



**Міністерство освіти і науки України
ДЕРЖАВНИЙ БІОТЕХНОЛОГІЧНИЙ
УНІВЕРСИТЕТ
Факультет ветеринарної медицини
Кафедра фізіології та біохімії тварин**

В. О. Приходченко, Н. І. Гладка, О. М. Денисова

MIXED FUNCTION COMPOUNDS

СПОЛУКИ ЗІ ЗМІШАНИМИ ФУНКЦІЯМИ

Навчально-методичний посібник

**Харків
2023**

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для здобувачів другого (магістерського) рівня вищої освіти
денної форми навчання зі спеціальності 211 Ветеринарна медицина

Затверджено
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П-77 Mixed function compounds [Текст]: навч.-метод. посіб. для здобувачів другого (магістерського) рівня вищої освіти денної форми навчання зі спеціальності 211 Ветеринарна медицина / В. О. Приходченко, Н. І. Гладка, О. М. Денисова ; Держ. біотехн. ун-т. – Харків, 2023.– 44 с.

Навчальний посібник призначений для аудиторної роботи іноземних студентів, які навчаються англійською мовою за спеціальністю "Ветеринарна медицина". У посібнику викладено основні питання хімії, зокрема біоорганічної. Значну увагу приділено хімічній структурі, номенклатурі, фізичним та хімічним властивостям гідроксикислот та різних груп вуглеводів, які зустрічаються в природі та є структурними компонентами живих організмів.

УДК 54(07)

Відповідальний за випуск О. М. Денисова, канд. біол. наук.

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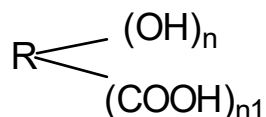
BRIEF CONTENTS

Mixed function compounds	4
1. Hydroxy Acids	54
2. Carbohydrates	15
2.1. Monosaccharides	18
2.2. Disaccharides	2830
2.3. Polysaccharides	35
Recommended books.....	43

1. Hydroxy Acids

Hydroxy Acids are the derivatives of carboxyl acids that contain –OH group (one or more).

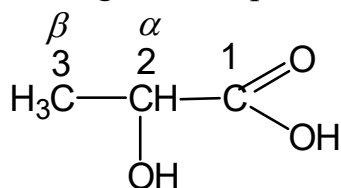
Common formula:



The number of carboxyl groups determines the basicity of hydroxy acids, and the number of hydroxyl groups, including the hydroxyl carboxyl group, determines the atomicity of hydroxy acids.

In accordance with international standards (IUPAC), the main group in hydroxy acids is an acid carboxylic group. Therefore, the basis of the name hydroxy acids are called acid and the position of hydroxyl groups indicate numbers.

Trivial acid names are often used in the literature. In this case, the location of the hydroxyl groups is indicated by the letters of the Latin alphabet (α -, β -, γ -, etc.). Among this class of organic compounds is widely used trivial nomenclature.



2-hydroxypropanoic acid
***a*-hydroxypropionic acid**
lactic acid

The most common natural hydroxy acids

Lactic acid, found in sour milk, sauerkraut, and dill pickles (fig. 1.1), has the functional groups of both a carboxylic acid and an alcohol. Lactic acid is the end product when our muscles use glucose for energy in the absence of oxygen, a process called *glycolysis*.



Figure 1.1. Sources of lactic acid

Salicylic acid is both a carboxylic acid and a phenol (fig. 1.2). It is of special interest because a family of useful drugs – the salicylates – is derivatives of this acid. The salicylates include aspirin and function as *analgesics* (pain relievers) and as *antipyretics* (fever reducers).



Figure 1.2. Salicylic acid

Malic acid. It is present in green apples and some berries (fig. 4.3). It takes part in biological processes in human organisms and organisms of other alive creatures. It is used in medicine for synthesis of some medical preparations.



Figure 1.3. Malic acid (structure and sources)

Tartaric acid. It is present in grape. It is used in medicine for synthesis of some medical preparations (fig. 1.4).



Figure 1.4. Tartaric acid (structure and sources)

Citric acid. It is present in orange, lemon and other citric fruits. It takes part in biological processes in human organism (fig. 1.5).

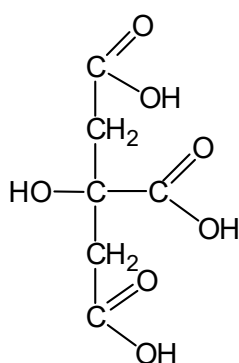


Figure 1.5. Citric acid (structure and sources)

Physical properties

Hydroxy acids are colorless liquid or crystalline substances, soluble in water. A characteristic property of most hydroxy acids is their **optical activity**.

Optical activity

Many naturally occurring substances are able to rotate the plane of polarized light. Because of this ability to rotate polarized light, such substances are said to be **optically active**. When plane-polarized light passes through an optically active substance, the plane of the polarized light is rotated. If the rotation is to the right (clockwise), the substance is said to be **dextrorotatory (+)**; if the rotation is to the left (counterclockwise), the substance is said to be **levorotatory (-)**.

Plane-polarized light is light that is vibrating in only one plane. Ordinary (unpolarized) light consists of electromagnetic waves vibrating in all directions (planes) perpendicular to the direction in which it is traveling. When ordinary light passes through a polarizer, it emerges vibrating in only one plane and is called *plane-polarized light* (fig. 1.6).

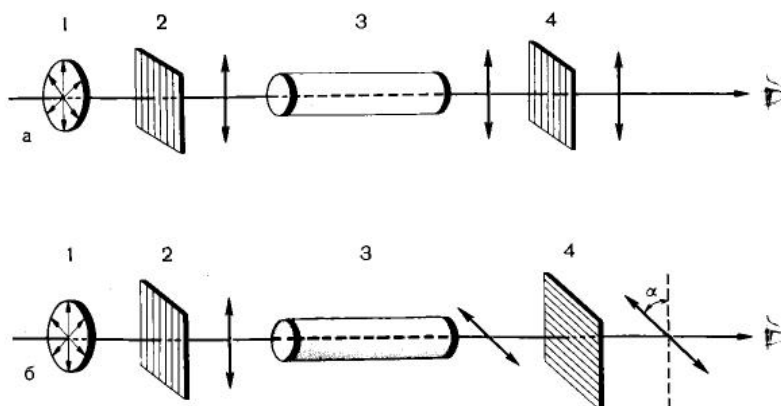


Figure 1.6. Polarimeter

The rotation of plane-polarized light is quantitatively measured with a polarimeter (fig. 1.7). The essential features of this instrument are (1) a light source (usually a sodium lamp), (2) a polarizer, (3) a sample tube, (4) an analyzer (which is another matched polarizer), and (5) a calibrated scale (360°) for measuring the number of degrees the plane of polarized light is rotated.

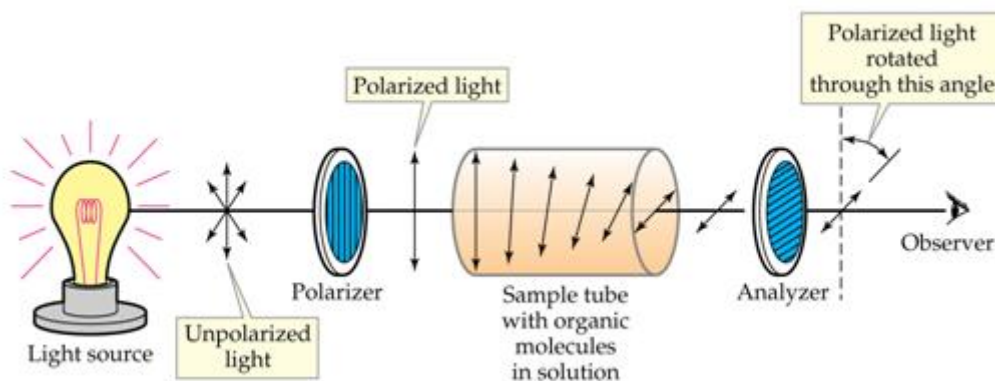


Figure 1.7. Polarimeter

The calibrated scale is attached to the analyzer. When the sample tube contains a solution of an optically inactive material, the axes of the polarizer and the analyzer are parallel, and the scale is at zero degrees; the light passing through is at maximum intensity. When a solution of an optically active substance is placed in the sample tube, the plane in which the polarized light is vibrating is rotated through an angle (α).

The analyzer is then rotated to the position where the emerging light is at maximum intensity. The number of degrees and the direction of rotation by the solution are then read from the scale as the observed rotation (fig. 1.8).



Figure 1.8. Polarizer and analyzer

In 1848, Louis Pasteur (1822–1895) observed that sodium ammonium tartrate, a salt of tartaric acid, exists as a mixture of two kinds of crystals. Pasteur carefully hand separated the two kinds of crystals. Investigating their properties, *he found that solutions made from either kind of crystal would rotate the plane of polarized light, but in opposite directions.* Since this optical activity was present in a solution, it could not be caused by a specific arrangement within a crystal. Instead, Pasteur concluded that this difference in optical activity occurred because of a difference in molecular symmetry.

The tetrahedral arrangement of single bonds around a carbon atom makes asymmetry (lack of symmetry) possible in organic molecules. When four different atoms or functional groups are bonded to a carbon atom, the molecule formed is asymmetric, and the carbon atom is called an **asymmetric carbon atom**.

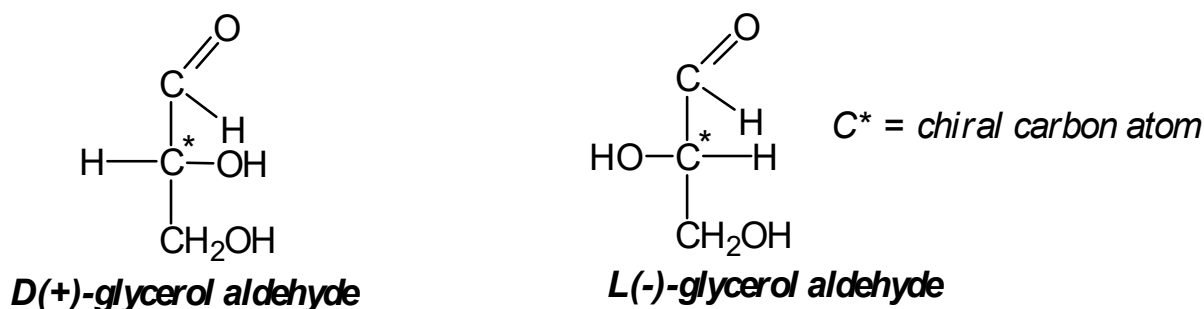
Your right and your left hands are mirror images of each other; that is, your left hand is a mirror reflection of your right hand, and vice versa. Furthermore, your hands are not superimposable on each other. **Superimposable** means that, when we lay one object upon another, all parts of both objects coincide exactly. A molecule that is not superimposable on its mirror image is said to be **chiral**.

An asymmetric carbon atom is also called a **chiral carbon atom** or chiral center. Molecules or objects that are superimposable on each other are **achiral**. A molecule cannot be chiral if it has a plane of symmetry. For example, if you can pass a plane through a molecule (or an object) in such a way that one-half of the molecule is the mirror image of the other half, the molecule is not chiral.

Molecules of a compound that contain one chiral carbon atom occur in two optically active isomeric forms. This is because the four different groups bonded to the chiral carbon atom can be oriented in space in two different configurations.

Chiral molecules that are mirror images of each other are stereoisomers and are called **enantiomers**.

Let's consider the spatial arrangement of a glycerol aldehyde molecule, that contains one chiral carbon atom:



The letter designations D (d) or L (l) determine the spatial orientation of atoms

or atomic groups around the asymmetric C-atom, and the signs (+) - right rotation, (-) - left rotation (fig 1.9).

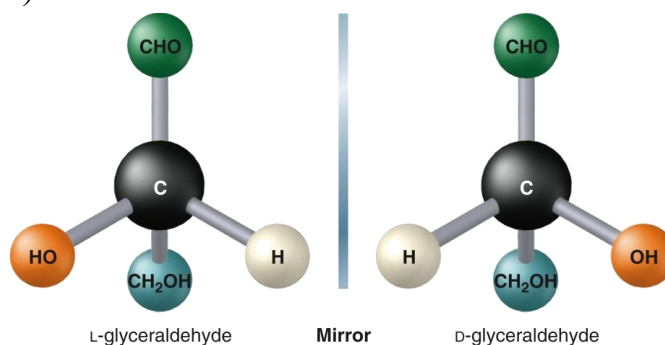


Figure 1.9. The spatial orientation of atoms or atomic groups

A mixture containing equal amounts of a pair of enantiomers is known as a **racemic mixture**. Such a mixture is optically inactive and shows no rotation of polarized light when tested in a polarimeter. Each enantiomer rotates the plane of polarized light by the same amount, but in opposite directions. Thus, the rotation by each isomer is canceled. The (\pm) symbol is often used to designate racemic mixtures. For example, a racemic mixture of lactic acid is written as (\pm)-lactic acid because this mixture contains equal molar amounts of (+)-lactic acid and (-)-lactic acid.

The number of stereoisomers increases as the number of chiral carbon atoms increases. The maximum number of stereoisomers for a given compound is obtained by the formula 2^n , where n is the number of chiral carbon atoms.

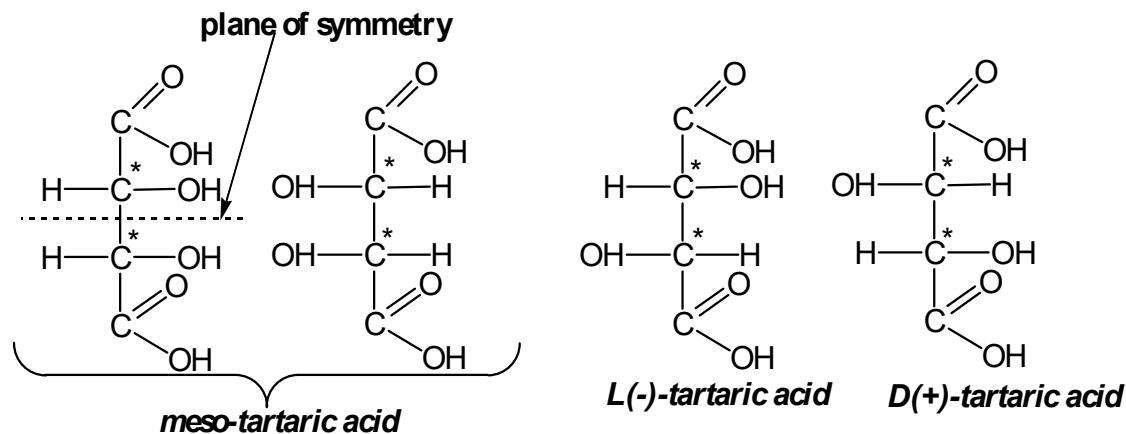
2^n = Maximum number of stereoisomers for a given chiral compound

n = Number of chiral carbon atoms in a molecule

As we have seen, there are two ($2^1 = 2$) stereoisomers of glycerol aldehyde.

Stereoisomers that contain chiral carbon atoms and are superimposable on their own mirror images are called **meso compounds**, or **meso structures**. All meso compounds are optically inactive.

The four stereoisomers of tartaric acid are represented and designated in this fashion:



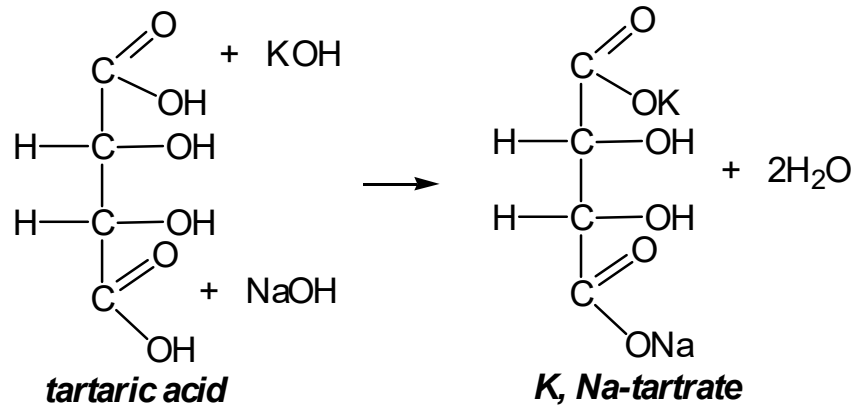
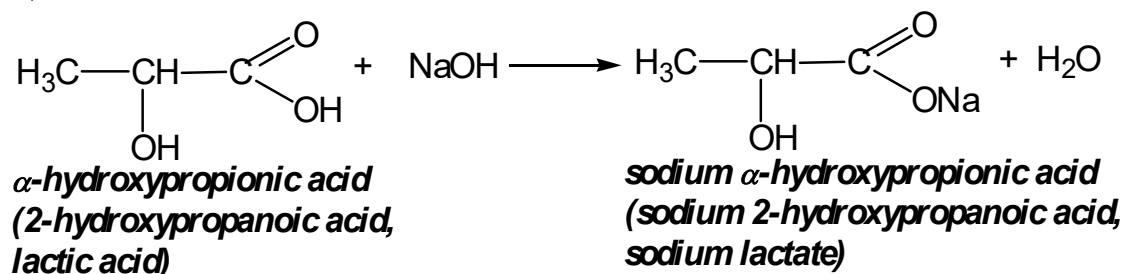
The value of optical isomerism. The constant characterizing the optical activity of a substance is called the specific rotation, from which the authenticity of the substance can be determined.

Optical isomerism has very great biological significance. Enzymes that catalyze biochemical reactions in living organisms have optical specificity, namely they act only on certain optical isomers (for example, on D-monosaccharides, on L-amino acids, etc.). Enzymes do not act on the optical antipodes of these substances; they do not entail their metabolism. Accumulation in tissues of such isomers can cause pathological processes. This should be taken into account when using various biologically active additives, which are most often racemates.

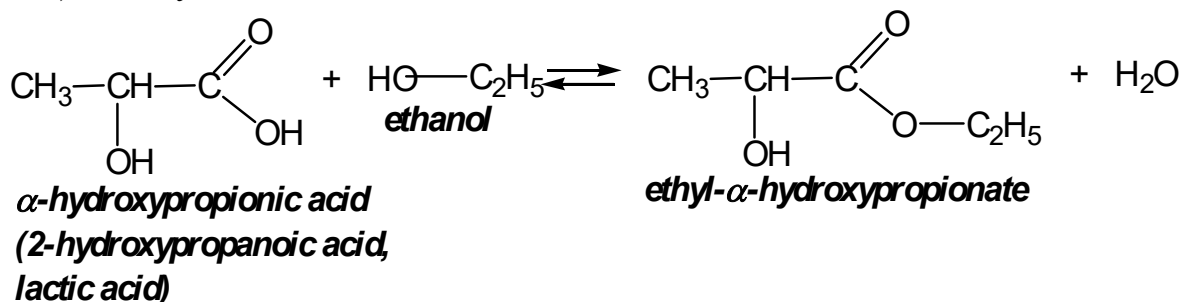
Chemical properties

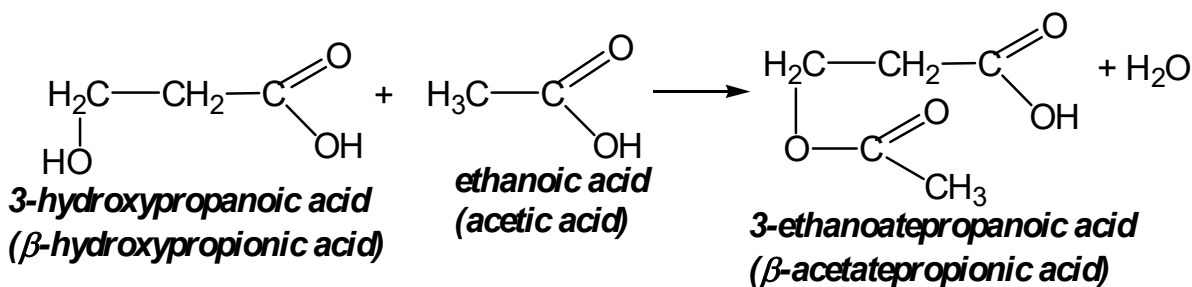
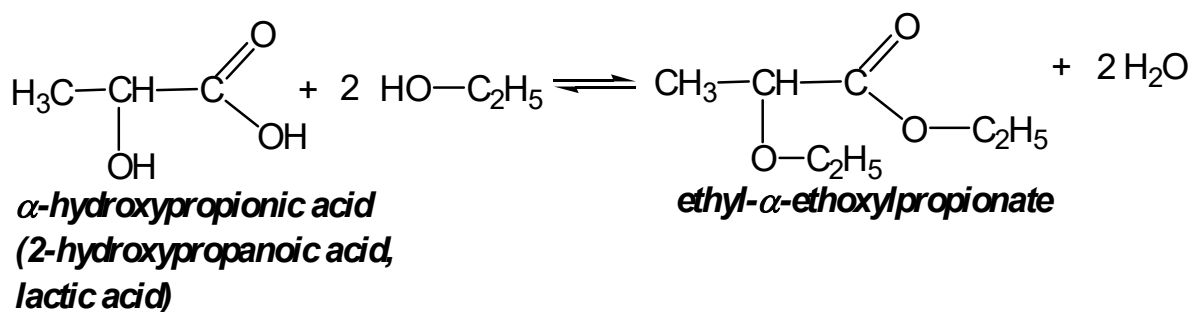
I. Carboxyl group can react forming:

1). Salts

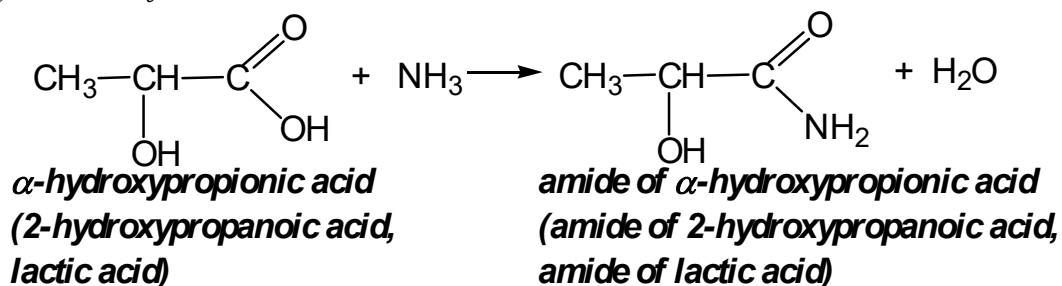


2). Ester formation



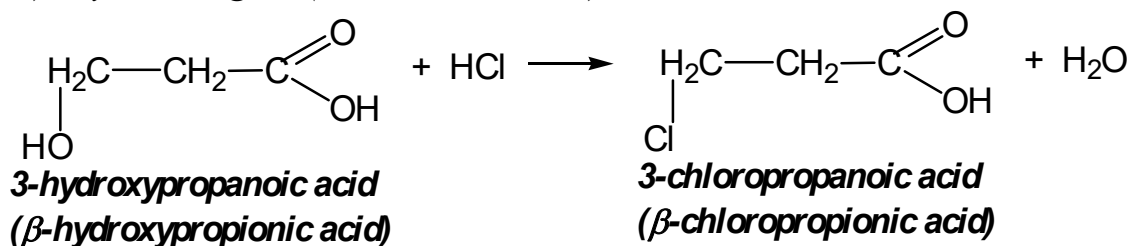


3). Amides formation

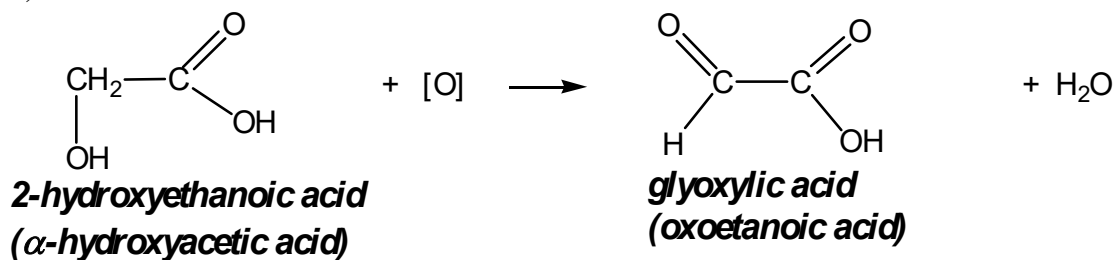


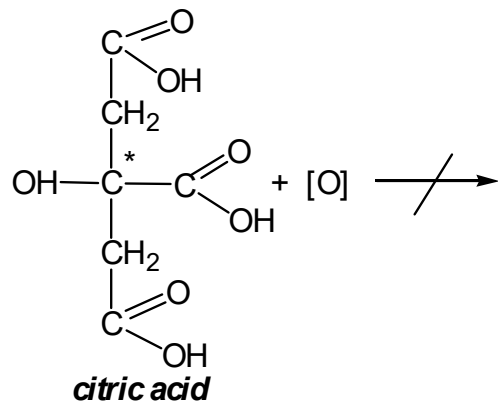
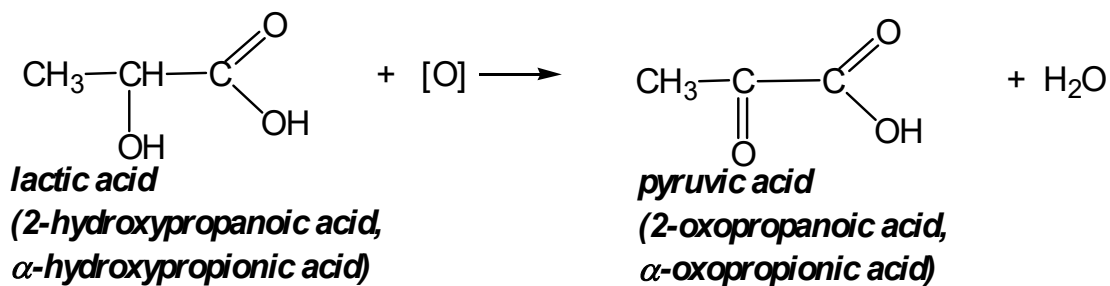
II. Hydroxyl group reaction:

1). Hydrohalogens (HCl, HBr, HI, HF)



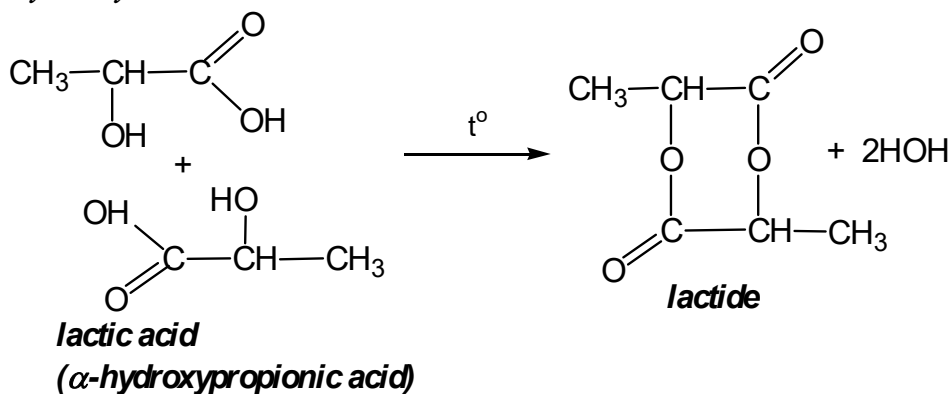
2). Can oxidize



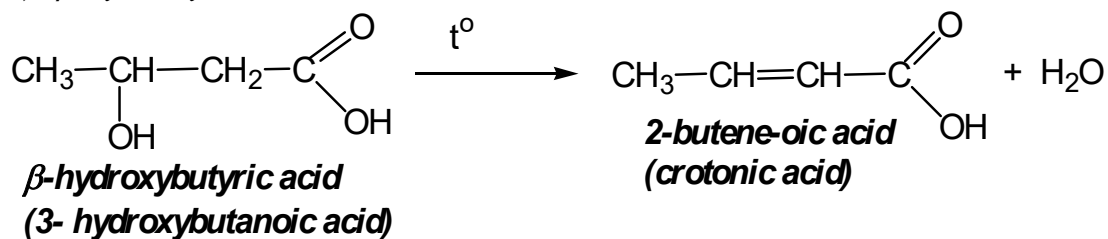


III. Specific properties of hydroxy acids:

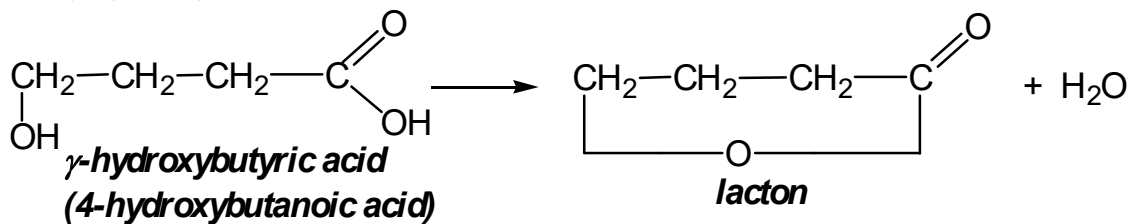
1). α-hydroxy acids



2). β-hydroxy acids

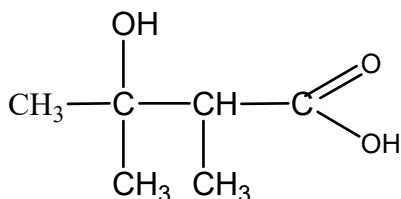


3). γ-hydroxy acids



Learning Check

1. Name the following compound by the IUPAC method:



2. Write the structural formula for *β*-hydroxyvaleric acid

3. Draw projection formulas of malic acids enantiomers, determine dissymmetric carbon atom and establish whether it is a D or L isomer.

4. Write the reaction of the interaction of *2*-hydroxypropanoic acid with HCl and name the reaction products.

5. Write reaction when *4*-methyl-*3*-hydroxypentanoic acid is oxidized with [O] and name the reaction products.

6. Write the reaction of the interaction of *3*-hydroxy-*2*-methylhexanoic acid with NH₃ and name the reaction products.

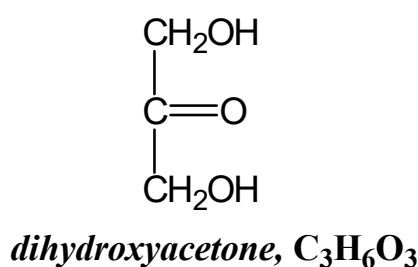
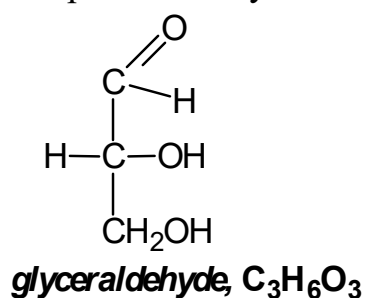
7. Write reaction when heated *4*-ethyl-*3*-hydroxypentanoic acid and name the reaction products.

8. Write the reaction of the interaction of *2*-hydroxyethanoic acid with NaOH and name the reaction products.

2. Carbohydrates

The name *carbohydrates* was given to this class of compounds many years ago by French scientists, who called them *hydrates de carbone* because their empirical formulas approximated $C_m(H_2O)_n$. It was found later that not all substances classified as carbohydrates conform to this formula (e.g., rhamnose, $C_6H_{12}O_5$, and deoxyribose, $C_5H_{10}O_4$). It seems clear that carbohydrates are not simply hydrated carbon; they are complex substances that contain from three to many thousands of carbon atoms. **Carbohydrates** are generally defined as polyhydroxy aldehydes or polyhydroxy ketones or substances that yield these compounds when hydrolyzed.

The simplest carbohydrates are glyceraldehyde and dihydroxyacetone:



These substances are “polyhydroxy” because each molecule has more than one hydroxyl group. Glyceraldehyde contains a carbonyl carbon in a terminal position and is therefore an aldehyde. The internal carbonyl of dihydroxyacetone identifies it as a ketone.

Importance of Carbohydrates for Life

Carbohydrates are used by essentially all cells as an energy source. Almost all cells, from the most primitive bacteria to complex human cells, have the metabolic machinery (called glycolysis) necessary to oxidize carbohydrates to smaller carboxylic acids. Sore muscles after exercise tell you that muscle tissue produces lactic acid as the muscle derives important energy from carbohydrates. Higher plant and animal cells (eukaryotic cells) also contain mitochondria, subcellular bodies that specialize in carbon oxidation. So, in eukaryotic cells (including human cells), carbons from carbohydrate can be completely oxidized to carbon dioxide.

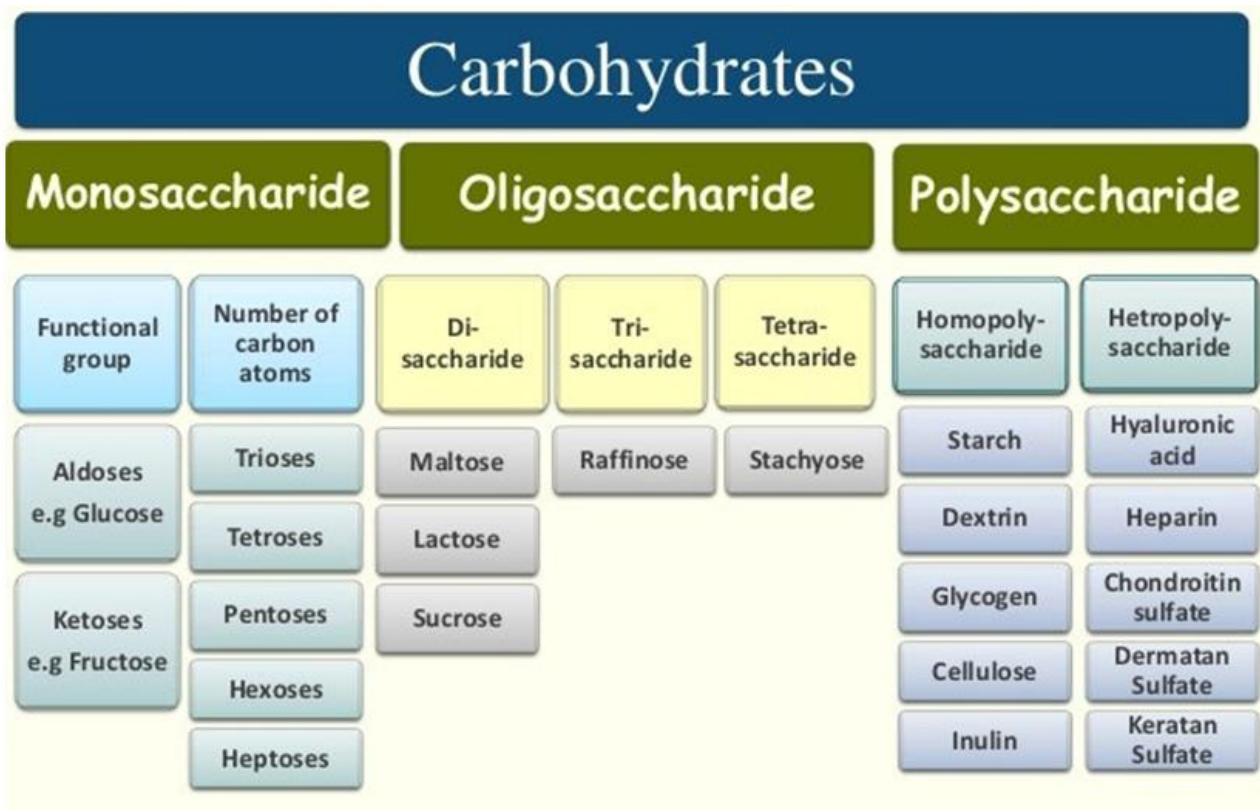
Carbohydrates are easily transported between and within cells. The smaller carbohydrates (e.g., mono- and disaccharides) are water soluble and are transported from cell to cell as a source of energy. The most important

monosaccharide, glucose, is sometimes termed “blood sugar” because glucose is carried in the bloodstream from cell to cell. Mammals use the disaccharide lactose, dissolved in milk, to transport carbohydrates from mother to baby, while higher plants use sucrose as a transport carbohydrate. The water-solubility of the small carbohydrates makes these molecules especially useful in metabolism.

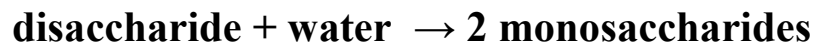
Carbohydrates provide essential structural support for both plant and animal cells. Large polymers (polysaccharides) with important structural characteristics can be formed from simple sugars. Carbohydrate polymers are found in essentially all animal connective tissue. For example, these carbohydrates provide the cushion that allows our joints to move smoothly. Another polymer, cellulose, forms at least part of the cell wall for all higher plants. Cellulose is such an effective structural polymer that it has been adopted for such diverse materials as strong, relatively rigid wood construction; flexible, comfortable cotton clothing; and disposable, biodegradable paper products.

Classification of Carbohydrates

A carbohydrate is classified as a *monosaccharide*, a *disaccharide*, an *oligosaccharide*, or a *polysaccharide*, depending on the number of monosaccharide units linked to form the molecule.



A **monosaccharide** is a carbohydrate that cannot be hydrolyzed to simpler carbohydrate units. The monosaccharide is the basic carbohydrate unit of cellular metabolism. A **disaccharide** yields two monosaccharides – either alike or different – when hydrolyzed:



Disaccharides are often used by plants or animals to transport monosaccharides from one cell to another. The monosaccharides and disaccharides generally have names ending in *-ose* – for example, glucose, sucrose, and lactose. These water-soluble carbohydrates, which have a characteristically sweet taste, are also called ***sugars***.

An **oligosaccharide** has two to six monosaccharide units linked together. *Oligo-* comes from the Greek word *oligos*, which means “small or few.” Free oligosaccharides that contain more than two monosaccharide units are rarely found in nature.

A **polysaccharide** is a macromolecular substance that can be hydrolyzed to yield many monosaccharide units:



Polysaccharides are important as structural supports, particularly in plants, and also serve as a storage depot for monosaccharides, which cells use for energy.

Carbohydrates can also be classified in other ways. A monosaccharide might be described with respect to several of these categories:

1. As a triose, tetrose, pentose, hexose, or heptose:

Trioses $C_3H_6O_3$

Hexoses $C_6H_{12}O_6$

Tetroses $C_4H_8O_4$

Heptoses $C_7H_{14}O_7$

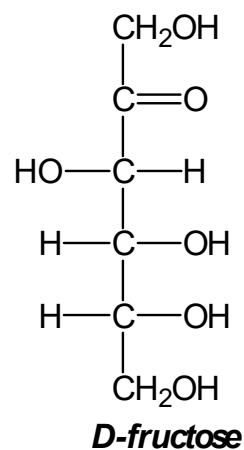
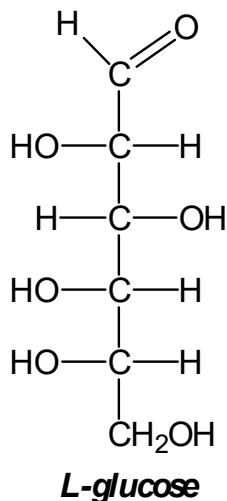
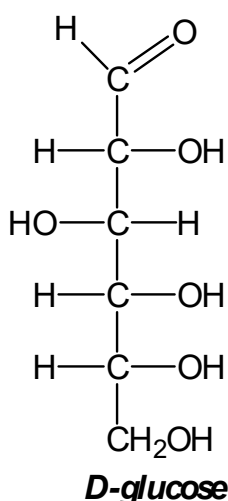
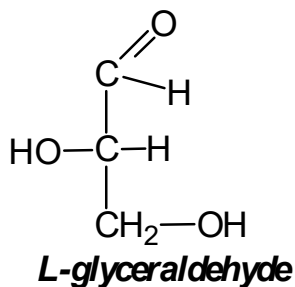
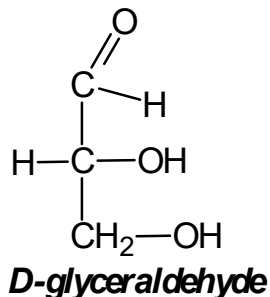
Pentoses $C_5H_{10}O_5$

Theoretically, a monosaccharide can have any number of carbons greater than three, but only monosaccharides of three to seven carbons are commonly found in the biosphere.

2. As an aldose or ketose, depending on whether an aldehyde group (–CHO)

or keto group ($\begin{array}{l} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$) is present. For ketoses, the $\begin{array}{l} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$ is normally located on carbon 2.

3. As a D- or L-isomer, depending on the spatial orientation of the H and OH groups attached to the carbon atom adjacent to the terminal primary alcohol group. When the OH is written to the right of this carbon in the projection formula, the D-isomer is represented. When this OH is written to the left, the L-isomer is represented. The reference compounds for this classification are the trioses D-glyceraldehyde and L-glyceraldehyde, whose formulas follow. Also shown are two aldohexoses (D- and L-glucose) and a ketohexose (D-fructose).



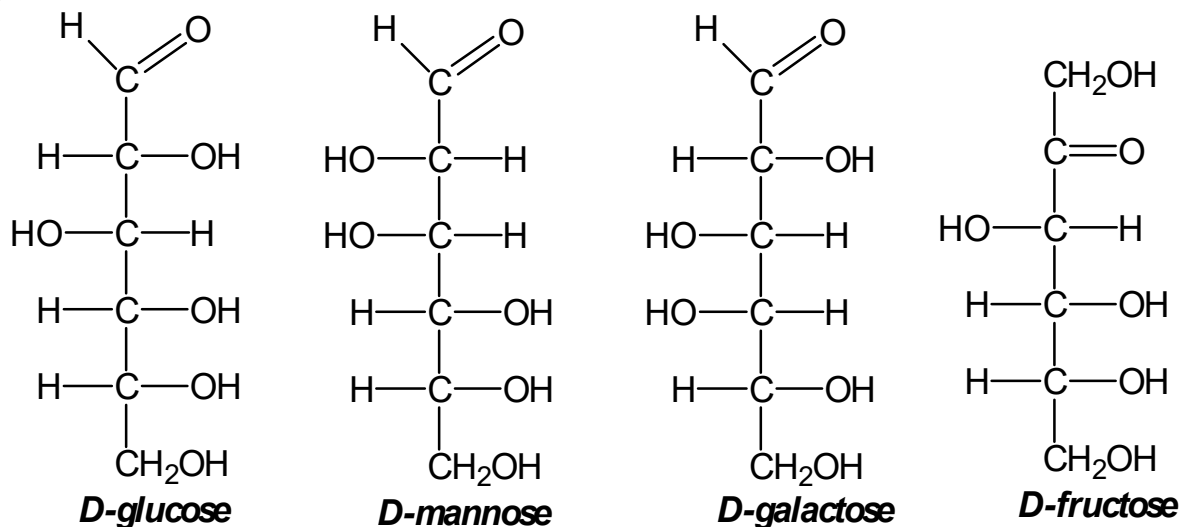
2.1. Monosaccharides

Although a great many monosaccharides have been synthesized, only a very few appear to be of much biological significance. One pentose monosaccharide (ribose) and its deoxy derivative are essential components of ribonucleic acid (RNA) and of deoxyribonucleic acid (DNA). However, the hexose monosaccharides are the most important carbohydrate sources of cellular energy. Three hexoses – glucose, galactose, and fructose – are of major significance in nutrition. All three have the same molecular formula, $\text{C}_6\text{H}_{12}\text{O}_6$, and thus deliver the same amount of cellular energy. They differ in structure, but are biologically interconvertible.

Glucose is the most important of the monosaccharides. It is an aldohexose and is found in the free state in plant and animal tissue. Glucose is also known as *dextrose* or *grape sugar*. It is a component of the disaccharides sucrose, maltose, and lactose and is the monomer of the polysaccharides starch, cellulose, and glycogen. Among the common sugars, glucose is of intermediate sweetness.

Glucose is the key sugar of the body and is carried by the bloodstream to all body parts. The concentration of glucose in the blood is normally 80–100 mg per 100 ml of blood. Because glucose is the most abundant carbohydrate in the blood, it is commonly called *blood sugar*. Glucose requires no digestion and may therefore be given intravenously to patients who cannot take food by mouth. Glucose is found in the urine of those who have diabetes mellitus (sugar diabetes). The condition in which glucose is excreted in the urine is called glycosuria.

Galactose is also an aldohexose and occurs, along with glucose, in lactose and in many oligo- and polysaccharides such as pectin, gums, and mucilages. Galactose is an isomer of glucose, differing only in the spatial arrangement of the H and OH groups around carbon 4. It is a constituent of glycolipids and glycoproteins in many cell membranes, such as those in nervous tissue. Galactose is less than half as sweet as glucose.



Fructose, also known as levulose, is a ketohexose that occurs in fruit juices, honey, and, along with glucose, as a constituent of sucrose. Fructose is the major constituent of the polysaccharide inulin, a starchlike substance present in many plants. Fructose is metabolized directly but is also readily converted to glucose in the liver.

In ***Fischer projection formulas***, the molecule is represented with the aldehyde (or ketone) group at the top. The –H and –OH groups attached to interior carbons are written to the right or to the left as they would appear when projected toward the observer.

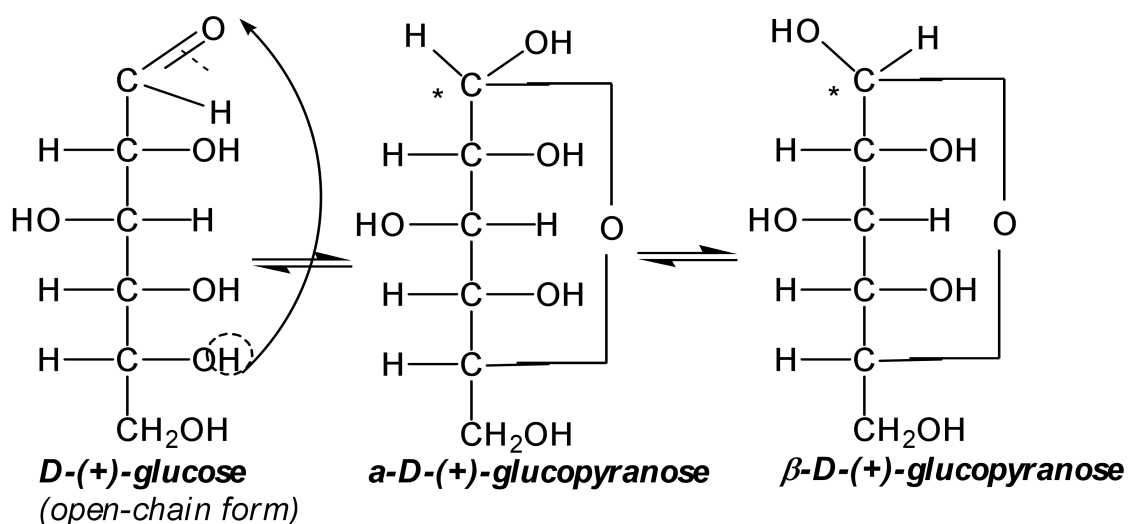
The structure called D-glucose is so named because the H and OH on carbon 5 are in the same configuration as the H and OH on carbon 2 in D-glyceraldehyde. The configuration of the –H and –OH on carbon 5 in L-glucose corresponds to the –H and –OH on carbon 2 in L-glyceraldehyde.

Cyclic Structure of Glucose; Mutarotation

Straight open-chain D-glucose is so reactive that almost all molecules quickly rearrange their bonds to form two new structures. These structures, which are six-membered rings containing one oxygen, are related to pyran and so are called *pyranose* sugars.

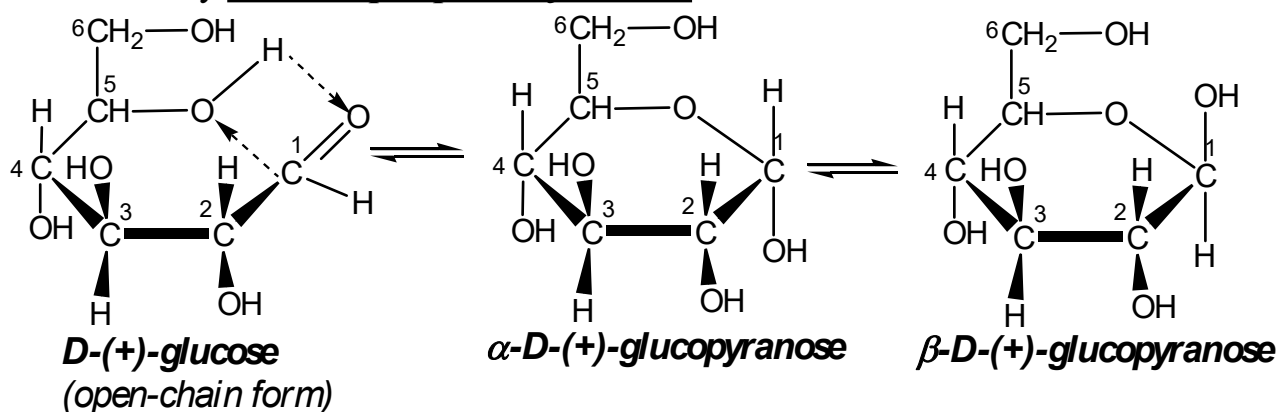
The two cyclic forms are diastereomers that differ with respect to their rotation of polarized light. One form, labeled α -D-glucopyranose, has a specific rotation, $[\alpha]$, of $+112^\circ$; the other, labeled β -D-glucopyranose, has a specific rotation of $+18.7^\circ$.

An interesting phenomenon occurs when these two forms of glucose are put into separate solutions and allowed to stand for several hours. The specific rotation of each solution changes to $+52.7^\circ$. This phenomenon is known as mutarotation. An explanation of mutarotation is that D-glucose exists in solution as an equilibrium mixture of two cyclic forms and the open-chain form.



The two cyclic molecules are optical isomers, differing only in the orientation of the –H and –OH groups about carbon 1. When dissolved, some α -D-glucopyranose molecules are transformed into β -D-glucopyranose, and vice versa, until equilibrium is reached between the α - and β -forms. The equilibrium solution contains about 36 % α -molecules and 64 % β -molecules, with a trace of open-chain molecules. When two cyclic isomers differ only in their stereo arrangement about the carbon involved in mutarotation, they are called **anomers**. For example, α - and β -D-glucopyranose are anomers. **Mutarotation** is the process by which anomers are interconverted.

The cyclic forms of D-glucose may be represented by either *Fischer projection* formulas or by *Haworth perspective formulas*.



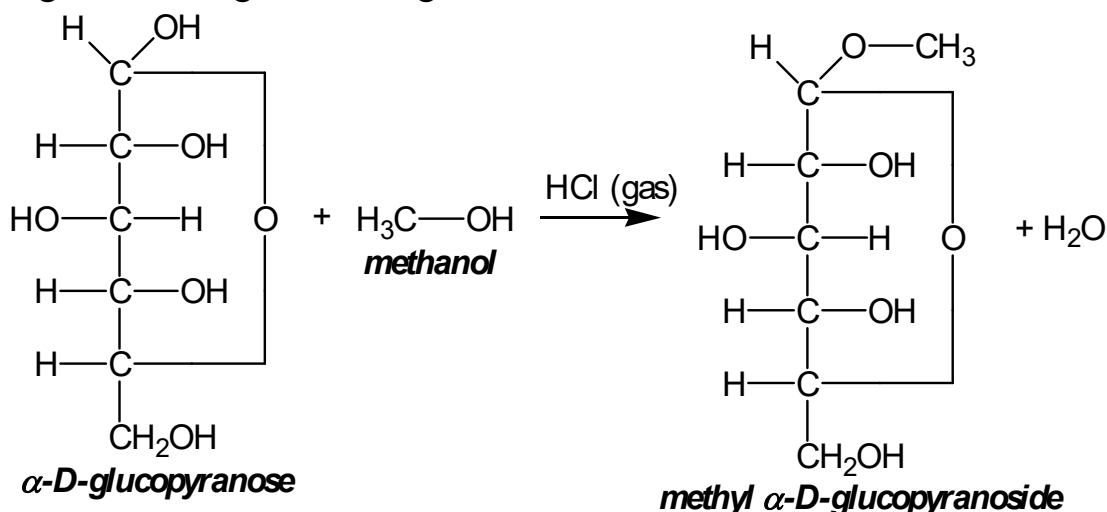
In the cyclic Fischer projection formulas of the D-aldoses, the α -form has the –OH on carbon 1 written to the right; in the β -form, the –OH on carbon 1 is on the left. The *Haworth formula* represents the molecule as a flat hexagon with the –H and –OH groups above and below the plane of the hexagon. In the α -form, the –OH on carbon 1 is written below the plane; in the β -form, the –OH on carbon 1 is above the plane. In converting the Fischer projection formula of a D-aldohexose to the Haworth formula, the –OH groups on carbons 2, 3, and 4 are written below the plane if they project to the right and above the plane if they project to the left. Carbon 6 is written above the plane.

The two cyclic forms of D-glucose differ only in the relative positions of the –H and –OH groups attached to carbon 1. Yet this seemingly minor structural difference has important biochemical consequences because the physical shape of a molecule often determines its biological use. For example, the fundamental structural difference between starch and cellulose is that *starch is a polymer of α -D-glucopyranose*, whereas *cellulose is a polymer of β -D-glucopyranose*. As a consequence, starch is easily digested by humans, but we are totally unable to digest cellulose.

Hemiacetals and Acetals. Cyclic structures of monosaccharides are intramolecular hemiacetals. Five- or six-membered rings are especially stable.

However, in an aqueous solution, the ring often opens and the hemiacetal momentarily reverts to the open-chain aldehyde. When the open chain closes, it forms either the α - or the β -anomer. Mutarotation results from this opening and closing of the hemiacetal ring.

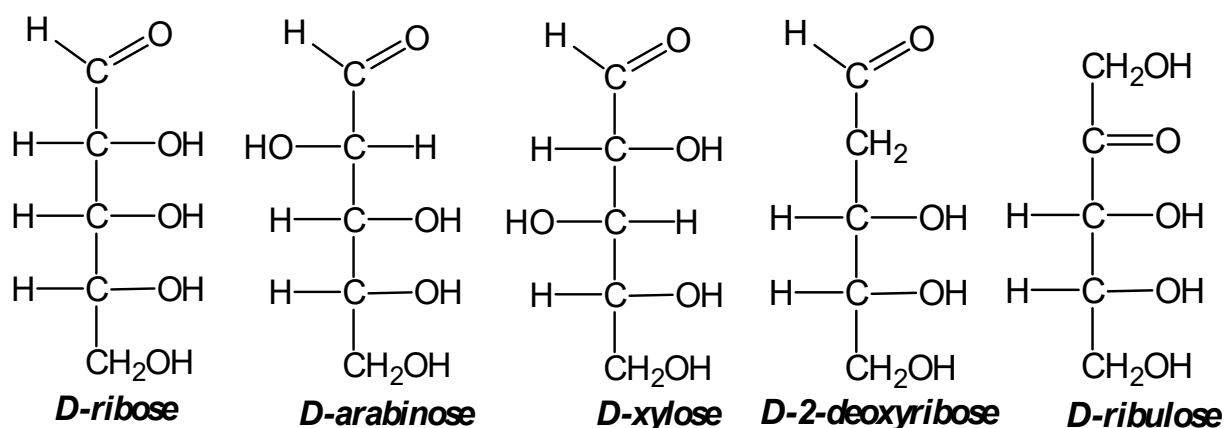
When an alcohol, ROH, reacts with another alcohol, R'OH, to split out H₂O, the product formed is an ether, ROR'. Carbohydrates are alcohols and behave accordingly. When a monosaccharide hemiacetal reacts with an alcohol, the product is an acetal. In carbohydrate terminology, this acetal structure is called a **glycoside** (derived from the Greek word *glykys*, meaning “sweet”). In the case of glucose, it would be a glucoside; if galactose, a galactoside; and so on.



The glycosidic linkage occurs in a wide variety of natural substances. All carbohydrates other than monosaccharides are glycosides. Heart stimulants such as digitalis and ouabain are known as heart glycosides. Several antibiotics such as streptomycin and erythromycin are also glycosides.

Pentoses

Arabinose and xylose occur in some plants as polysaccharides called pentosans. D-Ribose and its derivative, D-2-deoxyribose, are the most interesting pentoses because of their relationship to nucleic acids and the genetic code. Note the difference between the two names, D-ribose and D-2-deoxyribose. In the latter name, the 2-deoxy means that oxygen is missing from the D-ribose molecule at carbon 2. Check the formulas that follow to verify this difference.

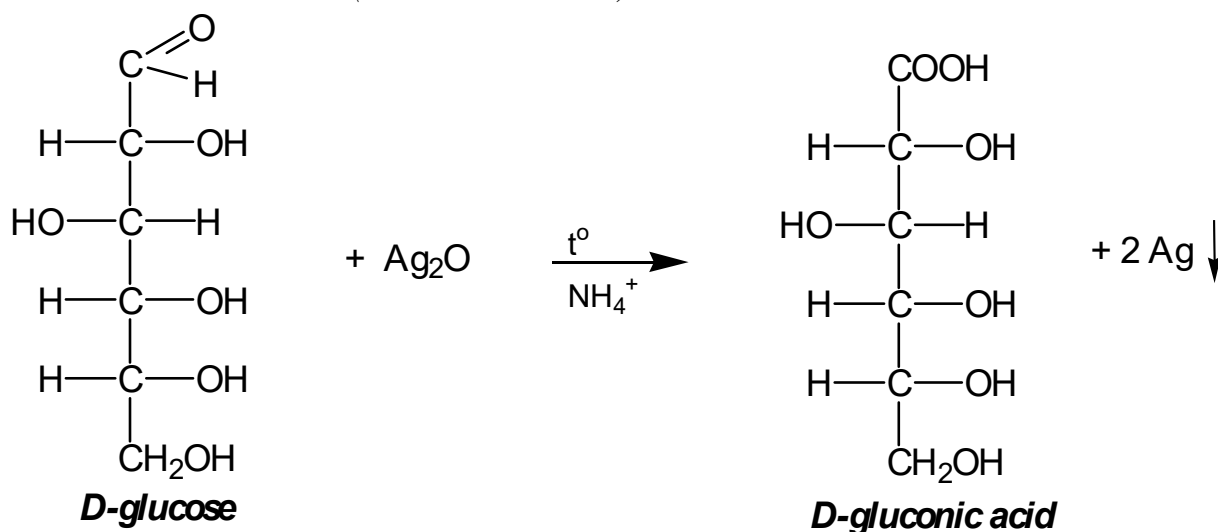


Chemical Properties

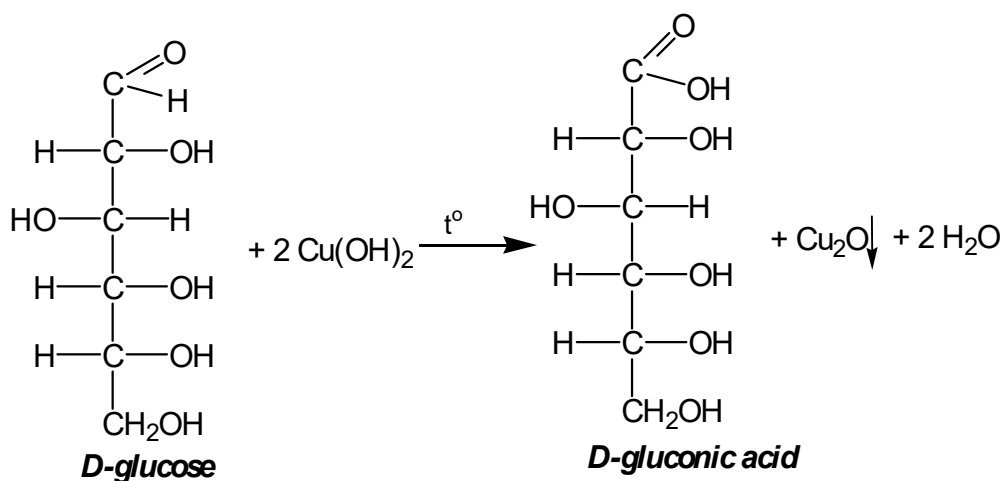
I. Oxidation

The aldehyde groups in monosaccharides can be oxidized to monocarboxylic acids by mild oxidizing agents such as bromine water. The carboxylic acid group is formed at carbon 1. The name of the resulting acid is formed by changing the *-ose* ending to *-onic acid*. *Glucose yields gluconic acid, galactose yields galactonic acid, and so on.*

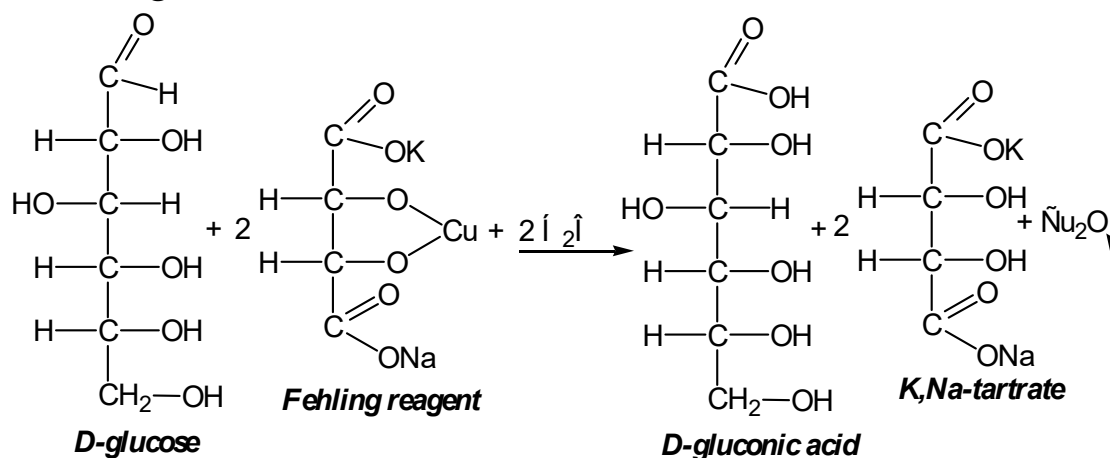
1. The Tollens test (silver-mirror test)



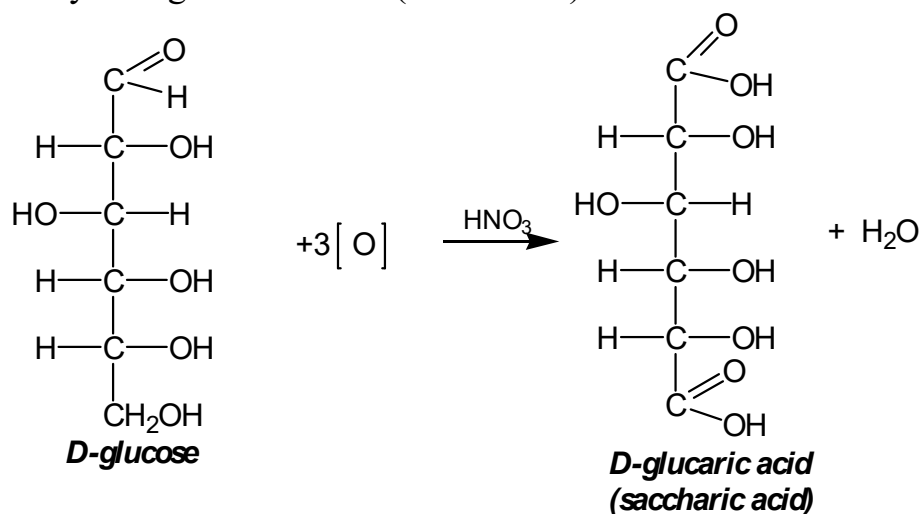
2. *Benedict's test* is similar to the Tollens test in that a metal ion is the oxidizing agent. In the Benedict tests, the aldehyde group is oxidized to an acid by Cu^{2+} ions. The blue Cu^{2+} ions are reduced and form brick-red copper (I) oxide (Cu_2O), which precipitates during the reaction. The tests use for detecting carbohydrates that have an available aldehyde group.



3. Fehling test



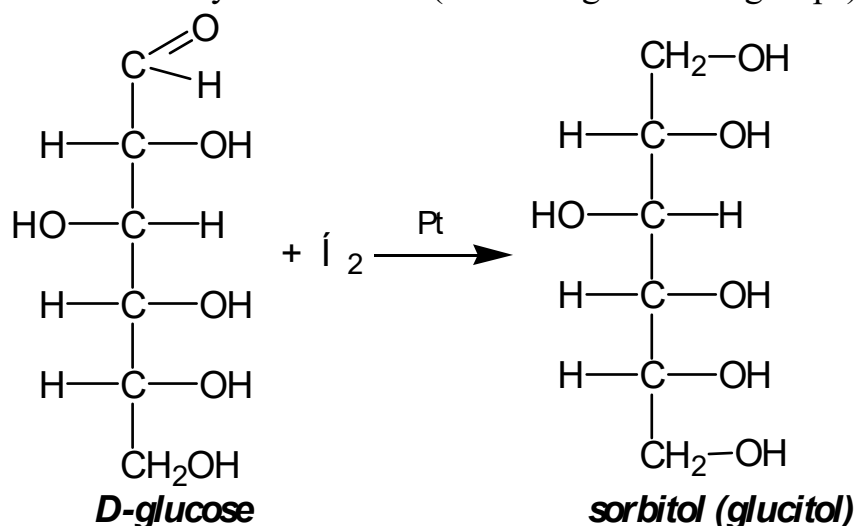
4. Dilute nitric acid, a vigorous oxidizing agent, oxidizes both carbon 1 and carbon 6 of aldohexoses to form dicarboxylic acids. The resulting acid is named by changing the *-ose* sugar suffix to *-aric acid*. Glucose yields glucaric acid (saccharic acid) and galactose yields galactaric acid (mucic acid):



II. Reduction

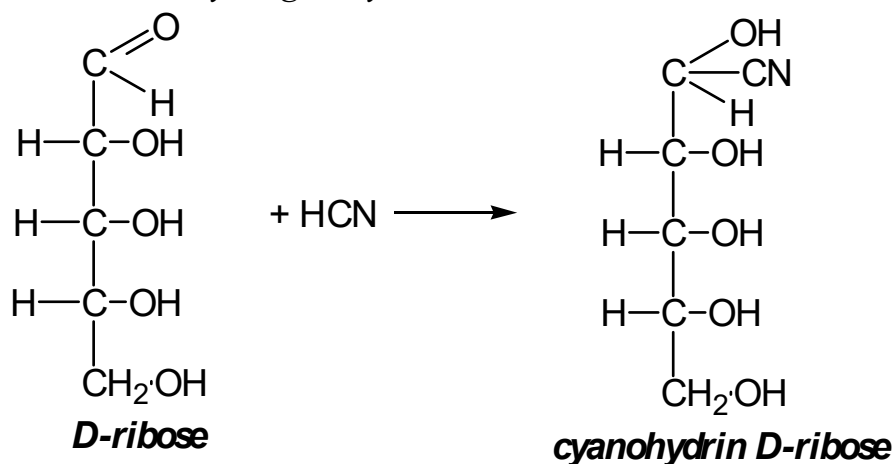
1. Interaction with Hydrogen

Monosaccharides can be reduced to their corresponding polyhydroxy alcohols by reducing agents such as H_2/Pt or sodium amalgam, $Na(Hg)$. For example, glucose yields sorbitol (glucitol), galactose yields galactitol (dulcitol), and mannose yields mannitol; all of these are hexahydric alcohols (containing six $-OH$ groups).



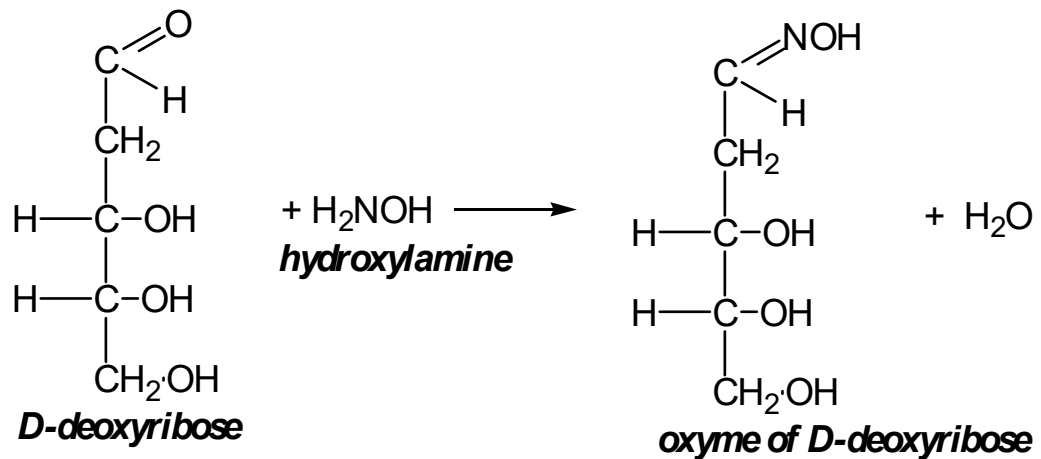
Many clinical tests monitor glucose as a reducing sugar. For example, Benedict and Fehling reagents are used to detect the presence of glucose in urine. Initially, the reagents are deep blue in color. A positive test is indicated by a color change to greenish yellow, yellowish orange, or brick red, corresponding to an increasing glucose (reducing sugar) concentration. These tests are used to estimate the amount of glucose in the urine of diabetics, in order to adjust the amount of insulin needed for proper glucose utilization.

2. Interaction with Hydrogen Cyanide

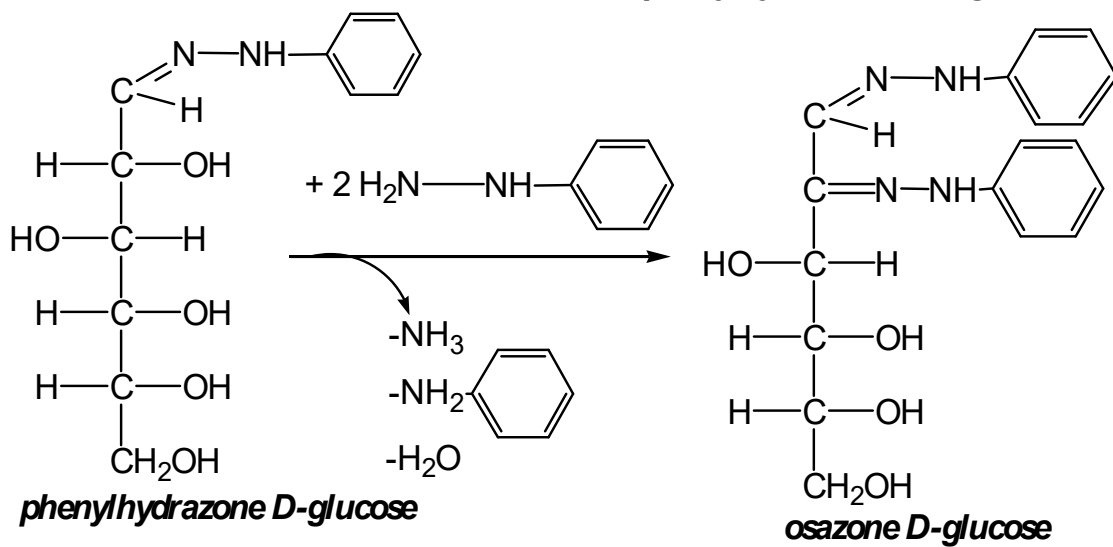
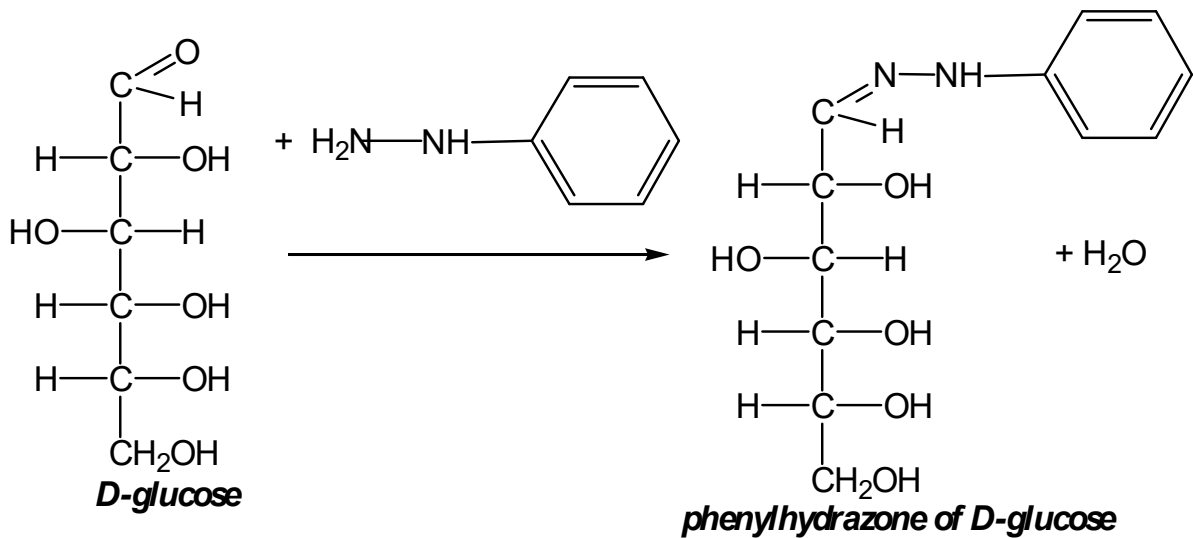


III. Substitution reactions

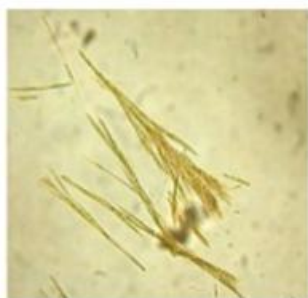
1. Interaction with hydroxylamine (getting oxymes)



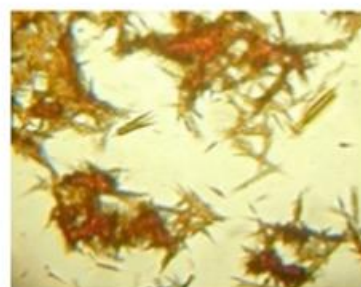
2. Interaction with phenylhydrazine



OSAZONE TEST



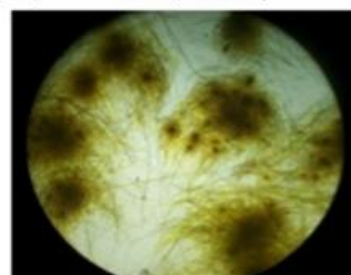
Needle shaped glucosazone crystals as viewed under the microscope



Galactosazone crystals as viewed under the microscope (Rhombic plates)



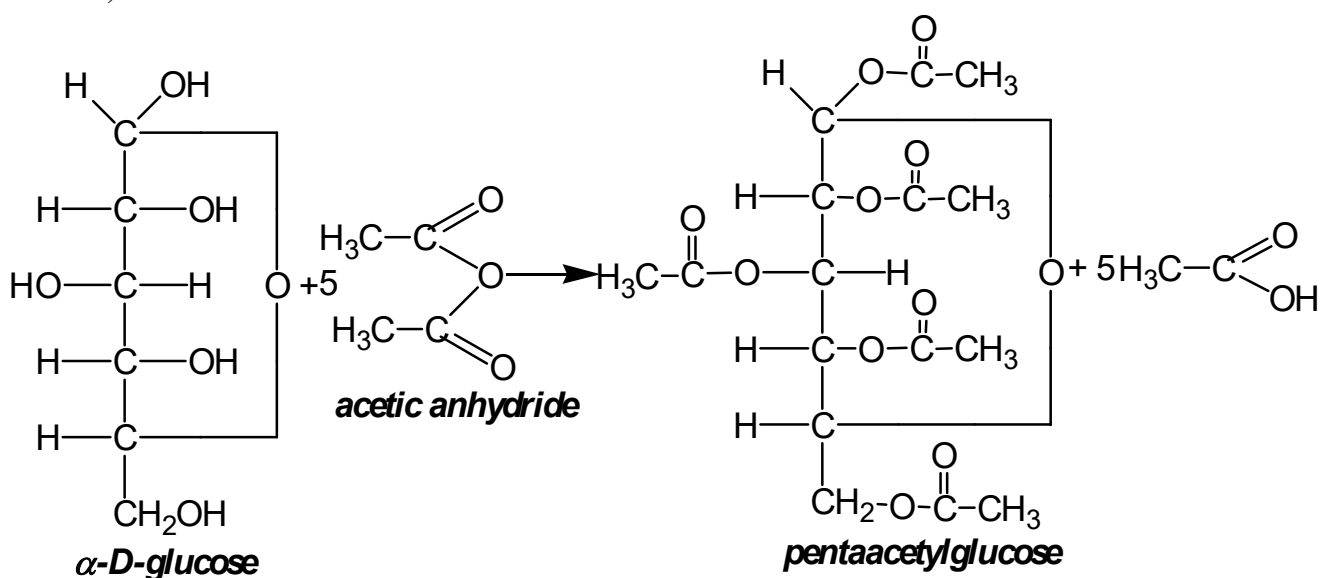
Sun flower shaped Maltosazone crystals as viewed under the microscope



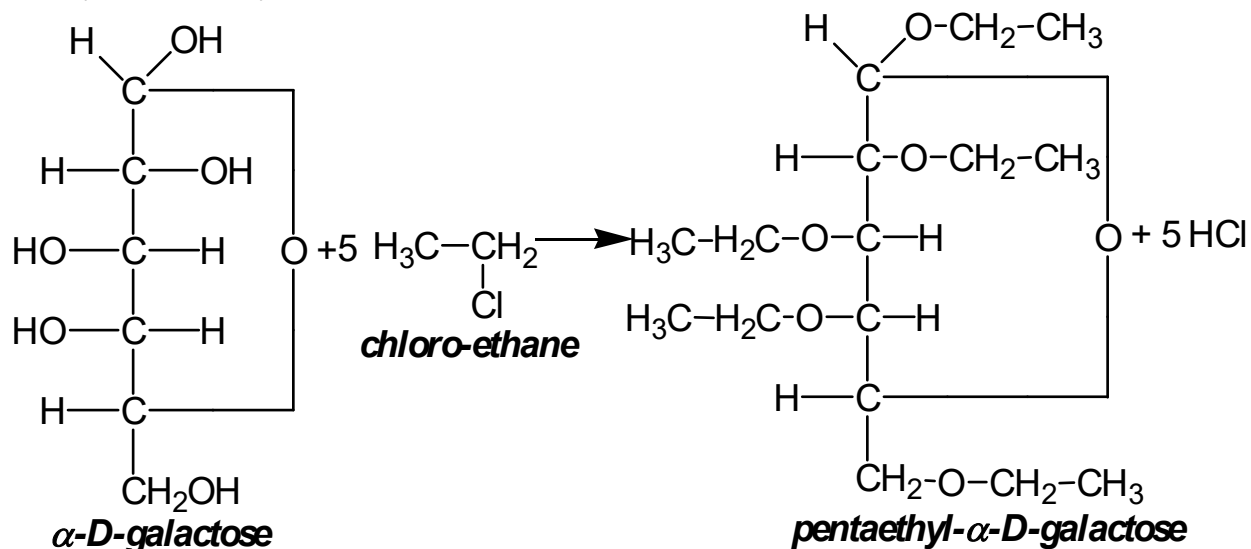
Powder puff/hedge hog shaped crystals of lactose as viewed under the microscope

IV. Alcohol properties

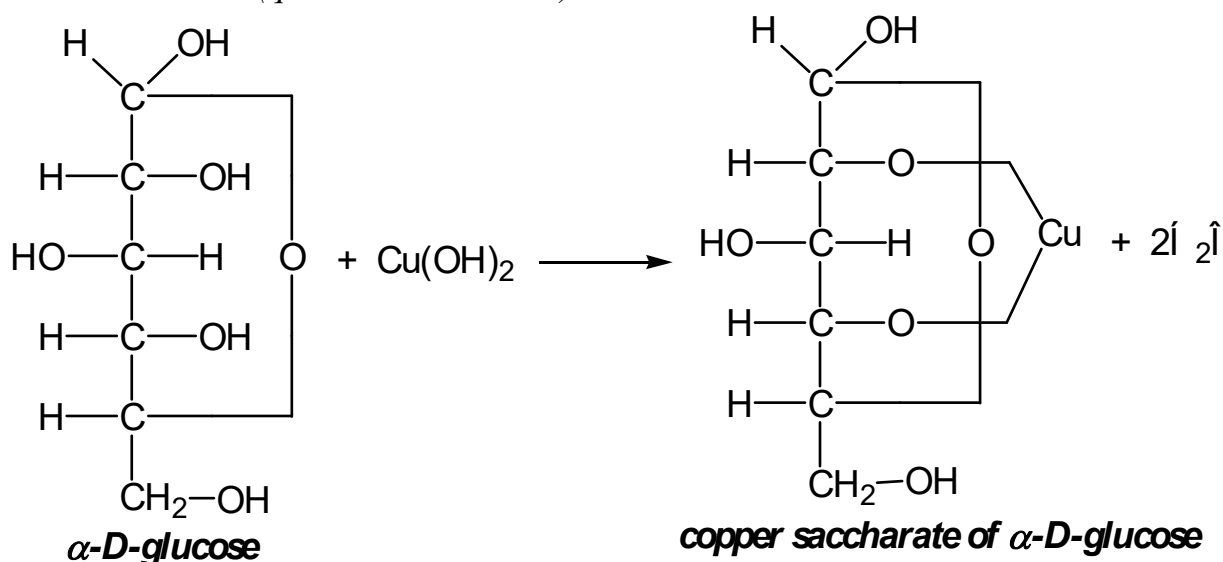
1. Formation of esters (interaction with carboxylic acids, anhydrides, acid halides)



2. The formation of ethers



3. Like all polyhydric alcohols, glucose with copper (II) hydroxide gives an intense blue color (qualitative reaction)



Learning Check

1. Indicate the number of hydroxyl groups in the D-mannose molecule.

1. 5
2. 6
3. 4
4. 3
5. 2

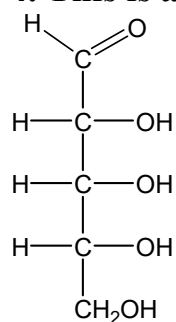
2. Depending on the ability to hydrolyze all carbohydrates are divided into three main groups:

1. Monosaccharides
2. Lipids
3. Oligosaccharides
4. Polysaccharides
5. Amino acids

3. The following three hexoses are most commonly found in higher animals:

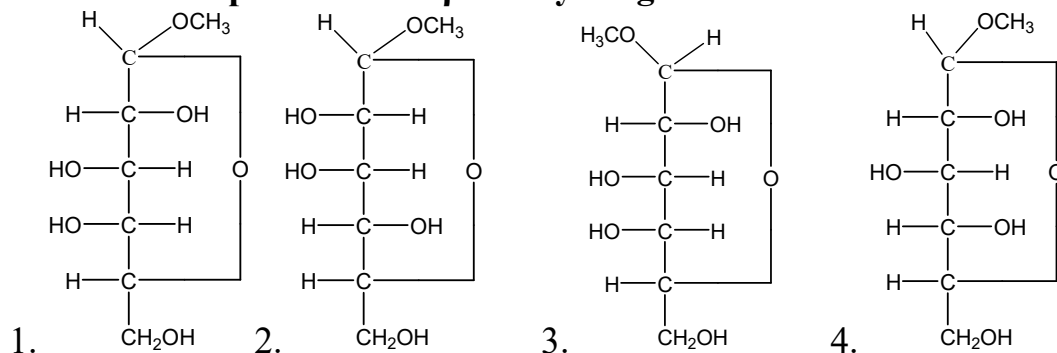
1. Glycogen
2. Glucose
3. Galactose
4. Maltose
5. Fructose

4. This is a formula ...



1. D-arabinose
2. D-xylose
3. D-ribose
4. D-deoxyribose
5. D-mannose

5. Choose a compound called β -methyl-D-galactoside:



6. Specify carbohydrate-free food.

1. Honey
2. Bread
3. Sugar
4. Vinegar

7. Write the reduction reaction of D-xylose H_2 .

8. Write the reaction between D-glucose and hydroxylamine ($\text{H}_2\text{N}-\text{OH}$). (This is the substitution reaction of carbonyl oxygen).

2.2. Disaccharides

Disaccharides are carbohydrates composed of two monosaccharide residues united by a glycosidic linkage.

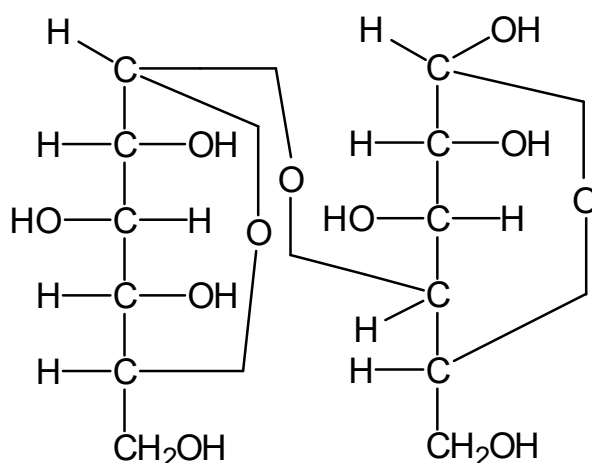
Disaccharides may be of two types, namely *non-reducing* and *reducing*.

The oxidation of a sugar's anomeric carbon by cupric or ferric ion (the reaction that defines a reducing sugar) occurs only with the linear form, which exists in equilibrium with the cyclic form(s). When the anomeric carbon is involved in a glycosidic bond, that sugar residue cannot take the linear form and therefore becomes a *nonreducing sugar (sucrose, trehalose)*. In describing disaccharides or polysaccharides, the end of a chain with a free anomeric carbon (one not involved in a glycosidic bond) is commonly called the *reducing end (lactose, maltose, cellobiose)*.

Reducing disaccharides

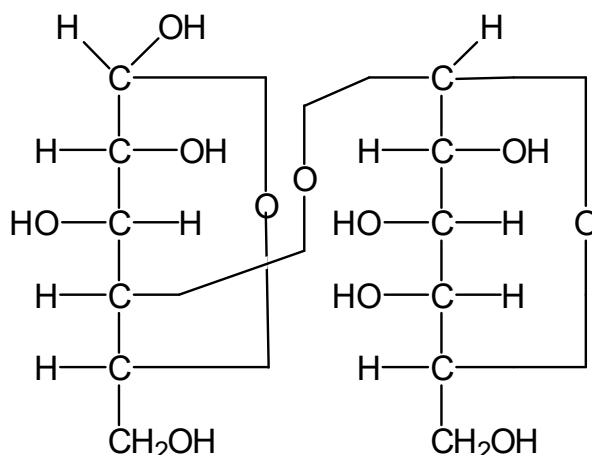
The disaccharide *maltose* contains two α -D-glucose residues joined by a glycosidic linkage between C-1 (the anomeric carbon) of one glucose residue and C-4 of the other. Because the disaccharide retains a free anomeric carbon (C-1 of the glucose residue on the right), *maltose is a reducing sugar*.

Maltose is the second member of an important biochemical series of glucose chains. Maltose is the disaccharide produced when amylase breaks down starch. It is found in germinating seeds as they break down their starch stores to use for food, which is why it was named after malt. It is also produced when glucose is caramelized.

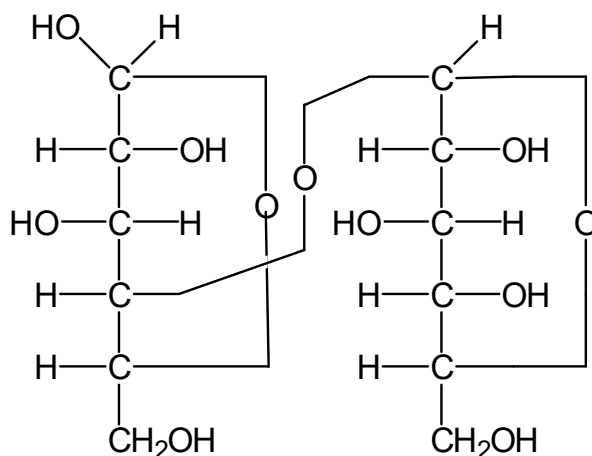


Lactose is a disaccharide sugar composed of galactose and glucose that is found in milk. Lactose makes up around 2–8% of milk (by weight), although the amount varies among species and individuals, and milk with a reduced amount of

lactose also exists. It is extracted from sweet or sour whey. The name comes from *lac* (gen. *lactis*), the Latin word for milk, plus the *-ose* ending used to name sugars.

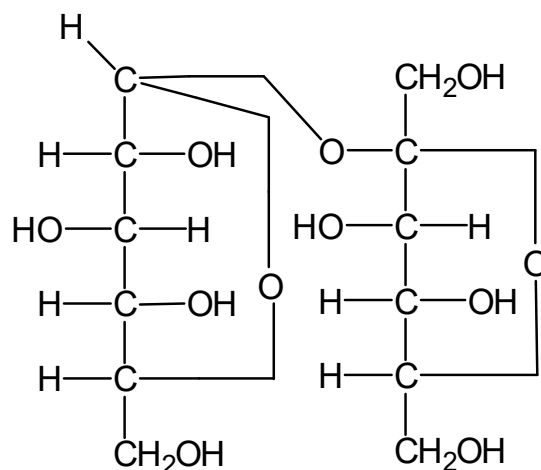


Cellobiose, a reducing sugar, consists of two β -glucose molecules linked by a $\beta(4\rightarrow1)$ bond. It can be hydrolyzed to glucose enzymatically or with acid. Cellobiose has eight free alcohol (OH) groups, one acetal linkage and one hemiacetal linkage, which give rise to strong inter- and intramolecular hydrogen bonds. It can be obtained by enzymatic or acidic hydrolysis of cellulose and cellulose rich materials such as cotton or paper.

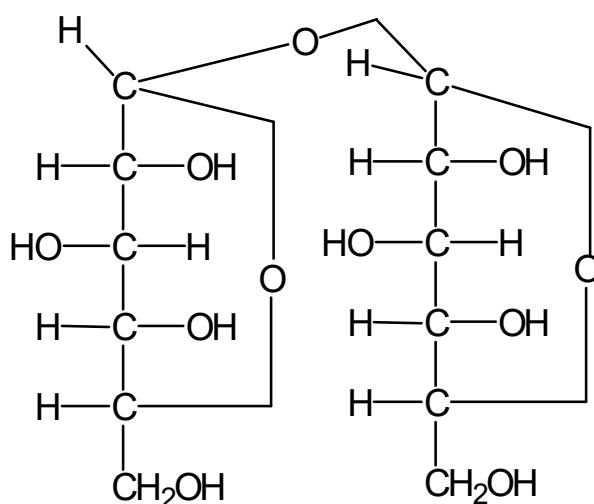


Non-reducing disaccharides

Sucrose is a common saccharide found in many plants and plant parts. The molecule is a disaccharide combination of the monosaccharides glucose and fructose. Sucrose, commonly known as *table sugar*, exists throughout the plant kingdom. Sugar cane contains 15–20% sucrose, and sugar beets 10–17%. Maple syrup and sorghum are also good sources of sucrose.

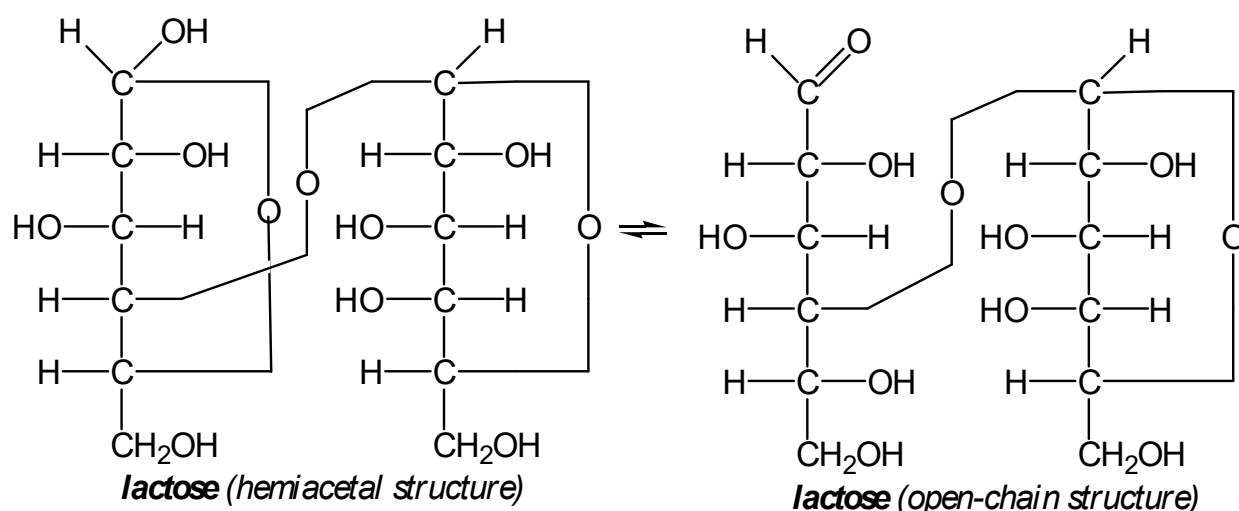


Trehalose, also known as **mycose** or **tremalose**, is a natural alpha-linked disaccharide formed by an α,α -1,1-glucoside bond between two α -glucose units. It can be synthesized by bacteria, fungi, plants, and invertebrate animals. It is implicated in anhydrobiosis – the ability of plants and animals to withstand prolonged periods of desiccation. It has high water retention capabilities, and is used in food and cosmetics. The sugar is thought to form a gel phase as cells dehydrate, which prevents disruption of internal cell organelles, by effectively splinting them in position.



Chemical properties

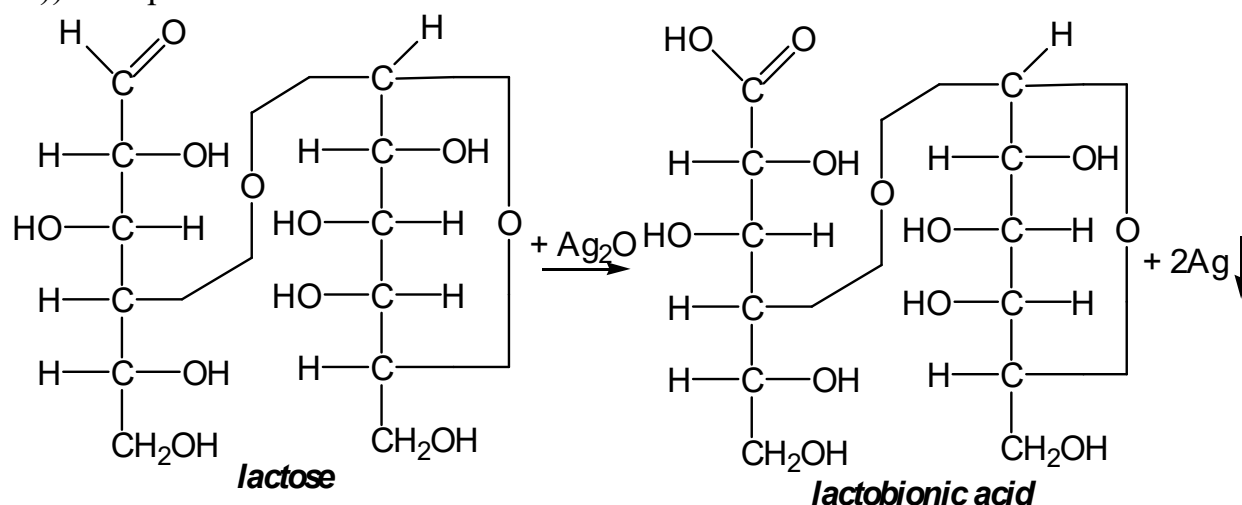
1. Lactose, maltose and cellobiose show mutarotation which indicates that one of the monosaccharide units has a hemiacetal ring that opens and closes to interchange anomers. Sucrose has no hemiacetal structure and hence does not mutarotate.

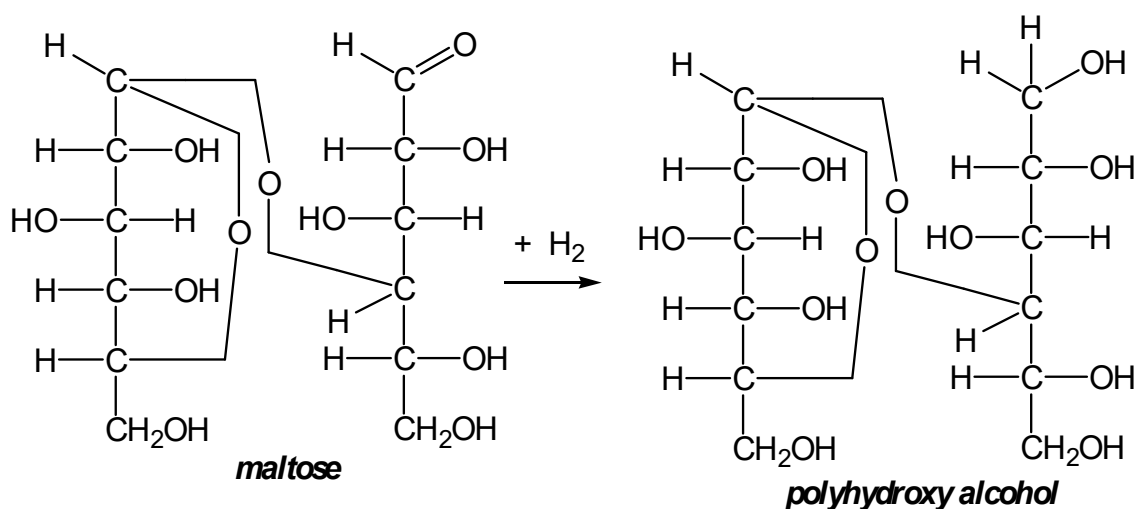


2. Reducing property of sugars

The reducing property is mainly due to the ability of these sugars to reduce metal ions such as copper or silver to form insoluble cuprous oxide, under alkaline condition.

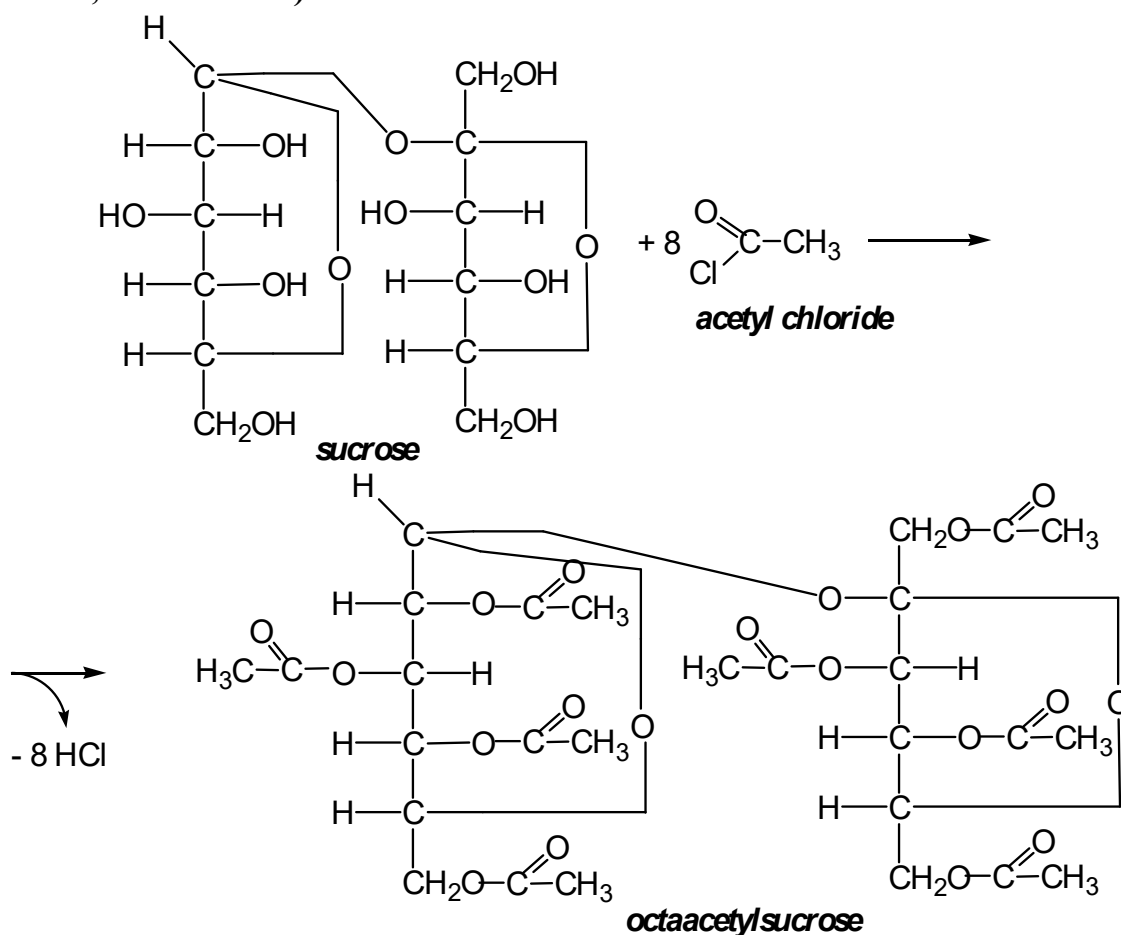
The aldehyde group of aldoses is oxidized to carboxylic acid. This reducing property is the basis for qualitative (Fehling's, Benedict's, Tollen's test (silver-mirror test)) and quantitative reactions.





3. Substitution reactions similar monosaccharides (*interaction with hydroxylamine, phenyl-hydrazine*).

4. Properties of disaccharides as polyhydroxy alcohols (preparation of esters, saccharates).



The non-reducing disaccharides have no aldehyde properties. They are characterized by the properties of polyhydroxy alcohols.

2.3. Polysaccharides

Most carbohydrates found in nature occur as polysaccharides, polymers of medium to high molecular weight. Polysaccharides, also called **glycans**, differ from each other in the identity of their recurring monosaccharide units, in the length of their chains, in the types of bonds linking the units, and in the degree of branching. *Homopolysaccharides* contain only a single type of monomer; *heteropolysaccharides* contain two or more different kinds.

Some homopolysaccharides serve as storage forms of monosaccharides that are used as fuels; *starch* and *glycogen* are homopolysaccharides of this type. Other homopolysaccharides (*cellulose* and *chitin*, for example) serve as structural elements in plant cell walls and animal exoskeletons. Heteropolysaccharides provide extracellular support for organisms of all kingdoms. For example, the rigid layer of the bacterial cell envelope (the peptidoglycan) is composed in part of a heteropolysaccharide built from two alternating monosaccharide units. In animal tissues, the extracellular space is occupied by several types of heteropolysaccharides, which form a matrix that holds individual cells together and provides protection, shape, and support to cells, tissues, and organs.

Starch

Starch $(C_6H_{10}O_5)_n$ is found in plants, mainly in the seeds, roots, or tubers. Corn, wheat, potatoes, rice, and cassava are the chief sources of dietary starch. The two main components of starch are *amylose* and *amylopectin*. *Amylose* molecules are unbranched chains composed of about 25–1300 α -D-glucose units joined by α -1,4-glycosidic linkages (fig. 2.10). The stereochemistry of the α -anomer causes amylose to coil into a helical conformation. Partial hydrolysis of this linear polymer yields the disaccharide maltose.

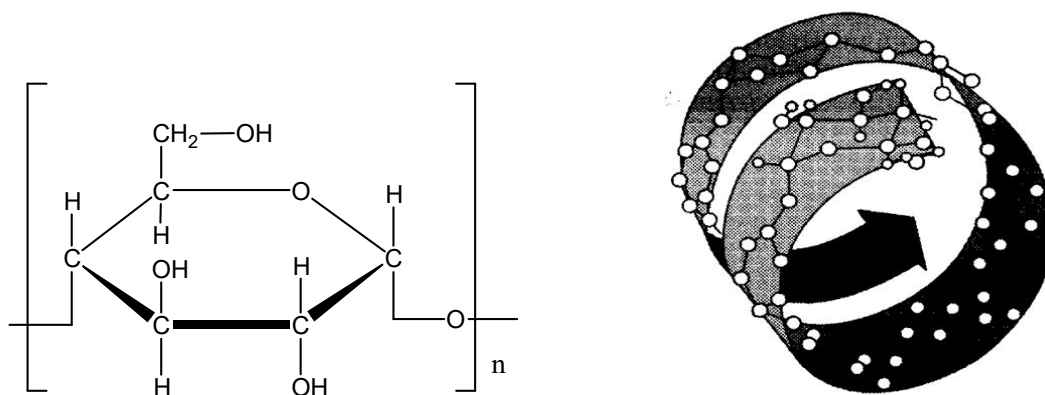


Figure 2.10. Structure of amylose

Amylopectin is a branched-chain polysaccharide with much larger molecules than those of amylose (fig. 2.11).

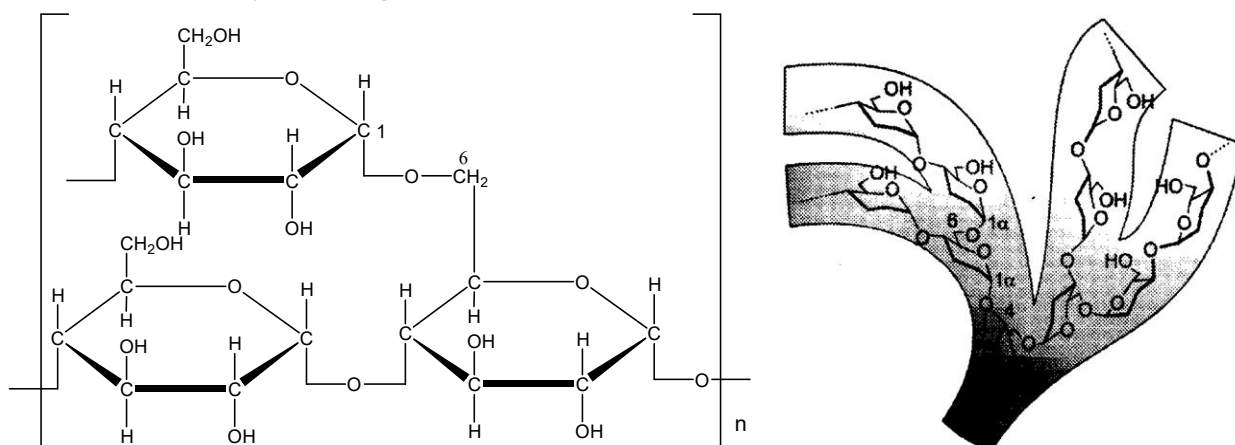


Figure 2.11. Structure of amylopectin

Amylopectin molecules consist, on average, of several thousand α -D-glucose units with molar masses ranging up to 1 million or more. The main chain contains glucose units connected by α -1,4-glycosidic linkages. Branch chains are linked to the main chain through α -1,6-glycosidic linkages about every 25 glucose units. This molecule has a characteristic treelike structure because of its many branch chains. Partial hydrolysis of amylopectin yields both maltose.

Despite the presence of many polar -OH groups, starch molecules are insoluble in cold water, apparently because of their very large size. Starch readily forms colloidal dispersions in hot water. Such starch “solutions” form an intense blue-black color in the presence of free iodine. Hence, a starch solution can be used to detect free iodine, or a dilute iodine solution can be used to detect starch.

Starch is readily converted to glucose by heating with water and a little acid (e.g., hydrochloric or sulfuric acid). It is also readily hydrolyzed at room temperature by certain digestive enzymes. The hydrolysis of starch to glucose is shown in the following equation:



The hydrolysis of starch can be followed qualitatively by periodically testing samples from a mixture of starch and saliva with a very dilute iodine solution. The

change of color sequence is *blue-black*→*blue*→*purple*→*pink*→*colorless*, as the starch molecules are broken down into smaller and smaller fragments.

Hydrolysis is a key chemical reaction in the digestion of starchy foods. If these foods are well chewed, salivary amylase normally decreases the starch polymer chain length from on the order of a thousand glucose units to about eight per chain. In the small intestine, pancreatic amylase continues digestion to form maltose. Enzymes in the small intestine membranes complete the conversion of starch to glucose, which is then absorbed into the bloodstream.

Glycogen

Glycogen ($C_6H_{10}O_5$)_n is the energy-storage carbohydrate of the animal kingdom. It is formed by polymerization of glucose and is stored in the liver and in muscle tissues. Structurally, it is very similar to the amylopectin fraction of starch, except that it is more highly branched. The α -1,6-glycosidic linkages occur on one of every 12–18 glucose units (fig. 2.12).

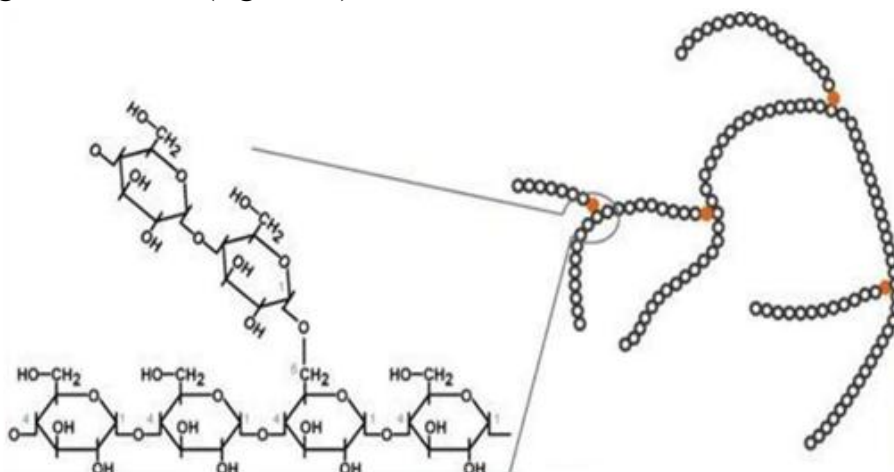


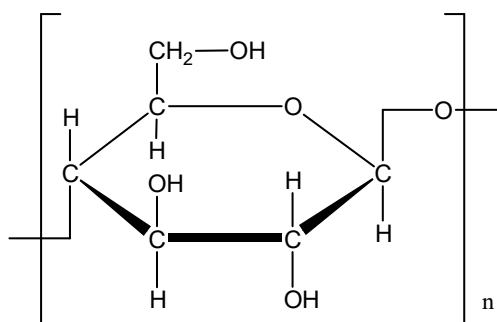
Figure 2.12. Structure of glycogen

Cellulose

Cellulose is the most abundant organic substance found in nature. It is the chief structural component of plants and wood. Cotton fibers are almost pure cellulose; wood, after removal of moisture, consists of about 50% cellulose. Cellulose is an important substance in the textile and paper industries.

Cellulose, like starch and glycogen, is a polymer of glucose. But cellulose differs from starch and glycogen in that the glucose units are joined by α -1,4-glycosidic linkages instead of β -1,4-glycosidic linkages. The stereochemistry of the β -anomer allows the polymer to form an extended chain that can hydrogen-

bond to adjacent cellulose molecules. The large number of hydrogen bonds so formed partially accounts for the strength of the resulting plant cell walls.

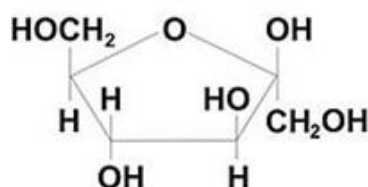


When partial hydrolysis of cellulose occurs, it produces the disaccharide cellobiose. However, cellulose has greater resistance to hydrolysis than either starch or glycogen. It is not appreciably hydrolyzed when boiled in a 1% sulfuric acid solution. It does not show a color reaction with iodine. Humans cannot digest cellulose, because they have no enzymes capable of catalyzing its hydrolysis.

Fortunately, some microorganisms found in soil and in the digestive tracts of certain animals produce enzymes that do catalyze the breakdown of cellulose. The presence of these microorganisms explains why cows and other herbivorous animals thrive on grass and why termites thrive on wood.

Inulin

$(C_6H_{10}O_5)_n$ – organic substance from the group of polysaccharides, polymer D- fructose.

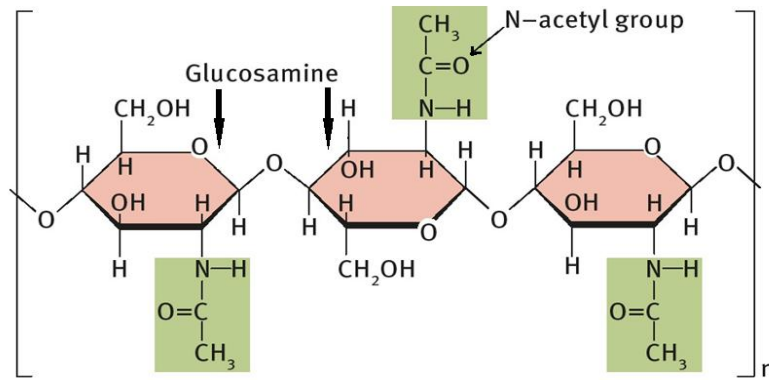


Inulin is not digested by the digestive enzymes of the human body and belongs to the group of dietary fibers. In connection with this, it is used in medicine as a prebiotic. Serves as the starting material for the industrial production of fructose.

It is used as a starch and sugar substitute in diabetes mellitus.

Chitin

Chitin is a linear homopolysaccharide composed of *N*-acetylglucosamine residues in β -linkage. The only chemical difference from cellulose is the replacement of the hydroxyl group at C-2 with an acetylated amino group.



Chitin forms extended fibers similar to those of cellulose, and like cellulose cannot be digested by vertebrates. Chitin is the principal component of the hard exoskeletons of nearly a million species of arthropods – insects, lobsters, and crabs, for example – and is probably the second most abundant polysaccharide, next to cellulose, in nature (fig. 2.13).

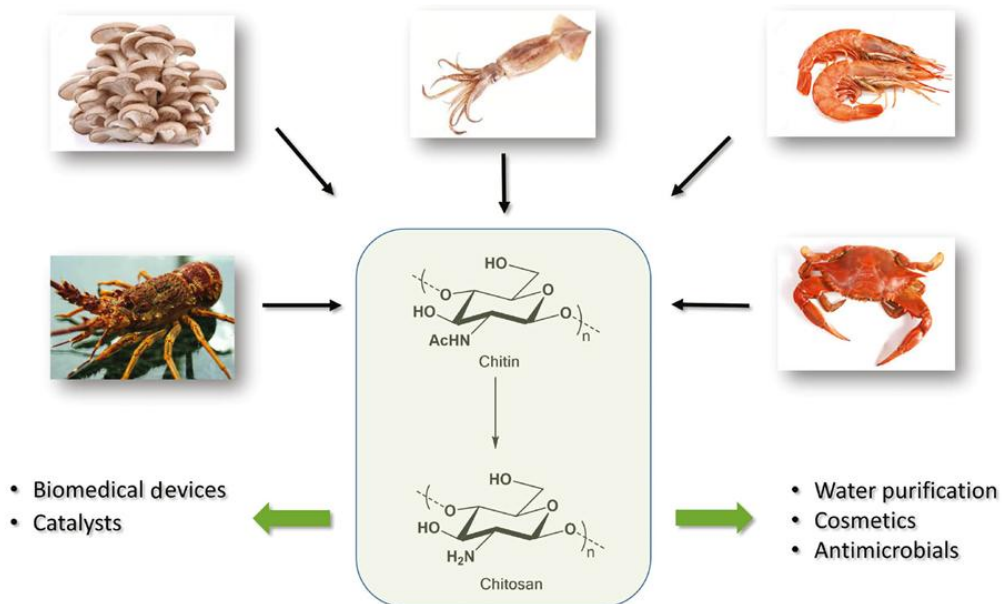
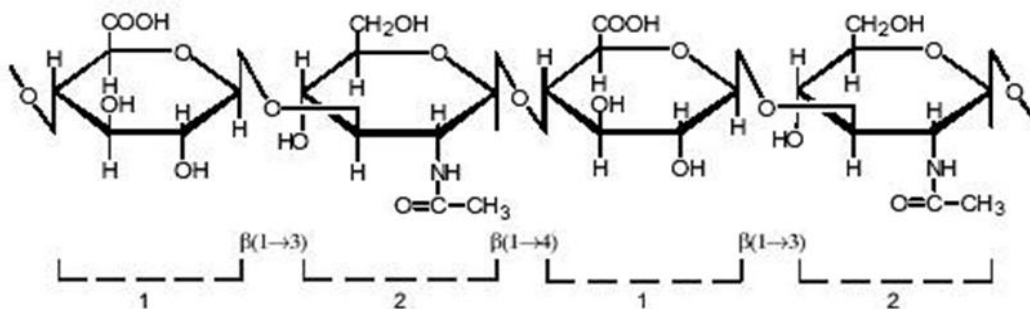


Figure 2.13. Chitin

Hyaluronic acid



1. *β -glucuronic acid*; 2. *N-acetyl-glucosamine*

Heteropolysaccharide, that is found in extracellular tissue space, the synovial fluid of joints, and the vitreous humor of the eyes and acts as a binding, lubricating, and protective agent.

Properties of Hyaluronic acid: is a substance naturally produced by the body in order to moisturize and protect the tissues (fig. 2.13).

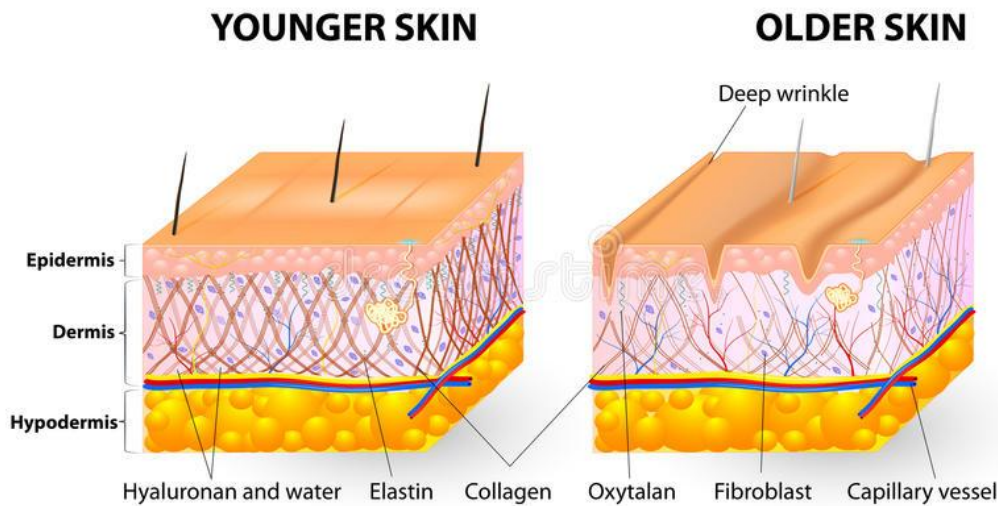
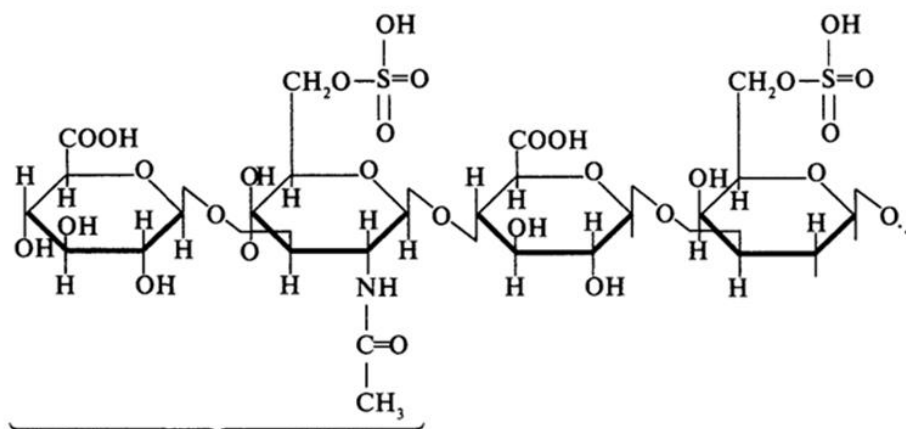


Figure 2.13. Hyaluronic acid in the skin

Chondroitin sulfuric acid

Chondroitin sulfates contain in a connecting tissue, skin, cartilages and tendons (fig. 2.14). They are esters of a sulfuric acid.

It is a product of polymerization of N-acetylgalactosamine sulfate and glucuronic acid, which are interconnected β -1,3- and β -1,4-glycoside bonds.



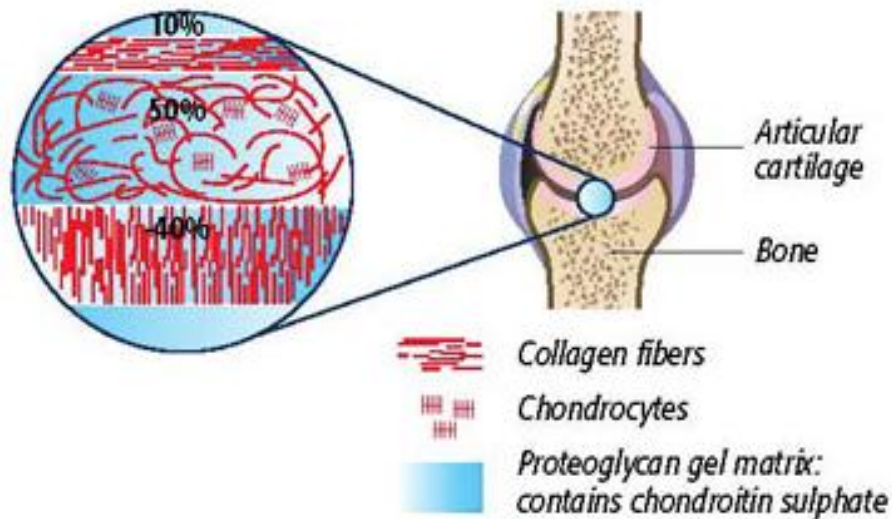
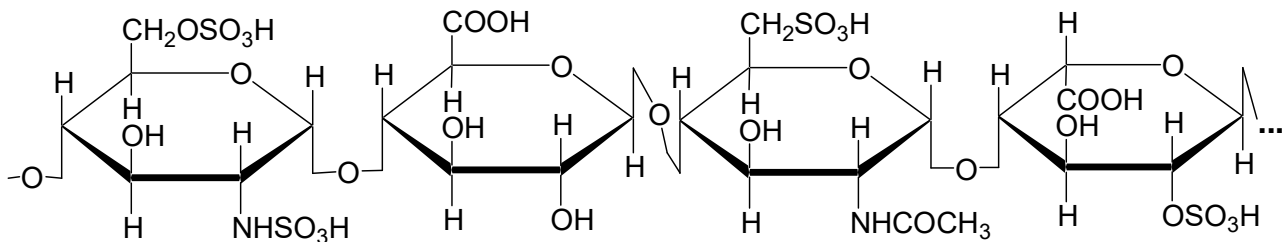


Figure 2.14. Structure of articular cartilage

Heparin

The molecule of this substance is formed by residues of α -D-glucosamine, glucuronic acid and sulfate acids.



Heparin is an anticoagulant (blood thinner) that prevents the formation of blood clots. Heparin is used to treat and prevent blood clots in the veins, arteries, or lung. Heparin is also used before surgery to reduce the risk of blood clots.

Learning Check

1. The sucrose molecule is consisting from residues...

1. α -D-glucose and α -D-glucose (linkage 1 \rightarrow 4)
2. α -D-glucose and β -D-glucose (linkage 4 \rightarrow 1)
3. α -D-glucose and β -D-galactose (linkage 4 \rightarrow 1)
4. α -D-glucose and β -D-fructose (linkage 1 \rightarrow 2)
5. 2 molecules of α -D-glucose (linkage 1 \rightarrow 1)

2. To the reducing disaccharides are the following three:

1. Maltose

2. Lactose
3. Sucrose
4. Trehalose
5. Cellobiose

3. Disaccharides are the following two oligosaccharides:

1. Raffinose
2. Lactose
3. Sucrose
4. Trifruktosan

4. Establish a sequence of produced products of reactions of enzymatic hydrolysis of starch:

1. Maltose
2. Starch
3. Dextrin
4. Glucose

5. Set match:

<i>Disaccharide</i>	<i>Product in which is located</i>
1. Lactose	A. Grass, hay
2. Sucrose	B. Milk
3. Cellobiose	C. Sprouts of cereals
4. Maltose	D. Sugar beet

6. The following three polysaccharides have plant origin:

1. Starch
2. Heparin
3. Glycogen
4. Cellulose
5. Agar

7. The monomer of heparin consists of the following three compounds

1. Glucosamine
2. Glucuronic Acid
3. Sulfate acid
4. Acetic acid
5. Galactosamine

8. Choose two carbohydrates which are heteropolysaccharides

1. Glycogen
2. Hyaluronic acid
3. Sucrose
4. Starch
5. Heparin

9. The intermediate product of hydrolysis of cellulose is disaccharide...

1. Trehalose
2. Sucrose

3. Maltose
4. Cellobiose
5. Lactose

10. Most hyaluronic acid is found in the following tissues:

1. Liver
2. Blood
3. Glassy eye body
4. Articular fluid
5. Skeletal muscles

RECOMMENDED BOOKS

Basic:

1. Organic Chemistry (third edition): student study guide and solutions manual / David Klein, 2016.
2. Chemistry (third edition): introducing inorganic, organic and physical chemistry / A. Burrows, J. Holman, A Parsons, G. Pilling, G. Price – Oxford, 2017.
3. General, Organic and Biological Chemistry (seventh edition) / H. Stephan Stoker – Boston, 2014.

Additional:

4. Organic Chemistry by T. W. Graham Solomons, Craig B. Fryhle, Scott A. Snyder. – January 20, 2016.
5. Textbook of Organic Chemistry Paperback by V K Ahluwalia, Rakesh K Parashar – 1 January 2012.
6. Organic Chemistry (second edition) / Jonathan Clayden, Nick Greeves, Stuart Warren. – Oxford, 2012.

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MIXED FUNCTION COMPOUNDS

СПОЛУКИ ЗІ ЗМІШАНИМИ ФУНКЦІЯМИ

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