Kurta S.A. Chemistry of carbohydrates and polysaccharides

Lecture №2.Content module 2. Monosaccharides.

Topic 4. Features of the structure, production and use of monosaccharides

Topic 5. Cyclic structure of monosaccharides. Mutarotation. Glycosides.

Topic 6. Synthesis and decomposition of monosaccharides. Chemical properties. Reactions of monosaccharides. Proof of the structure of D-glucose.

Purpose: to give the student the necessary knowledge about the chemical properties, structure, classification, origin of names, production, use, use, distribution of carbohydrates and natural di- and polysaccharides, to systematize and summarize material on natural carbohydrates and polysaccharides studied during previous years; to acquaint with all typical classes of carbohydrates and natural di- and polysaccharides; to teach students the rules of work in the chemical laboratory, safety; to acquire skills of independent work on synthesis, isolation, study of properties and establishment of structure of carbohydrates and di- and polysaccharides.

Plan

1. Monosaccharides

1.1. Features of the structure

1.1.2. Cyclic structure of monosaccharides

1.1.3. Mutarotation

1.1.4. Glycosides

1.2. Obtaining monosaccharides

1.2.1. Synthesis and decomposition of monosaccharides

1.3.Chemical properties

1.3.1. Reactions of monosaccharides

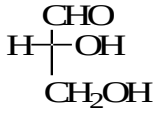
1.3.2. Proof of the structure of D-glucose

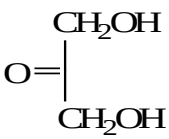
Lecture content

Section 1. Monosaccharides

1.1.Features of the structure

1.1.1 In nature, the most common monosaccharides are pentoses and hexoses, mostly aldose groups. The ancestors of the genetic series of monosaccharides are chiral glycerol aldehyde for aldosis and dihydroxyacetone for ketosis:

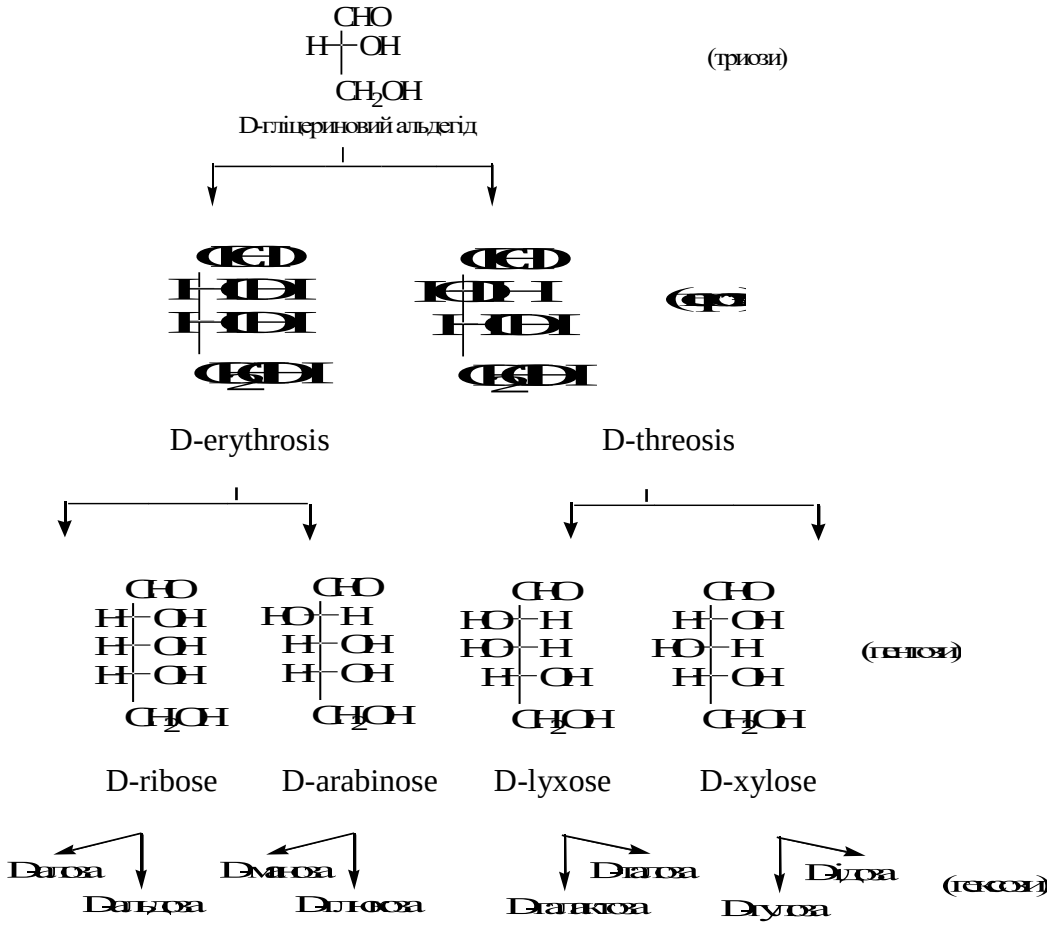




glycerol aldehyde dihydroxyacetone

From these compounds it is possible to obtain by synthetic method other monosaccharides which form a genetic series. The assignment of carbohydrates to the D- or L-series depends on the configuration of the lower chiral carbon atom in contrast to hydroxy acids and amino acids, for which the configuration is determined by the upper chiral atom.

The genetic series of D-aldosis is presented in the diagram:



A similar pattern is observed for L-glycerol aldehyde. Using the ancestor of ketosis dihydroxyacetone, you can build by analogy with the genetic series of D-ketosis:

Trivial names of tetra- and pentaketoses are formed from the names of the corresponding aldosis with the suffix -ulosa.

For monosaccharides, there are also systematic names according to IUPAC rules. Thus, the name aldosis is formed using configuration prefixes that correspond to the main name without ending in -za. Configuration prefix - Fisher projection of the corresponding base without taking into account the upper (carbonyl) and lower carbon atoms, denoted, for example: D-erythro- (this is the projection of D-erythrosis without the upper CHO- and lower CH2OH-group), D-arabino-, D -gluco-. Then the name of the base (tetrose, pentose, hexose, etc.) with the ending -oz is added to the configuration prefix, for example: D-threosa (trivial name) => D-threo-tetrose (systematic name), D-arabinose => D-arabino- pentose, D-glucose => D-glucose-hexose. Similarly, the names ketosis are formed, but the configuration prefix is based on the one that corresponds to the basis of aldose from the lower carbon atom to the keto group. For example, the configuration prefix arabino is used for D-fructose, because the configuration of D-fructose from the lower CH2OH group to the keto group corresponds to the configuration of aldose - D-arabinose. The ending -a is changed to -ulose, and the position of the keto group is denoted by a locant, for example: D-erythrulose => D-glycero-2-tetrulose, D-fructose => D-arabino-2-hexulose, D-tagatose => D -lexo-2-hexulose. More complex rules for monosaccharide derivatives.

The most common monosaccharides are D-glucose (grape sugar) and D-fructose (fruit sugar). Thus, glucose is found in grapes and most sweet fruits, is part of disaccharides (maltose, lactose, etc.), polysaccharides (starch, fiber, glycogen, dextrins, etc.). Fructose is also found mainly in sweet fruits,

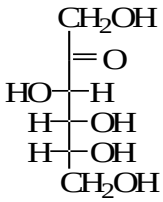
but in smaller quantities than glucose, and in addition, in honey, tomatoes; is a part of sucrose disaccharide, inulin polysaccharide, etc.

Based on the study of the chemical properties of glucose (in the reactions of reduction, acylation, oxidation, formation of oximes) A. Bayer and R. Fittig (1870) determined its structural formula:

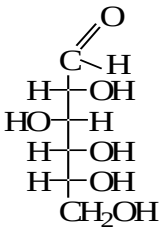
CH2OH-CH (OH) -CH (OH) -CH (OH) -CH (OH) -CH = O

Later, E. Fischer investigated the spatial configuration of glucose and

fructose and proposed for them modern projection formulas:



D-fructose



D-glucose

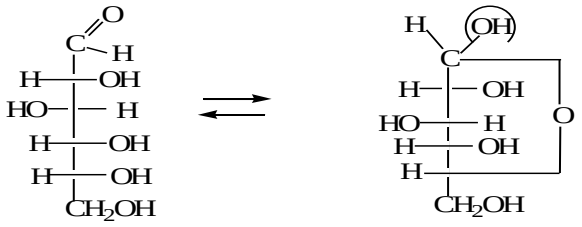
These formulas are called open or chain (carbonyl).

Numbering begins at the end of the chain to which the oxo group is closest. The notation α-, ß-, etc. is also used in relation to the oxo group.It was found that one hydroxyl is more reactive in chemical properties and differs from four other hydroxils.

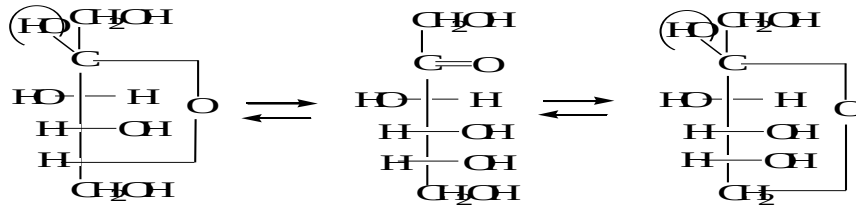
In addition, despite the ability of compounds such as glucose to reactions characteristic of oxo groups (interaction with HCN, oxidation by ammonia solution of silver oxide, reduction to hexahydric alcohol, formation of ozone with phenylhydrazine), they do not interact with NaH hydrosulfite. , do not enter into condensation and polymerization reactions. This indicates the existence of another form of monosaccharides, the so-called cyclic or semi-acetal (ring, form of O. Collie - B. Tollens), which occurs, for example, for glucose and fructose.

1.1.2. Cyclic structure of monosaccharides

The hemiacetal of glucose is formed by the intramolecular method by the interaction of the carbonyl group with the hydroxyl near the δ-carbon atom, and the fructose by the interaction of the carbonyl with the hydroxyl near the γ- or δ-carbon atoms according to the scheme:



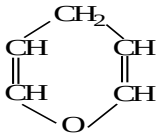
D-Glucose D-Glucopyranose



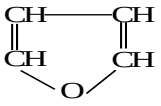
D-Fructofuranose D-Fructose D-Fructopyranose

This creates a new chiral center, or anomeric carbon atom. Hemiacetal hydroxyl differs in chemical properties from four other hydroxils. It is called glycoside hydroxyl (in the formula it is circled).Tautomerism of cyclic and open forms is called cyclo-chain tautomerism.

Hemiacetals exist in a six-membered pyranose form (δ-form), the name of which comes from the pyran cycle, and a five-membered furanose (γ-form) - from the furan cycle:



γ-Piran



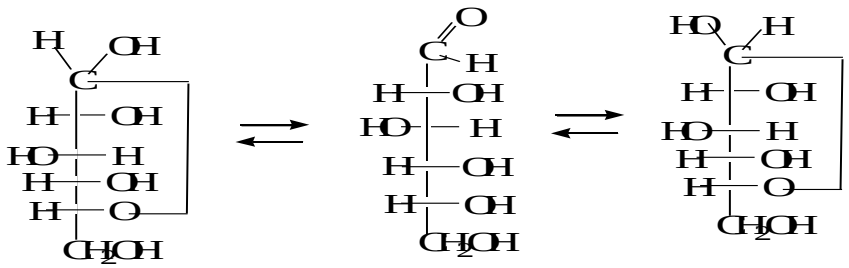
Furan

The hemiacetal form is characteristic of the crystalline state of hexoses. In the IR spectra of crystalline glucose there are no absorption bands -group.

An aqueous mixture of cyclic and open forms is formed in aqueous solutions, because tautomerism takes place only in aqueous solutions, ie monosaccharides react in both cyclic and open forms. In this case, according to the principle of Le Chatelier, if only the open form begins to react with any reagent, the tautomeric equilibrium is shifted towards the restoration of the concentration of compounds of the open form.

In general, the cyclic structure of monosaccharides is an α- or ß-form, which is called anomers (from the Greek apo - above).

Anomers are diastereoisomers that differ only in their configuration at the anomeric or hemisacetal carbon atom. Anomers have different melting temperatures, different angles of rotation of the plane of polarized light and are diastereoisomers with each other, but not enantiomers. The α-form is characterized by the location of the glycosidic hydroxyl on the same side as the hydroxyl, which determines the configuration of the monosaccharide as a whole (D- or L-) and participates in the formation of the cycle. The ß-form exists when placing these hydroxils on different sides of the cycle. X-ray diffraction analysis confirmed that the OH group at the anomeric carbon atom C1 is located on the right side for the α-D-series and on the left - for the ß-D-series:



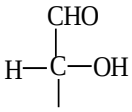
α-D-Glucopyranose D-Glucose ß-D-Glucopyranose

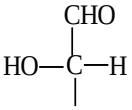
1.1.3.Mutarotation

It is known that a freshly prepared solution of α-D-glucose rotates the plane of polarized light to the right by an angle of 112º, and the solution of ß-D-glucose also rotates to the right, but by 19º. When dissolving one of these forms in water, there is always a partial isomerization of one anomer to another through the open form stage until an equilibrium is established between them with a final angle of rotation of 52.7 °. Such a change in the value of the angle of rotation of monosaccharides over time is called mutarotation (from the Latin mutare - to change, rotatio - rotation), or anomerization. It was found that an aqueous solution of glucose at 25 ° C contains 36%

α-D-glucopyranose and 64% ß-D-glucopyranose. Only about 0.02% of D-glucose in such solutions exists in open form, but, as already mentioned, this is sufficient for the course of a chemical reaction on the carbonyl group.Thus, glucose exists mainly in pyranose form. The furanose form for glucose is considered unstable mainly due to voltage of valence angles in the cycle. However, for aldotetrosis furanose form is essentially the only possible form of existence of monosaccharides in the crystalline state. The furanose form is more characteristic of fructose, the aqueous solution of which after mutarotation consists of approximately: 76% ß-D-fructopyranose, 20% ß-D-fructofuranose and 4% α-D-fructofuranose.

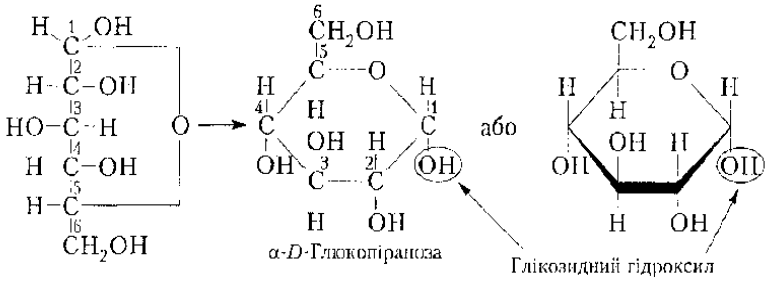
The difference in the configuration of another, often second, chiral carbon atom causes the formation of epimers. Epimers are diastereoisomers with several chiral atoms that differ in configuration with only one (epimeric) atom. For example, D-glucose and D-mannose, D-alose and D-altrose, D-galactose and D-talose, etc. are among the epimers:



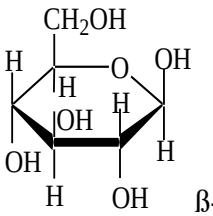


Glucose Mannose

The structure of monosaccharides in cyclic form can be conveniently represented by perspective formulas of W. Haworth (1929). In this case, the atoms placed in the Collie-Tollens formula on the left are located at the top, and placed on the right - at the bottom of the plane of the ring. Near the fifth carbon atom, hydrogen is located at the bottom, because the formation of the oxygen bridge C5-O requires rotation of the molecule around the valence axis C4-C5 to close the cycle:

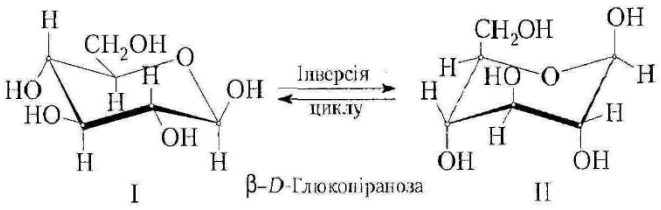


Similarly for ß-D-glucopyranose we obtain:



ß-D -Glucopyranose

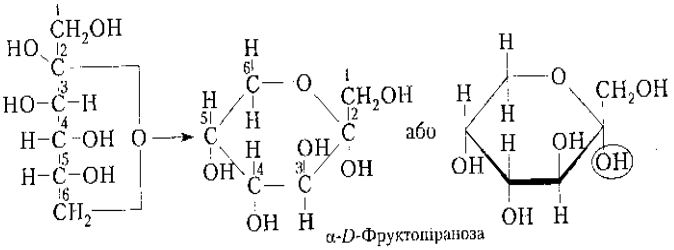
In fact, glucose and fructose, like all six-membered cycles, do not have a flat structure, but exist in the form of spatial conformers in the form of a bath (six conformers) or in a more energy-efficient chair (two conformers):



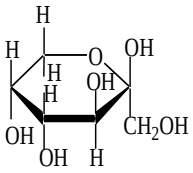
In this case, conformer I in the form of a chair prevails, because it contains all the large volume substituents OH and CH2OH in the equatorial position, and in conformer II they are in the axial (parallel) position. Due to this maximum thermodynamic stability of the conformer I ß-D-glucose and cellulose based on it are very common in nature.

For convenience, we will apply Haworth's formulas, remembering that the monosaccharide molecules actually exist in one or another conformational structure.

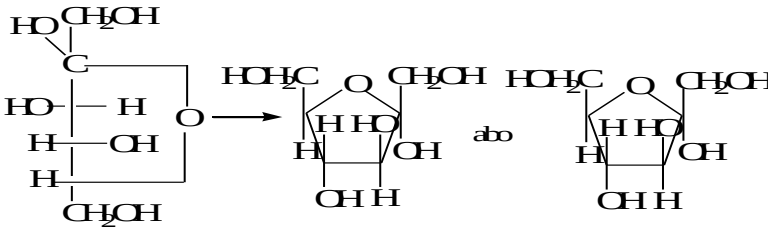
Accordingly, for fructose, as shown in the example of glucose, we can give pyranose and furanose Hawors formula:



Similarly for ß-D-fructopyranose we obtain:

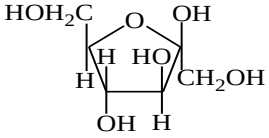


ß-D-fructopyranose



α-D-fructofuranose

Similarly for ß-D -fructofuranose we obtain:

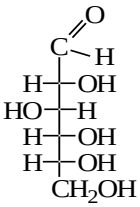


ß-D - fructofuranose

Thus, carbohydrates are characterized by all major types of isomerism: structural, steric and conformational. Aldohexoses in the open form contain four chiral carbon atoms, and, therefore, the total number of stereoisomers for them is 2n = 24 = 16. These 16 isomers form eight pairs of

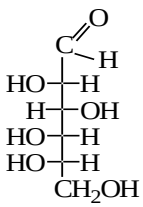
enantiomers: eight D-series and eight L-series (see genetic series of aldos). . All 16 enantiomers are known, and most

L-isomers are obtained synthetically. In the hemiacetal form for aldohexoses the number of chiral centers increases to five and aldohexoses correspond to 25 = 32 stereoisomers, ie each of them exists in α- or ß-form:



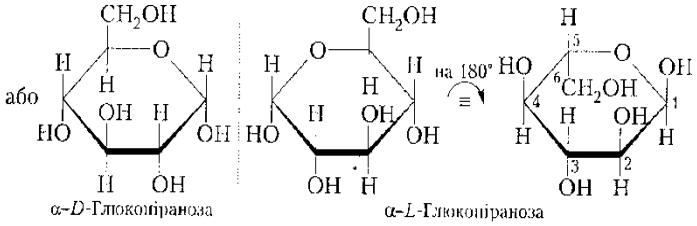
D-Glucose

(natural)

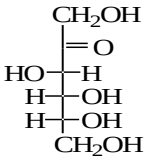


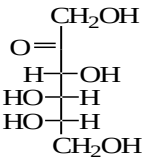
L-Glucose

(synthetic)



For ketohexoses containing three chiral carbon atoms in open form, the number of stereoisomers reaches 23 = 8, which form four pairs of enantiomers: four D-series and four L-series:



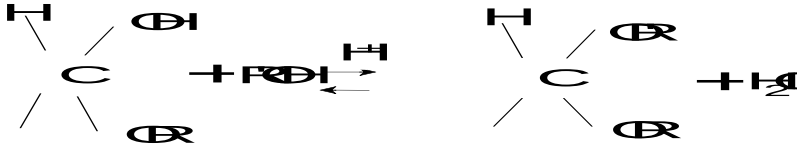


D-fructose (natural) L-fructose (synthetic)

α-D –Fructofuranose α-L – Fructofuranose

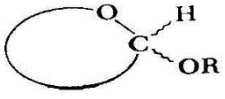
1.1.4.Glycosides

Reactions of simple pivacetals or hemiketals with alcohols form acetals or ketals, respectively. Aldoses and ketosis also give acetals and ketals.



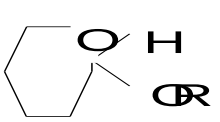
Pivacetal acetal

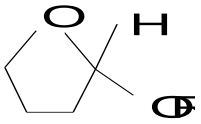
In the chemistry of carbohydrates, such substances are called glycosides.



Glycoside in General, shows only the anomeric carbon atom.

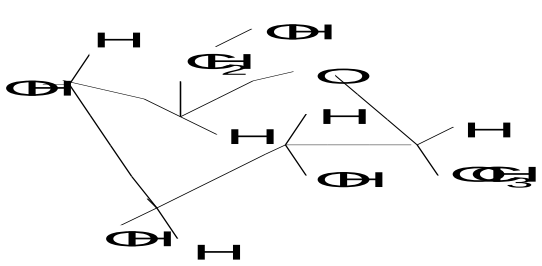
Cyclic glycosides that exist in the form of six-membered rings are called pyranosides. Cyclic glycosides, the ring of which contains five atoms, are called furanosides.

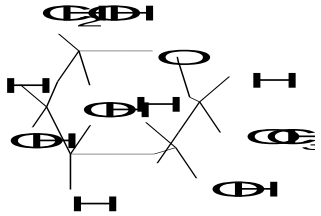


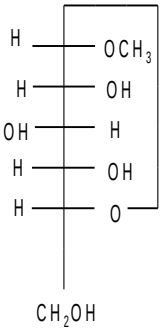


Pyranoside in General; furanoside in General;

Glucosides of glucose are widely distributed in nature - glucosides. Below are different ways of depicting the same α-D-glucopyranoside.

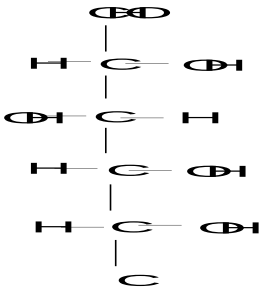


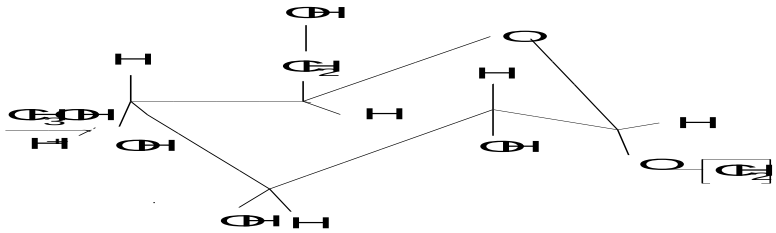




Different ways of imaging the same methyl α-D-glucopyranoside.

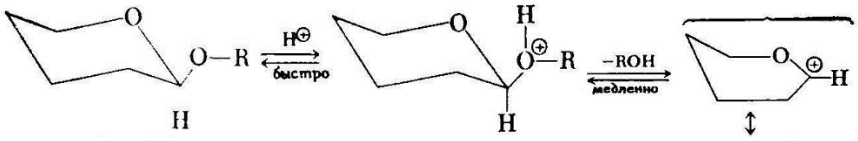
In the synthesis of glycosides by the reaction of monosaccharides with alcohols in the presence of acid are usually obtained acetals and ketals. The formation of glycosides is carried out, as a rule, in very mild conditions, so that the alcohol cannot be converted into ether, and only the hydrokyl group at C1 reacts.



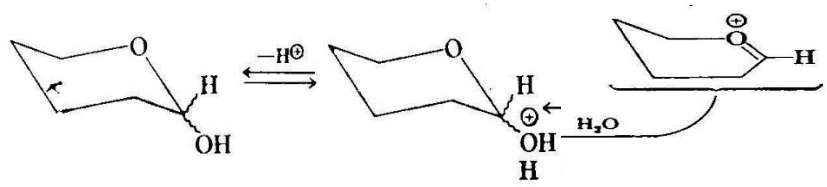


D-glucose methyl-α-D-glucopyranoside (also formed β-anomer)

The glycosidic bond is found in all natural carbohydrates, and therefore its cleavage methods play an important role in the analysis of carbohydrates. Like other acetals or ketals, glycosides are stable in slightly alkaline solutions, but easily hydrolyzed by acids. The mechanism of such hydrolysis is shown below:



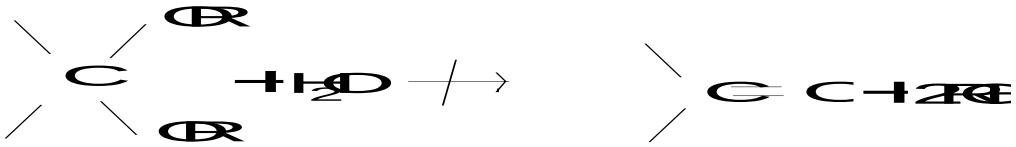
Glycoside in General;



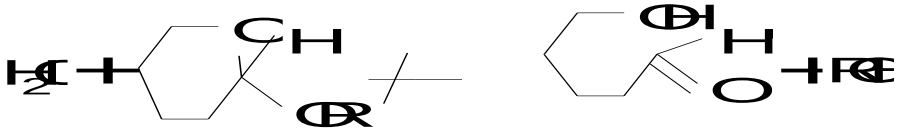
Despite the rate of acid-catalyzed hydrolysis, enzymatic hydrolysis should be preferred. The fact is that enzymes not only rapidly cleave glycosidic bonds, but also have high selectivity. For example, α-D-glucosidase from yeast acts only on glycosidic bonds at the C1 α-anomer of glucose. In contrast, β-D-glucosidase, which is contained in the almond emulsion, is specific for β-glucosidic bonds.

Pivacetals are easily cleaved to give carbonyl bonds and alcohol.

And acetals, on the contrary, are quite stable and do not undergo spontaneous hydrolysis.

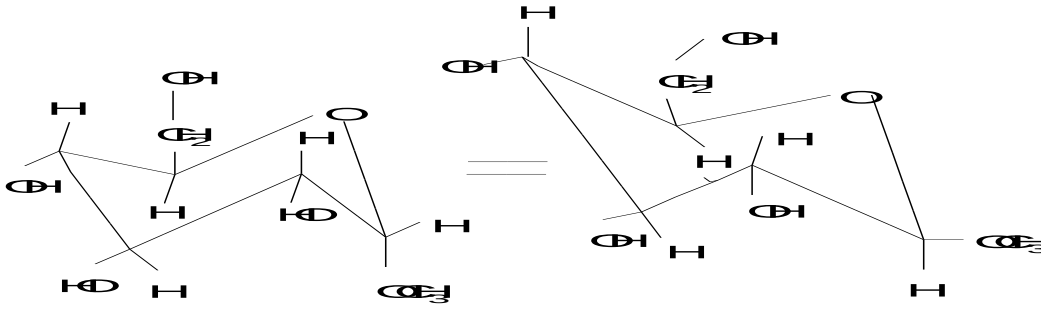


Glycosides are acetals. Therefore, they are not able to spontaneously convert to the corresponding monosaccharide.



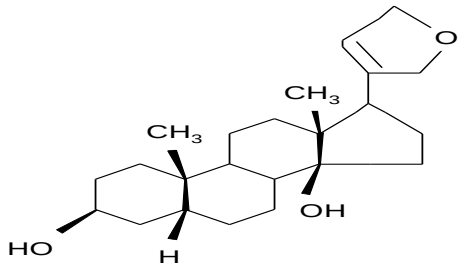
monosaccharide

In order for spontaneous equilibrium to be established between anomeric glycosides, they must be able to form a free monosaccharide, as it is an intermediate in the interconversion of α- and β-glucosides. Otherwise, spontaneous interconversion of anomeric glycosides is excluded. furanosides and pyranosides do not show mutarotation. The most interesting aglycones. Many natural products contain sugars, which are connected by glycosidic bonds with interesting aglycones. Simple glycosides of medical interest are cardiac glycosides, which contain a steroid aglycone and are used to stimulate the heart



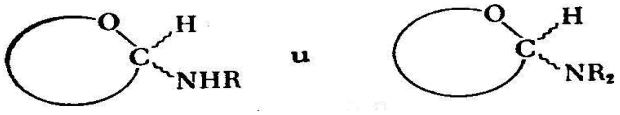
Spontaneous mutual transformation does not occur.

Digitalis plants (Digitalis purperia) can be extracted with a mixture known as degitalis. This mixture is rich in glycosides, the main aglycone of which is digethoxygenin - a polycyclic alcohol used in heart disease.



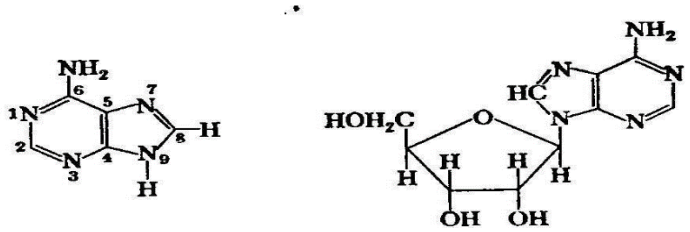
digethoxygenin

In addition to O-glycosides, there are other types of glycosides in which the aglycone is attached to the sugar not through an oxygen atom, but through some other atom. For example, in N-glycosides, the aglycone is attached to C1 through a nitrogen atom.



N-glycosides in generalized form

The most important N-glycosides are nucleosides, which consist of ribose or deoxyribose and heterocyclic amine. Below is the formula of adenosine nucleoside, built of adenine and ribose.

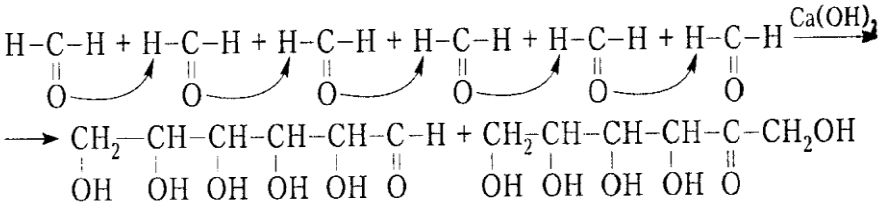


Adenine is a nucleoside made up of ribose and adenine

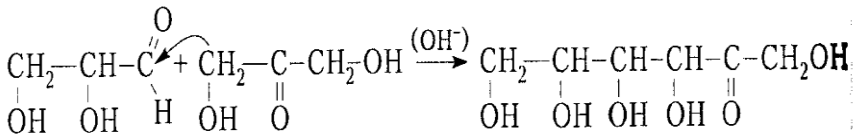
1.2. Obtaining monosaccharides

Monosaccharides can be obtained by synthetic methods, but this is not necessary, because it is more profitable to extract them from natural products. The following are the main industrial and synthetic methods for producing monosaccharides.

Aldol condensation. He was the first to synthesize sugars O. Butlerov (1861), which is made of formaldehyde under the action of lime water received a complex mixture of hexoses (aldose and ketosis):



Later, E. Fischer isolated from this mixture racemate D- and L-fructose. Aldol condensation of glycerol aldehyde and dihydroxyacetone also leads to the formation of ketohexoses:



2. Hydrolysis of disaccharides and polysaccharides. This method is basic for extraction of monosaccharides in industry:

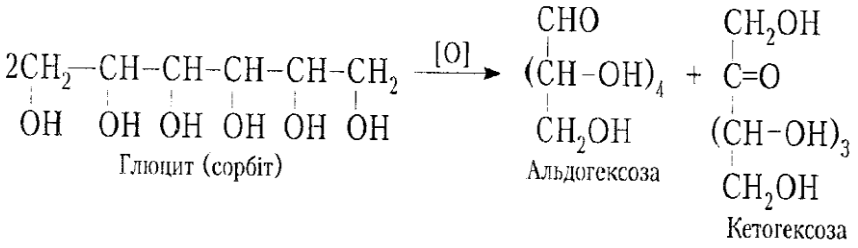
$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$

disaccharide (sucrose) monosaccharide

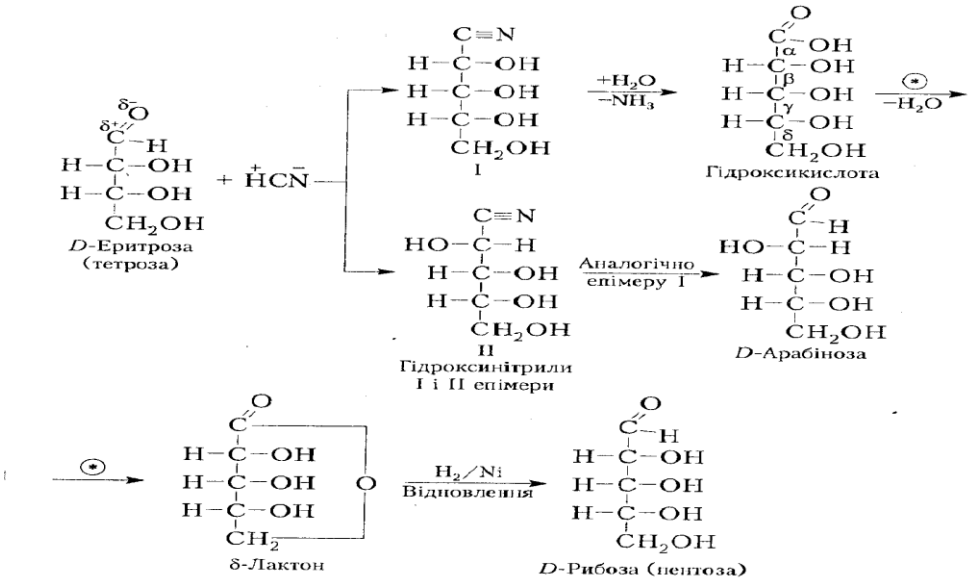
$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6$$

polysaccharide monosaccharide

3. Incomplete oxidation of hexahydric alcohols. Under normal conditions, the oxidation of polyhydric alcohols is formed as as a rule, a mixture of carbohydrates of aldotic and ketotic nature:



4. Hydroxynitrile synthesis of G. Kiliani - E. Fischer. This method can increase the length of the carbon chain of the monosaccharide. In this way were obtained heptoses, octoses and even decoses $C_{10}H_{20}O_{10}$, from the lower monosaccharides formed higher:



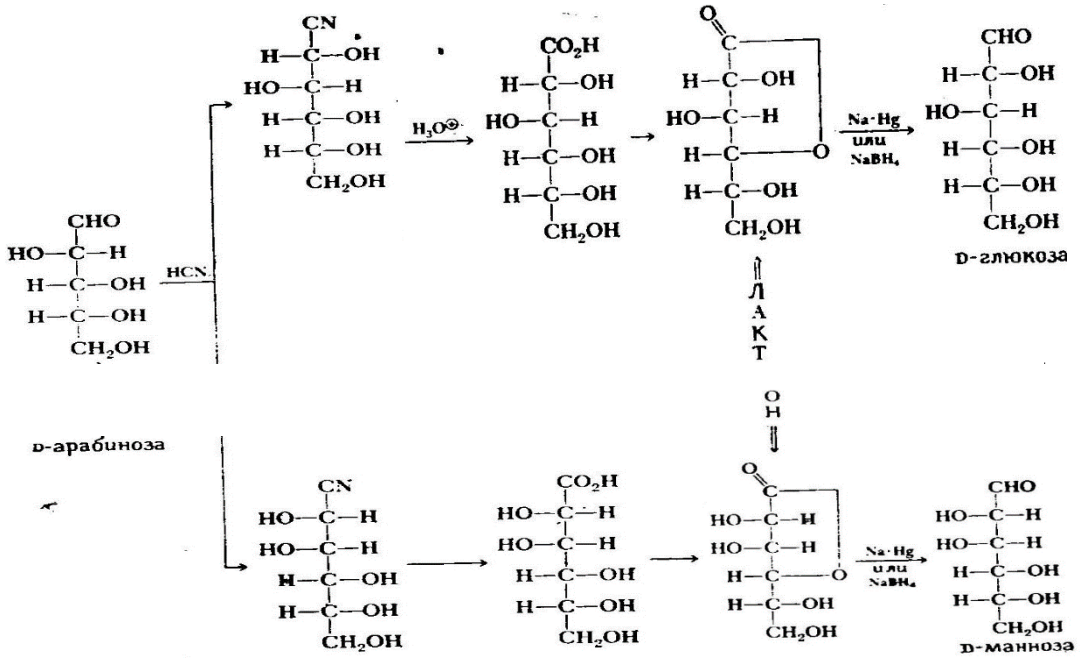
Hydroxynitrile synthesis occurs due to the ability of the carbonyl group of the monosaccharide to interact with cyanide acid to form a mixture of epimers (hydroxynitriles I and II), which differ in the configuration of the upper chiral carbon atom C1. Such hydroxynitrile is hydrolyzed to the corresponding hydroxy acid, which is easily dehydrated when heated to form a predominantly more stable six-membered δ-lactone compared to the five-membered γ-lactone. The obtained δ-lactone is easier than hydroxy acid to reduce to aldopentose by the action of amalgams of sodium or catalytic hydrogen.

The diagram shows the transformations only for epimer I, because for epimer II they are similar.

1.2.1 Synthesis and decomposition of monosaccharides;

Synthesis by the Killiani-Fischer method.

This method is used to increase the length of the carbohydrate chain of aldose by one carbohydrate atom, resulting in the formation of two diastometric aldos.

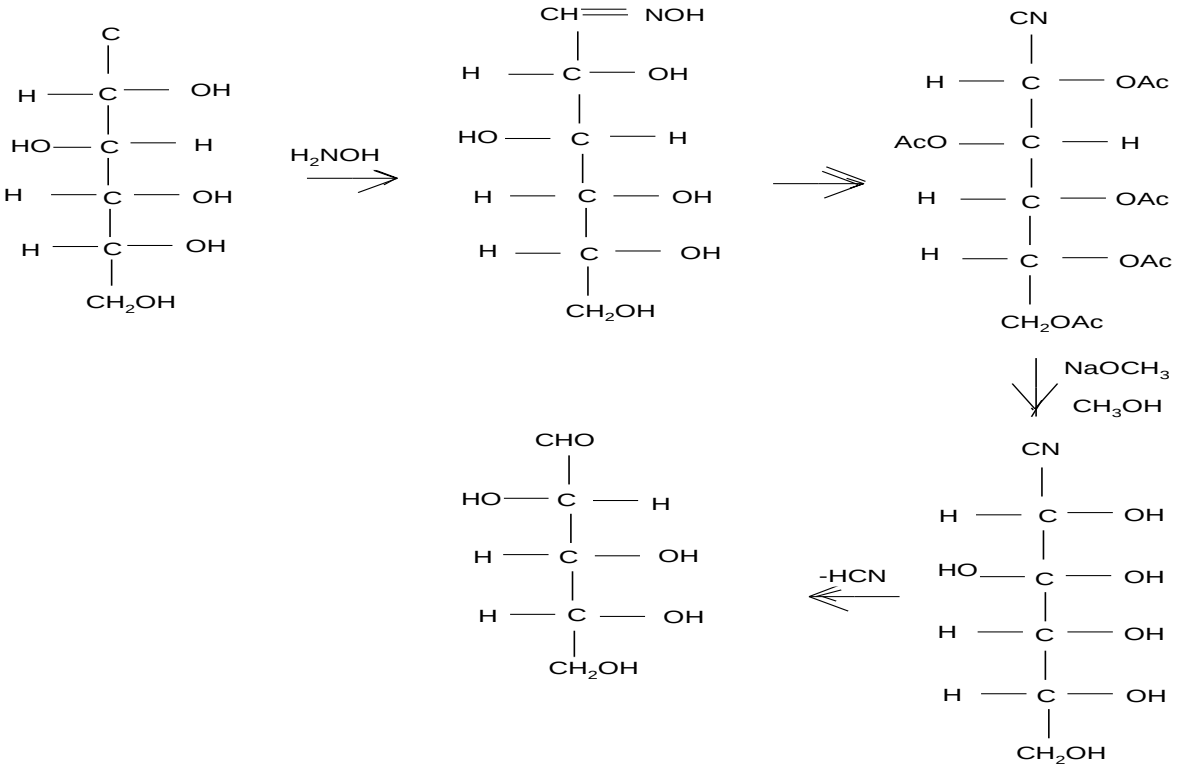


Already at the first stage of synthesis isomeric cyanhydrides are formed, after hydrolysis and dehydration of which lactones are formed, which are reduced to aldose, which contain one atom of carbohydrate more than the original monosaccharide. The formation of D-glucose and D-mannose from aldopeptose is shown above. The mixture of distereomeric products can be divided into different stages of synthesis, but it is better to do before the last recovery, as the separation of the two formed sugars is associated with some difficulties.

The same reactions can be performed in reverse order if you want to reduce the hydrocarbon chain of the monosaccharide by one atom. This Killiani-Fischer retroreaction begins with the conversion of aldose to oxime by reaction with hydroxylamine. Under the action of acetic anhydride, the oxime is dehydrated to nitrile. This reaction is accompanied by acetylation of free hydroxyl groups of free sugars. Transesterification of the acetylated product gives the cyanhydrin monosaccharide, which as a result of cleavage of hydrogen cyanide, is converted into aldose, which contains one atom of carbohydrate less than the original sugar.

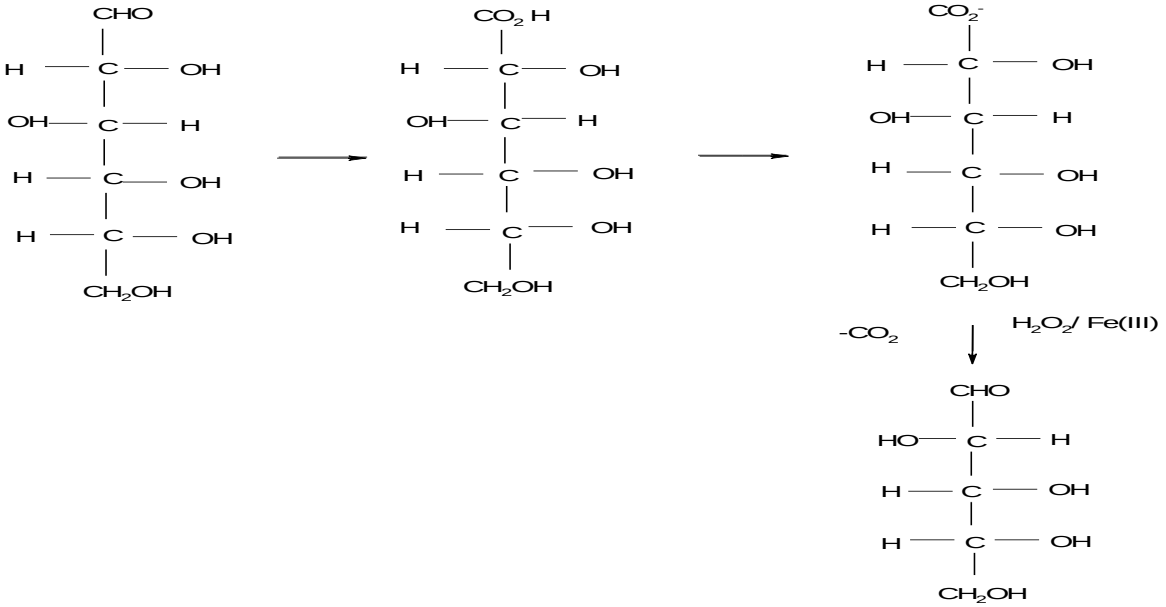
Conversion of D-glucose to D-arabinose by Killiani-Fischer retroreaction.

In this case, receive only one final product, as new chiral centers in the reactions are not formed. If in excess of Killian-Fisher synthesis, excess hydrogen cyanide is taken to ensure a high yield of cyanhydrin, for the successful reverse sequence of the reaction (so-called Will dehydration) it is necessary to continuously remove the formed hydrogen cyanide.



Synthesis of D-glucose and D-mannose by Killian-Fisher

Ruff degradation. Ruff aldose degradation is a free radical decarboxylation of a salt of glyconic acid, as a result of which the carbon chain of aldose is reduced by one atom. Decarboxylation is carried out with a mixture of hydrogen peroxide and ferric iron (so-called Fenton's reagent). Unfortunately, the product yield is only about 30-40%. Ruff's dehydration of glucose is shown below.



Conversion of D-glucose to D-arabinose by Ruff degradation.

1.1.3. Chemical properties

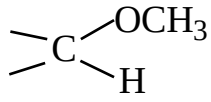
1.3.1. Reactions of monosaccharides;

Due to the peculiarities of the structure of monosaccharides exhibit the properties of alcohols, carbonyl compounds and hemispheres. Consider first their reactions for the open (carbonyl) form.

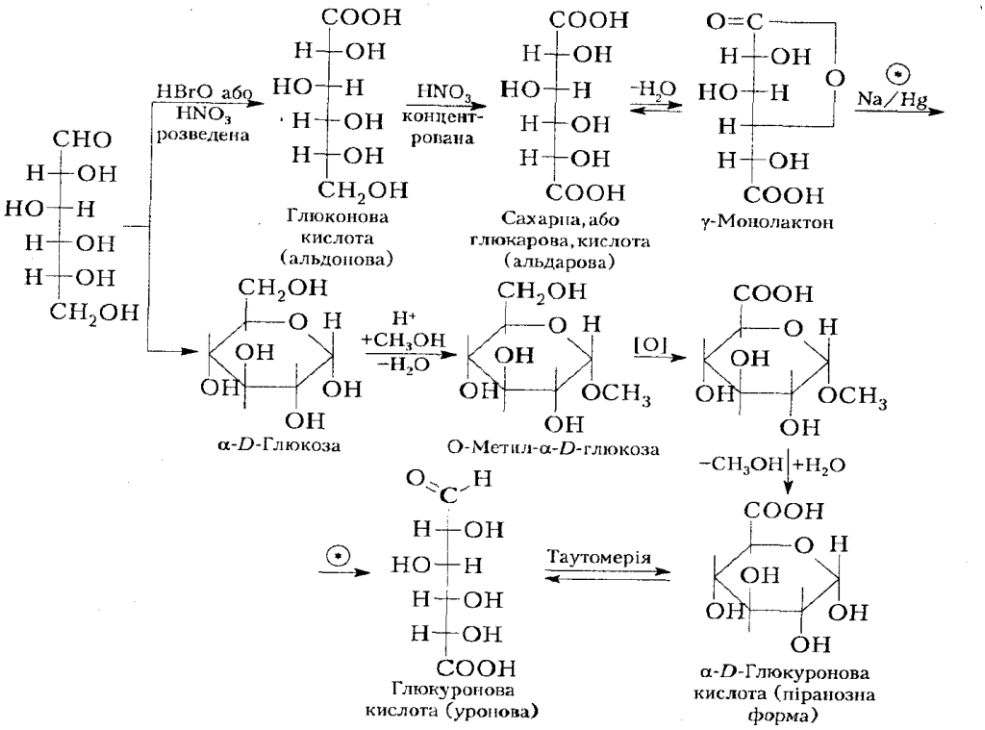
1 Recovery. Upon reduction of monosaccharides, the corresponding polyhydric alcohols are formed, the reaction is reversed to incomplete oxidation. Under the action of strong reducing agents such as NO is their complete recovery. For example, from glucose get 2-iodohexane:

$CH_2OH\text{-}(CHOH)_4\text{-}CH{=}O \xrightarrow{HI} CH_3{-}(CH_2)_3\text{-}CHI\text{-}CH_3$ Glucose 2-Iodohexane

2. Oxidation. Monosaccharides are easily oxidized and depending on the nature of the oxidant give different products. Thus, soft oxidants (HNO3, dilute or bromine water) in acidic and neutral media oxidize only the aldehyde group with the formation of so-called aldonic acids. When using a stronger oxidant, monosaccharides or aldo-new acids are oxidized to aldaric (dibasic). Thus, from gluconic acid during the oxidation of the primary alcohol group, sugar acid is obtained. During oxidation, mainly not the acids themselves, but their lactones are extracted.

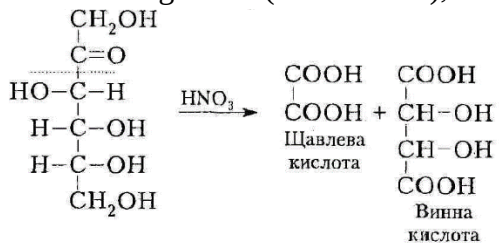
Uronic acids are obtained by oxidation of monosaccharide derivatives with a pre-protected aldehyde group. The use of protection of the aldehyde group is explained by the need to preserve it from oxidation. To do this, first form a glycoside or monomethyl ether of α-D-glucopyranose by the action of methanol on α-D-glucopyranose in a weakly acidic environment. Oxidation of such a glycoside followed by hydrolysis gives glucuronic acid. 

Another method is the reduction of sodium amalgam mono lactones of sugar acids, which are easily formed by the reaction:



Of these γ-monolactones of sugar acid, the carboxyl group, which forms lactone more easily, will be the first to be reduced.

Fructose (ketohexose) is more difficult to oxidize than glucose (aldo-hexose), and often with the splitting of the carbon chain:



In an alkaline environment, monosaccharides are oxidized with the cleavage of the carbon chain and the formation of oxidation products, which are characterized by strong reducing properties. This is the basis of the application for the qualitative determination of carbohydrates of the silver mirror reaction - the so-called Tollens test, which consists in the oxidation of the aldehyde group under the action of ammonia solution of silver oxide (Tollens reagent):

D-glucose + Ag (NH3)2+ → Oxidation products + Ag ↓ + 2HN3

For the same purpose, the reduction of carbohydrates of copper (II) hydroxide to bright red copper (I) oxide is used:

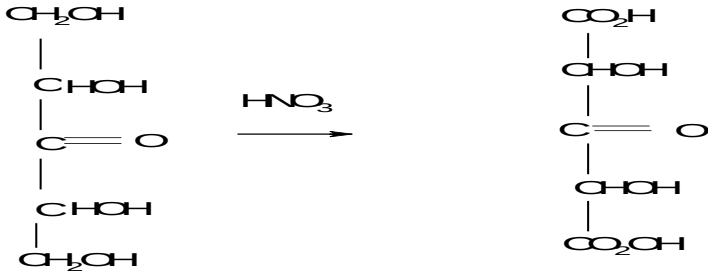
D-glucose + 2Cu(OH) 2 → Oxidation products + Cu2O + H2O

Fructose also reduces both of these compounds, in contrast to ketones. But this is not due to fructose itself, but due to the formation in an alkaline environment of a certain amount of glucose and mannose during the epimerization of fructose.

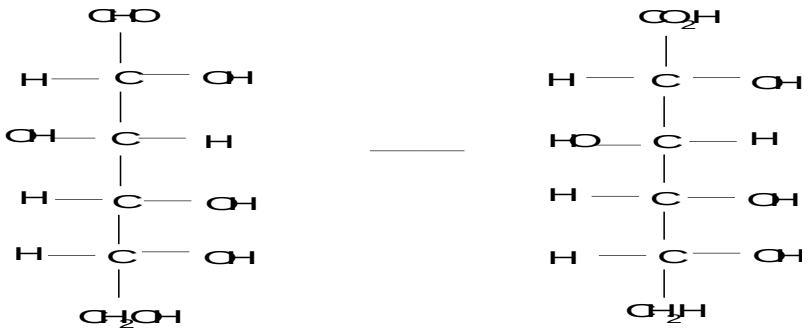
Concentrated alkali solutions monosaccharides are resinized to form a complex mixture of oxidation, cleavage, polycondensation, and the like.

Oxidation to glyceric acids.

Simple tsurkas contain a larger number of functional groups that can be oxidized by various agents. Nitric acid oxidizes aldose and ketosis to dicarboxylic glyceric (or sugar) acids.

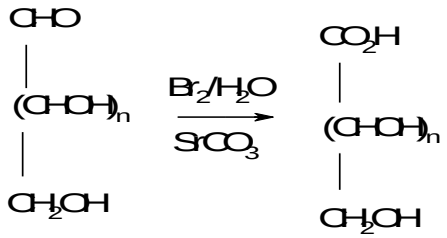


Thus, D-glucose is formed from D-glucose.



D-glucose D-glucaric acid

As a result of such a reaction, the oxidation of primary hydroxyl groups and aldehyde groups of monosaccharides occurs.

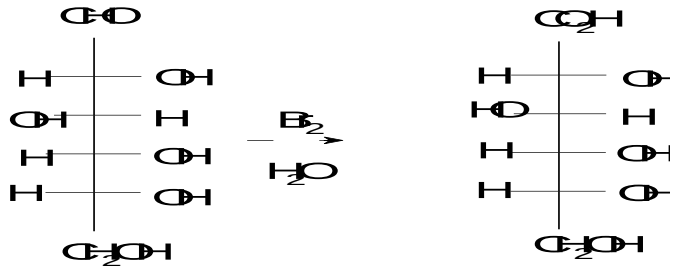


Oxidation to glyconic acids.

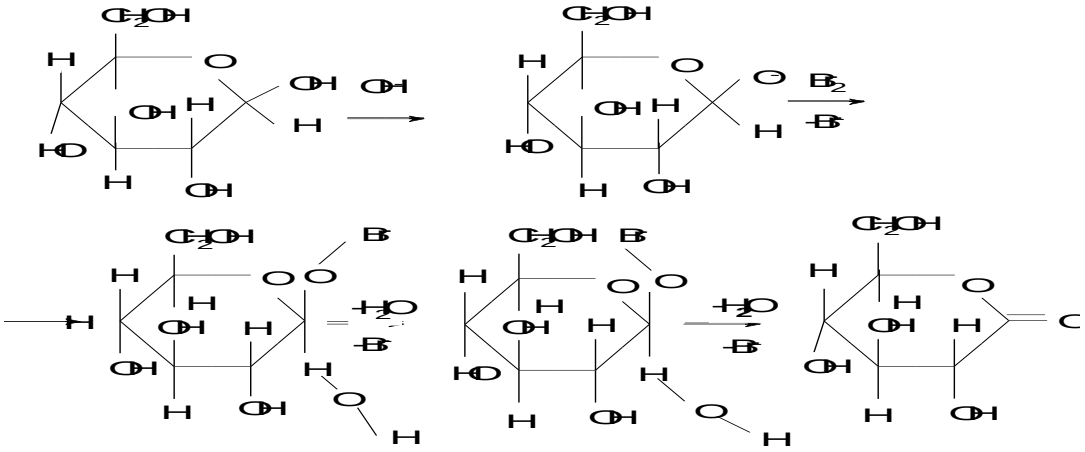
If you take a milder oxidizing agent than nitric acid, the oxidation of the functional groups will be more selective. Bromine water (Br2 / H2O), for example, oxidizes only aldehyde aldose groups to carboxyl groups. Monocarboxylic acids are called glyconic or aldonic. Often the reaction is carried out in the presence of a small number of bases.

Glycon formation acids

Under the action of bromine water, D-glucose is oxidized to D-gluconic acid, the yield of which may exceed 75%.

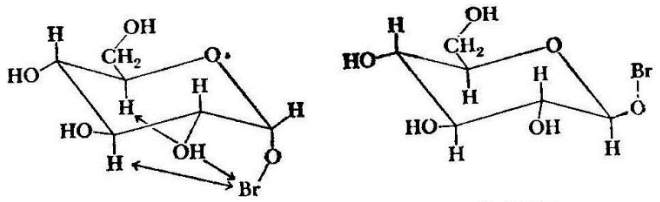


In fact, oxidation does not produce the glyconic acid itself, but the corresponding lactone. Accordingly, pivacetal compounds are not adapted to oxidation by carbonyl compounds. The role of bases is reduced to the formation of an alkoxide anion attacking bromine. Then there is a cleavage of hydrogen bromide by the mechanism E2. The following is an example of such reactions.



D-gluconolactone

α-D-Glucopyranose is oxidized more slowly by the β-anomer, due to unfavorable axial interactions in the conformer of the α-anomer, which is required for trans-lamination, In the conformer of the β-anomer, which is required for this reaction, such interactions do not occur Accordingly, the β-anomer requires less activation energy for trans-lamination than the α-anomer.



Conformer α-anomer conformer β-anomer, in the E2 reaction in the E2 reaction

Reagents Benedict, Fehleng (Fehleng liquid) and Tollens oxidize aldose to glyconic acids. Each of these reagents contains a metal ketone, which is reduced by aldose (hence the name of these sugars - reducing sugars),

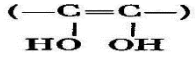
The Tollens reagent is prepared by mixing solutions of sodium hydroxide and silver nitrate, resulting in a precipitate of silver oxide.

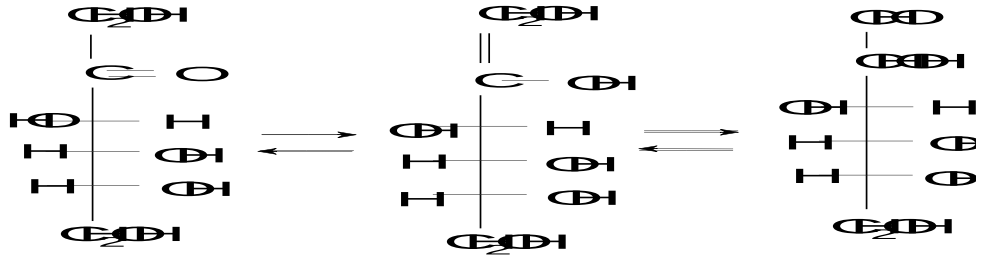
2Ag + 2OH → Ag2O + H2O

With careful addition of an aqueous solution of ammonia, the precipitate dissolves and the ion Ag (NH3) 2 is formed (do not precipitate). This solution is a Tollens reagent.

The addition of aldose to Tollens' reagent precipitates metallic silver, often in the form of a mirror coating on the walls of the test tube (hence the name-reaction of the "silver mirror"). As an example, the oxidation of D-glucose to D-gluconic acid is shown.

Ag (NH3) 2 + D-glucose → D-gluconic acid + Ag (

Fructose also reacts positively with Tollens' reagent, although it does not have an aldehyde group. The fact is that there is an equilibrium between glucose, mannose and fructose, which is catalyzed by bases. This equilibrium includes endiol as an intermediate, and is known as the Lobry de Bruyne-van Eckenstein rearrangement. 

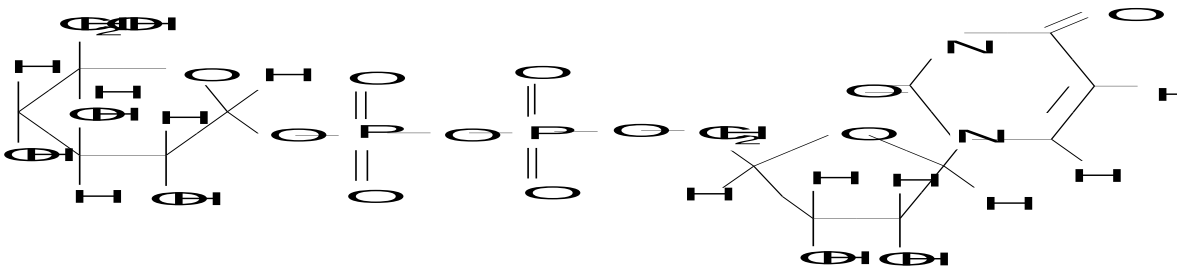


D-fructose intermediate endiol D-glucose and D-mannose

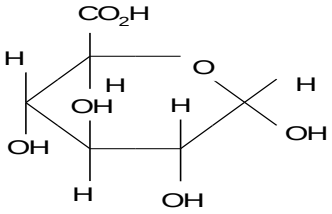
Thus, it is not fructose that reacts with Tollens' reagent, but alkali, mannose and glucose formed from it.

Oxidation to glycuronic acids.

Glycuronic (uronic) acids are compounds in which the terminal primary hydroxyl group of the monosaccharide is oxidized to the carboxyl group, while the carbonyl group is unchanged. They are quite difficult to synthesize in the laboratory, although they are common in nature, especially D-glucuronic acid, which is formed from vivo during the enzymatic oxidation of a complex molecule of uridine diphosphate-α-D glucose (UDF-glucose). An important biological role of D-glucuronic acid that many toxic substances are excreted in the urine in the form of glucuronides.

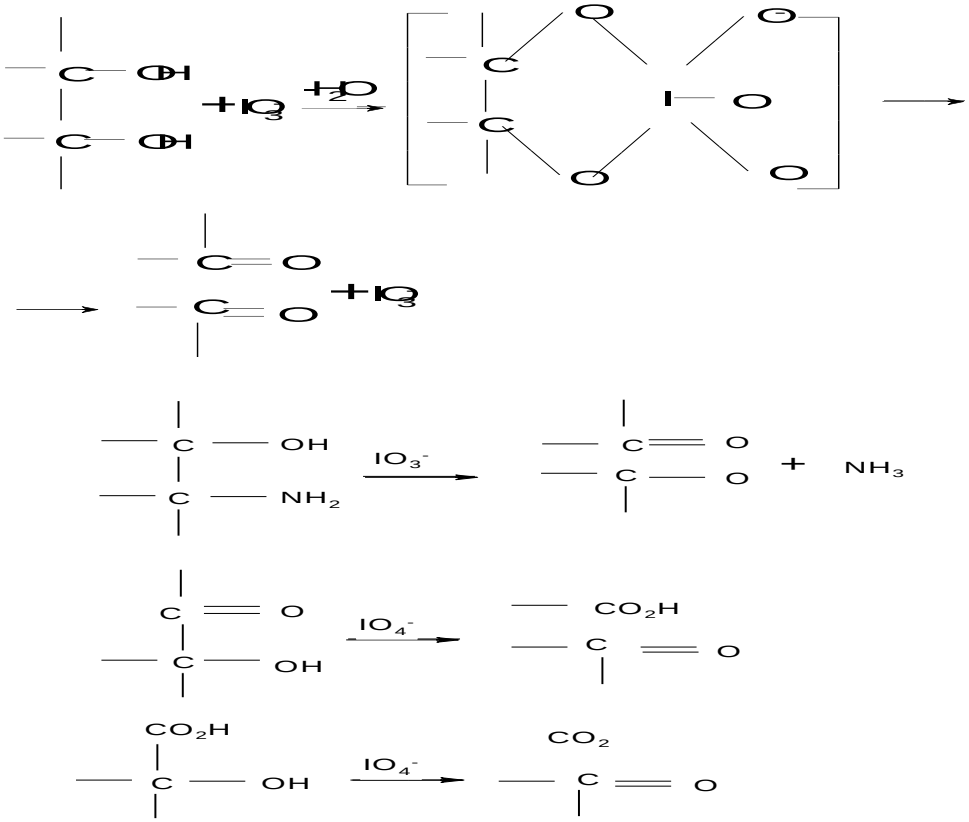


D-glucose uridine UDF

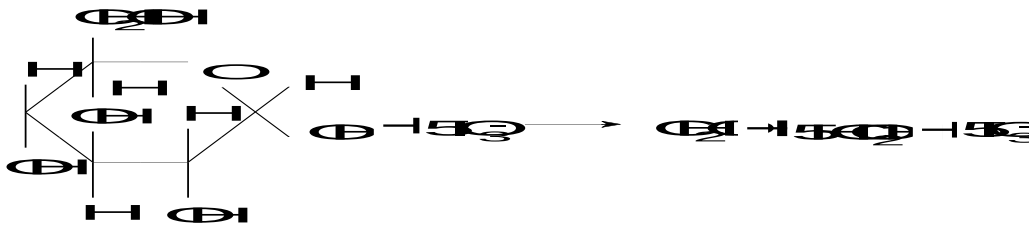


α-D-glucuronic acid (written as pivacetal)

Oxidized dehydration of sugars. Oxidation of diols by periodate ion IO4, this reaction is often used in the analysis of hydrocarbons, given below.



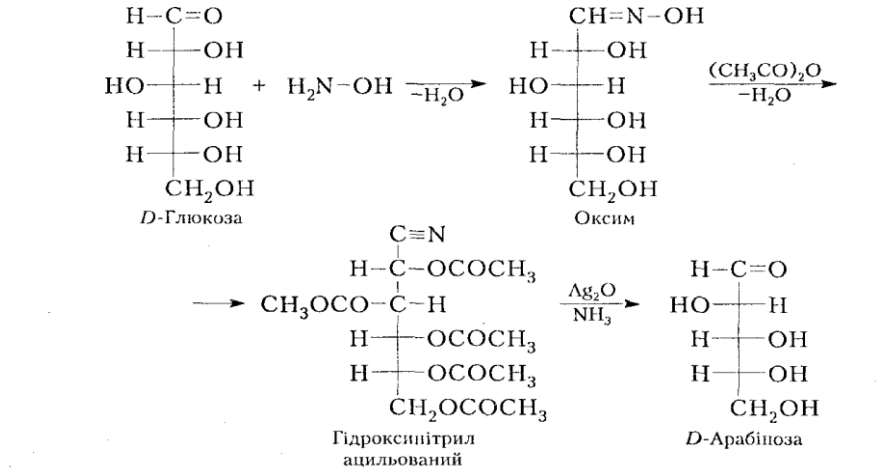
When glucose is oxidized by sodium metaperiodate, for example, 5 moles of formic acid and 1 mole of formaldehyde are formed. Which of the carbohydrate atoms of glucose is converted to formaldehyde.



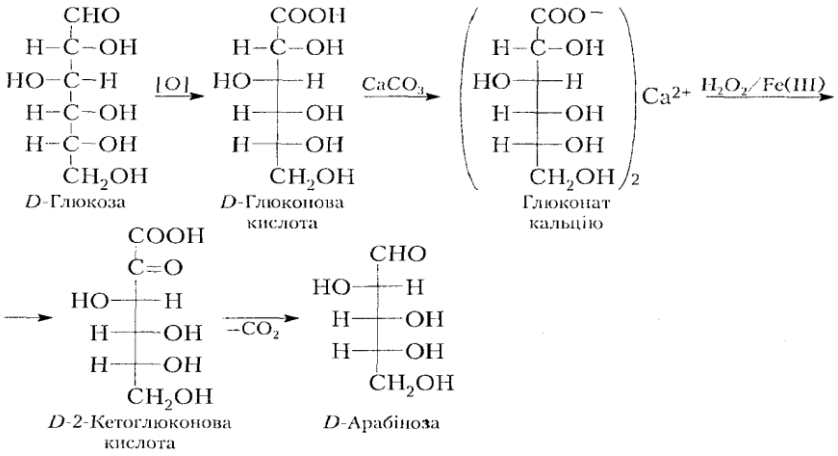
3. Transition from higher to lower monosaccharides.

There are several methods of transition from higher to lower monosaccharides. Noteworthy are the interaction with hydroxylamine (cleavage by A. Vol, 1893) and oxidative degradation by O. Ruff (1899)

Under the action of hydroxylamine from aldohexose the corresponding oxime is formed, which is dehydrated to hydroxynitrile by means of acetic anhydride. The reaction is also accompanied by acylation of free hydroxyl groups of glucose. The nitrile group in acylated hydroxynitrile is removed by treatment with an ammonia solution of silver oxide. At the same time under the action of ammonia there is an amonolysis of acetoxyl groups of a monosaccharide with regeneration of hydroxyl groups. The result is aldopentose with fewer carbon atoms:

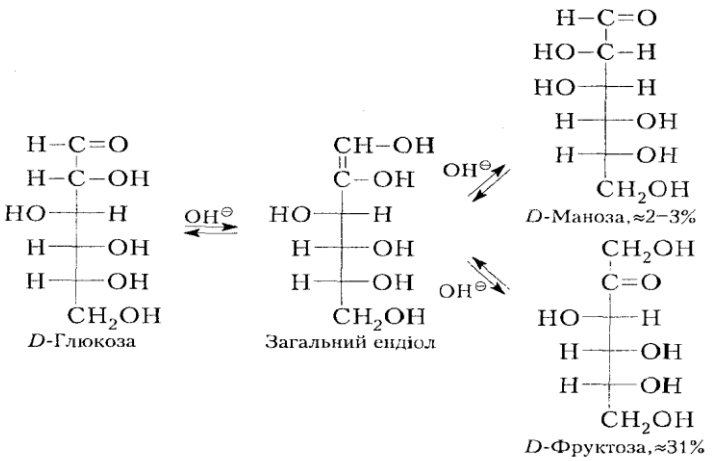


Ruff degradation (cleavage) is the oxidative decarboxylation of salts of aldonic acids, such as glucon under the action of a mixture of hydrogen peroxide and iron (III) salt:



4. The action of alkalis (epimerization).

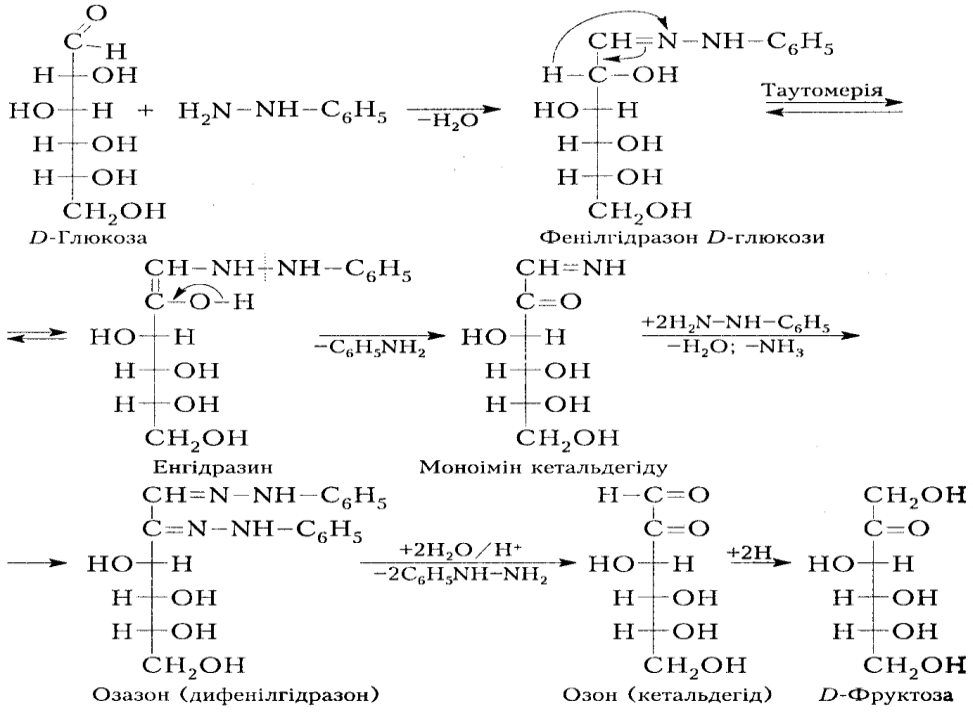
Under normal conditions, alkalis cause keto-enol tautomerism near the C1 and C2 carbon atoms of monosaccharides, which causes their epimerization. The corresponding epimers are formed from one monosaccharide. For example, when exposed to D-glucose with an alkali solution, it is 2-3% converted to D-mannose and 31% to D-fructose through the stage of intermediate endiol:



Transformations of this type also occur for D-fructose or D-mannose. Proof of these processes is that all three mentioned saccharides react equally with phenylhydrazine and differ only in the configuration near the second carbon atom (C2).

5. Interaction with phenylhydrazine.

The action of phenylhydrazine on monosaccharides allows you to isolate them in pure form, to establish the structure and most importantly to move from aldosis to ketosis. Phenylhydrazine first reacts with aldose as a regular aldehyde to form phenylhydrazone, which is capable of isomerizing to tautomerino to enhydrazine. The latter as a result of cleavage of aniline forms monoimine ketaldehyde. When interacting with the next two phenylhydrazine molecules, ozazone is synthesized, a crystalline substance that can be used to identify the original monosaccharides. In an acidic environment, ozones form ketaldehydes - ozones, from which the corresponding ketosis is extracted by reduction:



Monosaccharides are also involved in chemical reactions in the hemiacetal form.

6. Alkylation of monosaccharides.

When alkylating, for example, glucose with a weak alkylating agent, such as CH3OH, in the presence of an HCl solution, only the glycoside hydroxyl reacts to form the corresponding glycoside or acetal.

Glycoside is an acetabular or ketal monosaccharide that exists in α- and ß-forms.

The other four OH groups of glucose are not involved in the reaction.

Glycosides are derivatives of monosaccharides in which the glycoside hydroxyl is replaced by any non-carbohydrate residue - aglycone and connected to the monosaccharide cycle through an oxygen, nitrogen or carbon atom. Glucose acetals (glycosides) are called glucosides, galactose - galactosides, etc., and fructose ketals - fructosides.

The increased reactivity of the glycosidic hydroxyl is explained by the influence of the ether oxygen atom, which partially displaces the electrons of adjacent CO-bonds on themselves. This shift in electron density increases the polarity of the bond between the carbon atom and the OH group:

Glycosides such as methyl-α-D-glucose are not capable of mutarotation in aqueous solutions, do not reduce the ammonia solution of silver oxide to metallic silver or Cu (OH) 2 to Cu2O and are therefore non-reducing saccharides.

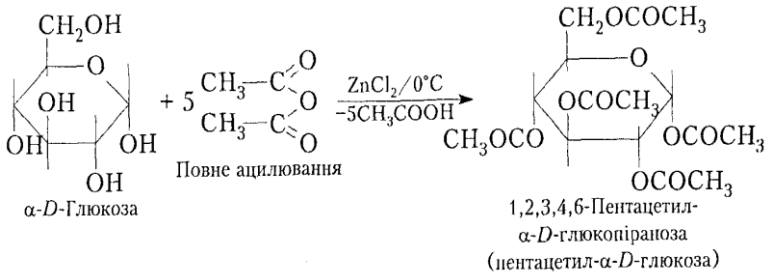
Under the action of an excess of stronger alkylating agents (alkyl halides, dialkyl sulfates (RO) 2 SO2, etc.), the other four hydroxyls are alkylated to form the complete ether.

The mechanism of alkylation by glycoside hydroxyl is its replacement by a CH3O group. When alkylating other hydroxyl groups with halogen alkyls, the reaction mechanism is to replace the hydrogen atoms of the OH groups with alkyl CH3- and similar to the mechanism of formation of ethers:

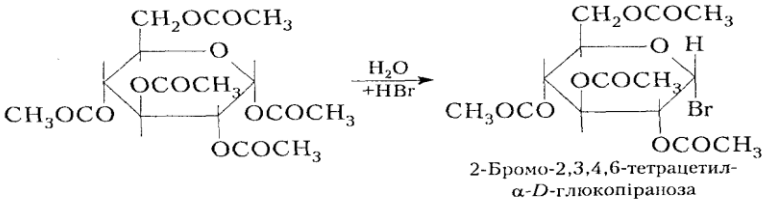
In the hydrolysis of fully alkylated monosaccharides under mild conditions, the acetal group formed by the glycosidic hydroxyl is primarily hydrolyzed. For dialkyl ethers R-O-R, hydrolysis is not observed. Under more severe conditions, the other four ether bonds are hydrolyzed to the original monosaccharide. Thus, fully methylated glucose contains acetal and ether bonds formed in different ways and hydrolyzed under different conditions.

7. Acylation of monosaccharides.

Monosaccharides are acylated with conventional acylating agents to esters:



Similarly to monosaccharide ethers, the ester group formed by the glycosidic hydroxyl is primarily hydrolyzed during the hydrolysis of esters. It is used for the synthesis of other derivatives of monosaccharides, as well as disaccharides. For example, under the action of hydrogen bromide under conditions of soft hydrolysis of pentacetyl-α-D-glucose there is only a monobromo derivative, because only the ester bond formed by glycosidic hydroxyl is hydrolyzed:



8. Fermentation of monosaccharides.

At anaerobic (without access of air) fermentation hexoses (fermentation is not peculiar to pentoses) there is a splitting

monosaccharides on simpler substances mainly under the influence of microorganisms.

The chemistry of fermentation is quite complex, multifaceted and not yet fully understood. Some hexoses are characterized by the breakdown of molecules into alcohol and carbon dioxide by enzymes such as zymase - alcoholic fermentation. This mixture of enzymes is produced by yeast fungi.

In alcoholic fermentation, the process of conversion of glucose into ethyl alcohol can be represented as a simplified scheme (glucose → glyceric aldehyde → glyceric acid → pyruvic acid → acetic aldehyde → ethyl alcohol) and a simplified equation:

C6H12O6 → 2C2H5OH + 2CO2

Hexose

Enzyme-derived ethyl alcohol is formed only from D-glucose, D-fructose and D-mannose.

When changing the nature of microorganisms and other process conditions for monosaccharides in addition to alcohol, several types of fermentation are known.

Lactic acid fermentation (lactate) occurs under the action of lactic acid bacteria, and up to 90% of the racemic mixture of lactic acid is extracted from glucose according to a simplified scheme and equation similar to glucose:

Glucose → glycerol aldehyde → glyceric acid → pyruvic acid → lactic acid:

$C_6H_{12}O_6 \rightarrow 2CH_3–CH–COOH$

|

OH

In addition to lactic acid, acetic acid, ethyl alcohol, and carbon dioxide are also obtained in the reaction medium. Lactic acid in the process of fermentation is formed in the manufacture of cheese, sauerkraut, silage.

Glycerin fermentation by chemistry is a deviation from the route of alcoholic fermentation: glucose → glycerol aldehyde → glycerin:

$$C_6H_{12}O_6 \xrightarrow{\text{Enzyme}} 2CH_2(OH) - CH(OH) - CH_2(OH)$$

To prevent the process by the alcohol route, sodium or ammonium hydrosulfite is added to the reaction of the mixture in order to bind the acetaldehyde, which arises at the appropriate stage from pyruvic acid.

Propionic acid fermentation undergoes a number of chemical transformations involving the following compounds:

glucose → glyceric aldehyde → glyceric acid → pyruvic acid → oxalic acetic acid → malic acid → fumaric acid → succinic acid → propionic acid:

$$C_6H_{12}O_6 \rightarrow CH_3 - CH_2 - COOH + CO_2$$

Butyric acid (butyric) fermentation by chemistry occurs ana-logically alcoholic to the formation of pyruvic acid is further converted into butyric:

glucose → pyruvic acid → butyric acid:

$$C_6H_{12}O_6 \rightarrow CH_3 - CH_2 - COOH + CO_2$$

Acetonebutanol fermentation in the early stages is similar to alcohol. The resulting pyruvic acid is converted into butyrate aldehyde (reduction leads to the formation of 1-butanol) or acetoacetic acid (decarboxylation of it causes the appearance of acetone) (X. Weizmann):

$$C_6H_{12}O_6 \xrightarrow{\text{enzyme}} C_4H_9OH + CH_3 - \underset{\underset{AT}{\|}}{C} - CH_3 + CO_2$$

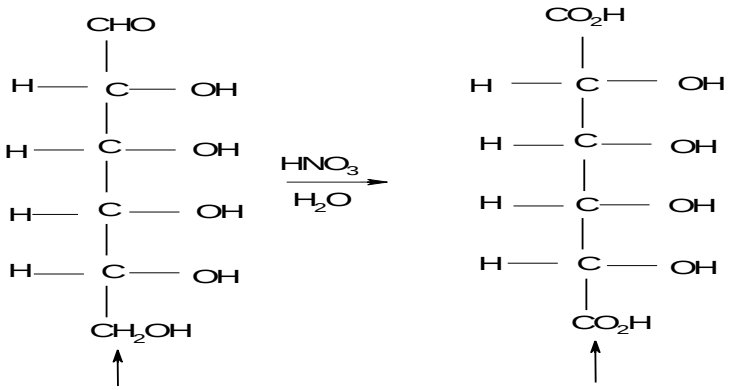
1.3.2.Proof of the structure of D - (+) glucose

Almost a hundred years ago (in 1888) Emil Fischer began his brilliant work, which led to the establishment of stereochemistry (+) - glucose. But he didn't have the equipment then, without which we can't imagine a chemical laboratory now. The most sophisticated device at the time was the polarimeter.

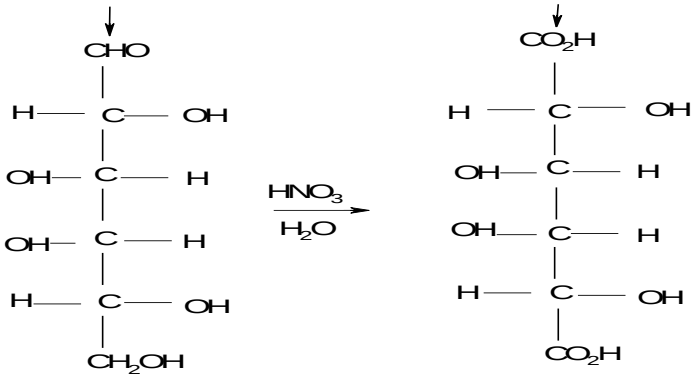
Fisher understood that he could distinguish the enantiomers of monosaccharides. Because he knew that (+) - glucose is an aldohexose, Fisher limited his experiments to eight enantiomers classified as D-series. configuration (+) - glucose.

1. (+) - Glucose is oxidized to optically active aldaric acid under the action of nitric acid. As a result, the reaction product - glucric acid - cannot have a plane of symmetry. Otherwise, it would be achiral,

but n optically active. And so, the structures now known as alloses and galactose must be discarded. Both of them would lead to the formation of meso-aldaric acids.

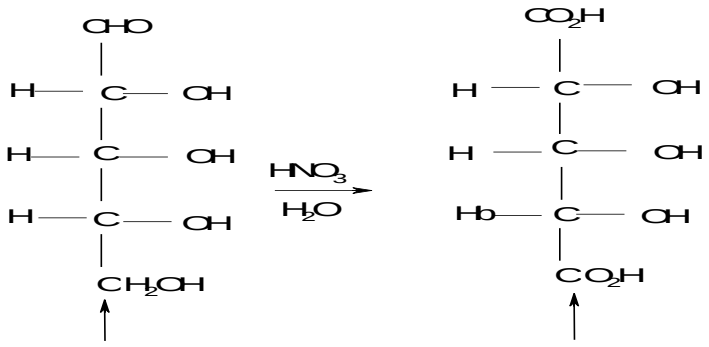


Meso-dicarboxylic acid cannot be glucose

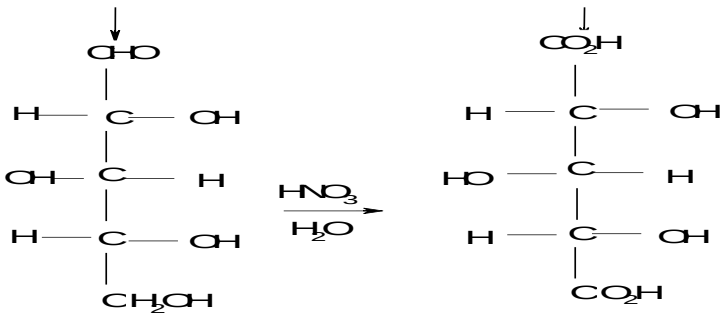


2. As a result of degradation of (+) -glucose (-) -arabinose is formed. But the structure of (-) -arabinose is not known, it is established that it is oxidized to optically active aldaric acid under the action of nitric acid.

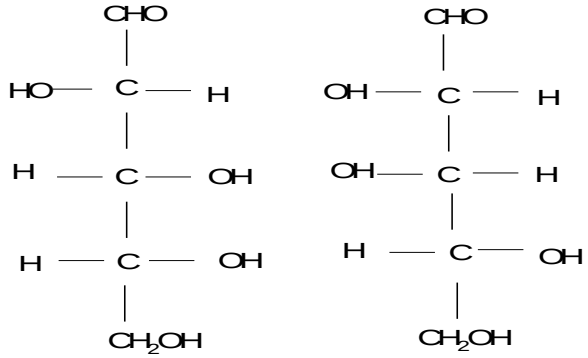
Accordingly, (-) - arabinose cannot have the structures that we now attribute to ribose or xylose, as their oxidation would give meso-dicarboxylic acid.



It cannot be arabinose meso-dicarboxylic acid

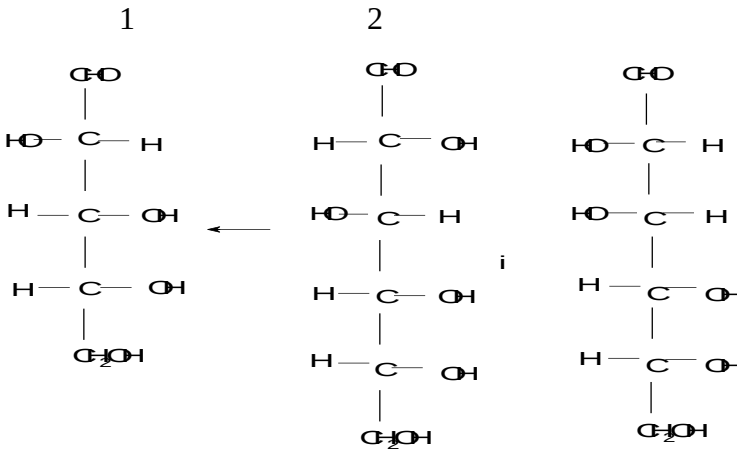


Because (-) - arabinose cannot have either of the two structures listed above, it must be assigned the first or second of the two structures shown below, as they are two aldopentoses that can give optically active aldaric acid:

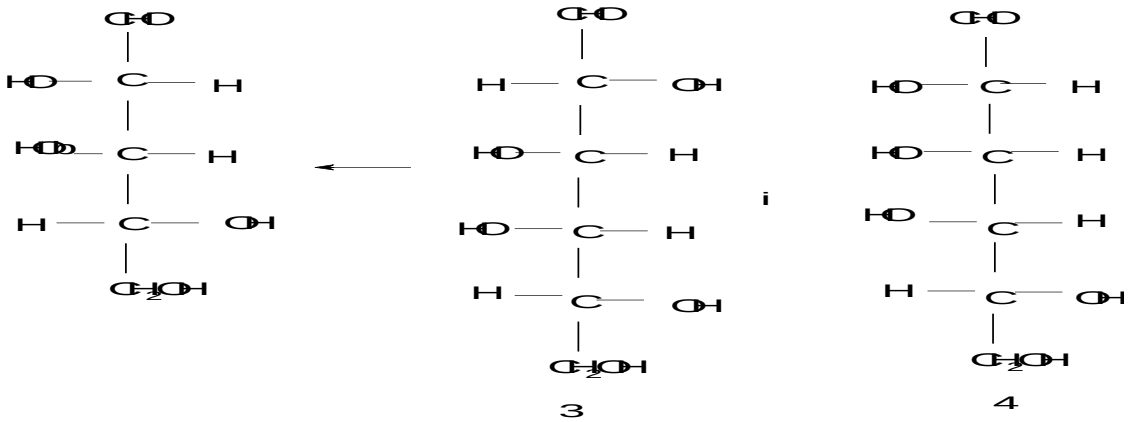


At this stage, Fischer knew that (-) - arabinose has one of these two structures

Therefore, (+) - glucose forms on dehydration (-) - arabinose, which must have one of two possible structures. Accordingly, glucose must be attributed to one of the four structures below:



If it is (-) - arabinose, then one of these compounds is (+) - glucose.

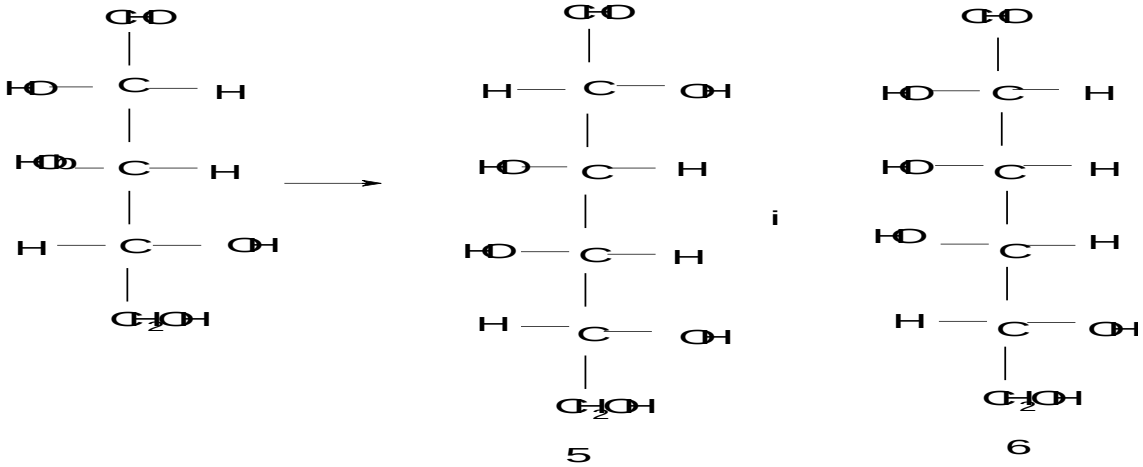


If it is (-) - arabinose, then one of these compounds is (+) - glucose.

However, structure 3 (see above) will result in the oxidation of optically inactive aldoric acid. The product of glucose oxidation is optically active aldoric acid. As a result, it remains to choose between structures 1,2 and 4.

3. If the Killian-Fisher synthesis is carried out on the basis of (-) - arabinose, two aldohexoses are formed: (* +) - glucose and (+) - mannose. Their oxidation under the action of nitric acid gives optically active aldar acids.

If (-) - arabinose has the configuration shown below, it will give two aldohexoses. However, the oxidation of one of them (5) will lead to optically inactive aldaric acid. As a result, (-) - arabinose can not have this structure. Kiliani-Fischer synthesis:



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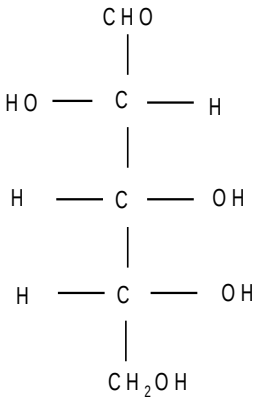
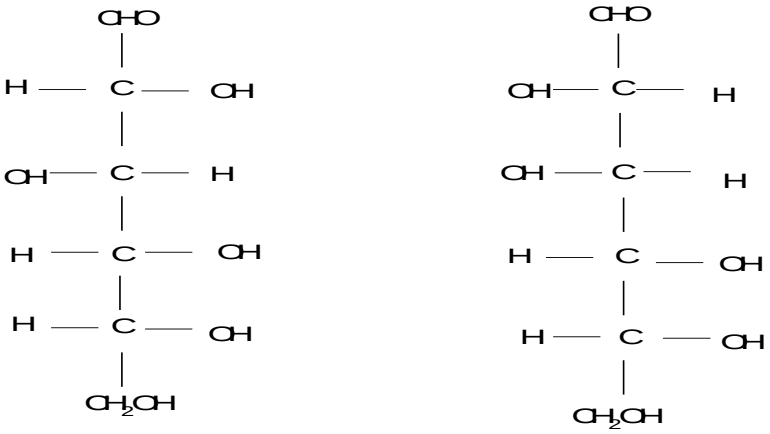
If it was (-) - arabinose, it would give these two aldohexoses

Since we have already shown that (-) - arabinose can have one of two alternative structures, it remains to prefer the structure below.



The correct structure (-) - arabinose

Given that the (-) structure of arabinose has already been elucidated, (+) glucose must have one of the structures shown below, and (+) mannose must have another.



One of these structures refers to (+) - glucose,and the other - to (+) - mannose.

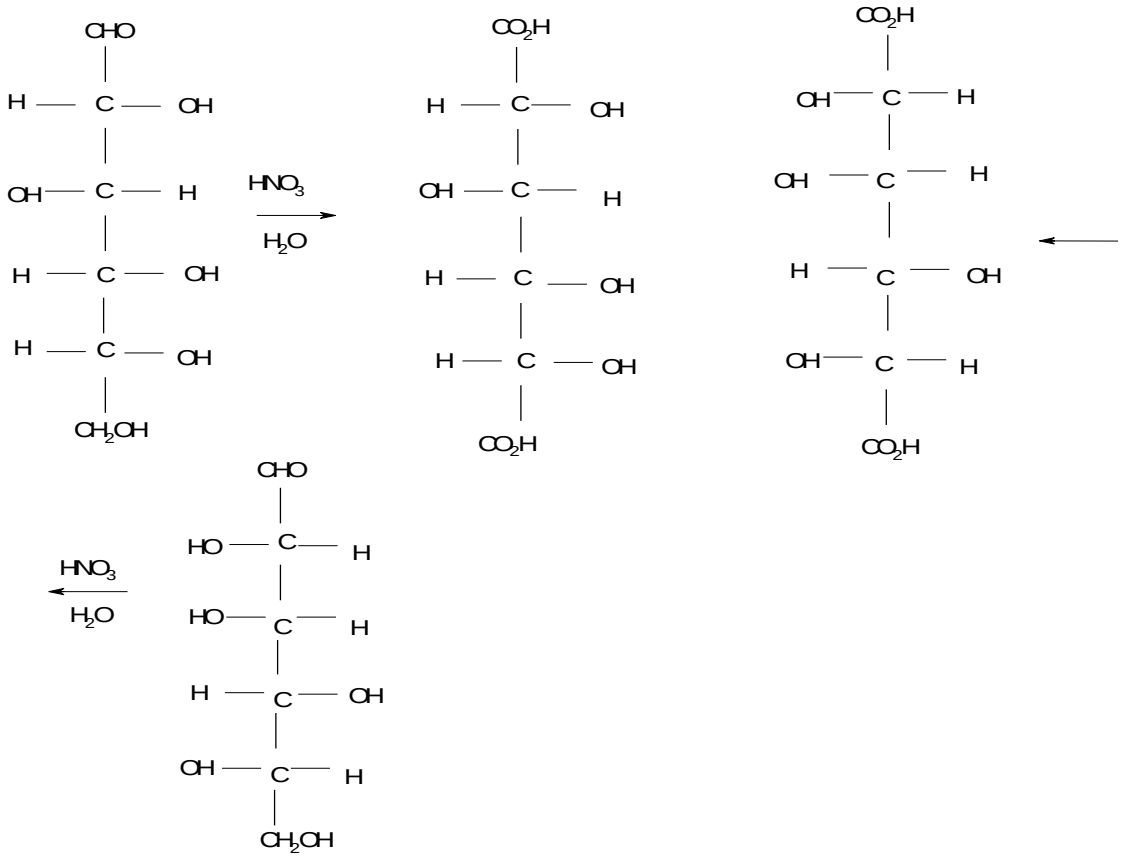
So, how to make the right decision at this stage. How do we do it?

Turning to the structures of aldohexoses, we will see that L-gulose gives the same acids as (+) - glucose, if glucose has the structure below.

4. Fisher synthesized L - (+) - gulose, it gave the oxidation of the same aldaric acid as (+) - glucose.

Thus, Fisher proved the relative configuration of all choral centers in (+) - glucose. Gradually, he established the structure of (+) - mannose.

Fisher also developed the synthesis of L - (+) - halos. This compound was known before Fischer began his research. Not surprisingly, Fischer was awarded the 1902 Nobel Prize in Chemistry for his brilliant work.



L-gulose

Recommended Books

1. Курта С.А.,Лучкевич Є.Р., Матківський М.П. Хімія органічних сполук. Підручник для вищих навчальних закладів. м. Івано-Франківськ: Прикарпат.нац.ун-т ім. В.Стефаника, 2013. – 599 с. вид-во. Прикарпат. нац. у-ту. Авторські права захищені свідоцтвом про реєстрацію авторського права на твір № 52578 від 13.12.2013 р. державним департаментом інтелектуальної власності МОН України.
2. Курта С.А. Природні вуглеводи і полісахариди. Навчальний посібник.ISBN 978-966-8969-84-3. Видав: Супрун В.П.76025, Івано-Франківськ, вул. В.Великого,12,аХ
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Questions for self-control

1. Monosaccharides. Structure of glucose and fructose. Fisher's projection formulas, cyclic Collie-Tolens formulas, Hawards perspective, conformational formulas.

2. Aldonic, sugar and uronic acids, hydrazones and ozones, fermentation of monosaccharides.

3. Chemical properties of monosaccharides. Aldonic, sugar and uronic acids, hydrazones and ozones, fermentation of monosaccharides.

4. Fermentation of glucose. Alcohol, glycerin, propionic, lactic, butyric acid fermentation.

5. The concept of glycosidic hydroxyl.

6. Proof of the structure of D (+) - glucose.

7. Features of the structure of monosaccharides. Nomenclature of carbohydrates.

8. Chemical properties of non-reducing disaccharides.

9. Types of spatial isomerism. Optical enantiomers and diastereoisomers. Rules for assigning molecules to D, L- and R, S-configurations. D- and L-glucose.