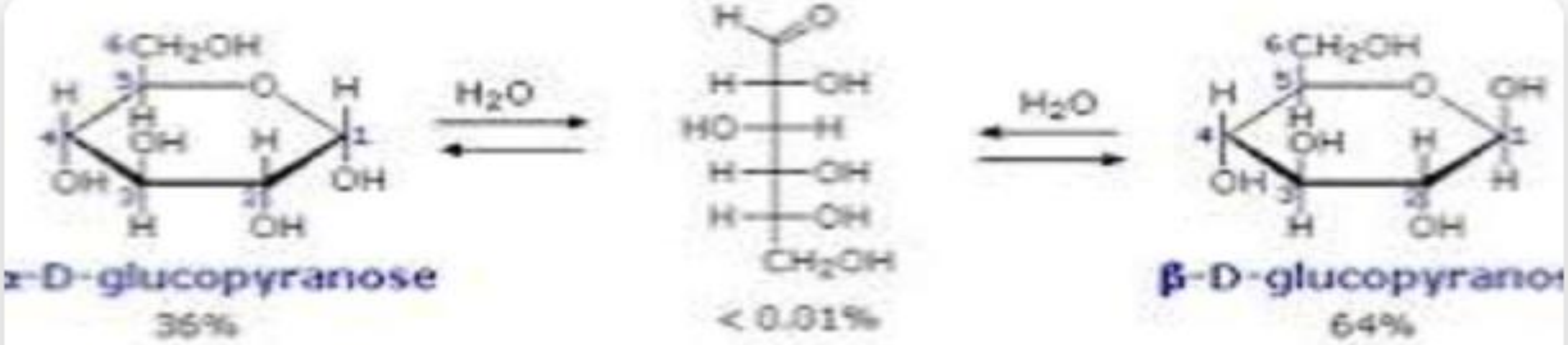

C2-epimers
C4-epimers
CHO
HO — C — H
HO — C — H
H — C — OH
H — C — HO
CH₂OH
1 CHO
2 H — C — OH
3 HO — C — H
4 H — C — OH
5 H — C — HO
6 CH₂OH
CHO
H — C — OH
HO — C — H
HO — C — H
H — C — HO
CH₂OH
D-mannose
D-glucose
D-galactose

Anomers

When a molecule such as glucose converts to a cyclic form, it generates a new chiral centre at C-1.



The carbon atom that generates the new chiral centre (C-1) is called the anomeric carbon.



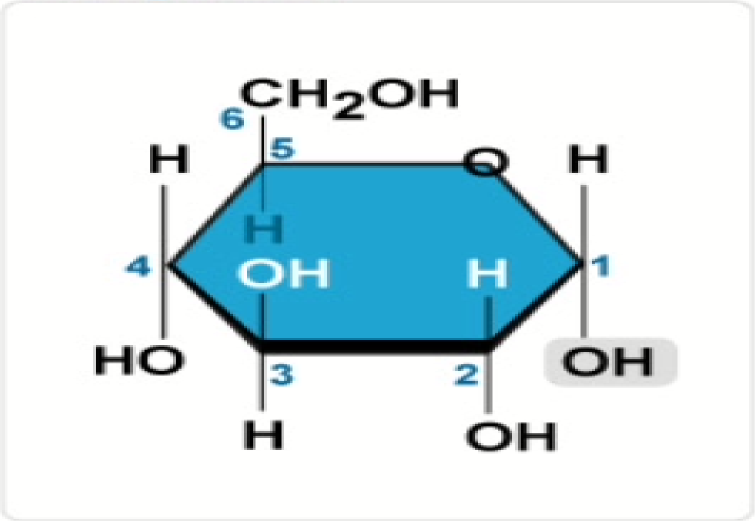
Mutarotation Equilibrium

"The hemiacetal carbon atom (C-1) becomes a new stereogenic center, commonly referred to as the **anomeric** carbon, and the α and β-isomers are called **anomers**.

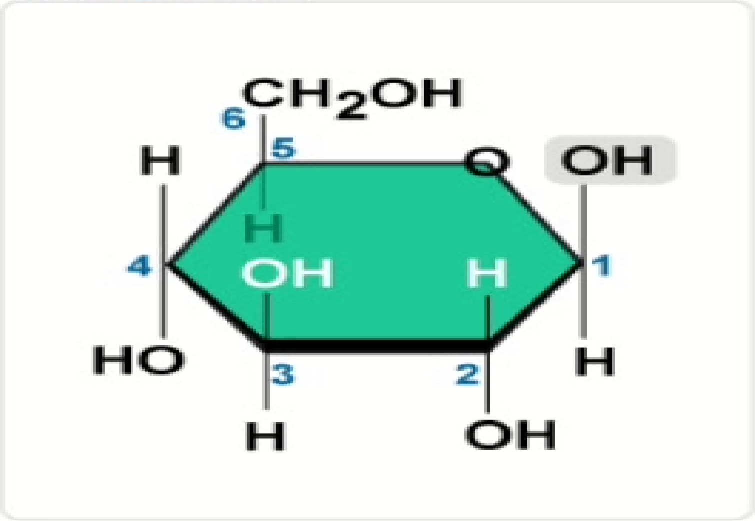
Anomers are special cases — they are epimers that differ in configuration only at the anomeric carbon.

For example, α-D-glucose and β-D-glucose are anomers.

α-D-glucose



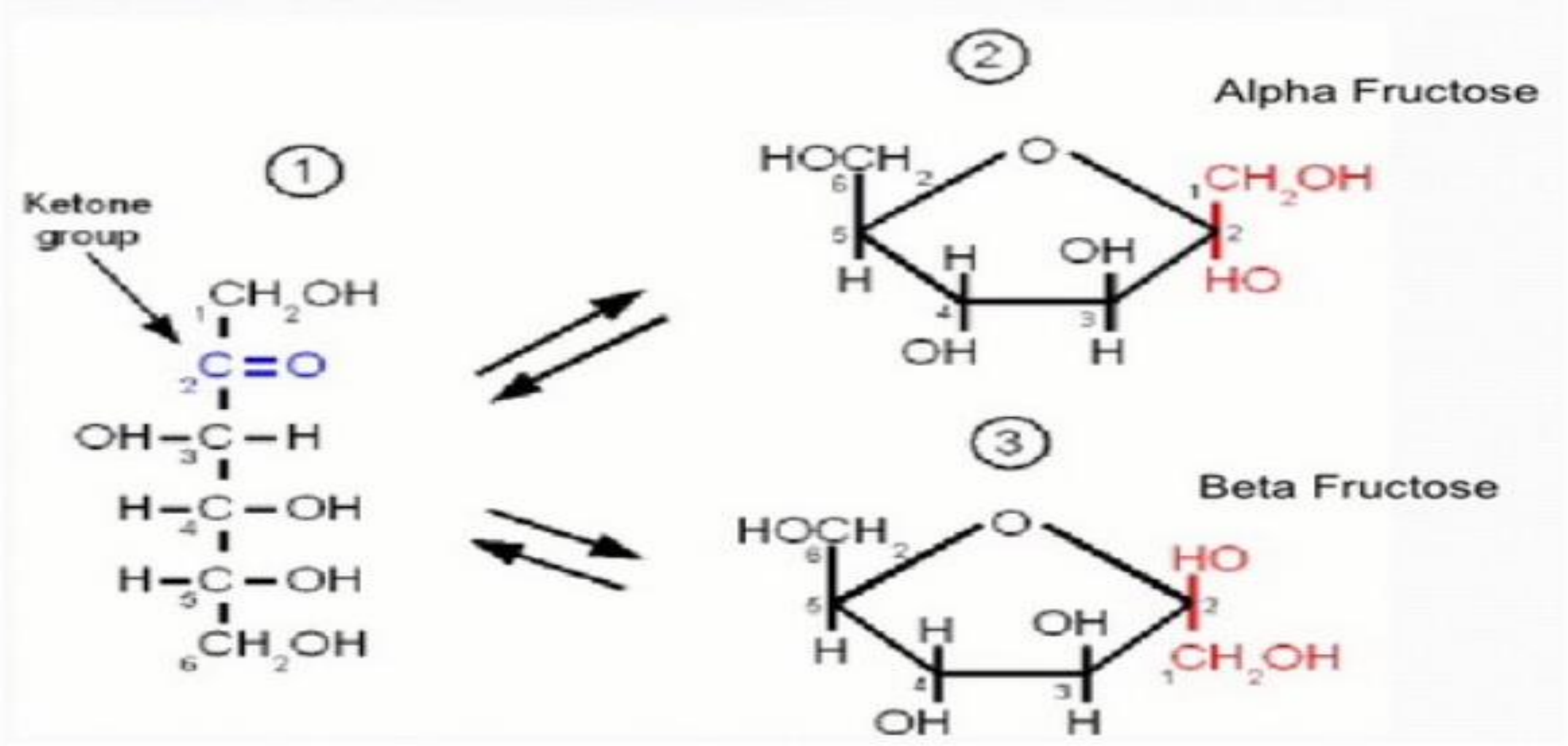
β-D-glucose



The α form has the anomeric OH group at $\mathrm{C{-}1}$ on the opposite side of the ring from the $\mathrm{CH_2OH}$ group at $\mathrm{C{-}5}$.

The β form has the anomeric OH group on the same side as the $\mathrm{CH_2OH}$.

Here, C-2 is the anomeric carbon.



α-D-Fructofuranose and β-D- fructofuranose are anomers.

Water soluble vitamins

Vitamin C

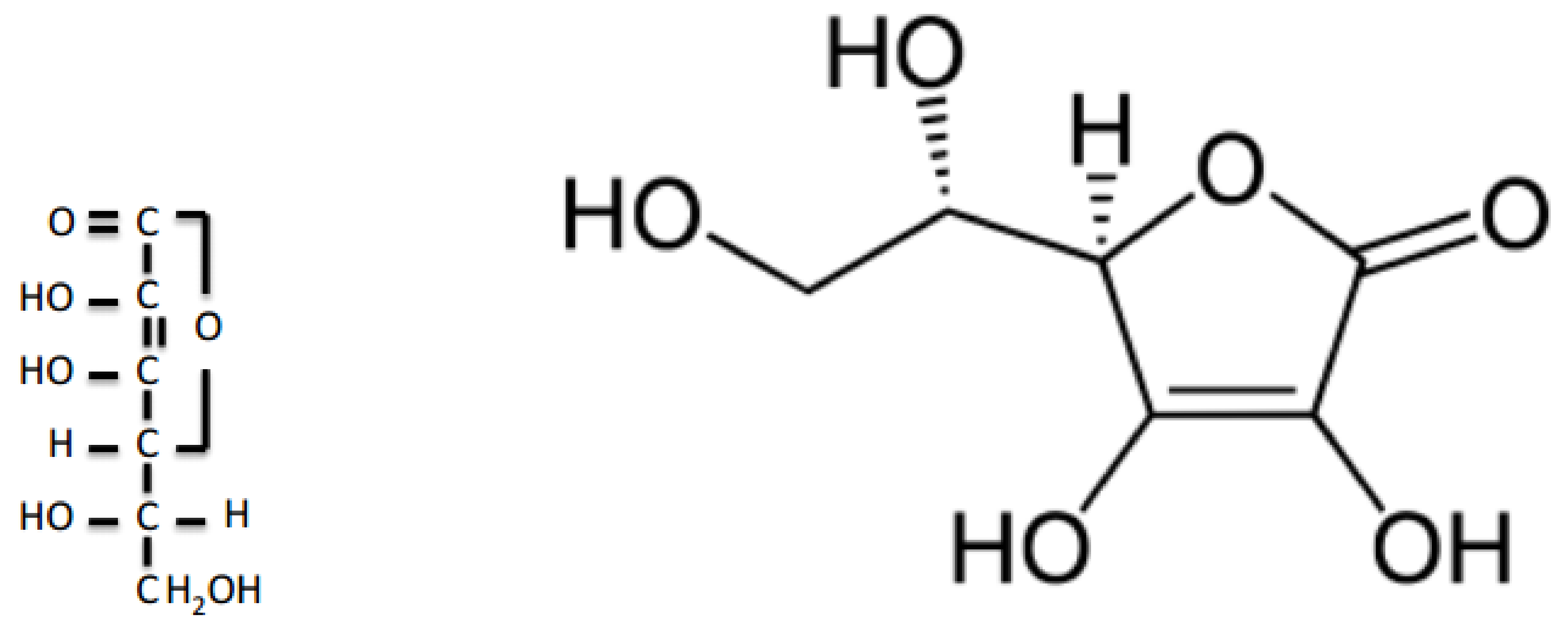
VITAMIN C

Vitamin C, also known as ascorbic acid and ascorbate, is a vitamin found in various foods and sold as a dietary supplement. It is used to prevent and treat scurvy. Vitamin C is an essential nutrient involved in the repair of tissue and the enzymatic production of certain neurotransmitters. It is required for the functioning of several enzymes and is important for immune system function. It also functions as an antioxidant.

- It is water-soluble vitamin.

- Most animals are able to synthesize all vitamin C they need from dietary sugars; but **humans are unable.**

- Also, animals are able to increase synthesis of vitamin C during stress but **humans' strictly depend on dietary sources, increases risk of deficiency during stress time.**


O = C
HO – C
O
HO – C
H – C
HO – C – H
CH$_2$OH
HO
H
O
HO
O
HO
OH

Natural Source of Vitamin C

Plum

Red pepper

Guava

Kiwifruit

Broccoli

Papaya

Strawberry

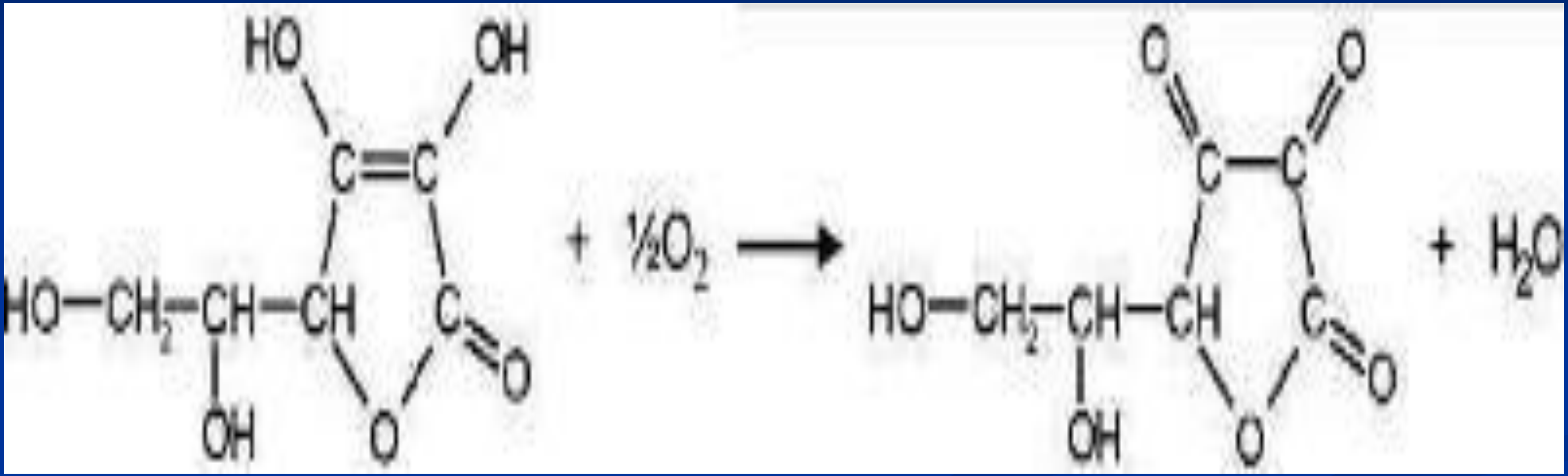
Orange

Lemon

Grapefruit

Mango

Vitamin C

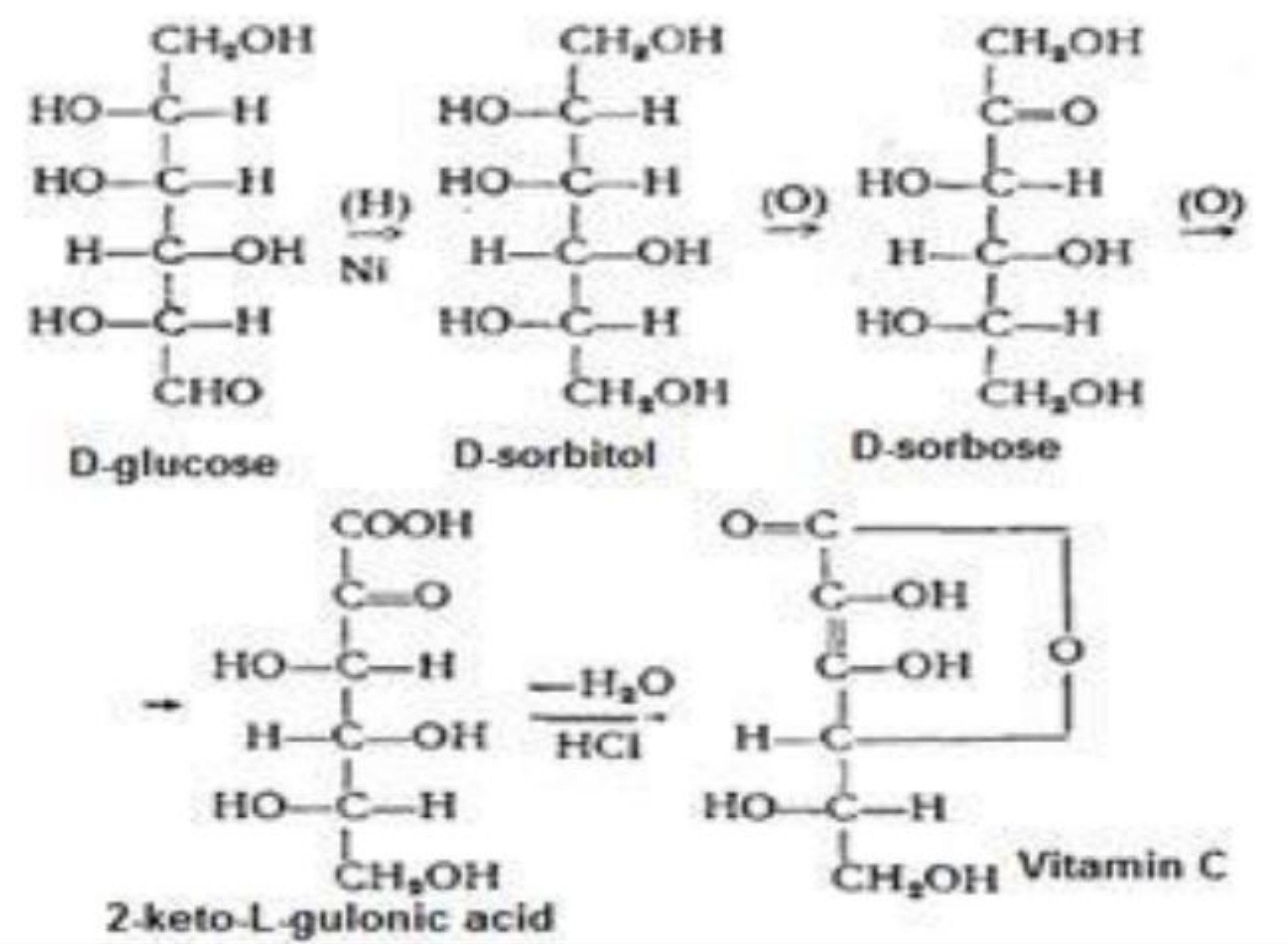


L- Ascorbic Acid
(Reduced Form)

L-Dehydroascorbic Acid
(Oxidised Form)

Physiologically active forms for vitamin C

RDA: Adults: 60 mg/day
Children: 30 mg/day


D-glucose
(H)
Ni
D-sorbitol
(O)
D-sorbose
(O)
2-keto-L-gulonic acid
—H₂O
HCl
Vitamin C

Chemistry and Stability of Vitamin C

- It is a weak acid and its salts called ascorbate.
- Unstable in alkaline pH, high temperature, and in the presence of oxygen or metals.
- The D-enantiomer of ascorbic acid shows no biological activity.
- Ascorbic acid is strong reducing agent, serves as an **anti-oxidant** and co-factor in hydroxylation reactions.
- Ascorbic acid is reversibly oxidized to L-dehydroascorbic acid and both L-ascorbic and L-dehydroascorbic acids are physiologically active forms for vitamin C.

Functions of Vitamin C

- Antioxidant function: It helps protect against oxidation by free radicals.
- Helps in detoxification and excretion of drugs : It maintains the enzyme systems in liver that detoxify and excrete drugs and toxic pollutants.
- Synthesis of collagen: The major component of connective tissue in skin, joints, muscles, bones ligaments, tendons, and cartilages.
- Involved in **carnitine** synthesis (along with niacin and vitamin B6) which is an amino acid required in breakdown of fats for energy.
- It is a cofactor in the synthesis of neurotransmitters as epinephrine , norepinephrine and serotonin.

- Important for healthy immune function: It is essential for optimum activity of WBCs and production of chemical mediators which direct the immune response. Vitamin C seems to increase T-lymphocyte activity, phagocyte function, leukocyte mobility, and possibly antibody and interferon production.

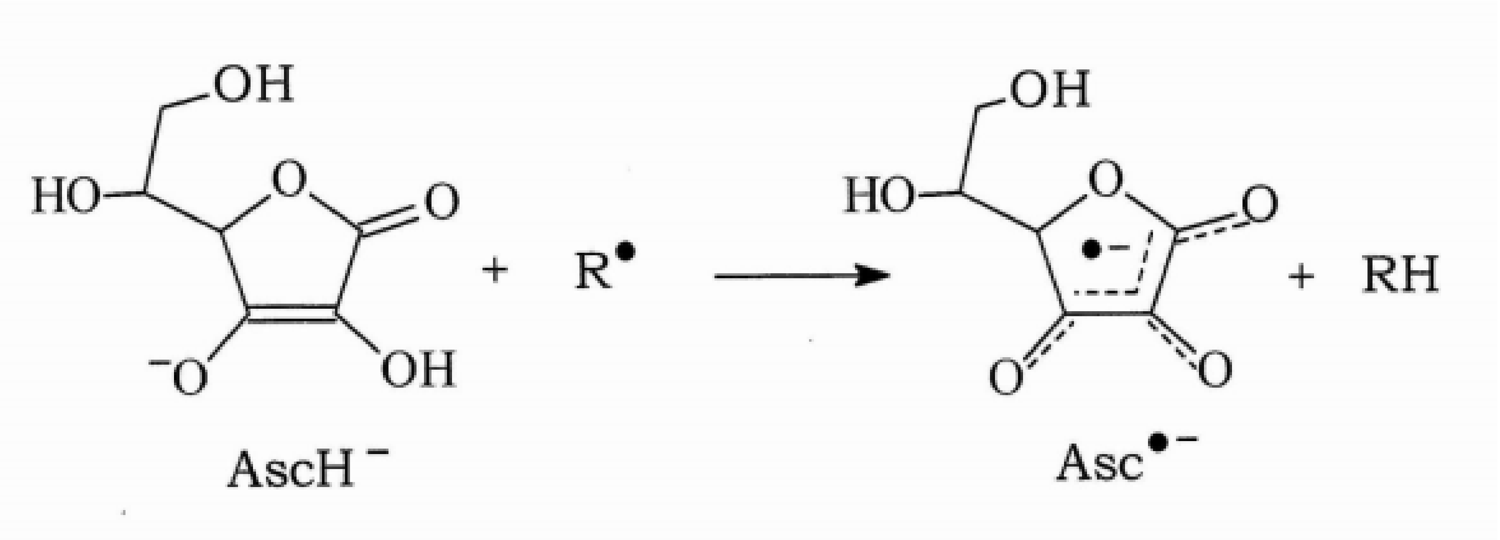
- Involved in cholesterol breakdown and excretion (cholesterol level increase if vitamin C status is impaired).

- Protection of folate and vitamin E from oxidation.

- Involved in control of histamine levels: When vitamin C status is poor → High levels of histamine → aggravate allergies, asthma, stomach ulcers, and certain psychiatric disorders.

Vitamin C is also a highly effective **antioxidant** =

it can absorb free oxygen radicals. Even in small amounts vitamin C can protect essential molecules in the body, such as proteins, lipids, carbohydrates, and nucleic acids (DNA and RNA) from damage by free radicals.



Symptoms of Vitamin C Deficiency

- **Scurvy:** Impaired connective tissue synthesis and fragility of blood vessels causes abnormal bleeding: easy bruising, subcutaneous hemorrhagic spots, inflamed and bleeding gums, joint stiffness and pain (due to bleeding into joints).

- Impaired wound healing.

- Build-up of keratin in hair follicles producing rough "sandpaper skin".
- Weakness, exhaustion, fatigue (due to impaired carnitine synthesis).
- Impaired immunity with increased risk of infection.
- Diminished antioxidant defenses: increase risk of cancer, heart disease, stroke, cataract.

Scurvy was common between Sailors, Pirates and others who were on ships for months without eating fresh fruits and

People at High Risk of Vitamin C Deficiency

1. **Increased physical stress** (e.g. infection, fever, burns, surgery, trauma to soft tissues or bones, and chronic illnesses such as hyperthyroidism, diabetes, rheumatoid arthritis, alcoholism, and kidney failure).
2. **Chronic use of drugs** such as aspirin and oral contraceptives impair vitamin C status.
3. **Older people, particularly** those with chronic illness, and aging.
4. **Periods of rapid growth**–childhood, adolescence, pregnancy, and lactation.
5. **Regular cigarette smoking** sharply increases breakdown and excretion of vitamin C.

Uses of Vitamin C in Prevention and Therapy

- **Enhance ability to fight infection:** Vitamin C stimulates the activity and ability of WBCs to destroy bacteria and viruses.

- **Treatment of cold and flu:** At doses of 1-2 g, it slightly increases body temp. → ↑ functions of WBCs and ↓ blood histamine → ↑ immune response and ↓ nasal and bronchial congestion → ↓ duration and symptoms of Cold and Flu.

- **Helps reduce risk of cancer:** particularly cancers of GIT, bladder, breast, pancreas, and uterus (antioxidant + enhancer for immune defenses against cancer and + helps detoxify carcinogenic food additives e.g. nitrates, pesticides, and other chemicals and heavy metals).

THANX

FATTY ACIDS AND LIPIDS

Lipids are heterogeneous group of molecules related to **fatty acids**. They are hydrophobic and are characterized by sparing solubility inwater but high solubility in non-polar solvents such as ether, benzene etc. The lipids may be classified into-

- **Simple or homolipids-**
    1) Fats and oils (triglycerol)
    2) Waxes
- **Compound or hetrolipids-**
    1) Phospholipids
    2) Shingolipids
    3) Glycolipid
    4) Lioprotein
- **Derived lipids-**
    1) Terpenes
    2) Steroids

Fatty acids- these are building blocks of lipids. They are monocarboxylic acid having a terminal carboxylate group. Since fatty acid are synthesized from 2C units. They consists of straight chain hydrocarbons with even number of C- atoms (4-30). The chain maybe **saturated** containing only single bond; or they maybe **unsaturated** having 0-6 double bonds mostly in 18-24C acids. Fatty acids are varied and may have acetylinic bond, epoxy, hydroxyl and keto group or cyclopropene and cyclopentene rings.

Saturated fatty acids- are generally solids at room temperature due to large number of carbon atoms. In plants occur in palm oil. They have hydrophobic tail of zig-zag configuration and because of single bond they are free to rotate and are thus more flexible and elongated. They form a fully extended and stable configuration in which the steric hindrances of neighboring atoms is minimized. These molecules can thus pack together tightly to form a nearly crystalline structure. General formula is $C_nH_{2n+1}COOH$.

Lauric acid (12 C) $CH_3(CH_2)_{10}COOH$ – members of Lauracea family

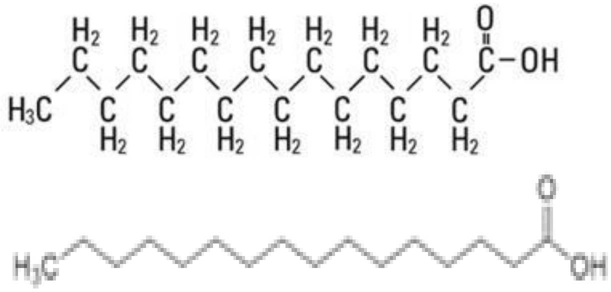
Myristic acid (14 C) $CH_3(CH_2)_{12}COOH$ – members of Myrtaceae family

Palmitic acid (16 C) $CH_3(CH_2)_{14}COOH$ – palm oil

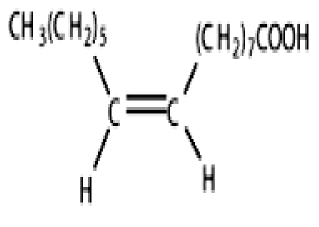
Stearic acid (18 C) $CH_3(CH_2)_{16}COOH$ - palm oil

Arachidinic acid (20 C) $CH_3(CH_2)_{20}COOH$ – peanut oil

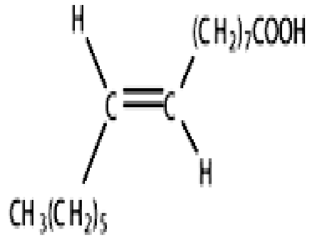
Palmitic acid
$C_{16}H_{32}O_2$



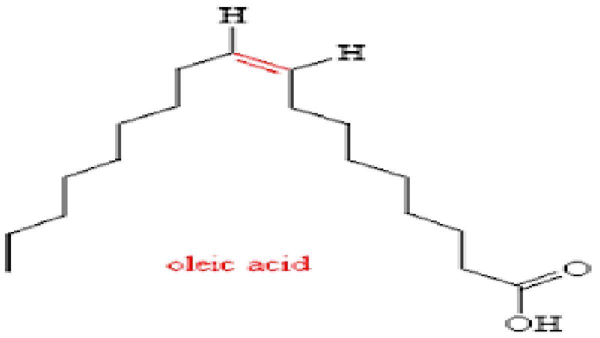
Unsaturated fatty acids- presence of double bond. Lowers melting point and therefore lipids with unsaturated acids are mostly oils at room temperature. The number of double bond show the degree of unsaturation. Double bonds produce rigid bends in the HC tail resulting in geometric isomerism. Most common are the less stable ‘cis’ form rather than ‘trans’ forms which are more stable.



cis fatty acid



trans fatty acid

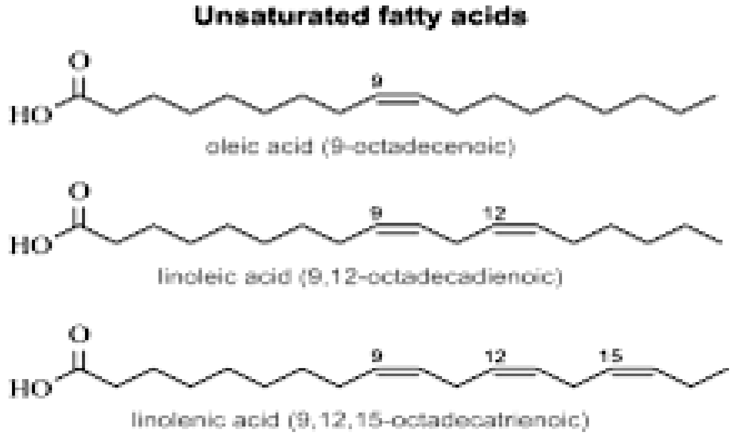


Fatty acids with double bonds have kinks in their structure and therefore cannot pack together like saturated FA and their interaction with each other is poor. These double bonds thus give a large bulky structure to fatty acids and thus require less thermal energy to disorder them resulting in lower melting points and therefore lipids with unsaturated acids are mostly oils at room temperature. Plants and animals contain polyunsaturated acids while bacteria has no polyunsaturated fatty acids except the unsaturated acid vaccenic acid eg. $CH3(CH_2)_5$-$CH=CH(CH_2)_9$-COOH. The double bond system may be

1) **Non- Conjugated double bond system**- where doble bond are interrupted by methylene grop and arrangement is a pentadine structure eg. linoleic acid CH_2-$CH=CH$-CH_2-$CH=CH$-CH_2
2) **Conjugated double bond system**- have triene system as in α-elaeostearic acid (….oil……) $CH_3(CH_2)CH=CHCH=CHCH=CH(CH_2)_7COOH$.

According to number of double bonds unsaturated acid may be:

1. **Monoenoic or monoethenoid acid-** $C_nH_{2n-1}COOH$ (18C); oleic acid $CH_3(CH_2)$ $CH=CH(CH_2)_7COOH$- palm oil; erucic acid (20 C) $CH_3(CH_2)_4CH=CH(CH_2)_{11}COOH$ - mustard oil.
2. **Dienoic or diethenoid acid** - $C_nH_{2n-3}COOH$ (18C); Linoleic acid in cotton seed, linseed and soybean $CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
3. **Trienoic or triethenoid** acid - $C_nH_{2n-5}COOH$ (18 C); Linolenic acid in palm and linseed oil $CH_3CH_2CH_{11}CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$.
4. **Tetraenoic or Tetraethenoid acid -** $C_nH_{2n-7}COOH$ (20); Arachidonic acid in peanut oil. $CH_3(CH_2)_4CH=CHCH_2CH=$ $CHCH_2CH=CHCH_2CH=CHCH_2(CH_2)_3COH$.

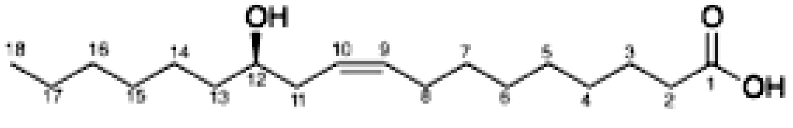


oleic acid (9-octadecenoic)

linoleic acid (9,12-octadecadienoic)

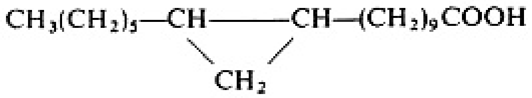
linolenic acid (9,12,15-octadecatrienoic)

Unusual fatty acid- hydroxy or oxygenated fatty acid eg. ricinoleic acid (18C) castor oil with OH group on C_{12}.



Ricinoleic acid in castor oil

Cyclic fatty acid – example – lactobacillic acid with a cyclopropyl group and methylene group across the double bond of vaccenic acid.



$$CH_3(CH_2)_5-\underbrace{CH-CH}_{CH_2}-(CH_2)_9COOH$$

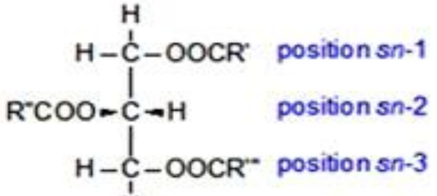
Lactobacillic acid

NOMENCLATURE :

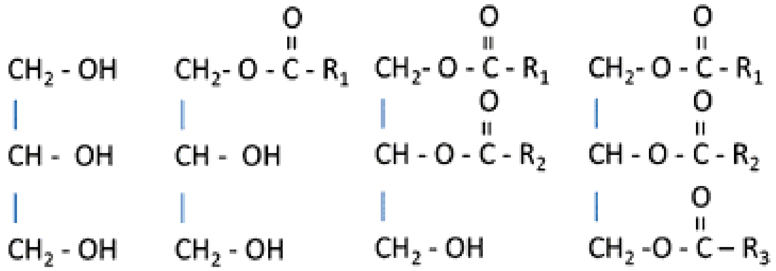
The fatty acids are numbered at the end. First we write no of C atoms then no of double bonds and finally position of first C of double bond counting from carboxylic end. Thus palmitic acid is 16:0 , oleic acid 18:1(9), linoleic acid 18:2 (9,12); linolenic acid 18:3(6+,9+,12); arachidonic acid 20:4 (5,8,11,14).

SIMPLE LIPIDS

These are esters of one or more fatty acids and an alcohol mostly glycerol generically known as **acylglycerols**. Most common are triacylglycerol but mono and diacylglycerol are also common. Because the polar OH group and the polar carboxyl of fatty acid are bound in ester linkage triacylglycerol are non-polar hydrophobic molecules. They have lower specific gravity than water hence they float on it. They are used as fuels more than carbohydrates as carbon atoms in fats are more reduced and therefore oxidation of fats gives more energy. They are present as fsimple ats and oils and complex waxes. When the glycerol is esterified with fatty acid then C-2 becomes asymmetric centre and the 2nd hydroxyl group of glycerol is always show to left of C-2 while C atom above C-2 is called C-1 and below C-2 is C-3. This is stereo specific numbering (SN). Accordingl to the no. of FA esterified to glycerol they may be called mono-,di- or triacylglyceral:



Fischer projection of a triacyl-sn-glycerol



Fats and oils- These are the triglycerides or triacylglycerols. They are esters of three fatty acids and glycerol (trihydric alcohol) formed by loss of three H_2O molecules. These are non polar and hydrophobic immiscible in water with general formula $CH_3(CH_2)_nCOOH$ where n= even number. They are most abundant storage form and serve as fuel having high calorie count. forming 95% of dietary lipids. They may exist as either Fats which are solid at room temperature with high proportion of saturated fatty acids resulting in high melting point as in animal triacylglycerols. Oils have low melting point due to presence of unsaturated fatty acid and therefore liquid at room temperature as in plant. Those with single type of fatty acid as simple triacylglycerol eg tristearylglycerol or mixed with two types of fatty acids eg. dietary fat

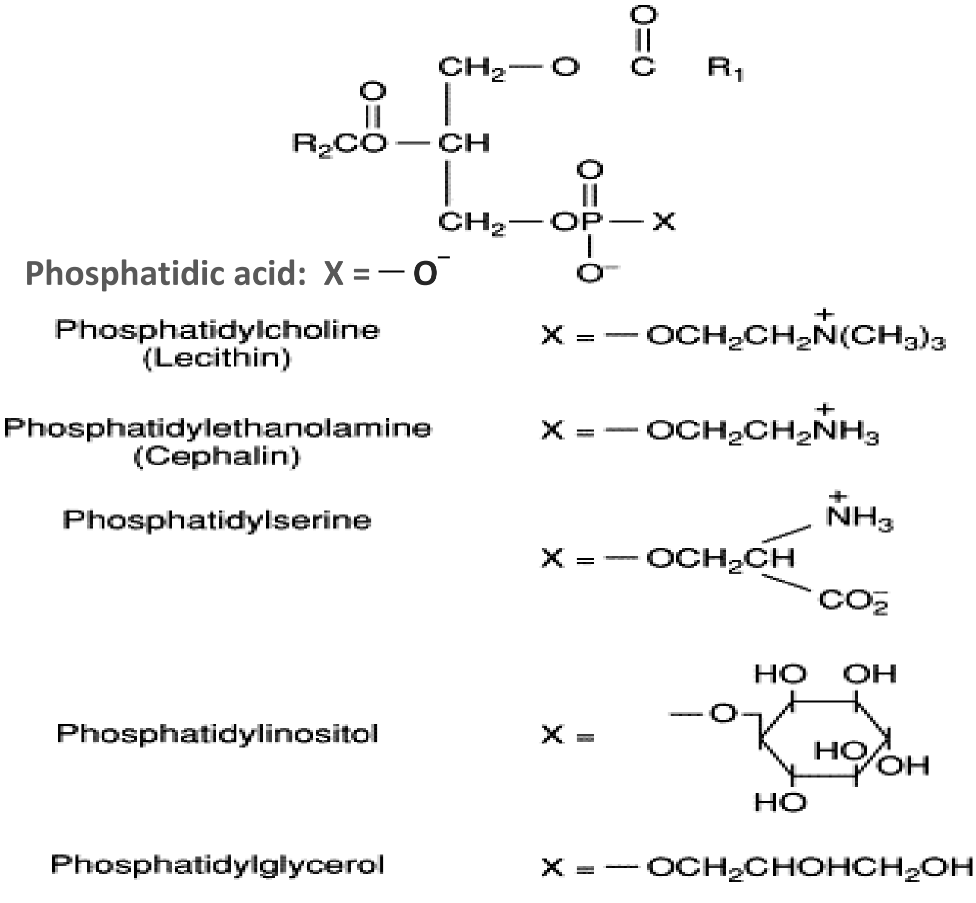
Waxes- occur as protective coating on fruits and leaves or secreted by insects (beewax). These are mixtures of long chain alkanes with odd number of carbon atom C_{25}-C_{35} and oxygenated derivative such as secondary alcohols and ketones. They are insoluble in water and are chemically enert resistant to atmospheric oxygen and therefore protect plants from water loss and abrasive damage. Mostly they are fatty acyl ester of long chain alcohols of long length. The myricyclic alcohol of beewax has 30C ($C_{30}H_{61}OH$-- triacontanol) and is myricyl palmitate RCOOR' R is C_{17}-C_{29} C atoms and R' C_{18} – C_{30} . Sperm whale wax is composed of palmitic acid esterified with hexacoscenol ($C_{26}H_{53}OH$). This was primary wax source for many years but now *Simmondsia chinensis*_a desert plant has large oxygen wax esters as storage lipid in its seed. These wax esters act as superior machine lubricants.

COMPOUND LIPIDS

These are esters of fatty acids containing other groups in additional to fatty acids and alcohols:

1. **Phospholipids-** are most abundant membrane stored in large amount lipid being their structural component and never stored in large amounts. These lipids contain a phosphorus atom as phosphoric acid. They differ from triglycerides in having one hydrophilic polar head formed by an ester linkage between 3rd OH group of glycerol and phosphoric acid (to which some other group maybe attached) and 2 hydrophobic non- polar tails of long chain fatty acid. They are thus called polar lipids and sometimes amphipathic lipid and they have negative charge on phosphoric acid at pH 7.0 The group attached to phosphoric acid may also be changed.

   Phosphatidic acid is most simple phospholipid and have two molecules of fatty acid esterified to glycerol with phosphoric acid at terminal end. This polar phosphoryl group generally forms a second ester with some alcohol may be amino alcohol, ethanol amine or its methylated derivative choline, or its carboxylated serine.



Lecithin – Phosphatidyl choline has methylated derivative of the alcohol, found in soybean and yeast. This is major constituent of all membrane lecithin helps in transport and utilization of lipids accumulation results in fatty liver. It can be broken down by lecithinase resulting in haemolysis of blood (Snake venom). It is yellowship grey soluble in ether alcohol, on exposure it absorbs water and darkens to form a dark greasy wax.

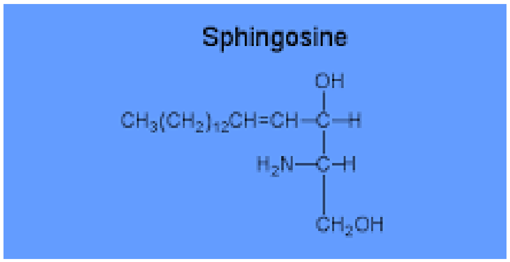
Cephalins – Found in soybean oil is association with lecithin phosphatidyl ethanol amine has the amino alcohol ethanol amine forming ester with phosphoric acids. Positively charged generally R` is palmitic or stearic or poly unsaturated acid.

Phosphatidyl serine – is neutral having amino- and carboxy- groups of serine attached to the amino group of ethanol.

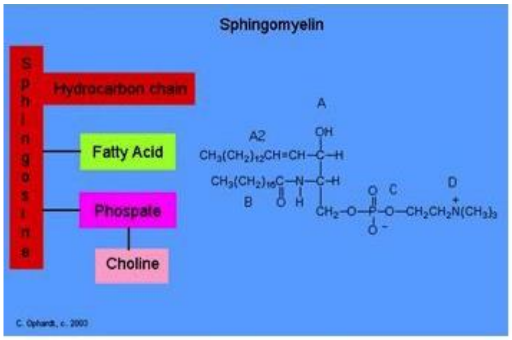
Plasmalgen - not significant in plant but in brain. Here first fatty acid is replaced by unsaturated unsaturated ether. Polar group may be choline and serine

Phosphatidyl inositol - Present in brain and soybean. Important because of the role in transport process of cells. Here cyclic hexahydroxy alcohol called myoinositol replace the base.

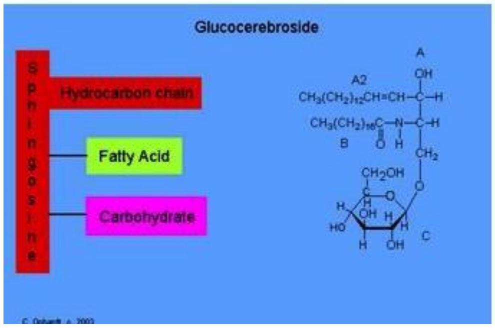
2. **Sphingolipids-** diverse group of complex lipids composed of derivatives of sphingosine now called 4-sphingenine which is a long chain amino alcohol formed from palmityl CoA and serine found in brain nerve and tissue. The sphingosine has a long chain fatty acid attached to it amino acid by amide linkage. This is called ceramide, basic structure and in association with phosphoryl choline it forms sphingomyelin. Glycosphingolipids in which amino alcohol is replaced by sugars. Replacement of phosphoryl choline in sphingomyelin by β-D-galactosyl group. Forms cerebroside.



Sphingosine has three parts, a three carbon chain with two alcohols an amine and a hydrocarbon chain

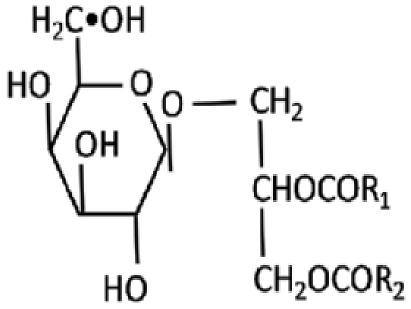


Sphingomyelin has a sphingosine backbone and a fatty acid is attached to the amine through amide bond. Phosphate is attached through a phosphate ester bond, and through a second phosphate ester bond to choline.

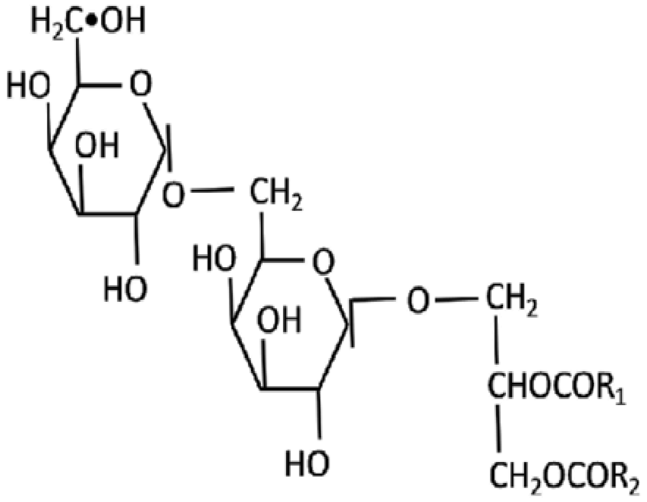


Phosphoryl choline is replaced with a sugar

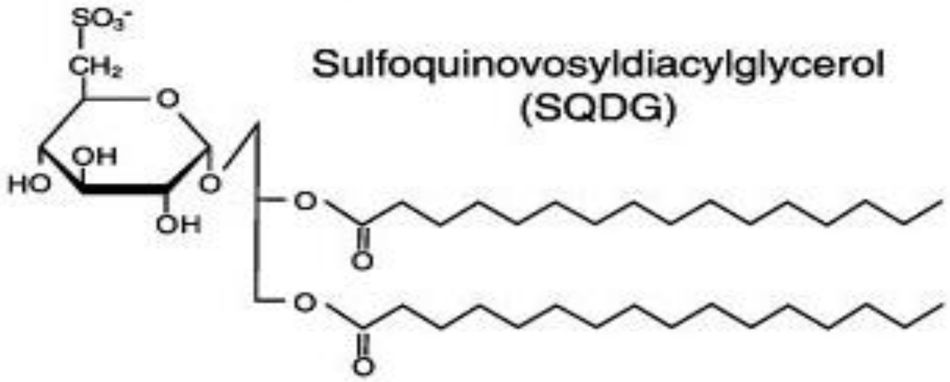
3. **<u>Glycolipids</u> -** these are primarily amphipathic carbohydrates – glyceride derivatives and do not contain phosphate. These include galactolipids and sulpholipid found primarily in chloroplast membranes



Monogalactosyldiacylglycerol (MGMG)



Digalactosyldiacylglycerol (DGMG)



Sulfoquinovosyldiacylglycerol (SQDG)

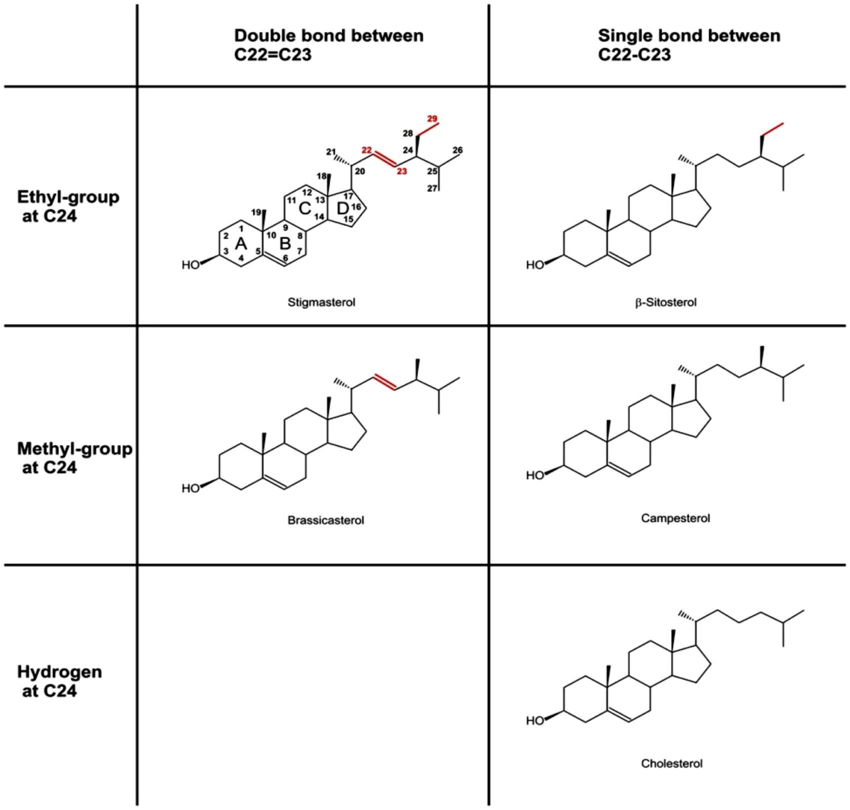
4. **<u>Lipoproteins-</u>** important component of cell membrane of mitochondria, endoplasmic reticulum, nuclei, chloroplast lamellae and play important role in ETS. Lipids maybe triacylglycerol phospholipid or cholesterol ester. The protein is made up of non-polar aminoacids and bonding is due to hyphobic interaction between proteins and lipids. In the plasma the lipids are associated with proteins in the form of lipoproteins. Classified in to 4 types: The lipoprotein of lowest density the chylomicrons are the largest in size and contain the most lipids and smallest percentage of proteins high density lipoproteins (HDL) are smallest in size and have highest percentage of protein and lowest of triacylglycerols.

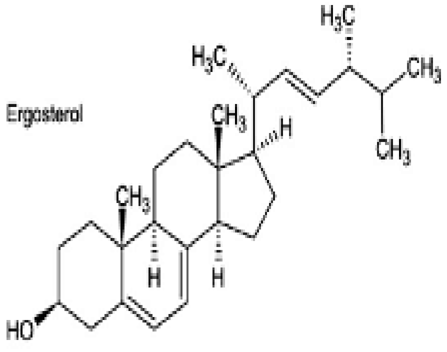
	Chylomicrons	**VLDL**	**LDL**	**HDL**
Diameter (mm)	500-1000	30-70	20-25	10-15
Protein %	1-2	10	25	33
Triacylglycerol	53	50	10	8
Cholesterol and cholesterol ester	8	22	46	30
Phospholipid	7	18	22	29

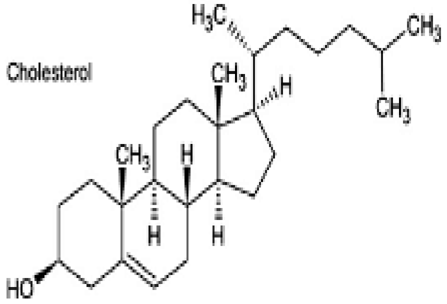
Each has a neutral lipid core of triacylglycerol and cholesterol ester. Around this core is a layer of protein , phospholipid and cholesterol. These lipoprotein serve as mode of transport of triacylglycerol and cholesterol enter from intestine to other tissues in the body. The cholesterol ester is derived from cholesterol and phosphatidycholine on the surface of high density lipoprotein by lecithin cholesterol acyl transferage (LCAT). Cholesterol ester is the storage form of cholesterol in cells and formed by cholesterol and acyl CoA by acyl CoA cholesterol acyl transferase (ACAT).

DERIVED LIPIDS

1. Steroids- polycyclic compound which is unsaponifiable, cannot be hydrolysed. They have a basic structure derived from fully saturated ring system sterane or perhydrocyclopentanephenanthrene which has 3 complex ring fused in a linear or phenanthrene manner and a terminal cyclopentane ring. The presence of C_{8}- C_{10} chain at position 17 and a OH group at 3 characterizes a large number of steroids called sterols. Sterols or steroid alcohol occurring in membrane as transporters of lipids and are soluble in organic solvents. Cholesterol is the best known sterol found in animals. Esterification of one group of cholesterol gives cholesteryl ester which are storage forms. Ultraviolet radiations give rise to Vit D. Deriatyives of cholesterol occur as vitamins such as vitamin E α-tocopherol in wheat germ oil, naphtoquinone/phylloquinone (Vit K). In plants sterols are abundantly present as- stigmasterol- from soybean and wheat germ oil, sitosterol- higher plants, spinasterol- spinach and cabbage.

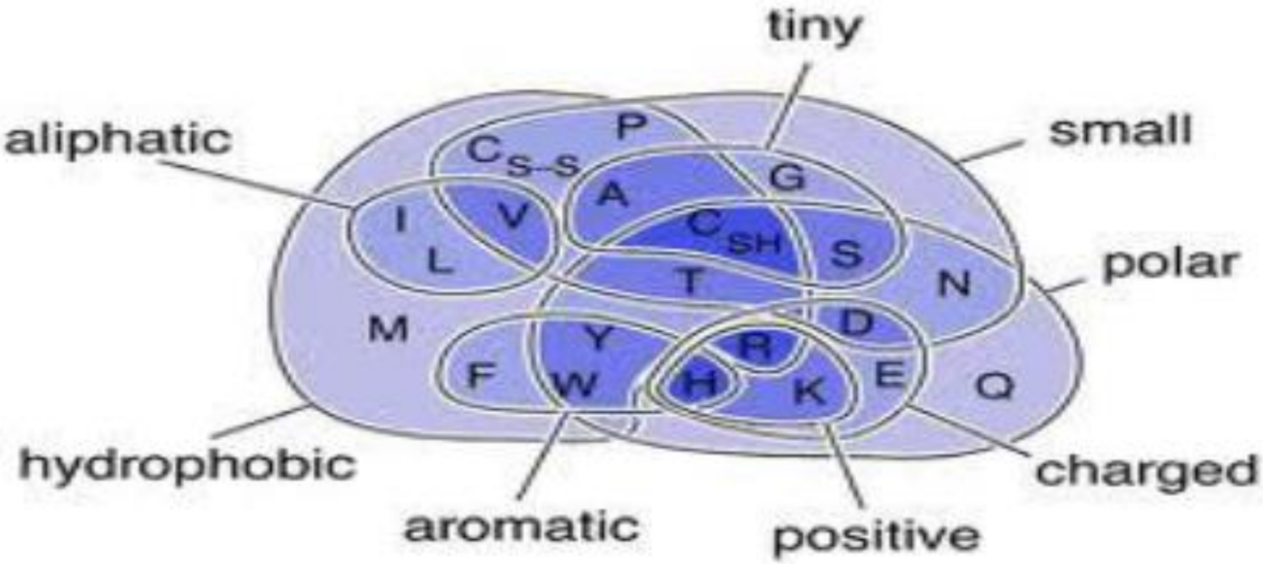




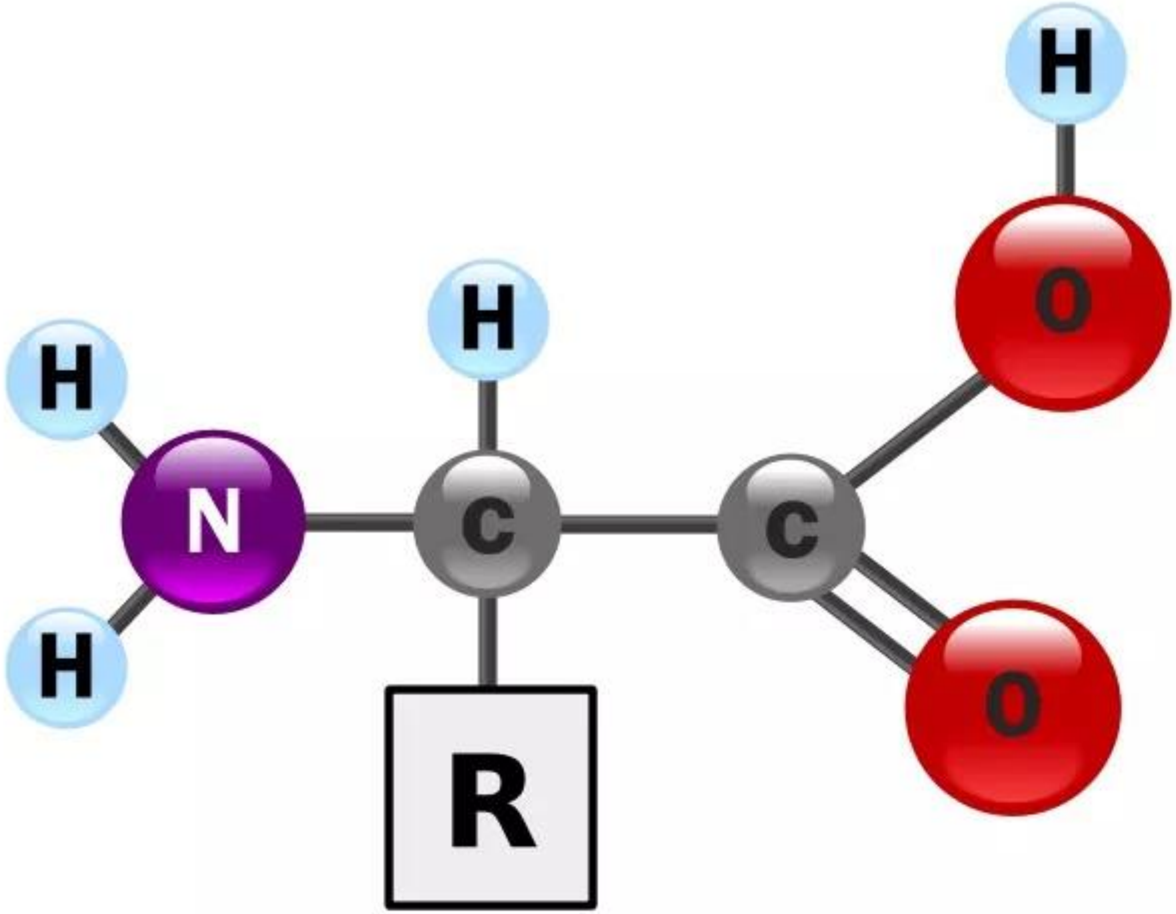


2. **Terpenes-** found in plants and made up of repeating unit of isoprene units derived from isopentyl pyrophosphate. Monoterpene consists of 2 isoprene units formed in higher plants. Their oxygenated derivative occur as essential oils e.g myrcene (oil of bay), geranoil (rose oil), limonene (lemon oil), menthol (peppermint oil). Diterpenes, triterpenes and tetraterpenes include important compounds like gierellins, phytol ring structure, carotenoids, xanthophylls, flavonoids,plant pigments, chalcone and stilbenes.

Amino Acids (AA)



Amino acids are organic compounds that contain amine (–NH_2) and carboxyl (–COOH) functional groups, along with a side chain (R group) specific to each amino acid.



Amino acid, any of a group of organic molecules that consist of a basic amino group (—NH2), an acidic carboxyl group (—COOH), and an organic R group (or side chain) that is unique to each amino acid. The term amino acid is short for α-amino [alpha-amino] carboxylic acid. Each molecule contains a central carbon (C) atom, called the α-carbon, to which both an amino and a carboxyl group are attached. The remaining two bonds of the α-carbon atom are generally satisfied by a hydrogen (H) atom and the R group.

Amino acids are organic compounds composed of nitrogen, carbon, hydrogen and oxygen, along with a variable side chain group.

Your body needs 20 different amino acids to grow and function properly. Though all 20 of these are important for your health, only nine amino acids are classified as essential (1Trusted Source).

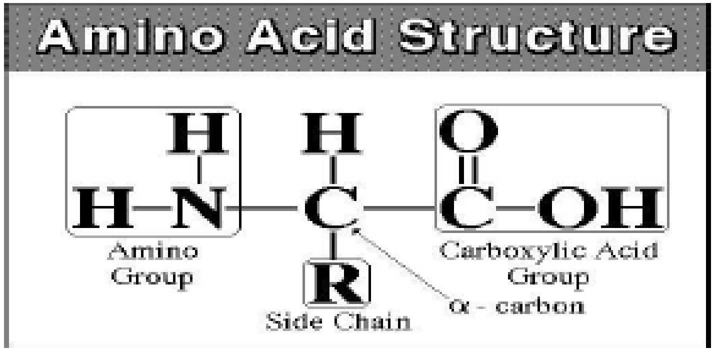
These are histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan and valine.

Unlike nonessential amino acids, essential amino acids can’t be made by your body and must be obtained through your diet.

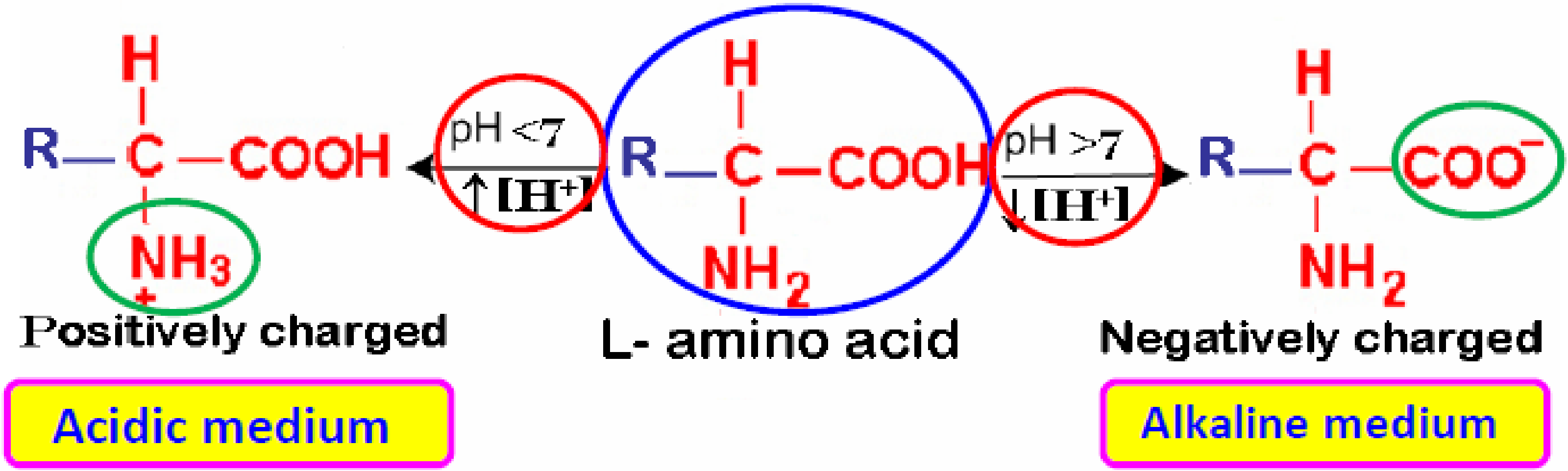
The best sources of essential amino acids are animal proteins like meat, eggs and poultry.

Ionic properties of amino acids

- Amino acids contain acidic (COOH) and basic (NH2) groups.



- Amino acids are usually ionized at physiologic pH
- Therefore, amino acids have amphoteric properties:
  - In acidic medium ; the amino acid is positively charged, so it behaves as a base (proton acceptor).
  - In alkaline medium ; the amino acid is negatively charged, so it behaves as an acid (proton donor).



$$R-\overset{H}{\underset{NH_3^+}{C}}-COOH \xleftarrow[\uparrow[H^+]]{pH<7} R-\overset{H}{\underset{NH_2}{C}}-COOH \xrightarrow[\downarrow[H^+]]{pH>7} R-\overset{H}{\underset{NH_2}{C}}-COO^-$$

Positively charged

L- amino acid

Negatively charged

Acidic medium

Alkaline medium

Amino Group

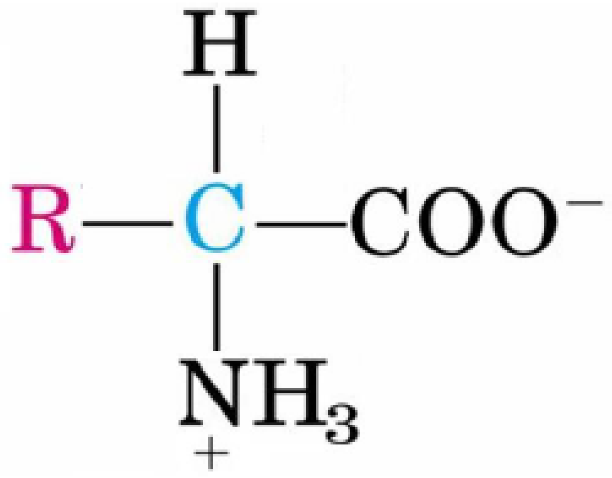
$$NH_3^+ \underset{\text{lower pH}}{\overset{\text{higher pH}}{\rightleftharpoons}} NH_2$$

Carboxyl Group

$$COOH \underset{\text{lower pH}}{\overset{\text{higher pH}}{\rightleftharpoons}} COO^- + H^+$$

Isoelectric point or "pI"

- At certain pH "specific for each amino acid" the amino acid can exist in the dipolar from: fully ionized but with no net electric charge.
- The characteristic pH at which the net electric charge is zero is called the Isoelectric point or "pI".
- The amino acid at the isoelectric pI is called "Zwitter Ion" and is electrically neutral (not migrating in an electric field).



$$R-\overset{\displaystyle H\\|}{\underset{\displaystyle |\\ \overset{+}{N}H_3}{C}}-COO^-$$

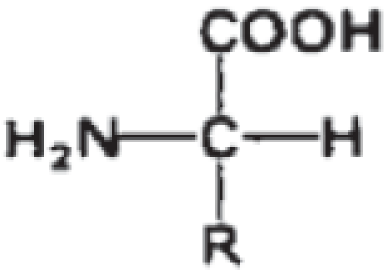
Zwitter ion

2-Configuration and Optical Activity

-Amino acids, except for glycine, have at least one chiral center and, hence, are optically active.

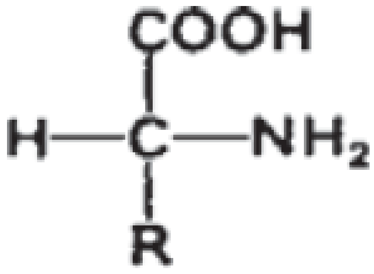
-All amino acids found in proteins have the same configuration on the α-C-atom: they are considered L-amino acids (with L-cysteine an exception; it is in the (R)-series).

-D-amino acids (or (R)-amino acids) also occur in nature, for example, in a number of peptides of microbial origin:



$$\begin{array}{c} COOH \\ | \\ H_2N-C-H \\ | \\ R \end{array}$$

L-Amino acid
(S)-Amino acid



$$\begin{array}{c} COOH \\ | \\ H-C-NH_2 \\ | \\ R \end{array}$$

D-Amino acid
(R)-Amino acid

3-Solubility

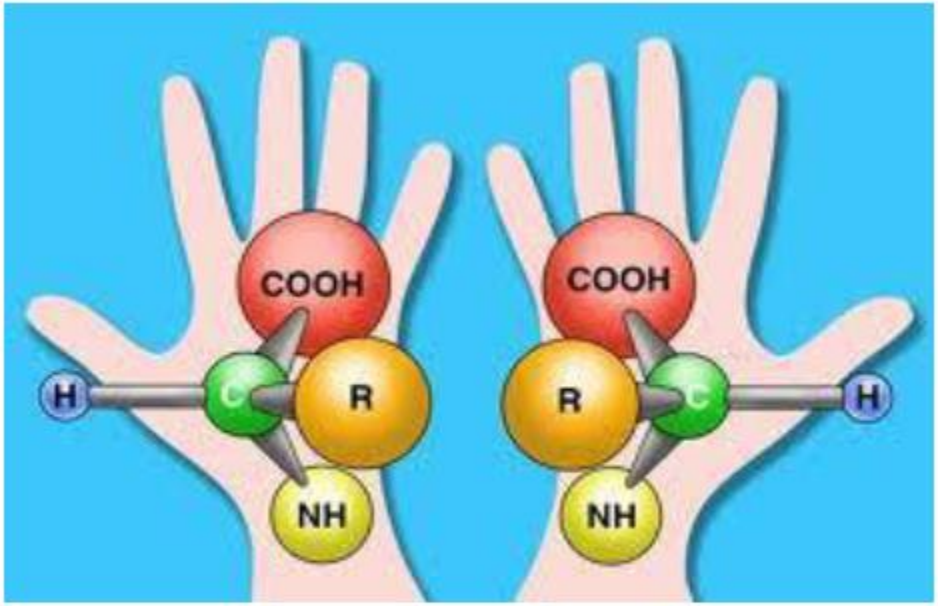
-The solubilities of amino acids in water are highly variable. Besides the extremely soluble proline, hydroxyproline, glycine and alanine are also quite soluble.

-Other amino acids are significantly less soluble, with cystine and tyrosine having particularly low solubilities.

-Addition of acids or bases improves the solubility through salt formation.

-The presence of other amino acids also brings about an increase in solubility. Thus, the extent of solubility of amino acids in a protein hydrolysate is different than that observed for the individual components.

Chemical Reactions of Amino Acids

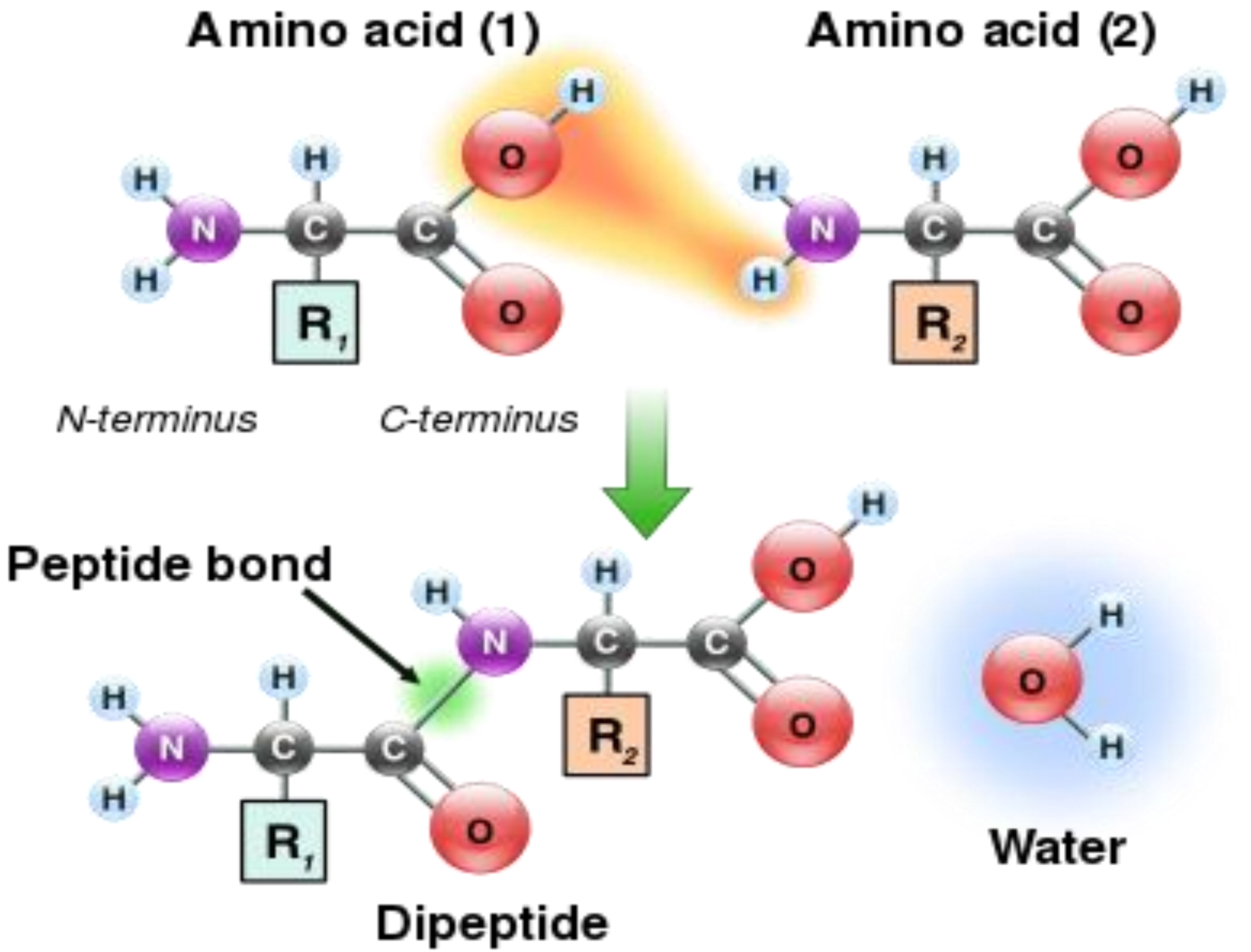


-Amino acids show the usual reactions of both carboxylic acids and amines.

-Reaction specificity is due to the presence of both carboxyl and amino groups and of other functional groups.

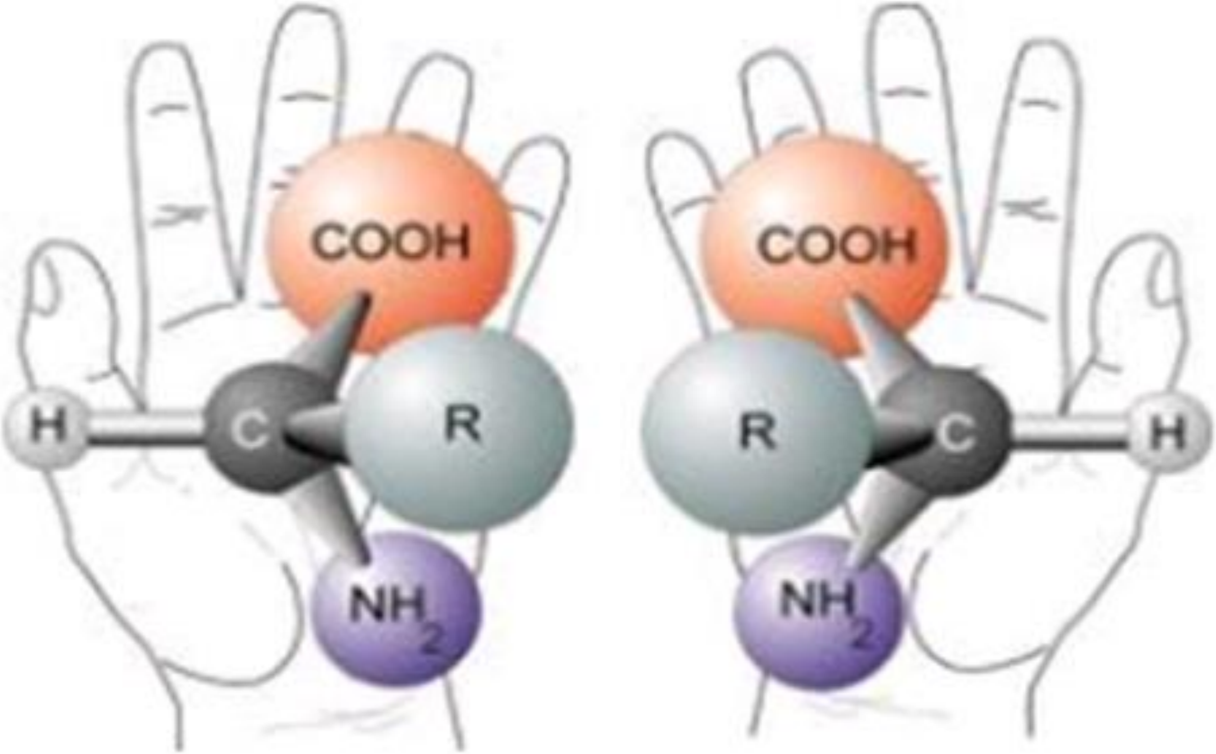
-Reactions occurring at 100–220 ◦C, such as in cooking, frying and baking, are particularly relevant to food chemistry.

Formation of protein



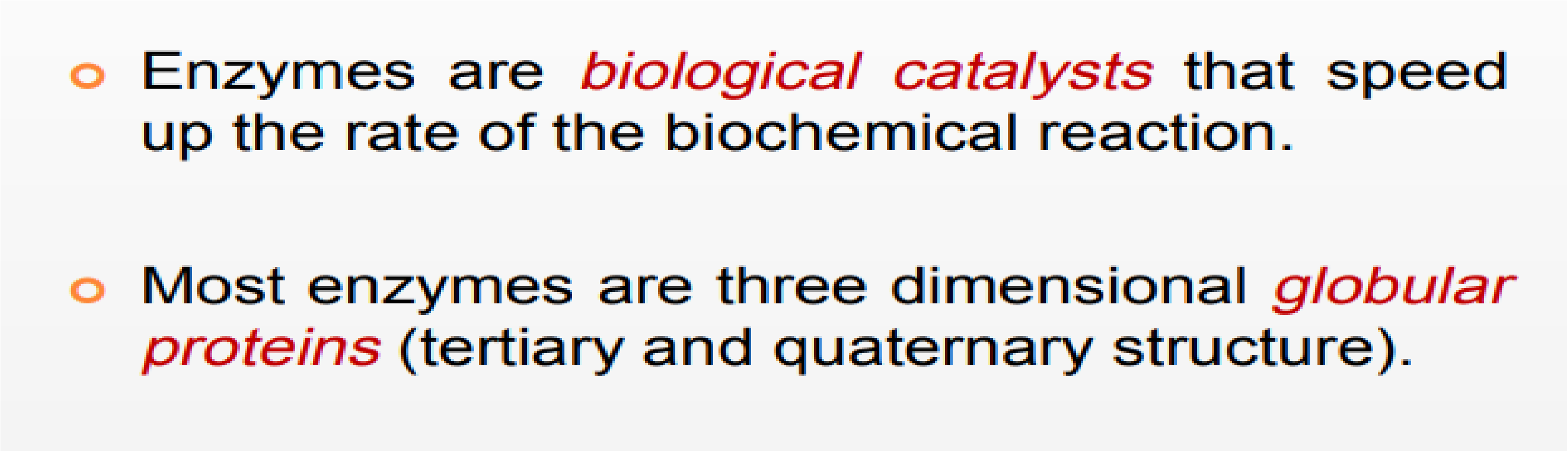
Chirality

All the amino acids but glycine are chiral molecules. That is, they exist in two optically active asymmetric forms (called enantiomers) that are the mirror images of each other. (This property is conceptually similar to the spatial relationship of the left hand to the right hand.) One enantiomer is designated D and the other L. It is important to note that the amino acids found in proteins almost always possess only the L-configuration. This reflects the fact that the enzymes responsible for protein synthesis have evolved to utilize only the L-enantiomers. Reflecting this near universality, the prefix L is usually omitted. Some D-amino acids are found in microorganisms, particularly in the cell walls of bacteria and in several of the antibiotics. However, these are not synthesized in the ribosome.

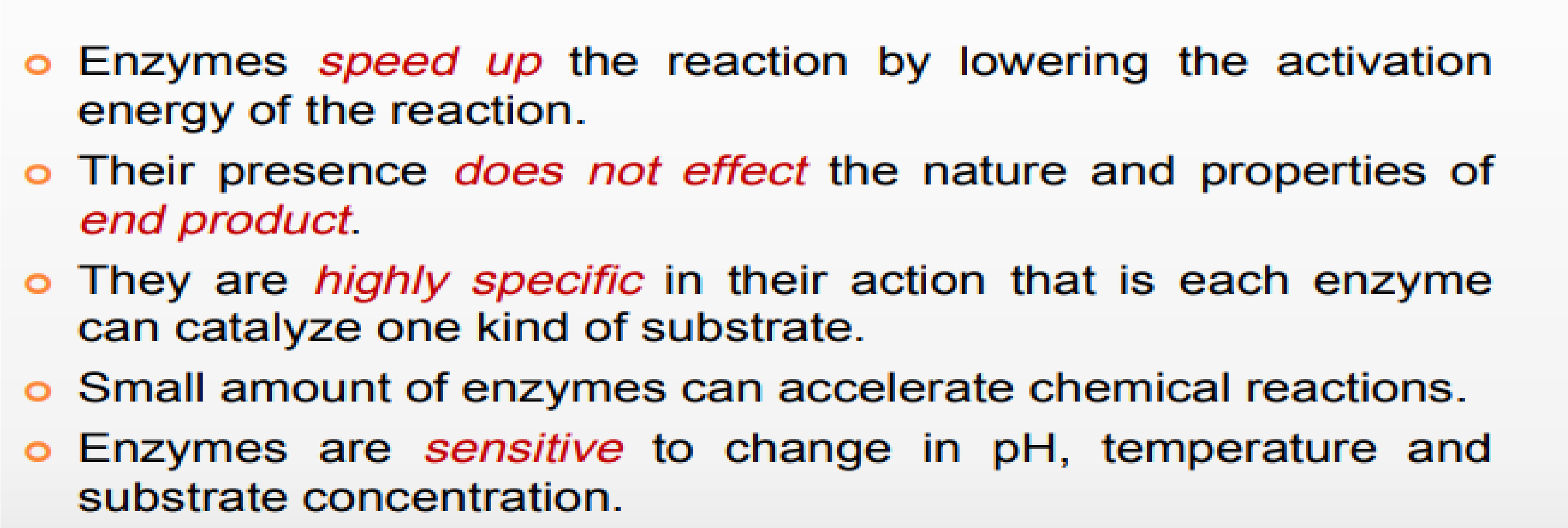

COOH
H
C
R
NH2
COOH
R
C
H
NH2

ENZYMES

- They accelerate the rate of chemical reaction **without being consumed in the reaction**.



- Enzymes are *biological catalysts* that speed up the rate of the biochemical reaction.
- Most enzymes are three dimensional *globular proteins* (tertiary and quaternary structure).

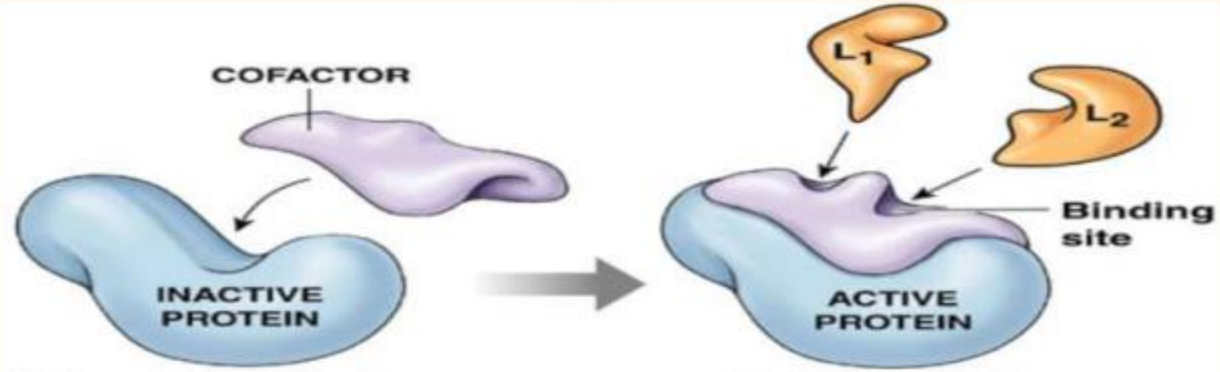


- Enzymes *speed up* the reaction by lowering the activation energy of the reaction.
- Their presence *does not effect* the nature and properties of *end product*.
- They are *highly specific* in their action that is each enzyme can catalyze one kind of substrate.
- Small amount of enzymes can accelerate chemical reactions.
- Enzymes are *sensitive* to change in pH, temperature and substrate concentration.

CO-FACTORS

- Co-factor is the non protein molecule which carries out chemical reactions that can not be performed by standard 20 amino acids.

- Co-factors are of two types:
  - Organic co-factors
  - Inorganic cofactors



Without the cofactor attached, the protein is not active.

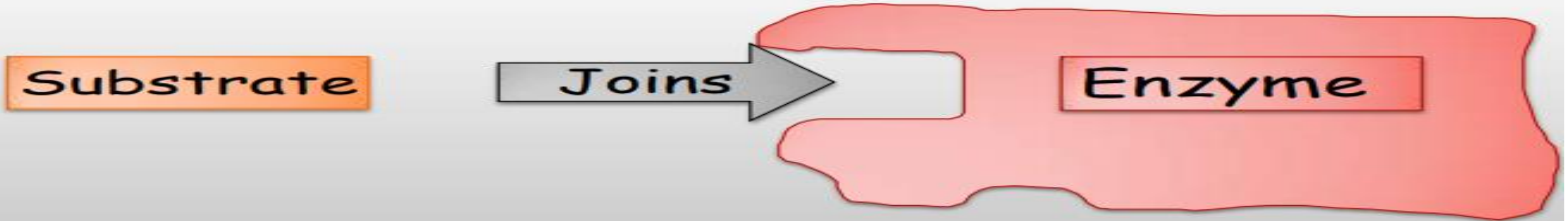
Cofactor binding activates the protein.

Fig. 2-18

Chemical Nature of Enzymes

- All enzymes are **protein** in nature except ribozymes (RNA in nature).

- The reactant in biochemical reaction is termed as substrate.
- When a substrate binds to an enzyme it forms an enzyme-substrate complex.



Enzymes vocabulary

substrate

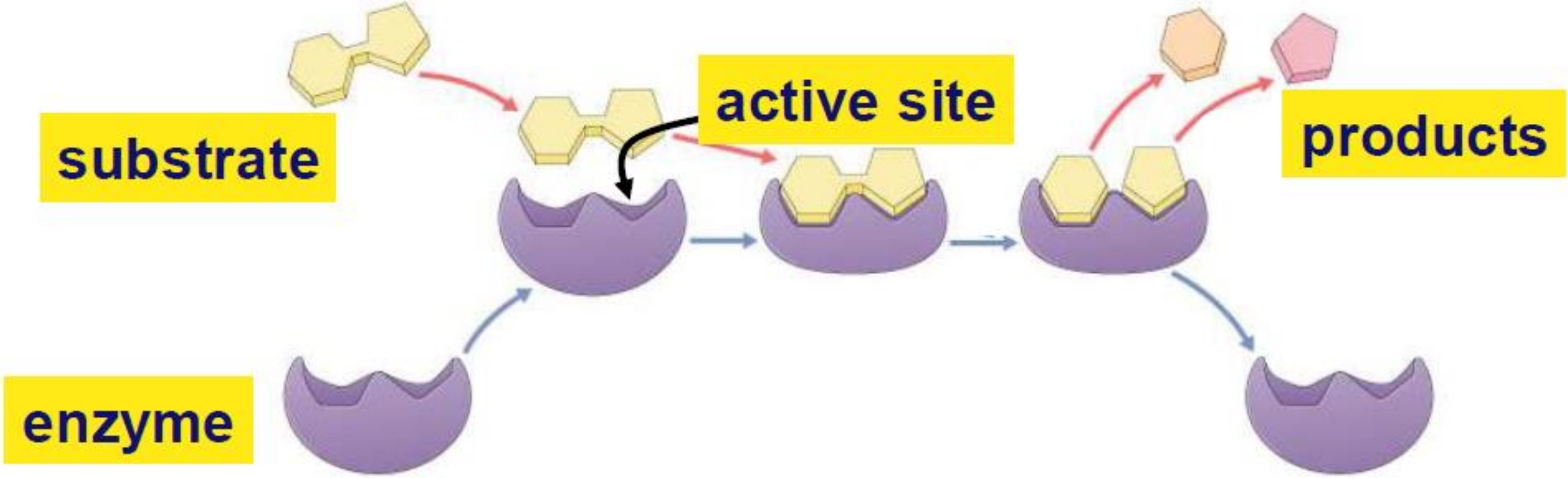
- reactant which binds to enzyme
- enzyme-substrate complex: temporary association

product

- end result of reaction

active site

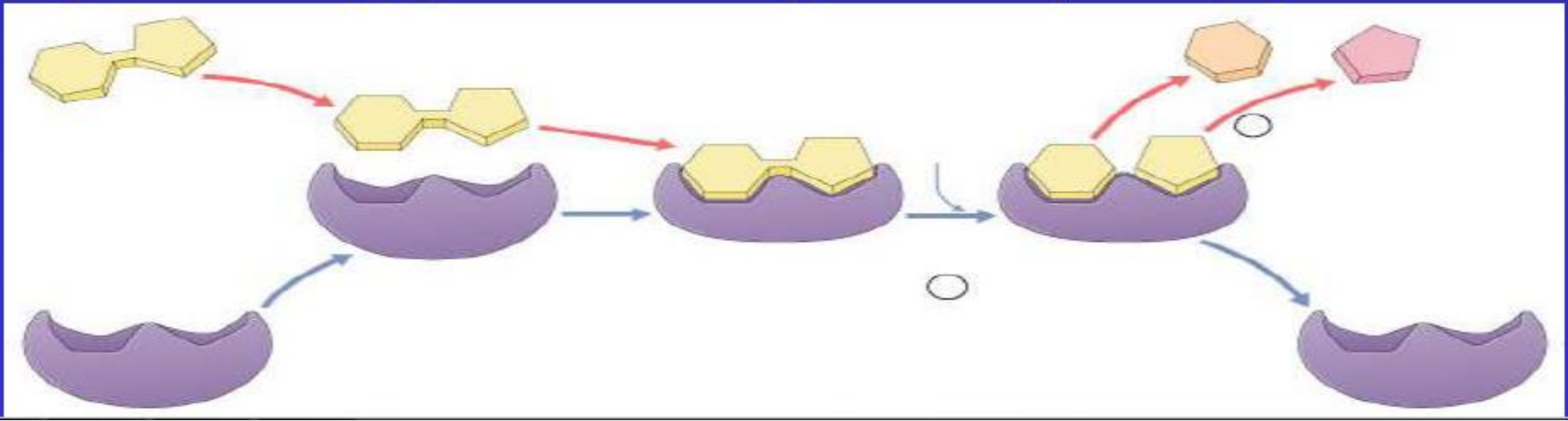
- enzyme's catalytic site; substrate fits into active site



Mechanism of enzyme action

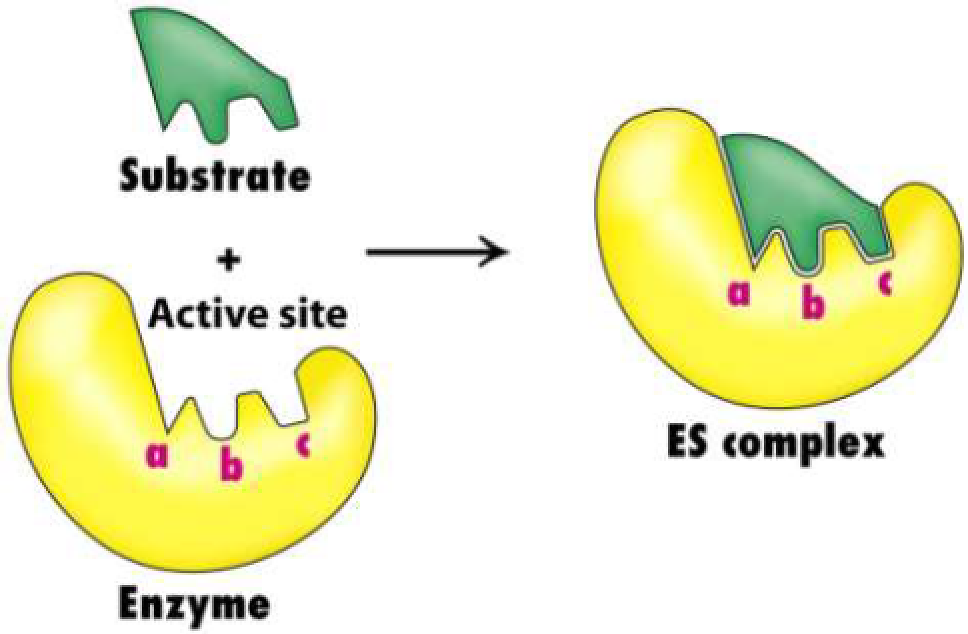
1- The **substrate (S)** binds to the **enzyme (E)** at its active catalytic site to form activated intermediate **enzyme substrate complex (ES).**

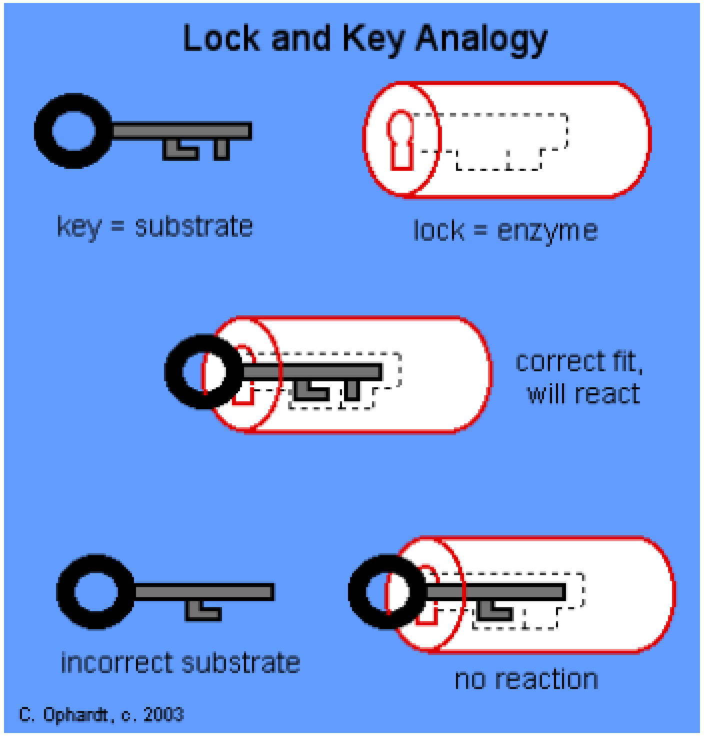
2- The activated complex (ES) **cleaved** to the **products (P)** and the original **enzyme (E)**



Lock and Key model

Proposed by Fischer in 1894





C. Ophardt, c. 2003

In this model, the active sites of the unbound enzyme is complementary in shape to the substrate

- The word **enzyme** is formed from two Greek words: **en** means **inside** and **zyme**, which means **yeast** i.e., the word enzyme means **inside yeast**.
- **There are many methods for naming enzymes:**

1- The **old trivial name** as **pepsin** and **trypsin.**

2- The name of **substrate and the suffix – ase** added to it as **lactase** acting on lactose and **sucrase** acting on sucrose.

3- Two words, one for the **substrate** and the other for the **type of reaction** e.g. **succinate dehydrogenase, pyruvate decarboxylase** and **glutamine synthetase**.

NOMENCLATURE OF ENZYMES

- An enzyme is named according to the name of the substrate it catalyses.
- Some enzymes were named before a systematic way of naming enzyme was formed.

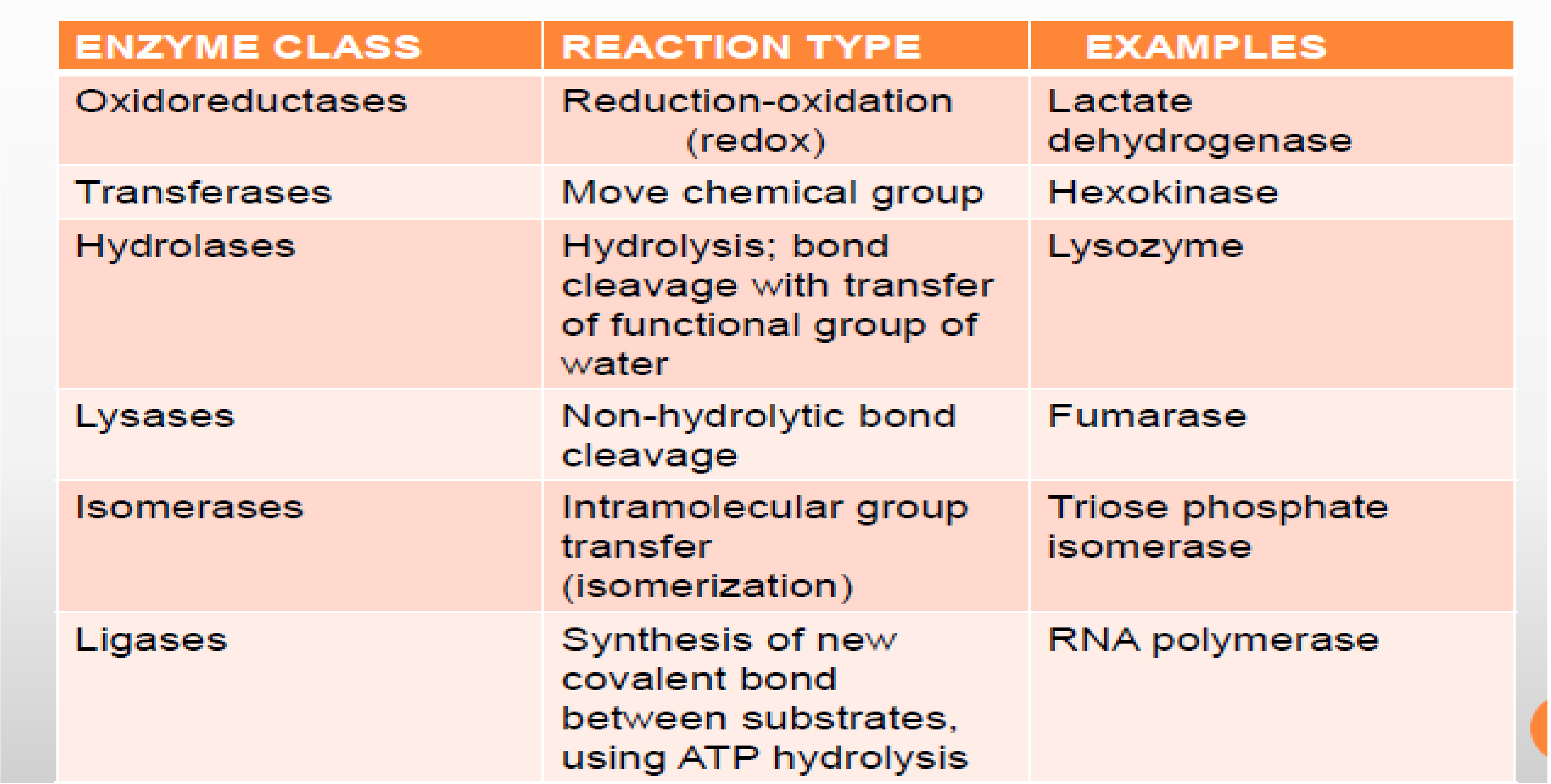
  Example: pepsin, trypsin and rennin
- By adding suffix ***-ase*** at the end of the name of the substrate, enzymes are named.
- Enzyme for catalyzing the hydrolysis is termed as hydrolase.

  Example :

maltose + water $\xrightarrow[\text{maltase}]{}$ glucose + glucose

EXAMPLES

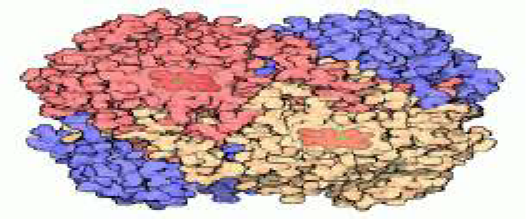
substrate	enzymes	products
lactose	lact**ase**	glucose + galactose
maltose	malt**ase**	Glucose
cellulose	cellul**ase**	Glucose
lipid	lip**ase**	Glycerol + fatty acid
starch	amyl**ase**	Maltose
protein	prote**ase**	Peptides + polypeptide



ENZYME CLASS	REACTION TYPE	EXAMPLES
Oxidoreductases	Reduction-oxidation (redox)	Lactate dehydrogenase
Transferases	Move chemical group	Hexokinase
Hydrolases	Hydrolysis; bond cleavage with transfer of functional group of water	Lysozyme
Lysases	Non-hydrolytic bond cleavage	Fumarase
Isomerases	Intramolecular group transfer (isomerization)	Triose phosphate isomerase
Ligases	Synthesis of new covalent bond between substrates, using ATP hydrolysis	RNA polymerase

Factors Affect Rate of Enzyme Action

- Enzyme concentration
- Substrate concentration
- Temperature
- pH
- Concentration of coenzymes
- Concentration of ion activators
- Time
- Inhibitors



catalase

1- Effect of enzyme concentration

The rate of enzyme action is **directly proportional** to the concentration of enzyme **provided** that there are sufficient supply of substrate & constant conditions.

2- Effect of substrate concentration

-The rate of reaction **increases** as the substrate concentration increases up to certain point at which the reaction rate is maximal **(Vmax.)**

3- Effects of temperature

- Rate of reaction **increases gradually** with the rise in temperature until reach a **maximum** at a certain temperature, called **optimum temperature**
- The optimum temperature is **37-40 C** in

The effect of temperature on reaction rate is due to:

1- Increase of temperature **increase the initial energy** of substrate and thus **decrease the activation energy**

4- Effect of PH

- Each enzyme has an **optimum PH** at which its **activity is maximal**

- E.g. Optimum PH of **pepsin = 1.5 - 2**
- Optimum PH of **pancreatic lipase = 7.5 - 8**
- Optimum PH of **salivary amylase = 6.8**

5- Concentration of coenzymes: In the conjugated enzymes that need coenzymes, the **increase** in the **coenzyme concentration** will **increase** the reaction rate.

6- Concentration of ion activators: The **increase** in metal ion activator **increase** the reaction rate

7- Effect of time:

- In an enzymatic reaction, **the rate of reaction is decreased by time.**

8- Presence of enzymes inhibitor: presence of enzyme **inhibitor decreases** or stops the enzyme activity.