Lecture 5. Carbohydrates

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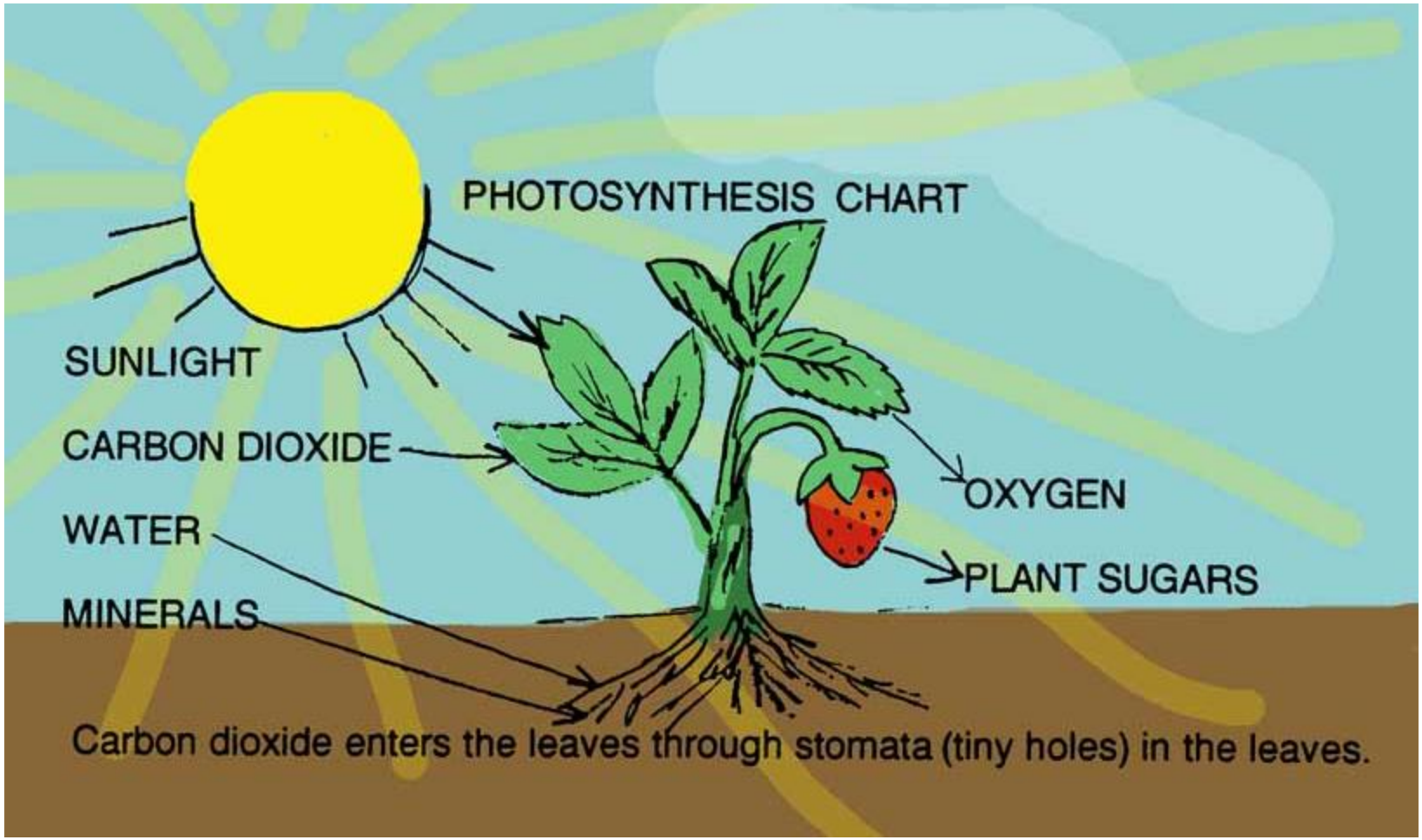
How carbohydrates form...

Using the sun's energy and the green pigment in plants called chlorophyll, plants convert carbon dioxide and water into glucose and oxygen. Glucose is the basic sugar molecule from which all carbohydrates (sugars, starches, and fiber) are made.

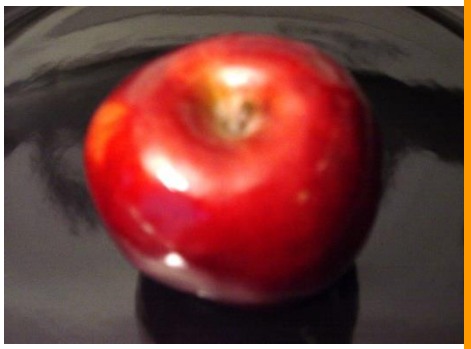


Sugars are simple carbohydrates...

A ‘saccharide’ is simply a sugar or a substance made from sugar. They are classified as ‘monosaccharides’ (simple sugars including glucose) or ‘disaccharides’ (two monosaccharides bonded together).

Granulated sugar (table sugar), brown sugar, and confectioners sugar (powdered sugar) are made from sugar cane or sugar beets. These are examples of the disaccharide <u>sucrose.</u>

<u>Maltose</u>, the sugar from grains, and <u>lactose</u>, the sugar from milk, are also disaccharides.

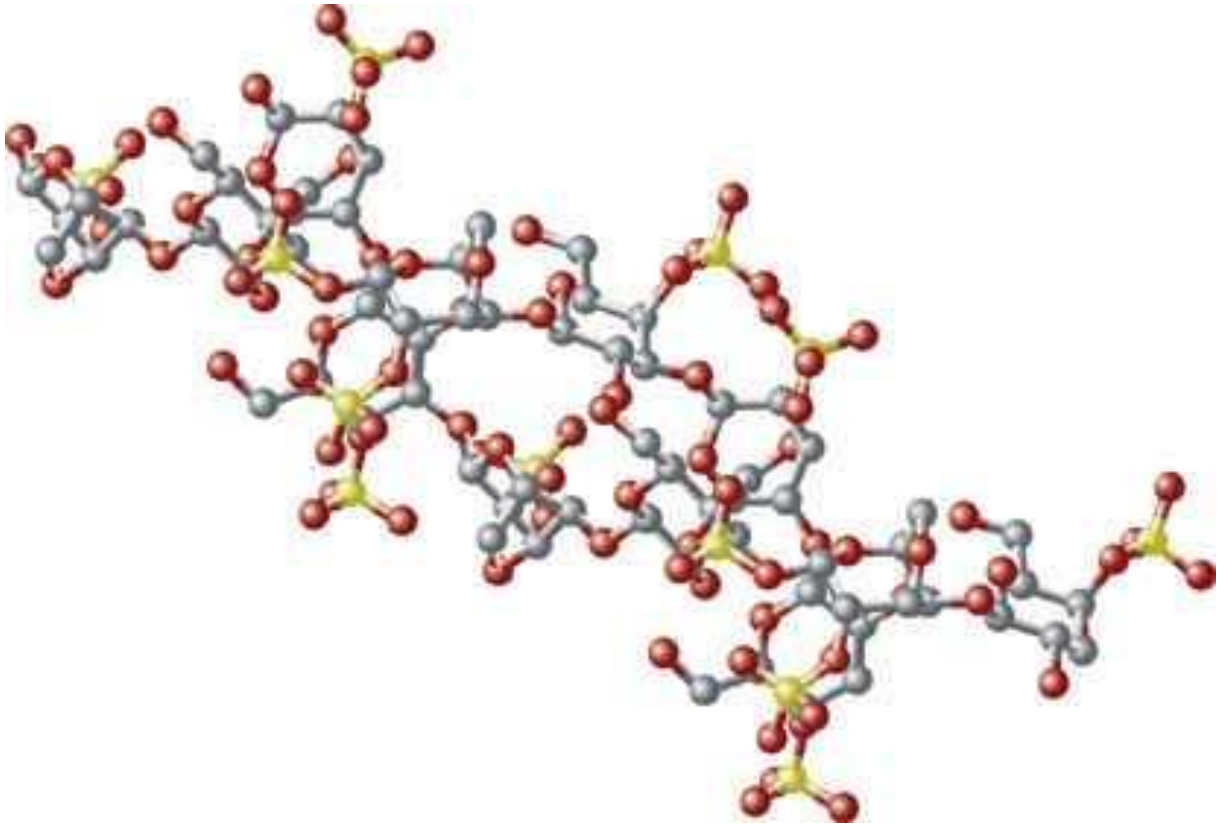


The monosaccharide <u>fructose</u> is found in fruit; <u>glucose</u> is found in corn syrup, honey, and tree sap (maple syrup).

What are carbohydrates?...

A carbohydrate is an organic compound that is the body's main source of energy. If you break down the word 'carbohydrate', you'll find part of the names of its main components: carbon and hydrogen. A carbohydrate molecule also includes oxygen.

$C_n(H_2O)_n$



Simple carbohydrates consist of one or two sugars, found in very small molecules.

Starches are complex carbohydrates, which are very large molecules made out of many simple carbohydrate units.

Carbohydrates hydrates of carbon: general formula $C_n(H_2O)_n$

- Made of carbon, hydrogen, and oxygen in a 1:2:1 ratio

Classification of the carbohydrates

Monosaccharaides which are simple sugars that cannot be broken down into smaller molecules by hydrolysis.

Glucose, fructose

Disaccharides which can be hydrolyzed to give two monosaccharaides.

Sucrose, lactose

Oligosaccharides which are made of two to ten monosaccharide units.

N-glycoproteins

Polysaccharides which are polymers consisting of many (hundreds and thousands) monosaccharide units

Starch, glycogen

Classification of Carbohydrates.

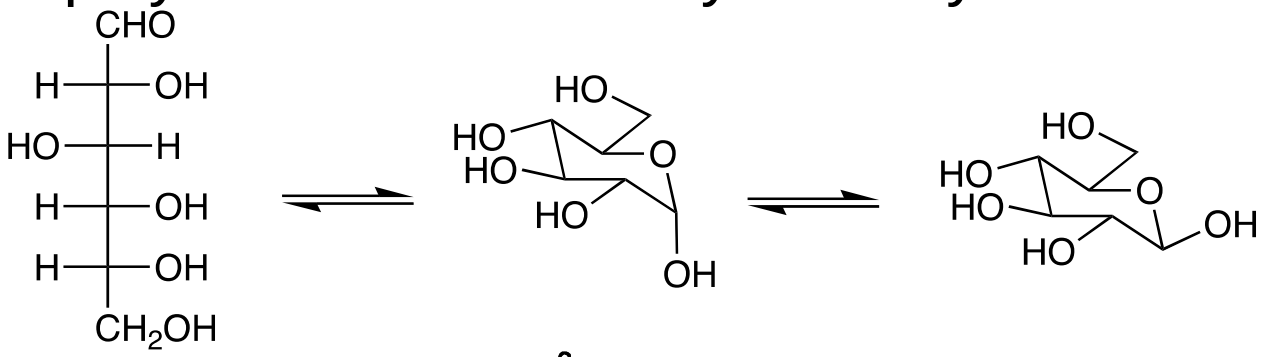
I. Number of carbohydrate units

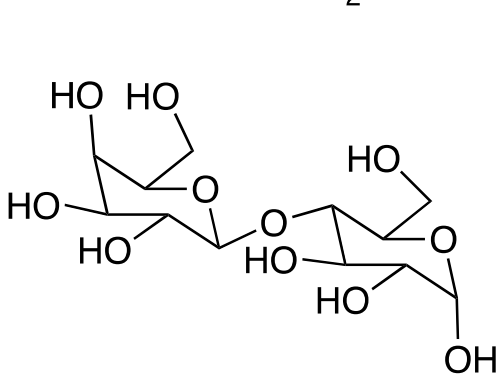
monosaccharides: one carbohydrate unit
(simple carbohydrates)

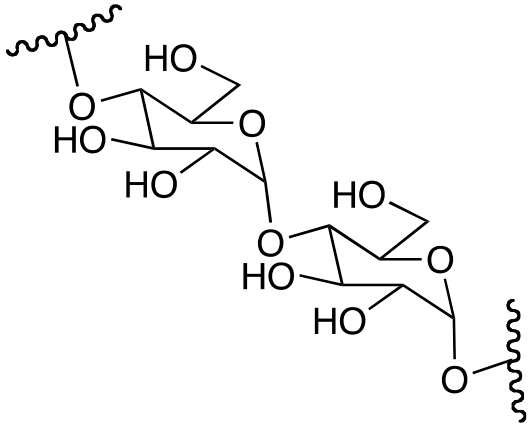
disaccharides: two carbohydrate units
(complex carbohydrates)

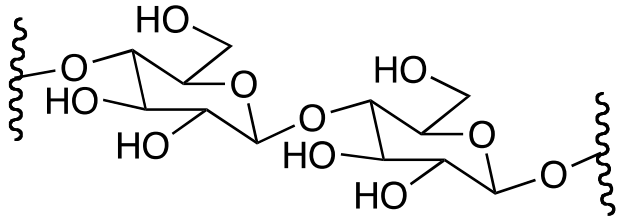
trisaccharides: three carbohydrate units

polysaccharides: many carbohydrate units









II. Position of carbonyl group

at C1, carbonyl is an aldehyde: aldose

at any other carbon, carbonyl is a ketone: ketose

III. Number of carbons

three carbons: triose

four carbons: tetrose

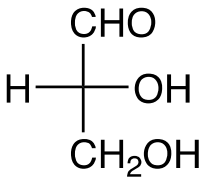
five carbons: pentose

six carbons: hexose

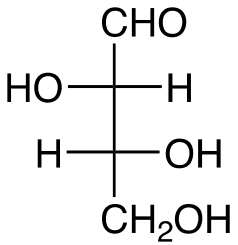
seven carbons: heptose

etc.

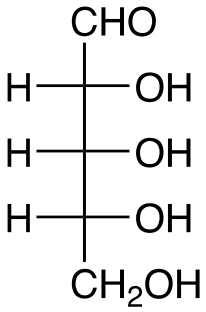
IV. Cyclic form



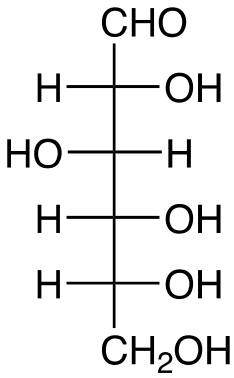
glyceraldehyde (triose)



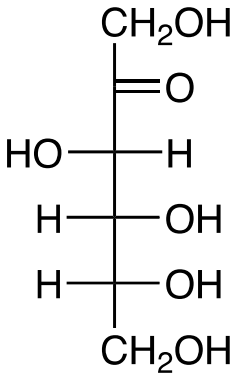
threose (tetrose)



ribose (pentose)



glucose (hexose) (aldohexose)

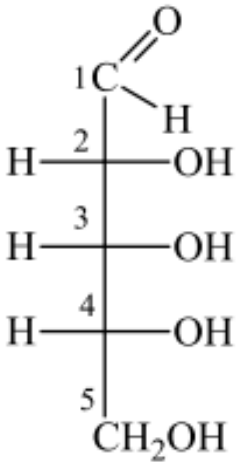


fructose (hexose) (ketohexose)

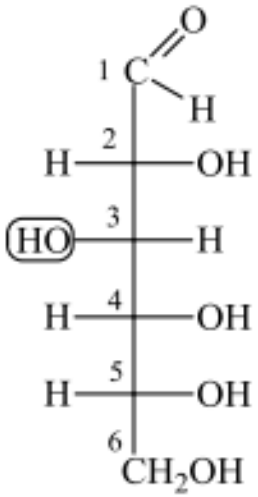
Monosaccharides

According to the number of carbon atoms they are trioses, tetroses, pentoses, hexoses.
$C_3H_6O_3$ – Glyceraldehyde
$C_5H_{10}O_5$ – Ribose
$C_6H_{12}O_6$ – Glucose, fructose

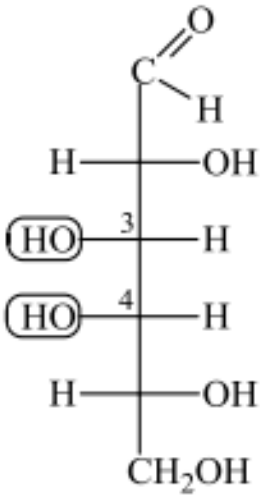
Depending on the presence of the aldehyde or the ketone group, the sugar is called aldose or ketose.



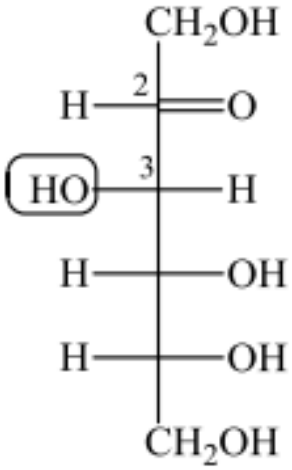
Ribose



Glucose

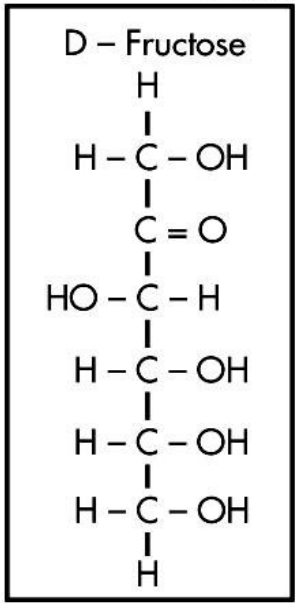


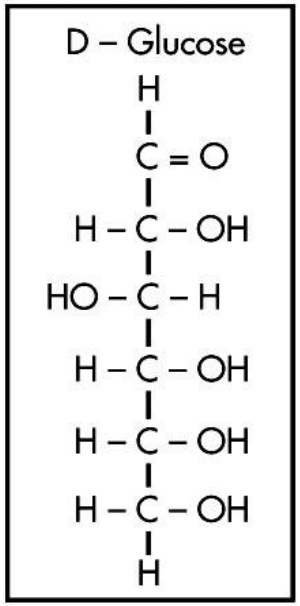
Galactose

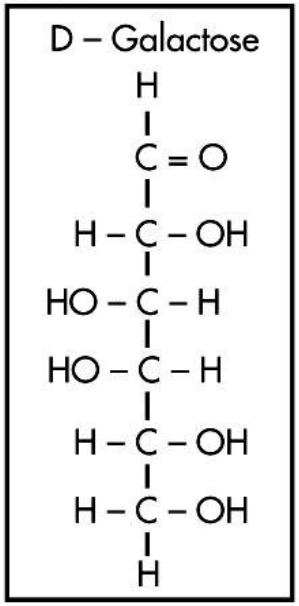


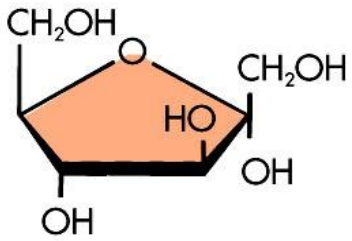
Fructose

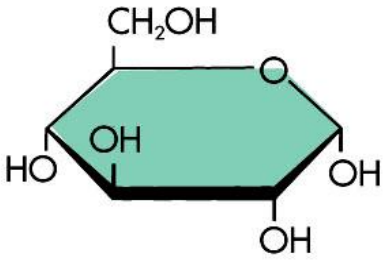
MONOSACCHARIDES

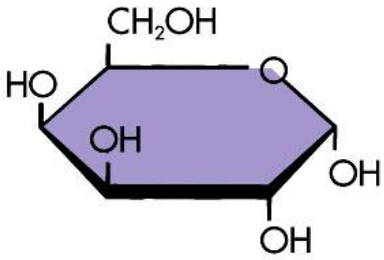


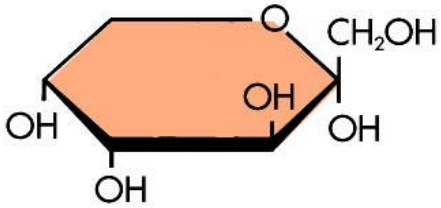






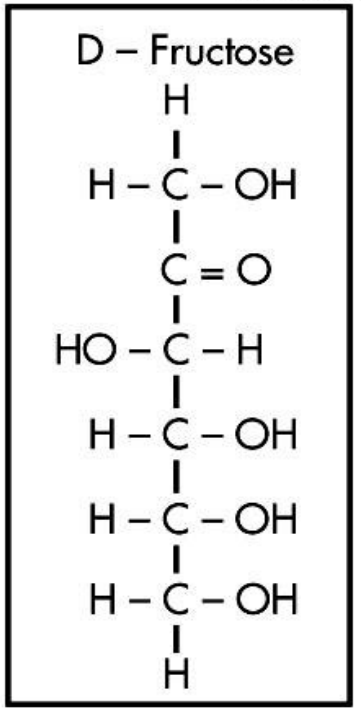


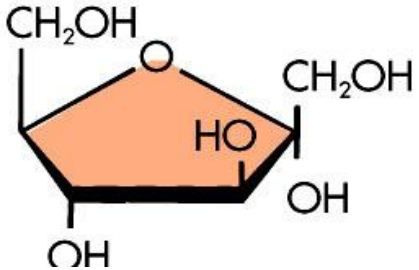




FRUCTOSE

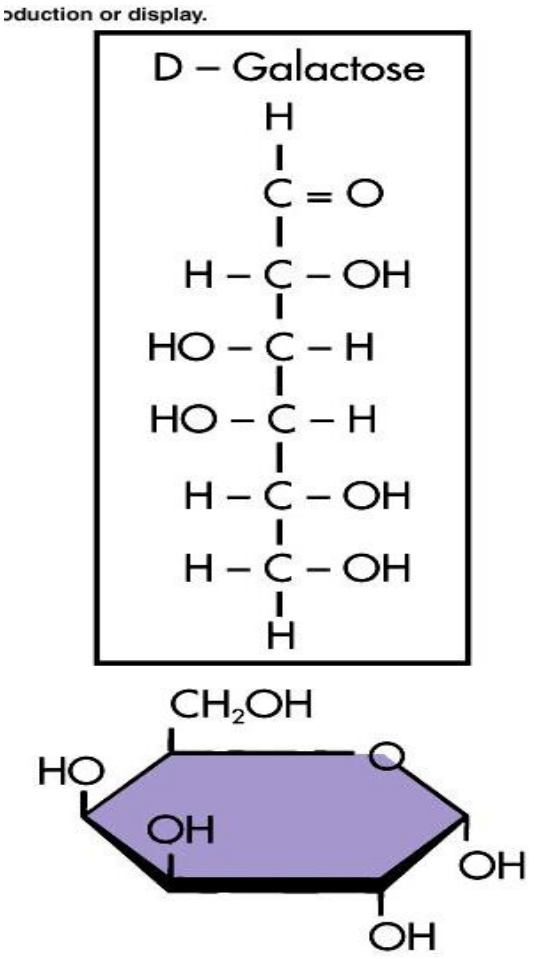
- Also called levulose
- Isomer of glucose
- Metabolized into glucose by the liver
- Small amounts are converted into glycogen, lactic acid, or fat
- Found in fruit, honey, and high fructose corn syrup





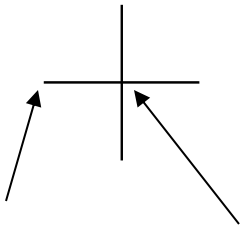
GALACTOSE

- Not usually found free in nature in large quantities
- Isomer of glucose
- Typically found as a subunit of lactose
- Converted to glucose by the liver
- Used as an immediate energy source or is stored as glycogen



Fischer Projections and the D, L Notation. Representation of a three-dimensional molecule as a flat structure. Tetrahedral carbon represented by two crossed lines:

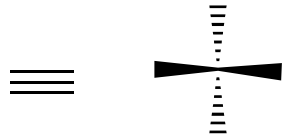
horizontal line is coming out of the plane of the page (toward you)



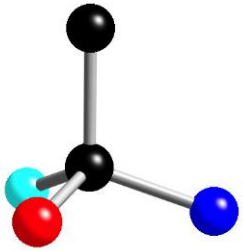
substituent

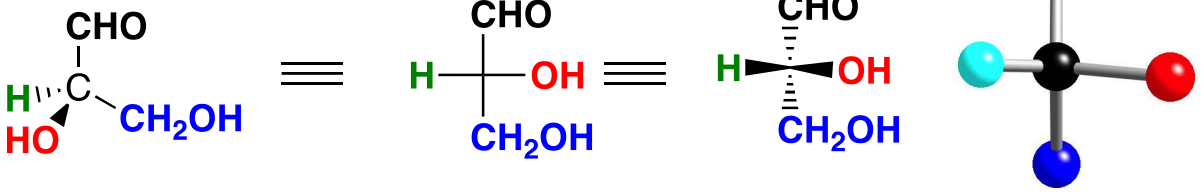
carbon

vertical line is going back behind the plane of the paper (away from you)

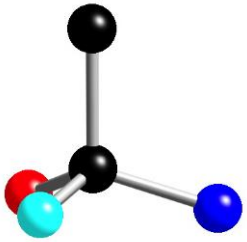


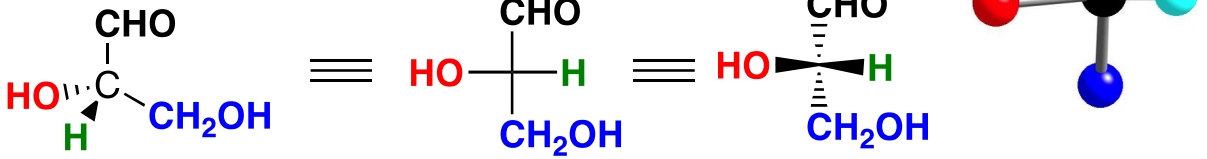
(*R*)-(+)-glyceraldehyde



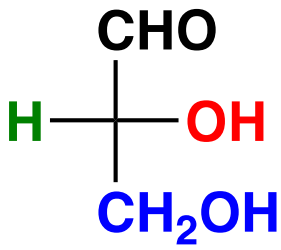


(*S*)-(-)-glyceraldehyde

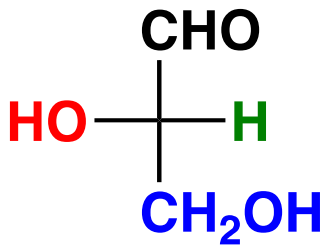




before the *R*/*S* convention, stereochemistry was related to (+)-glyceraldehyde



D-glyceraldehyde
R-(+)-glyceraldhyde
(+)-rotation = dextrorotatory = d

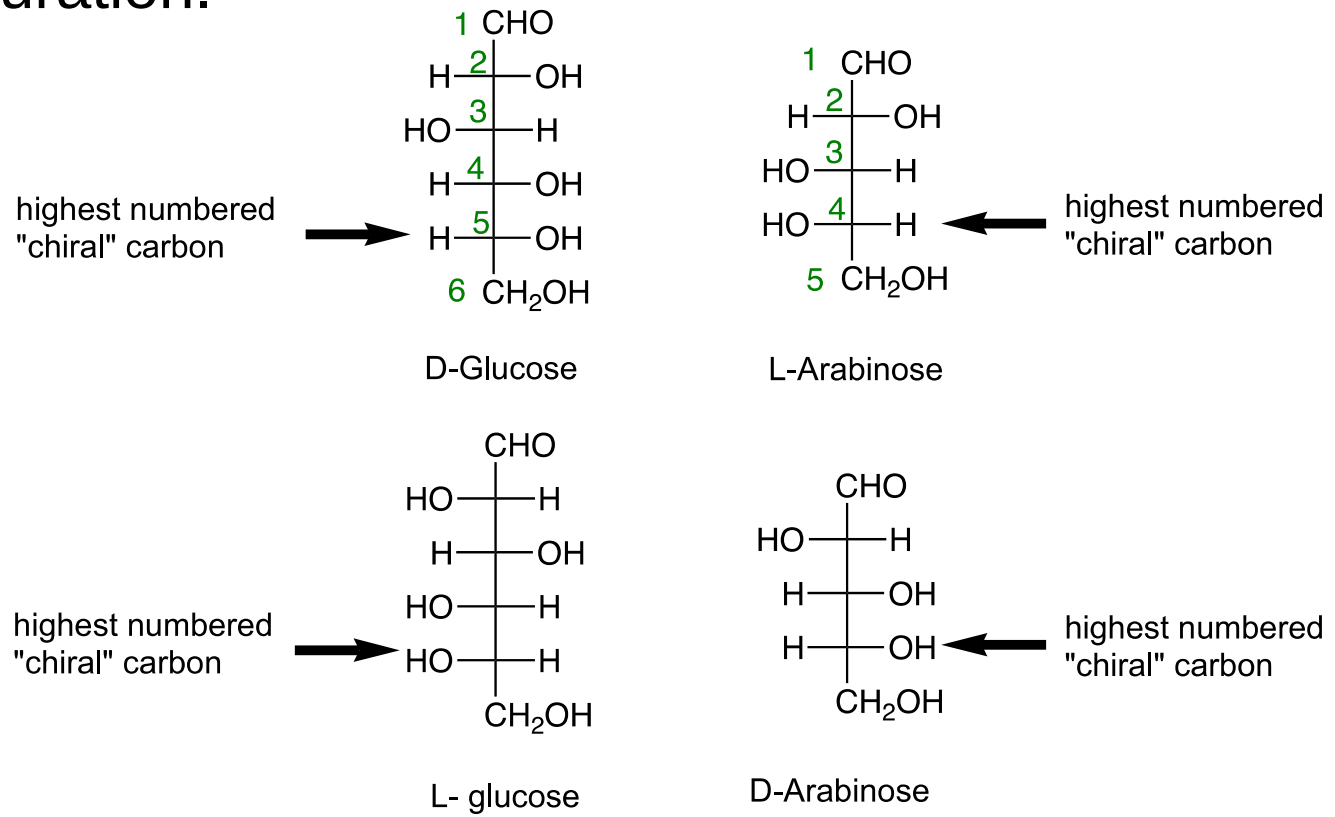


L-glyceraldehyde
S-(-)-glyceraldhyde
(-)-rotation = levorotatory = l

D-carbohydrates have the -OH group of the highest numbered chiral carbon pointing to the right in the Fischer projection as in R-(+)-glyceraldhyde

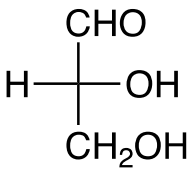
For carbohydrates, the convention is to arrange the Fischer projection with the carbonyl group at the top for aldoses and closest to the top for ketoses. The carbons are numbered from top to bottom.

Carbohydrates are designated as D- or L- according to the stereochemistry of the highest numbered chiral carbon of the Fischer projection. If the hydroxyl group of the highest numbered chiral carbon is pointing to the right, the sugar is designated as **D** (*Dextro*: Latin for *on the right side*). If the hydroxyl group is pointing to the left, the sugar is designated as **L** (*Levo*: Latin for *on the left side*). Most naturally occurring carbohydrates are of the D-configuration.

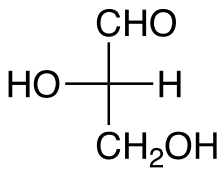


The Aldotetroses. Glyceraldehyde is the simplest carbohydrate (C_3, aldotriose, 2,3-dihydroxypropanal). The next carbohydrate are aldotetroses (C_4, 2,3,4-trihydroxybutanal).

aldotriose



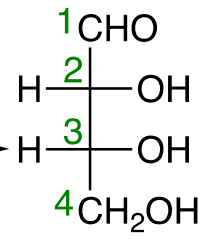
D-glyceraldehyde



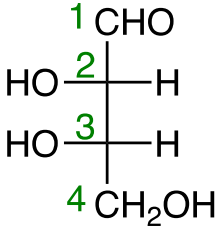
L-glyceraldehyde

aldotetroses

highest numbered "chiral" carbon



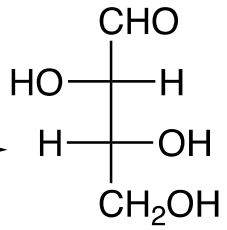
D-erythrose



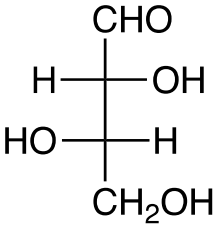
L-erythrose

highest numbered "chiral" carbon

highest numbered "chiral" carbon



D-threose

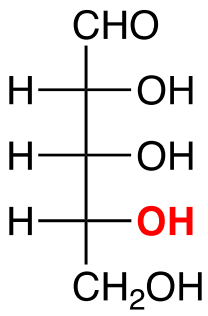


L-threose

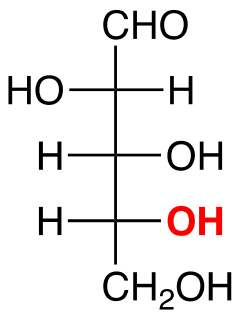
highest numbered "chiral" carbon

Aldopentoses and Aldohexoses.

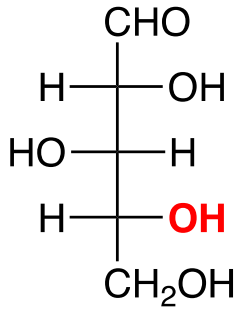
Aldopentoses: C_5, three chiral carbons, eight stereoisomers



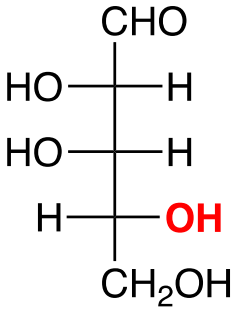
D-ribose



D-arabinose

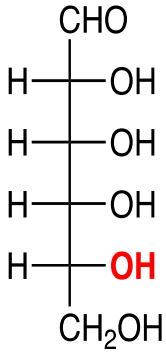


D-xylose

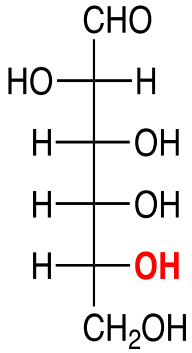


D-lyxose

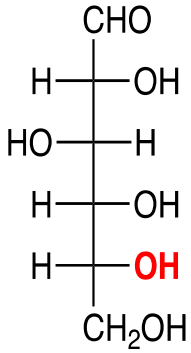
Aldohexoses: C_6, four chiral carbons, sixteen stereoisomers



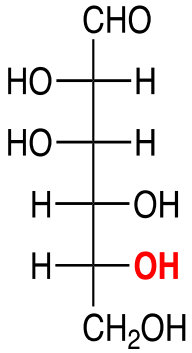
D-allose



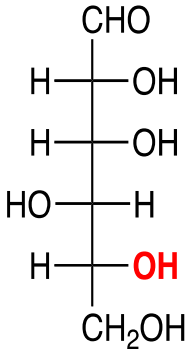
D-altrose



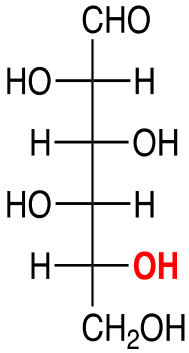
D- glucose



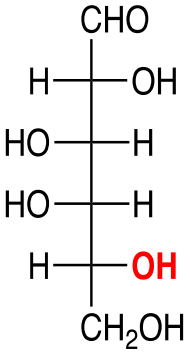
D-mannose



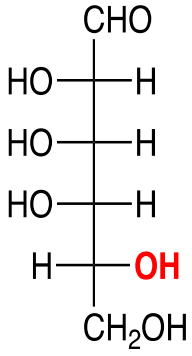
D-gulose



D-idose



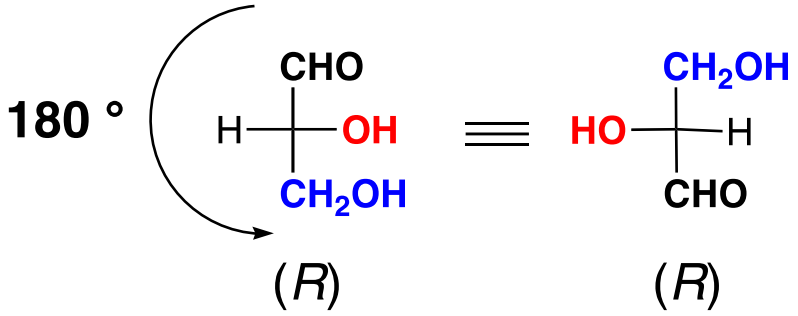
D-galactose

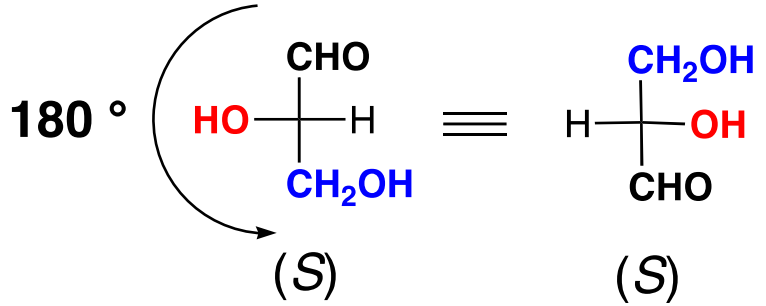


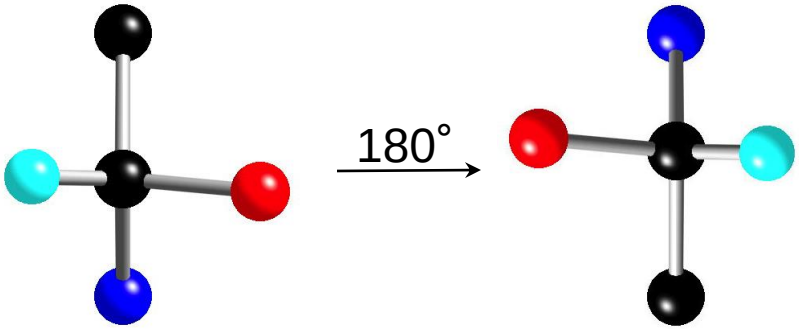
D-talose

Manipulation of Fischer Projections

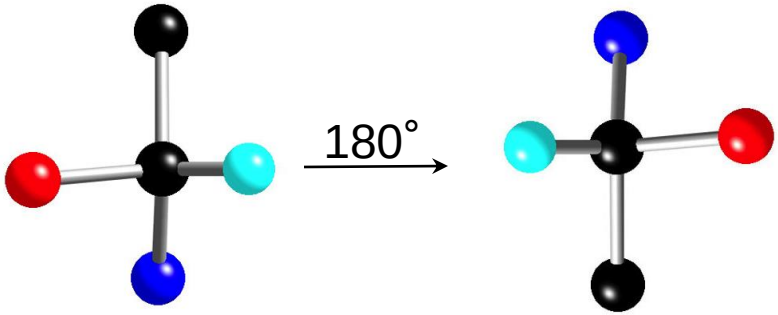
1. Fischer projections can be rotate by 180˚ (in the plane of the page) only!





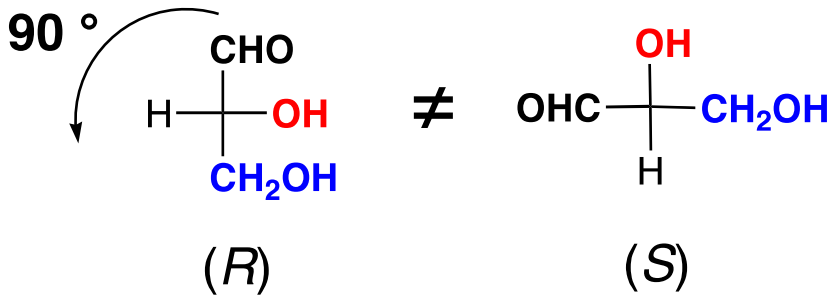


Valid Fischer projection

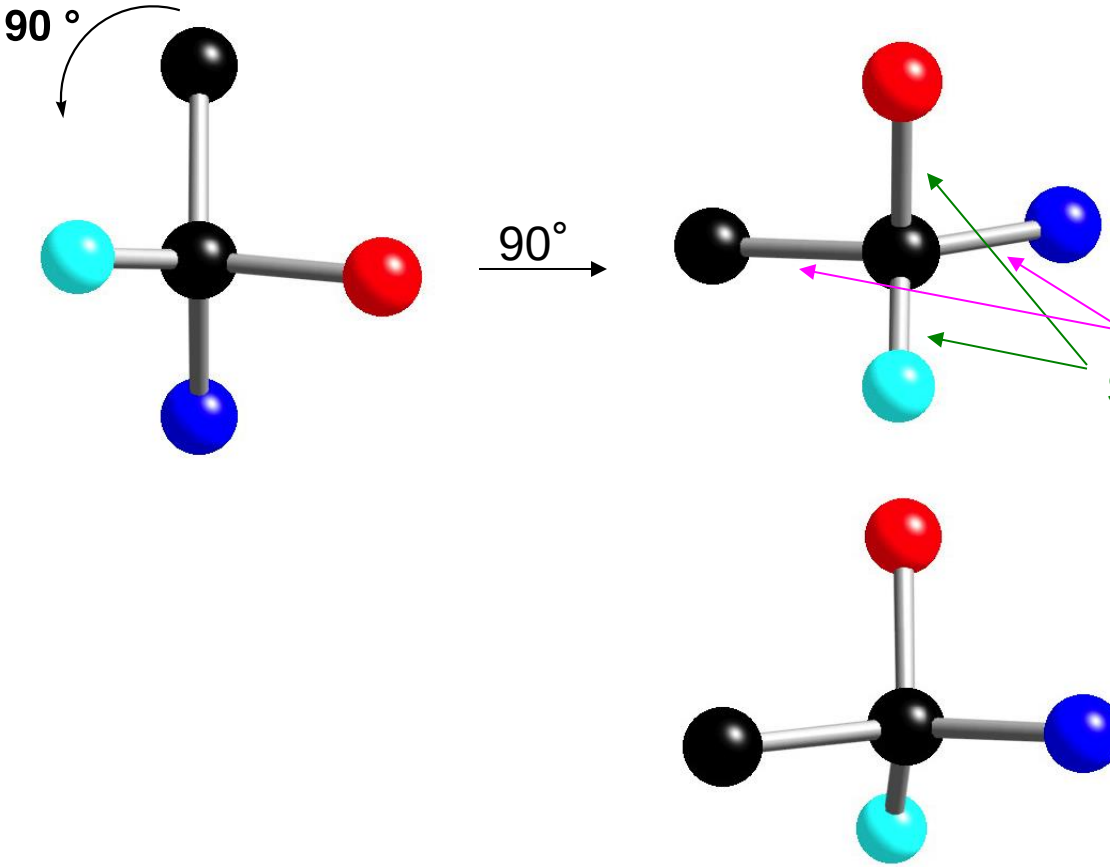


Valid Fischer projection

a 90° rotation inverts the stereochemistry and is illegal!



(*R*) (*S*)



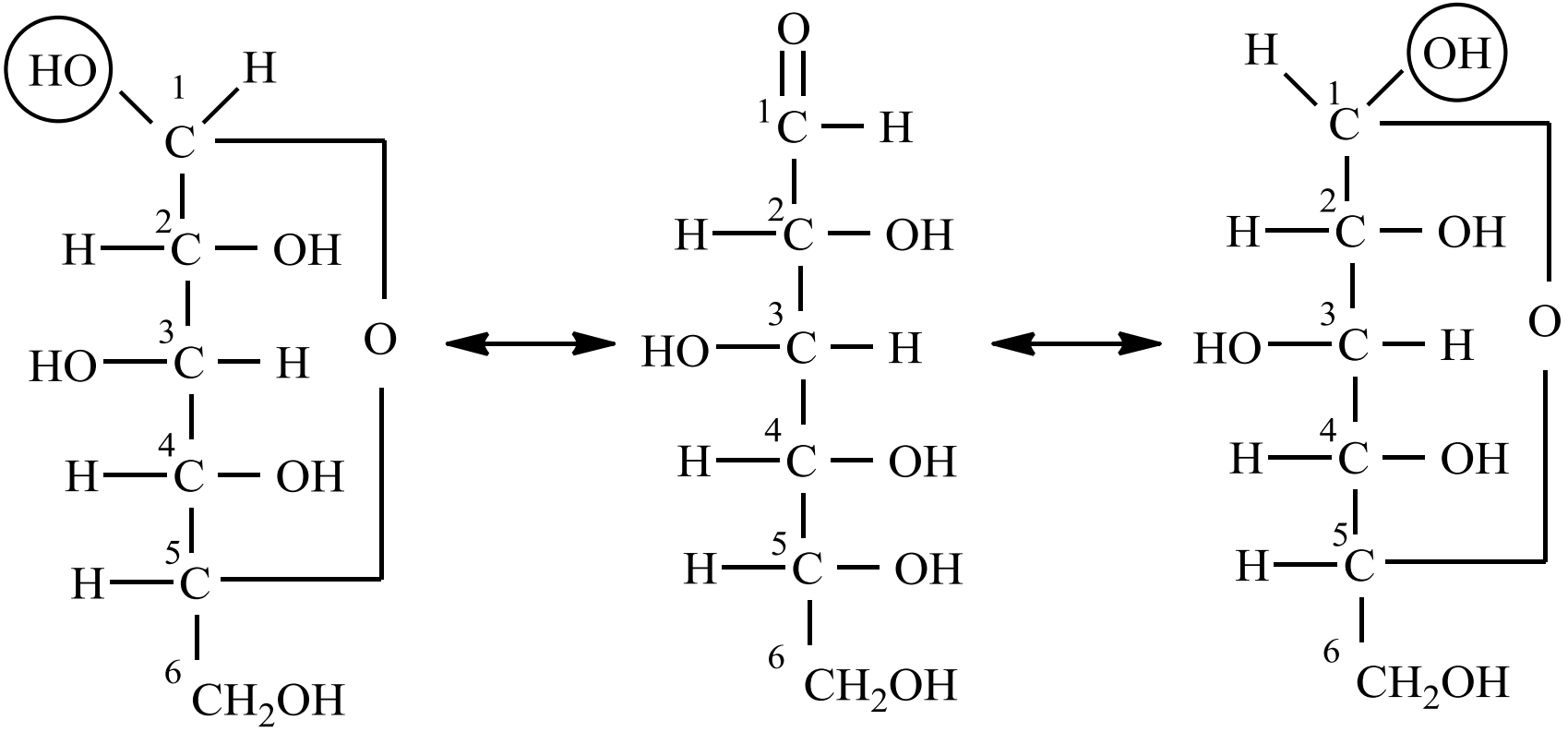
This is not the correct convention for Fischer projections

Should be projecting toward you

Should be projecting away you

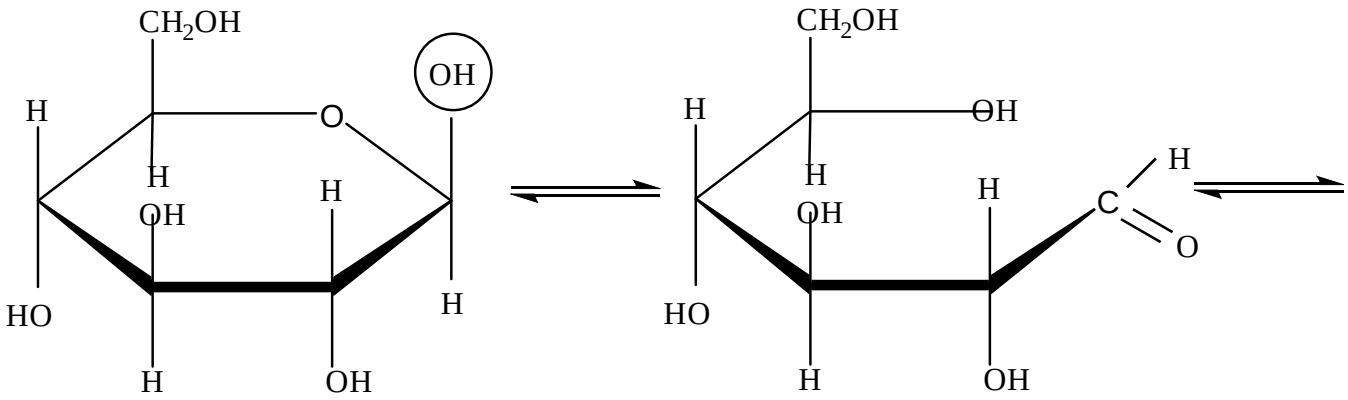
This is the correct convention for Fischer projections and is the enantiomer

Cyclic structures: As the two reacting groups aldehyde and alcoholic group belong to the same molecule, a cyclic structure takes place. C1 after cyclization becomes asymmetric – it is called “anomeric” carbon and α–D–glucose and β–D–glucose are “anomers”.



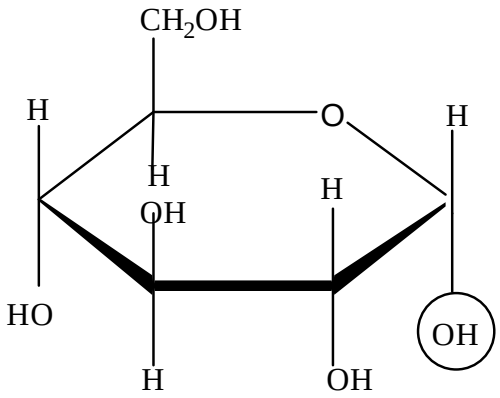
β-D-Glucose Aldehydo-D-Glucose *α*-D-Glucose

Haworth Projection



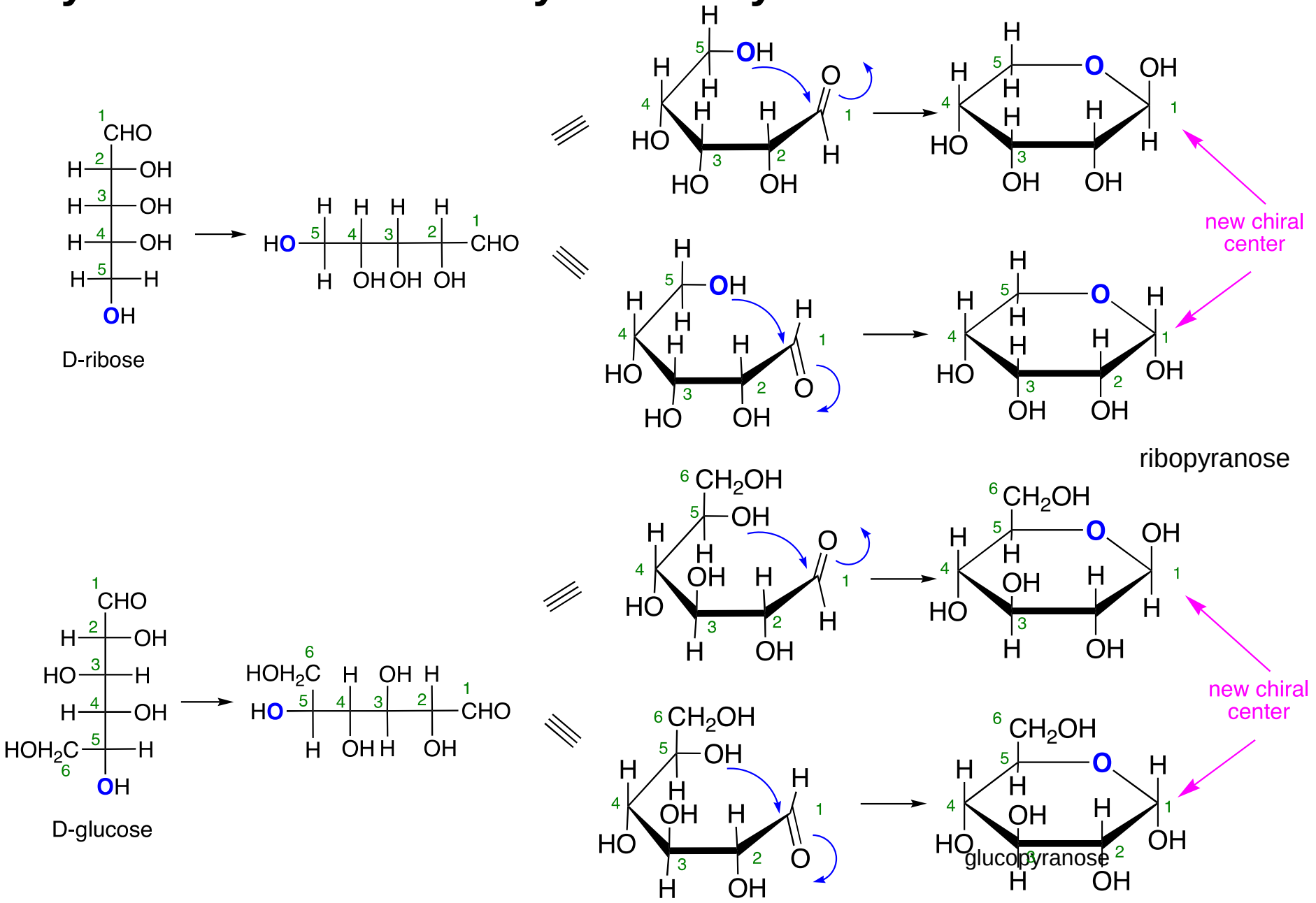
β-D-glucopyranose

aldehydo-D-glucose



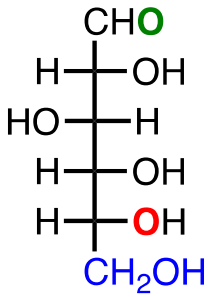
α-D-glucopyranose

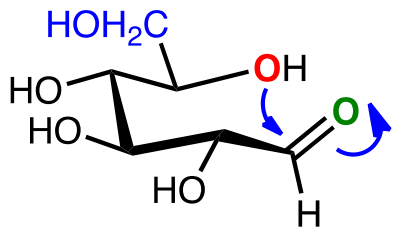
Cyclic Forms of Carbohydrates: Pyranose Forms.

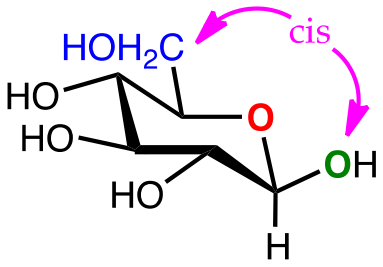


Note: the pyranose forms of carbohydrates adopt chair conformations.

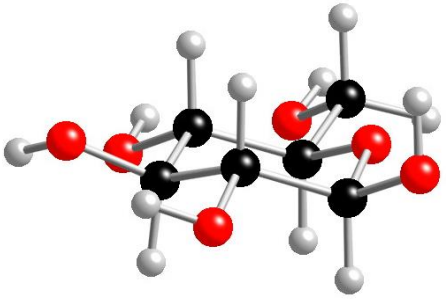
Mutarotation. The α- and β-anomers are in equilibrium, and interconvert through the open form. The pure anomers can be isolated by crystallization. When the pure anomers are dissolved in water they undergo mutarotation, the process by which they return to an equilibrium mixture of the anomer.



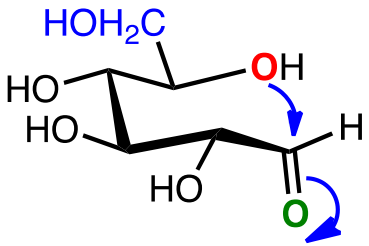


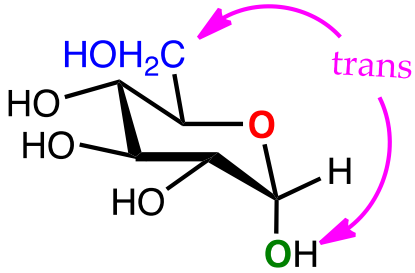


β-D-Glucopyranose (64%)
(β-anomer: C1-OH and
CH_2OH are cis)

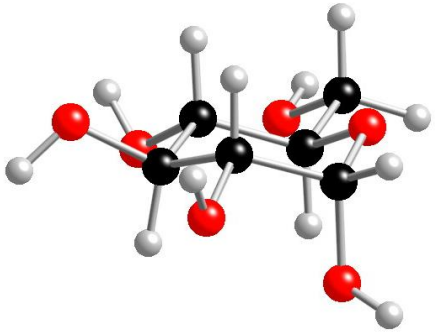


$[\alpha]_D$ +18.7°





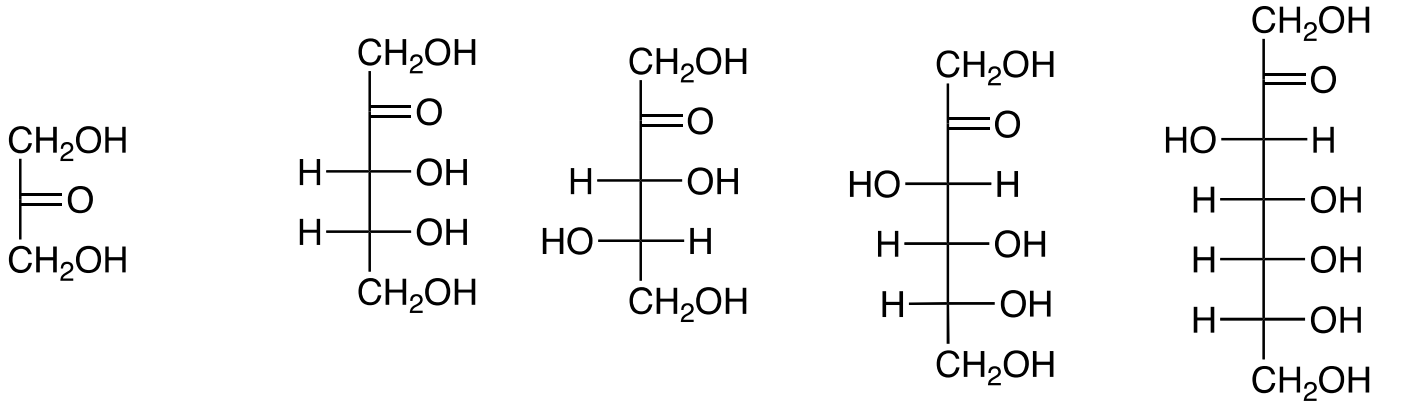
α-D-Glucopyranose (36%)
(α-anomer: C1-OH and
CH_2OH are trans)



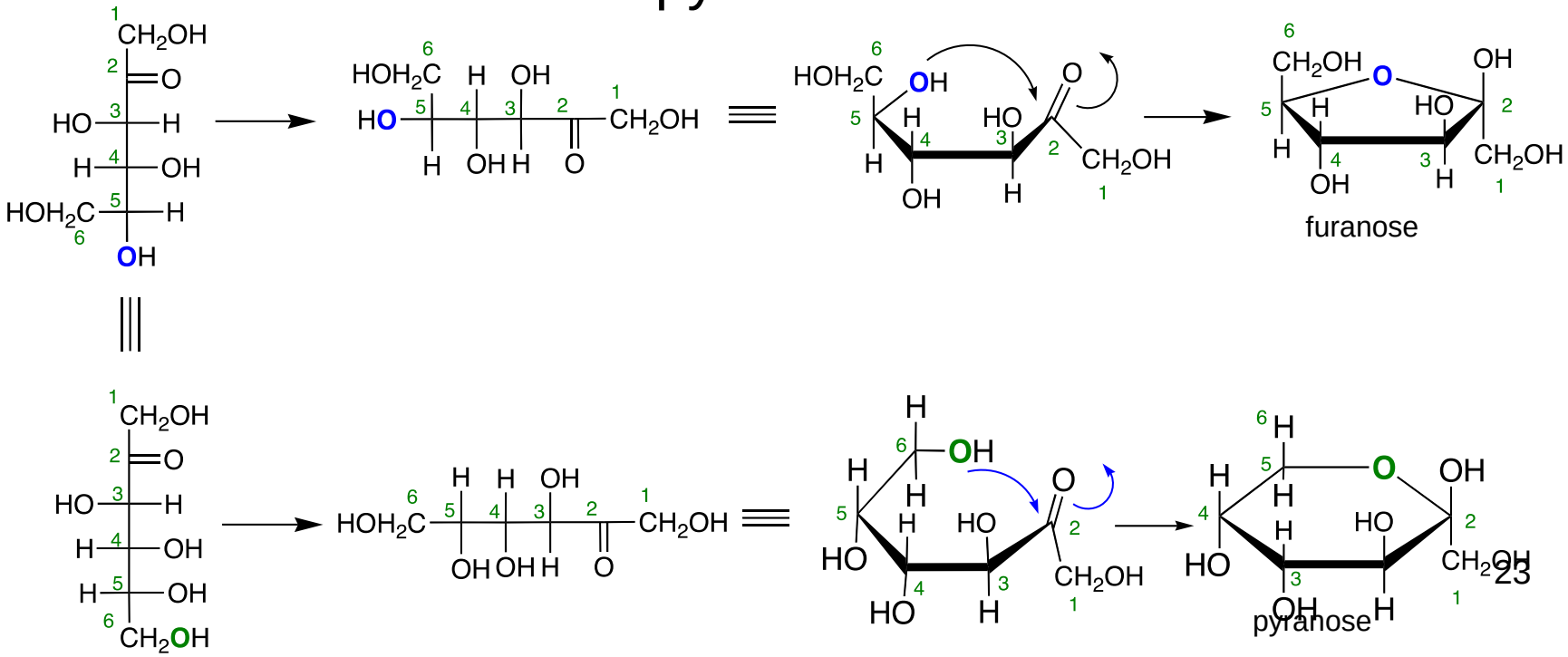
$[\alpha]_D$ +112.2°

Carbohydrate Conformation: The Anomeric Effect

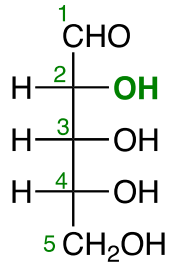
Ketoses. Ketoses are less common than aldoses

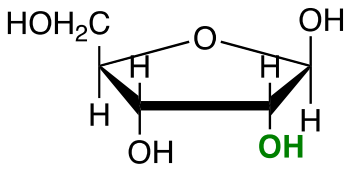


Fructofuranose and Fructopyranose

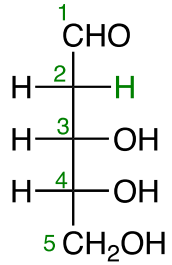


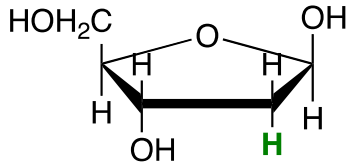
Deoxy Sugars. Carbohydrates that are missing a hydroxy group.



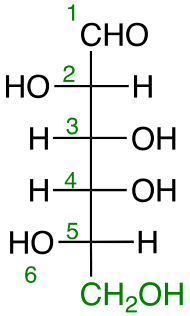


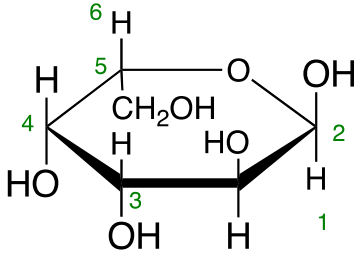
D-ribose



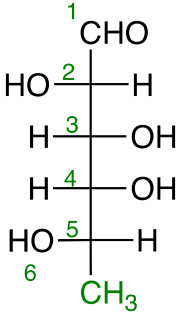


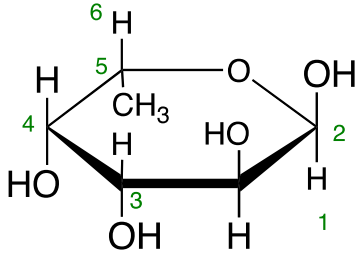
2-Deoxy-D-ribose





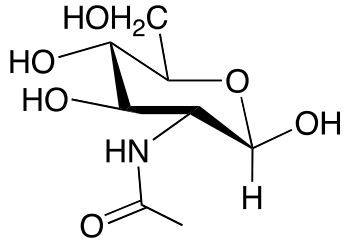
L-Galactose



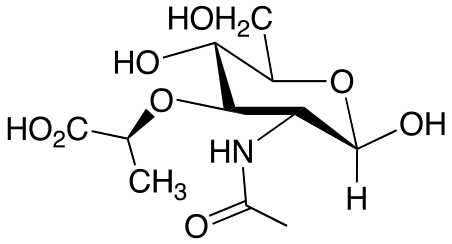


6-Deoxy-L-Galactose
(fucose)

Amino Sugars. Carbohydrates in which a hydroxyl group is replaced with an -NH_2 or -NHAc group

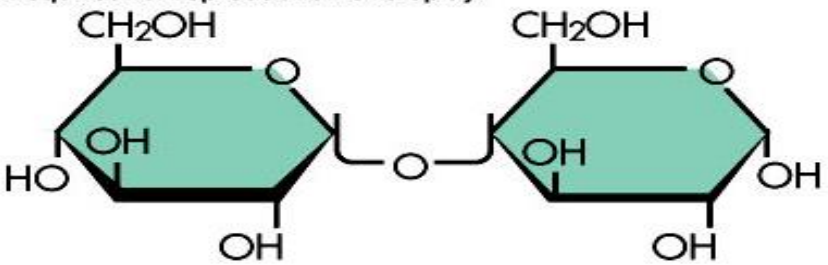


N-acetyl-D-glucosamine
(GlcNAc or NAG)

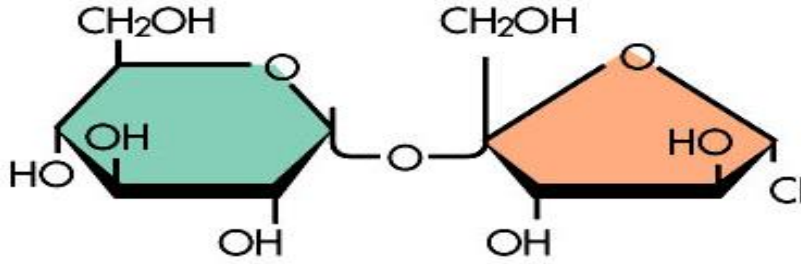


N-Acetylmuramic acid
(MurNAc)

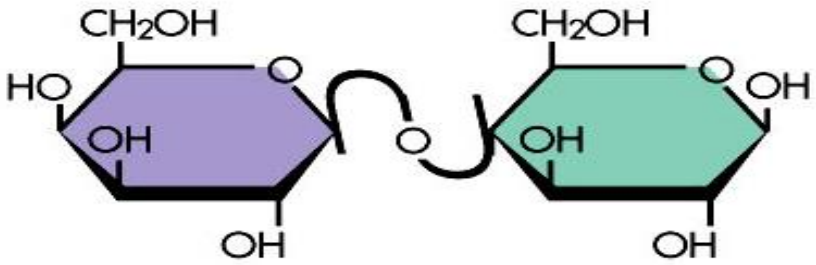
DISACCHARIDES



Maltose

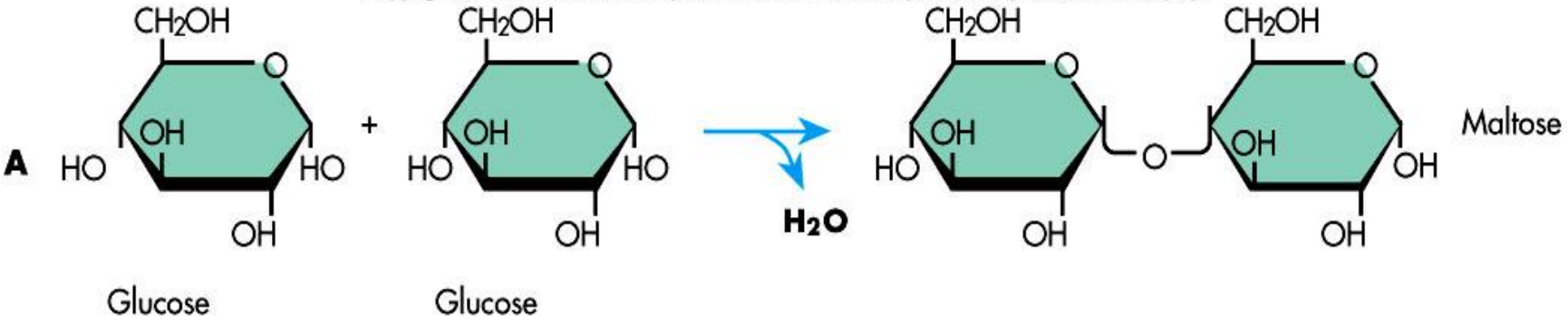


Sucrose



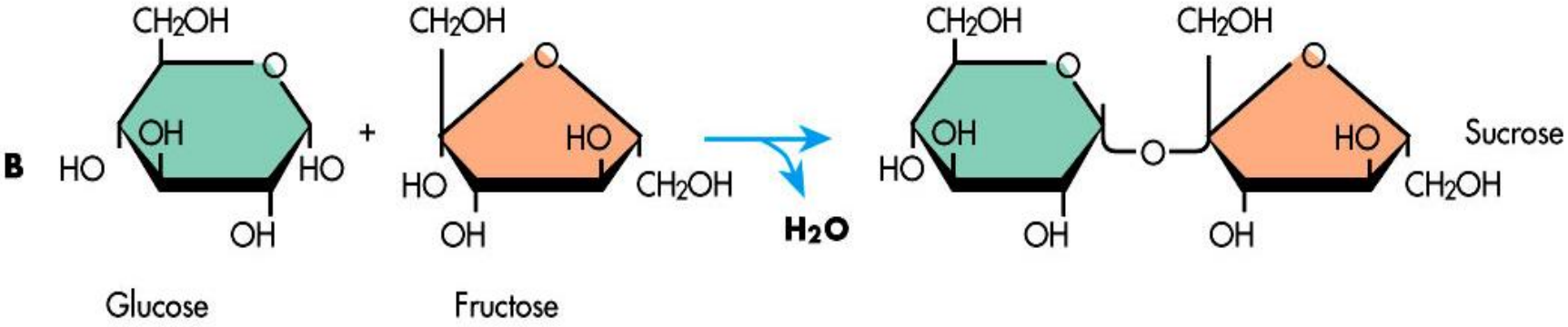
Lactose

MALTOSE



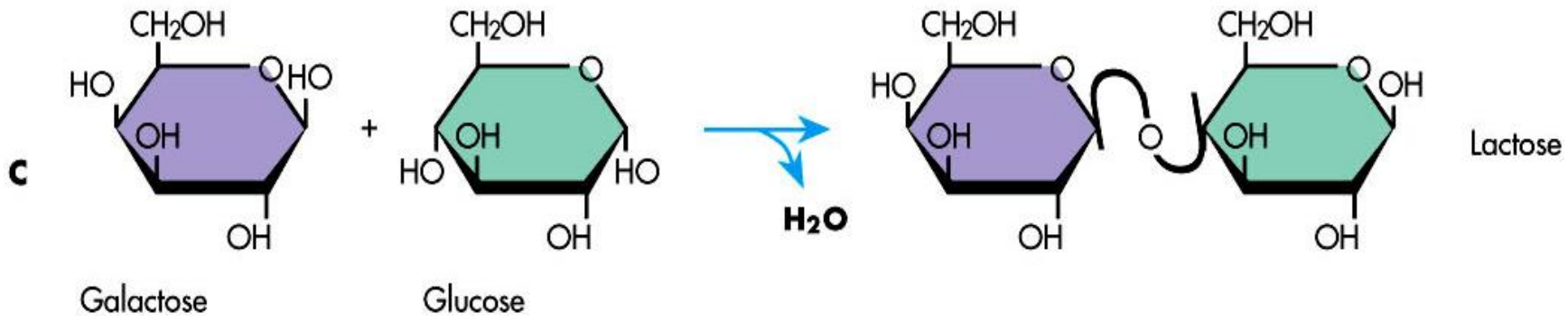
- Constructed by a condensation reaction
- Composed of two glucose molecules
- Possesses an alpha bond
- Commonly produced by fermentation reactions called malting
- Most maltose digested is the result of starch digestion

SUCROSE



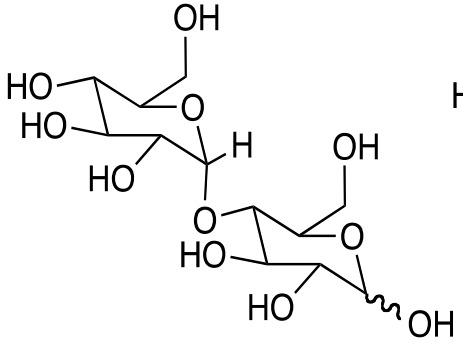
- Constructed by a condensation reaction
- Composed of one glucose and one fructose
- Possesses an alpha bond
- Commonly called table sugar and is found in plants such as sugar cane and maple syrup
- Purified to form brown, white, and powdered sugars

LACTOSE

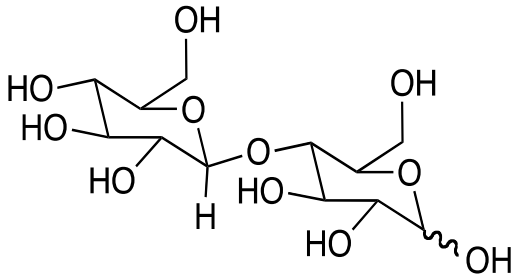


- Constructed by a condensation reaction
- Composed of one glucose and one galactose
- Possesses a beta bond
- Beta bonds are difficult to digest
- Primary sugar in milk and milk products

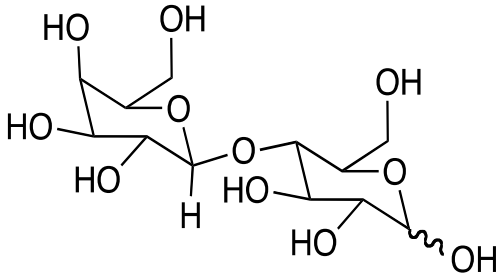
Disaccharides. A glycoside in which ROH is another carbohydrate unit (complex carbohydrate).



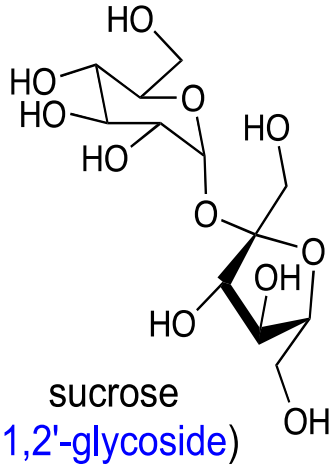
maltose
(1,4'-α-glycoside)



cellobiose
(1,4'-β-glycoside)

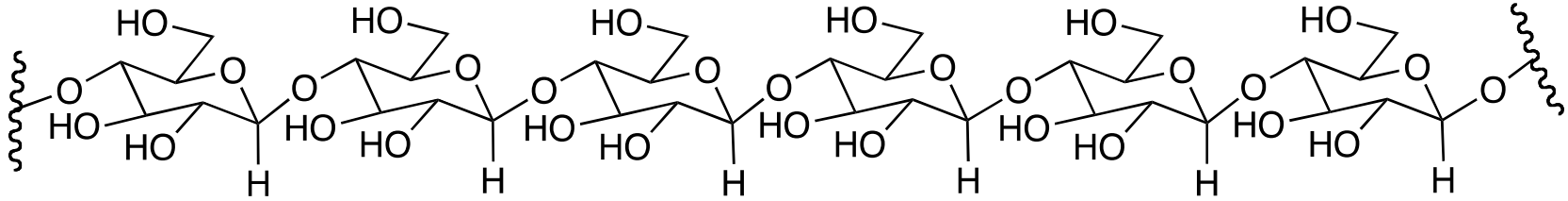


Lactose
(1,4'-β-glycoside)

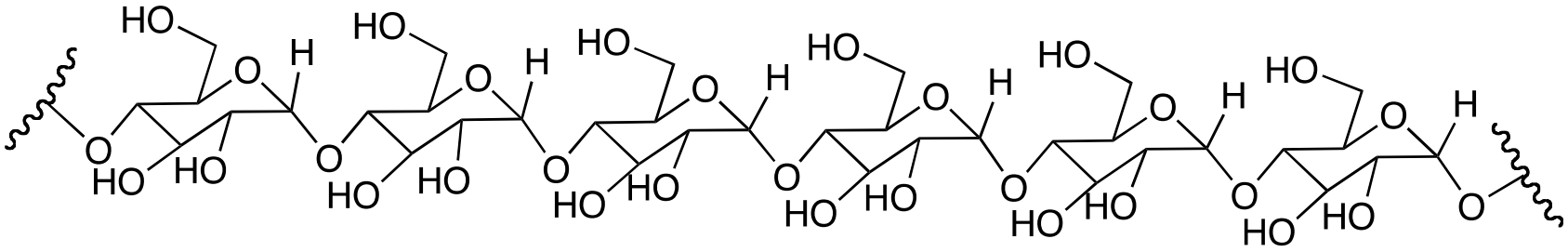


sucrose
(1,2'-glycoside)

Polysaccharides. *Cellulose*: glucose polymer made up of 1,4' -β-glycoside linkages

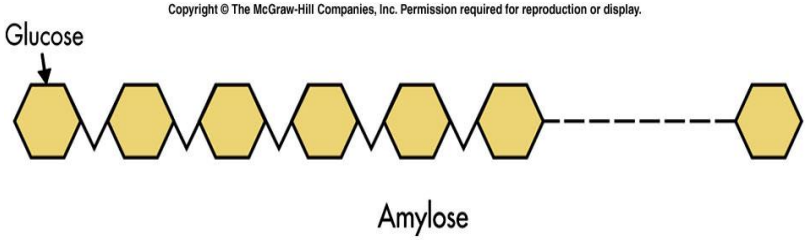


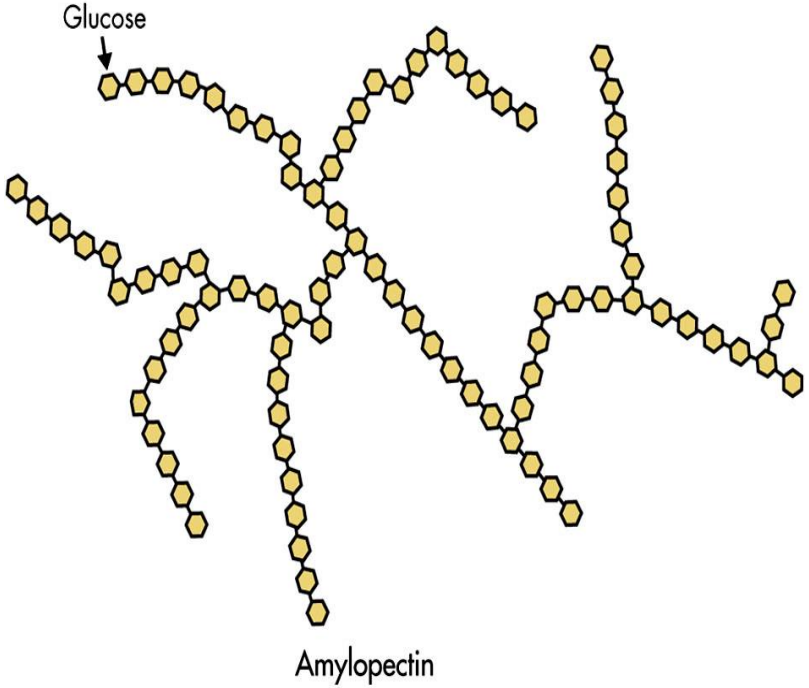
Amylose: glucose polymer made up of 1,4' -α-glycoside linkages



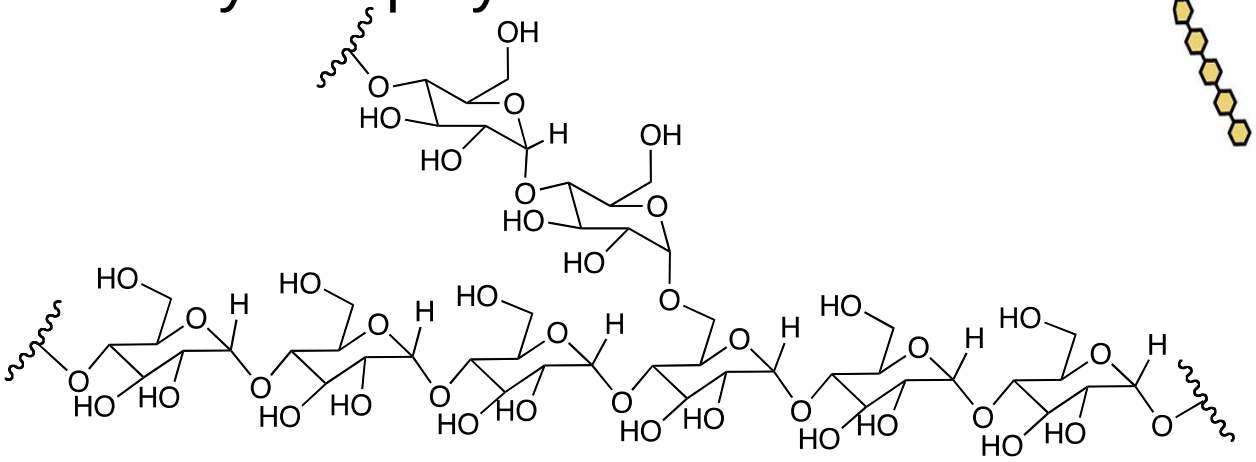
STARCHES

- 3000 monosaccharides
- Contain alpha bonds
- Amylose is straight chain
- Amylopectin is branched chain
- High Glycemic Index





Amylopectin: Branched amylose polysaccaride



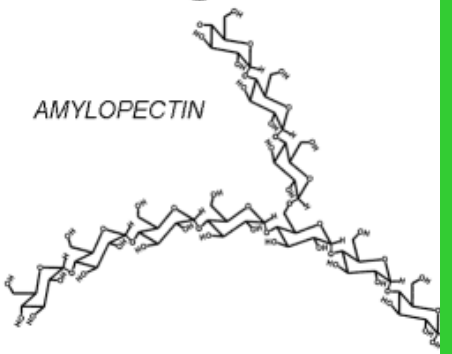
Properties of starches: gelatinization...

Starches are NOT water soluble like sugars. The molecules are too big to form solutions. When starches are heated in water, an irreversible thickening process called gelatinization occurs. The starch granules absorb the water and swell. Hydrogen bonds form between the starch and water molecules, and a paste is formed.

As gelatinization thickens a mixture, VISCOSITY increases. Viscosity is 'resistance to flow'. The greater the concentration of starch, the more viscous a paste becomes.

Properties of starches: thickening...

Amylopectin, because of its branched quality, does not mix with water as easily as amylose. Therefore, amylopectin does not thicken as easily and is a good type of starch for foods that always need to remain a bit runny… like ketchup and gravy. Amylose starches are used for foods that need to gel more firmly and permanently, like pudding.



The temperature at which a paste forms varies with the type of starch. Wheat starch thickens at a lower temperature than cornstarch.

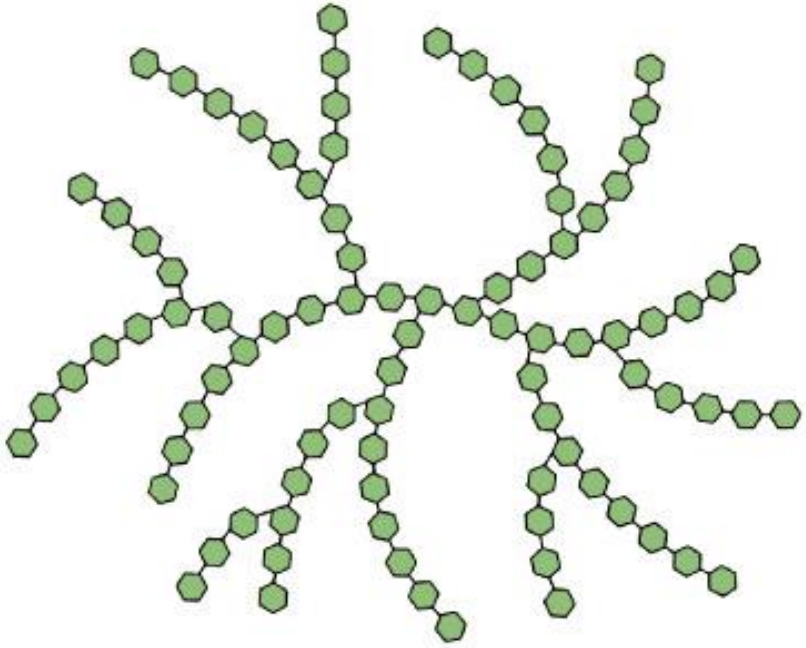
Properties of starches: retrogradation and syneresis...

When starch pastes cool without stirring (especially in the refrigerator), they change to gels, and lose the 'flow' properties they formerly had. After a period of time, however, the molecules shift and form a somewhat 'gritty' texture. This is called RETROGRADATION.

During retrogradation, a mixture may 'weep'. Water leaks from the gel as it ages. This is called SYNERESIS (sĭ-nĕr'ĭ-sĭs) . The starch molecules pull together more tightly, the gel network shrinks, and the water is pushed out of the gel. You can see liquid forming on the surface.

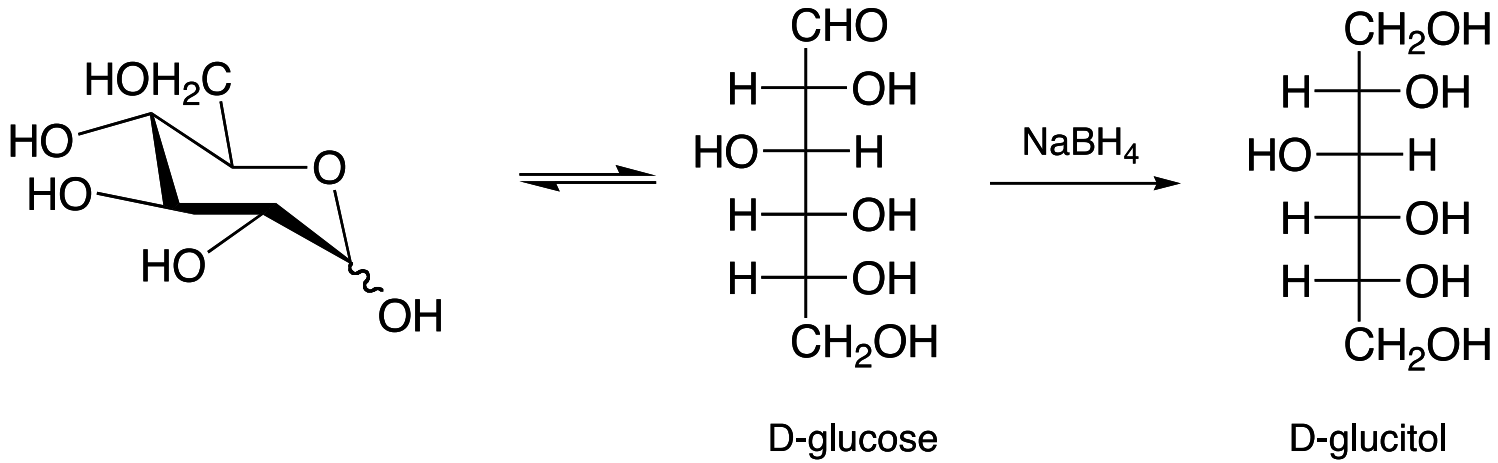
GLYCOGEN

- Storage form of glucose in animals and humans
- Structure is similar to amylopectin but with more complex branching
- Numerous alpha bonds
- Found in liver (400 kcal) and muscles (1400 kcal)



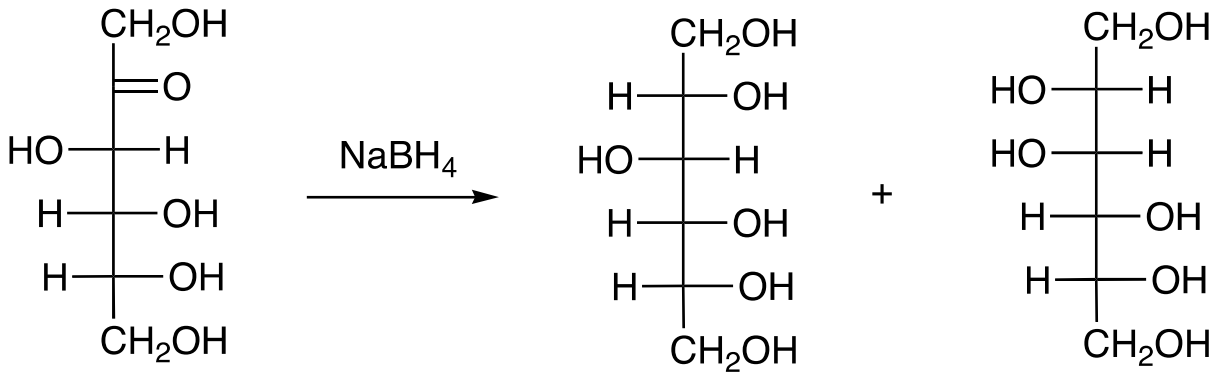
Reactions of Carbohydrates. Glycoside formation is related to acetal formation.

Reduction of Monosaccharides. C1 of aldoses are reduced with sodium borohydride to the 1° alcohol (*alditols*)



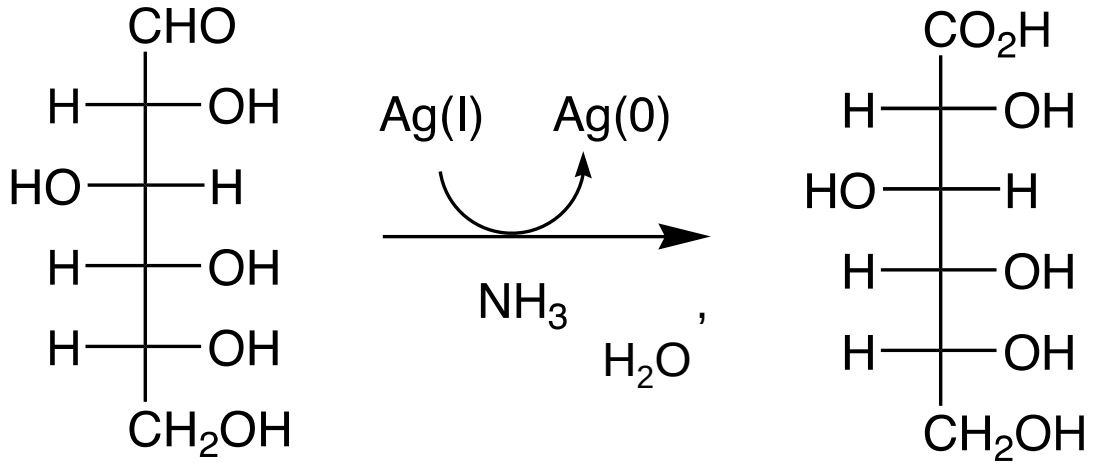
D-glucose D-glucitol

Reduction of ketoses

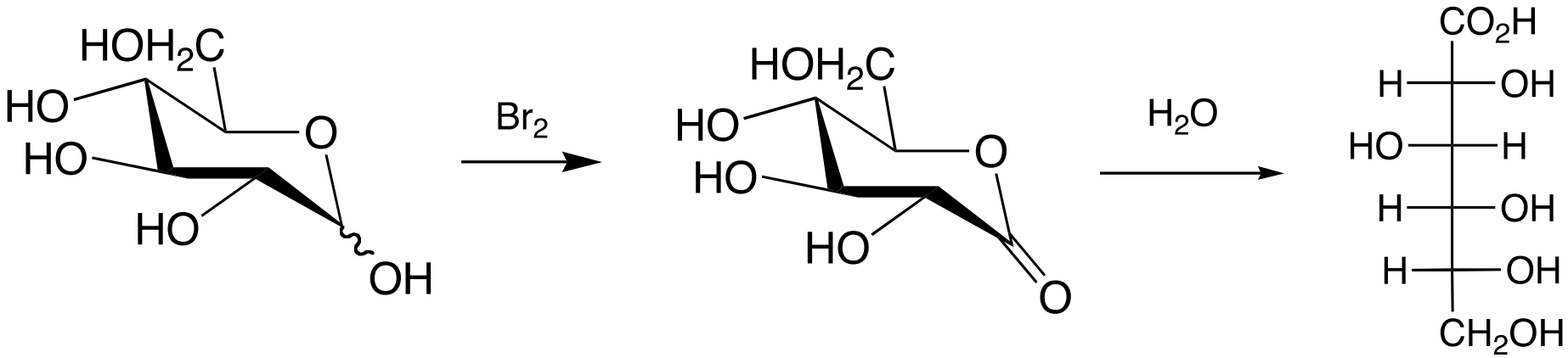


D-fructose D-glucitol D-mannitol

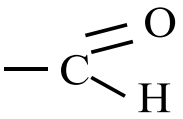
Oxidation of Monosaccharides. C1 of aldoses can be selectively oxidized to the carboxylic acid (*aldonic acids*) with Br_2 or Ag(I) (Tollen's test).

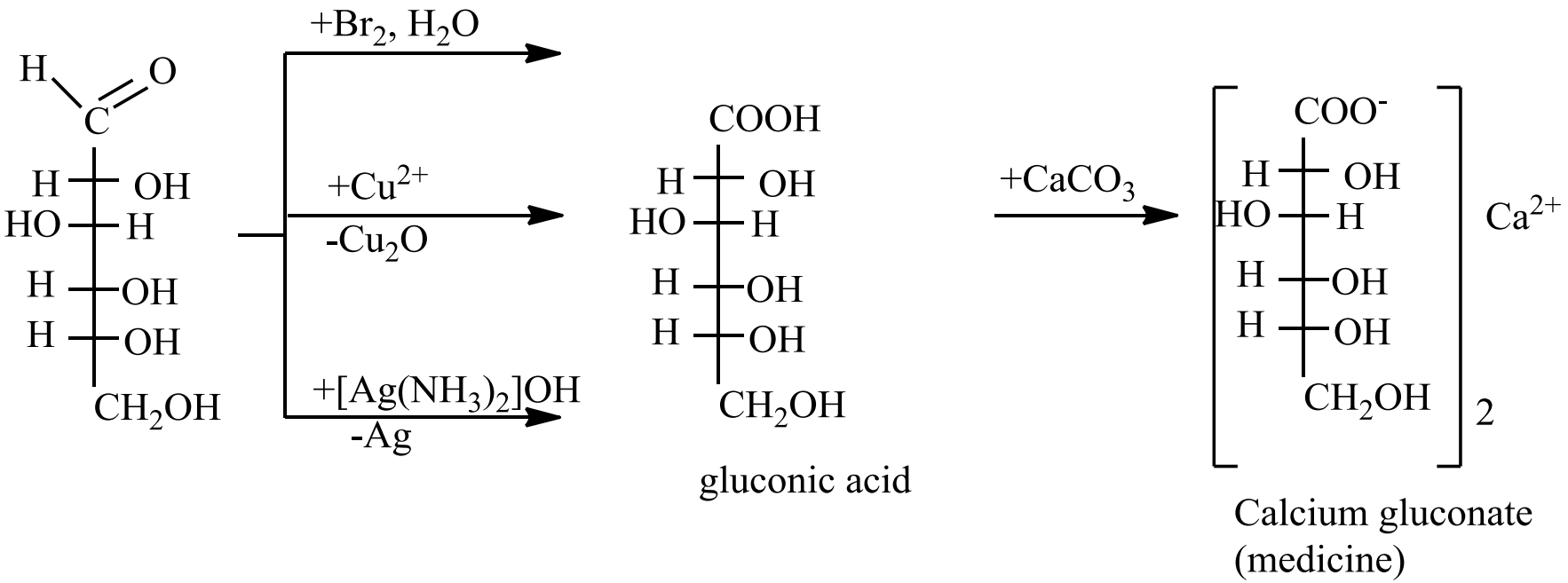


aldonic acid

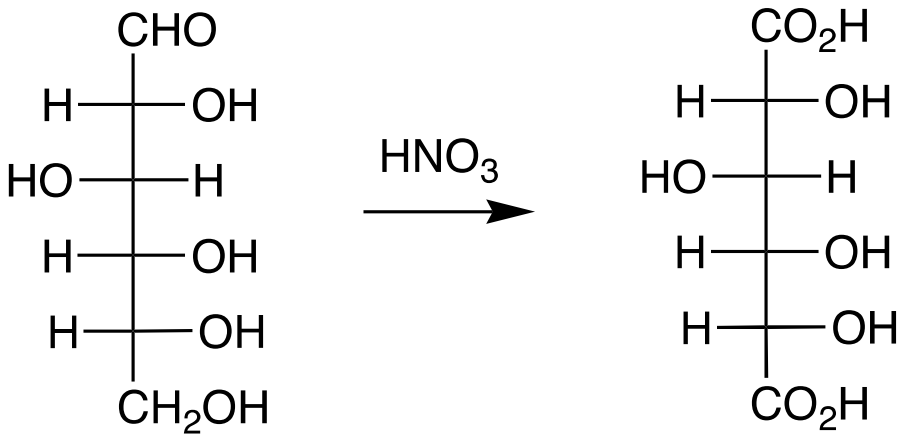


Reducing sugars: carbohydrates that can be oxidized to aldonic acids.

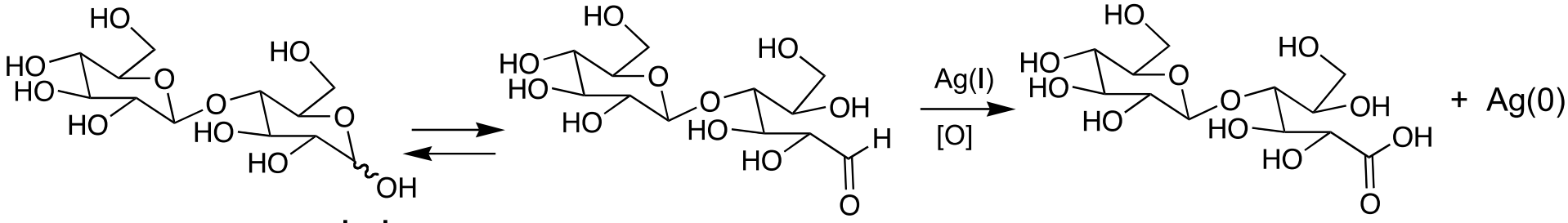
Oxidation of the  group. When the aldehyde carbon is oxidized, the **aldonic** acids form.



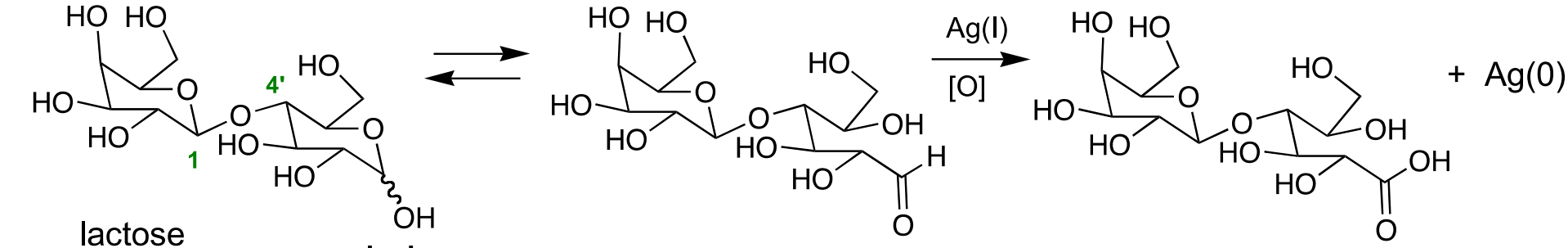
Oxidation of aldoses to *aldaric acids* with HNO_3.



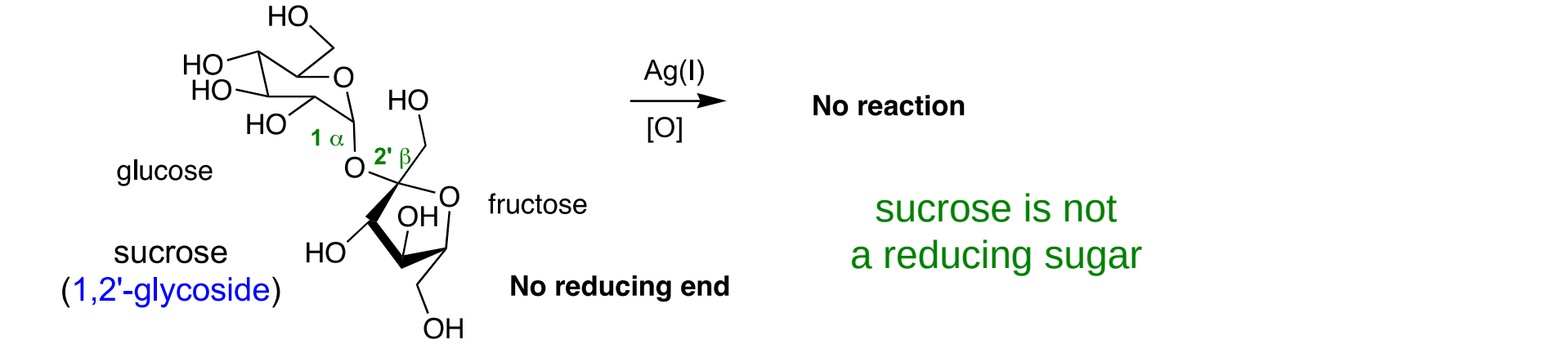
Reducing sugars: carbohydrates that can be oxidized to aldonic acids.



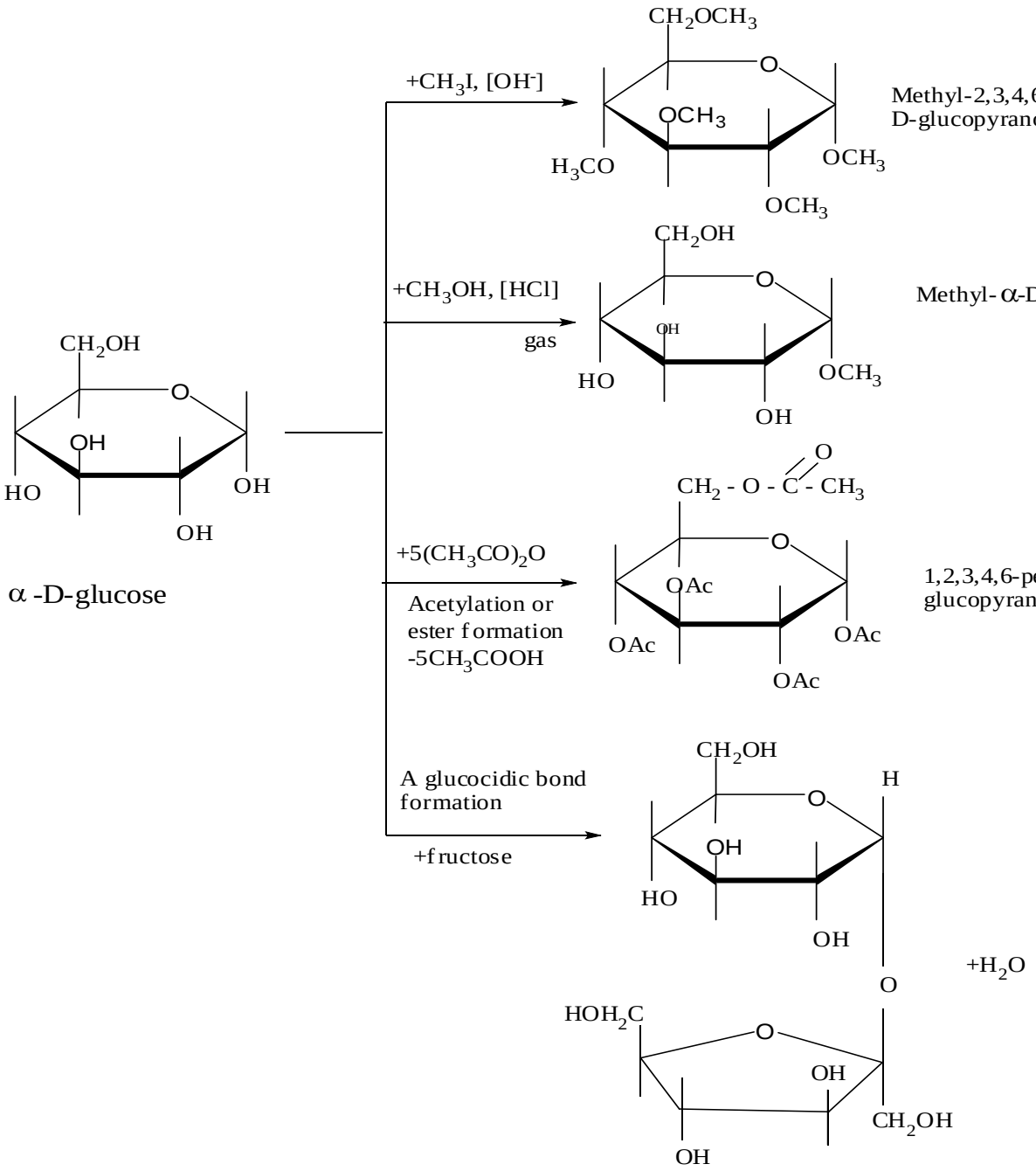
cellobiose and maltose are reducing sugar



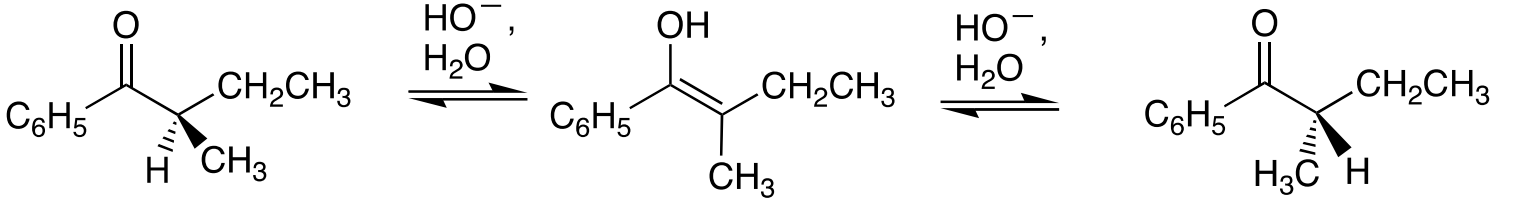
lactose is a reducing sugar



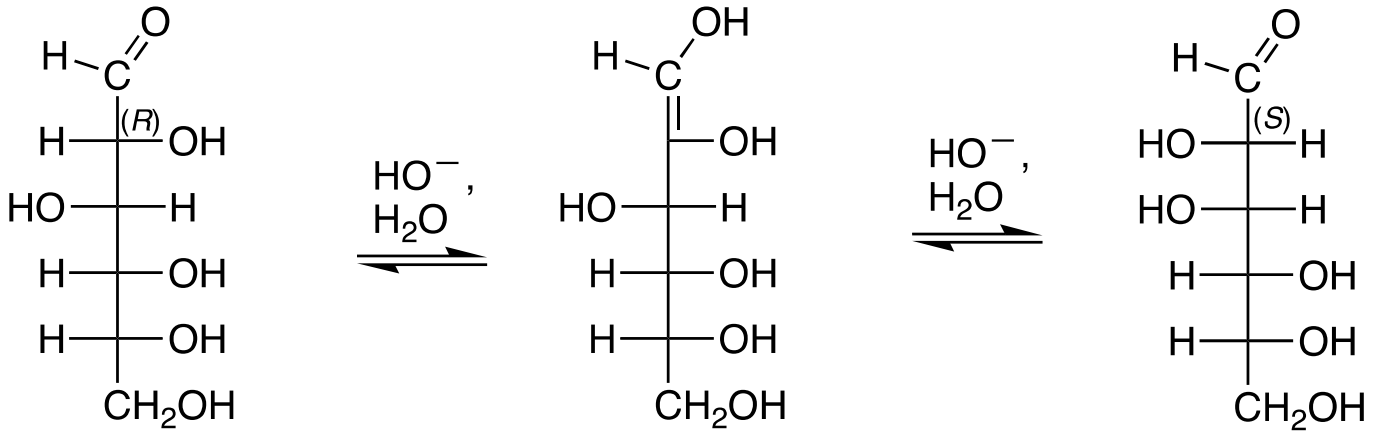
sucrose is not a reducing sugar


α -D-glucose
+CH3I, [OH-]
Methyl-2,3,4,6-tetramethyl- α–D-glucopyranoside
+CH3OH, [HCl]
gas
Methyl- α-D-glucopyranoside
+5(CH3CO)2O
Acetylation or ester formation
-5CH3COOH
1,2,3,4,6-penta acytyl-D-glucopyranoside
A glucocidic bond formation
+fructose
+H2O
Sucrose

Epimerization, Isomerization and Retro-Aldol Cleavage.

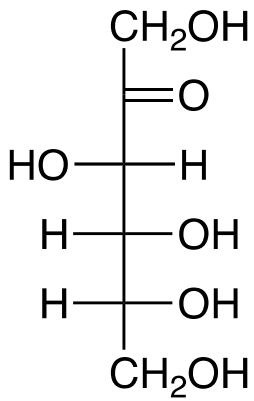


from Ch 20.16



D-glucose

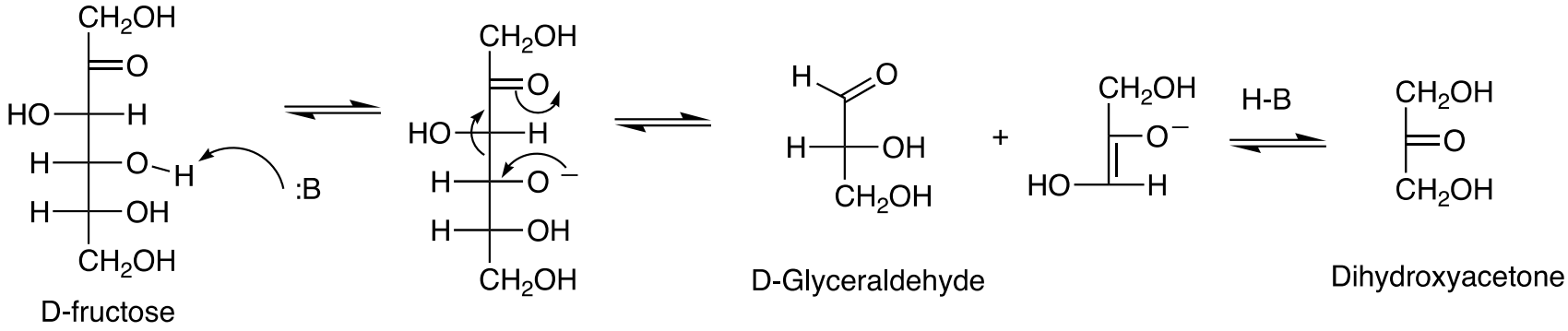
D-mannose



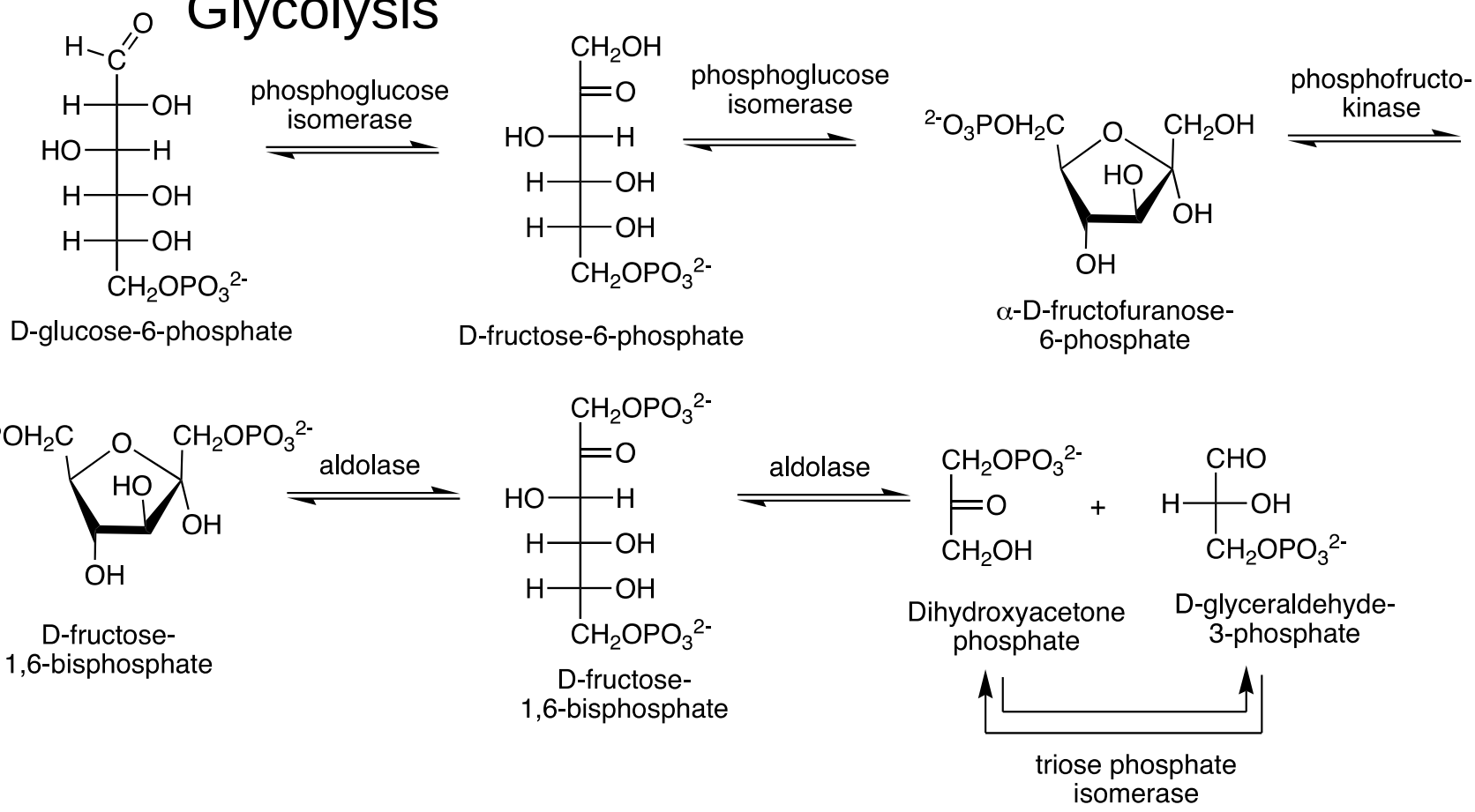
D-fructose

fructose is a reducing sugar (gives a positive Tollen's test)

Retro-aldol reaction of carbohydrates

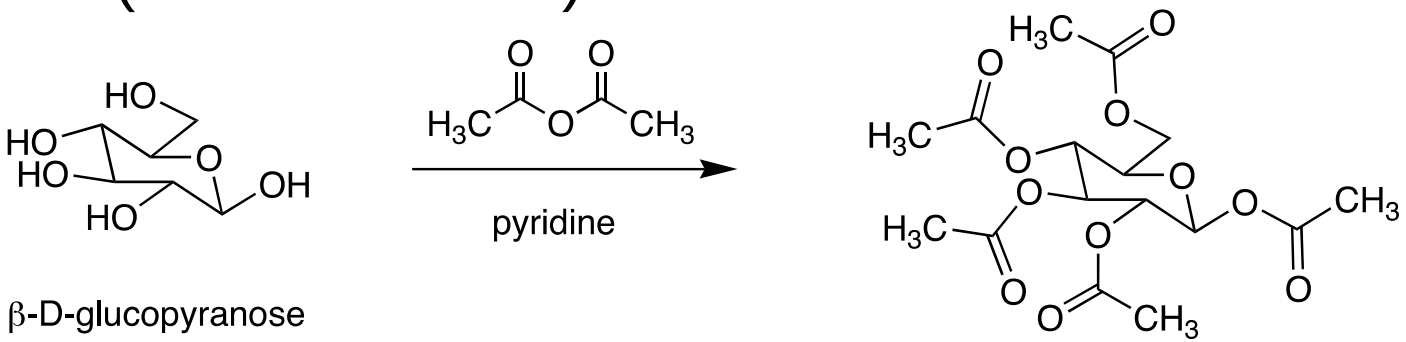


Glycolysis

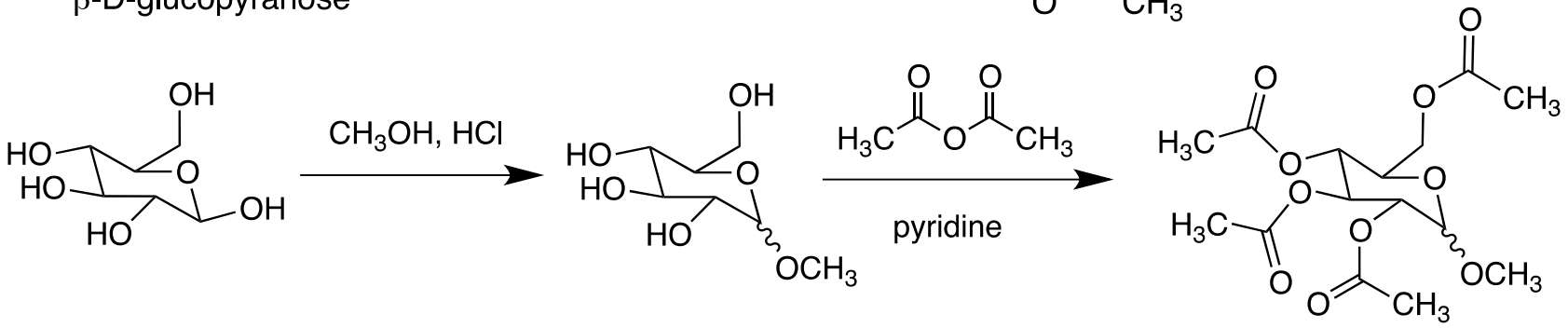


Acylation and Alkylation of Hydroxyl Groups

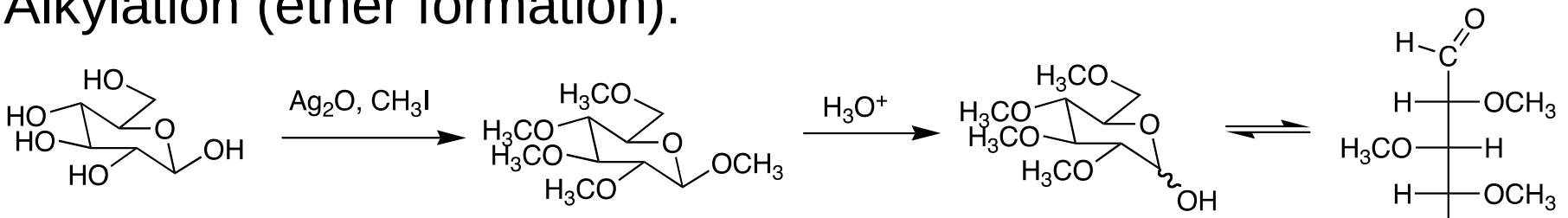
Acylation (ester formation):



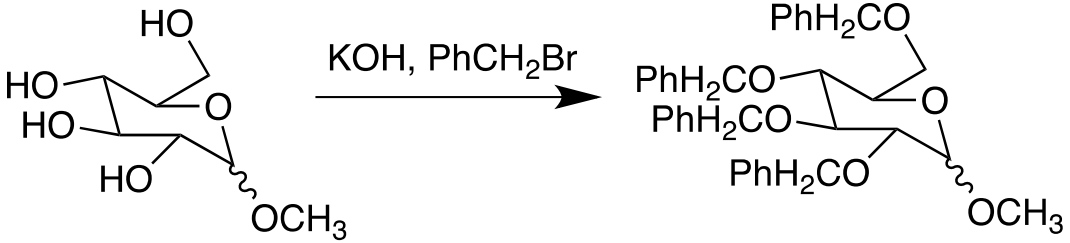
β-D-glucopyranose



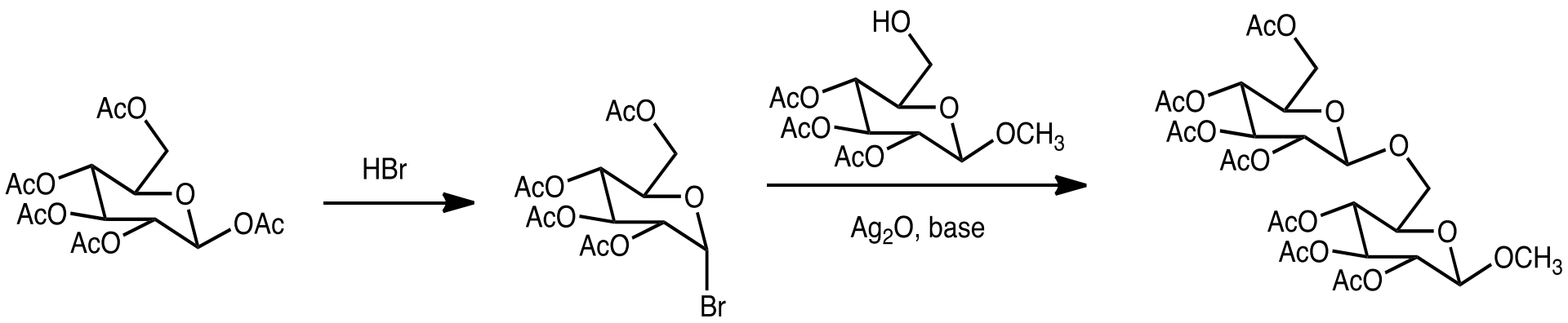
Alkylation (ether formation):



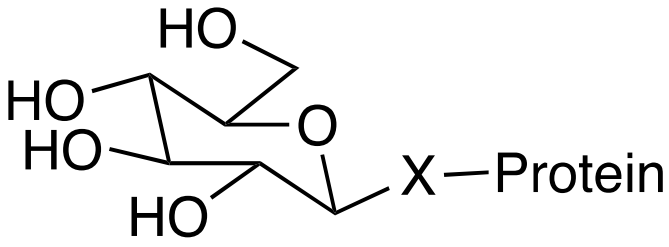
β-D-glucopyranose



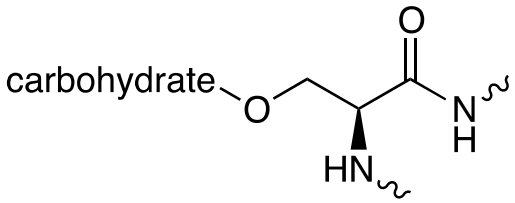
Glycosides: Synthesis of Oligosaccharides mechanism



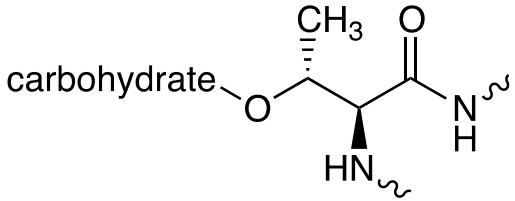
Glycoproteins: glycosides of proteins



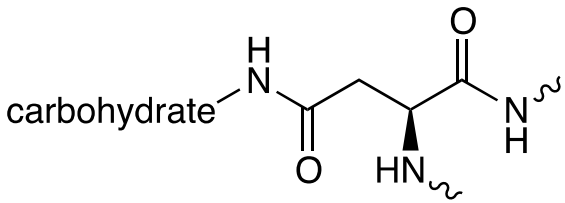
X= -O- or -NH-



serine



threoine



asparagine

Blood sugar and diabetes...

Diabetes (dī'ə-bē'tĭs, -tēz) is a condition in which the body cannot regulate blood glucose levels. In Type I diabetes that affects children and young adults, the pancreas secretes little or no insulin. In the more common Type II diabetes that can affect people of all ages, the pancreas does produce insulin, but either not enough or the insulin isn't used effectively.

Both types of diabetes cause abnormally high blood sugar levels that can strain and damage the heart and kidneys. This high blood sugar level is called 'hyperglycemia'. The kidneys filter some of the glucose and excrete it in the urine; very little actually reaches the cells.

Blood sugar levels consistently above 150 mg. are indicative of hyperglycemia.

The diabetic monitors their own blood sugar levels, injecting insulin when levels are high and eating carbohydrates when levels are low.

Hypoglycemia...

An abnormally LOW level of blood sugar is called ‘hypoglycemia’. There are several causes of this condition. If it occurs for a diabetic, it may be a reaction to an insulin injection. In some cases, it appears to be associated with malfunctions or diseases of the liver, pituitary, adrenals, liver, or pancreas. It sometimes happens after long periods without food, and occasionally following strenuous exercise.

Blood sugar levels consistently below 70mg. are indicative of hypoglycemia.

Other factors sometimes associated with hypoglycemia include:
pregnancy , a weakened immune system, a poor diet, prolonged use of drugs including antibiotics, chronic physical or mental stress, heartbeat irregularities, allergies, breast cancer, high blood pressure treated with some medications, and upper gastrointestinal tract surgery.

Ketosis...

It is important to consume a minimum amount of carbohydrates to prevent ketosis, a condition resulting from the breakdown of fat or muscle protein for energy in the absence of carbohydrates.

Ketosis can occur in previously healthy people during prolonged fasting or starvation, after persistent vomiting, or on a very high fat and low carbohydrate diet; or it can occur because of disordered hormonal control of metabolism in diabetes.

The high rate of breakdown of fatty acids by the liver produces the 'ketone bodies' (acetoacetate and b-hydroxybutyrate) which are released into the blood and alter normal pH balance (this is particularly harmful to an unborn fetus). Some of the acetoacetate is converted to acetone — another 'ketone body' — mainly in the lungs, and this becomes noticeable on the breath. The breath smells like nail polish remover.

Recommended daily allowance...

No RDA for carbohydrates has been set, but a minimum of 50-100 grams should be consumed daily for normal brain function. Carbohydrates should make up 55% of your daily total caloric intake. Sugars and starches that occur naturally in foods is preferred over those that are 'added' to foods, such as refined sugars.

Foods from the fruits, vegetables, and breads & cereals group on the food pyramid provide carbohydrates.

The 2005 Dietary Guidelines for Americans recommends no more than 8 teaspoons per day of added sugar based on a 2,000 calorie/day diet. That's 32 grams if you're reading labels.

8 teaspoons x 4 grams per teaspoon = 32 total grams sugar

With 40 grams in a can, a single non-diet Coke provides 10 teaspoons of sugar.