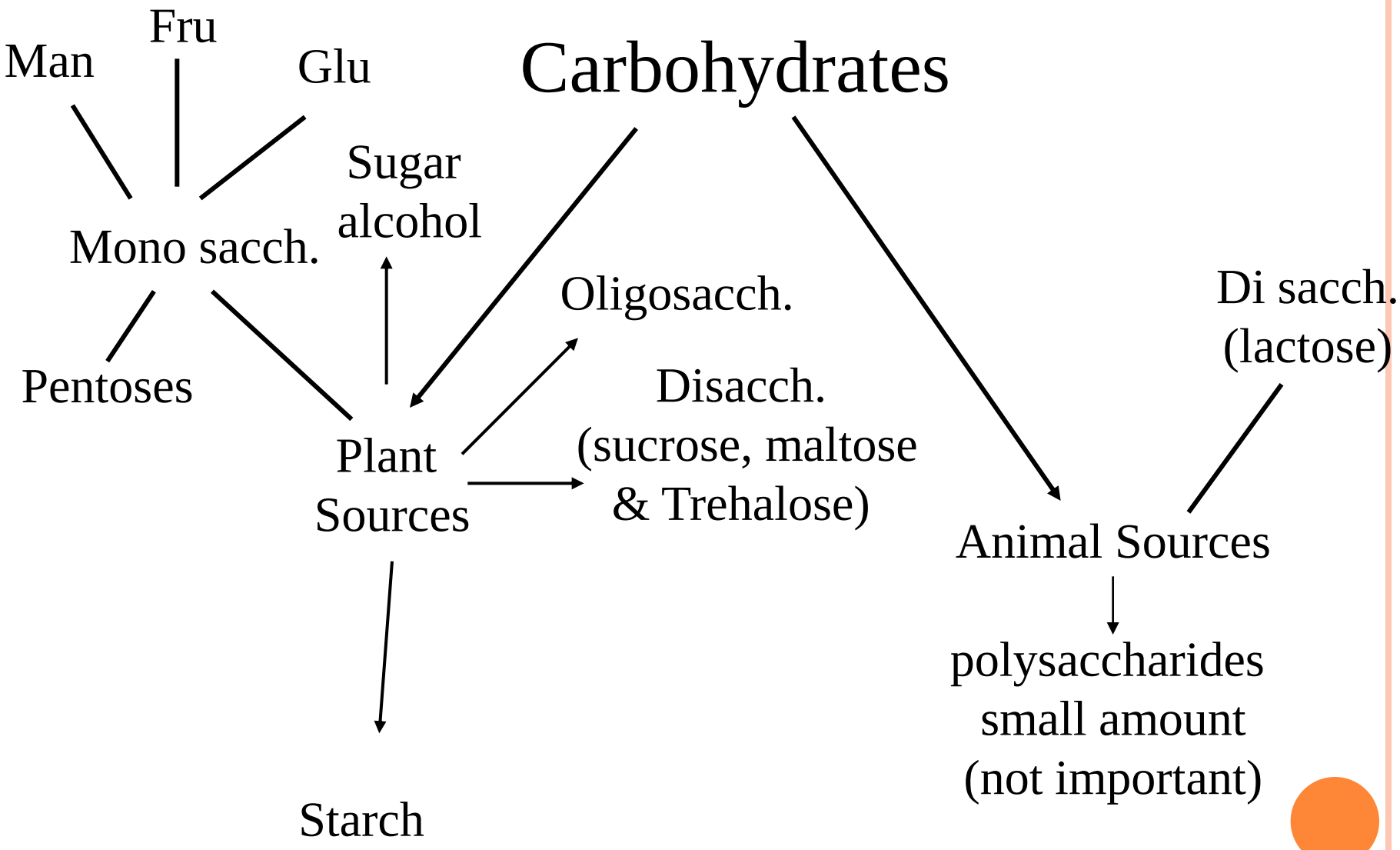
CARBOHYDRATES

Dr. Phadnaik


Carbohydrates
Man
Fru
Glu
Mono sacch.
Sugar alcohol
Pentoses
Oligosacch.
Disacch. (sucrose, maltose & Trehalose)
Plant Sources
Starch
Di sacch. (lactose)
Animal Sources
polysaccharides small amount (not important)

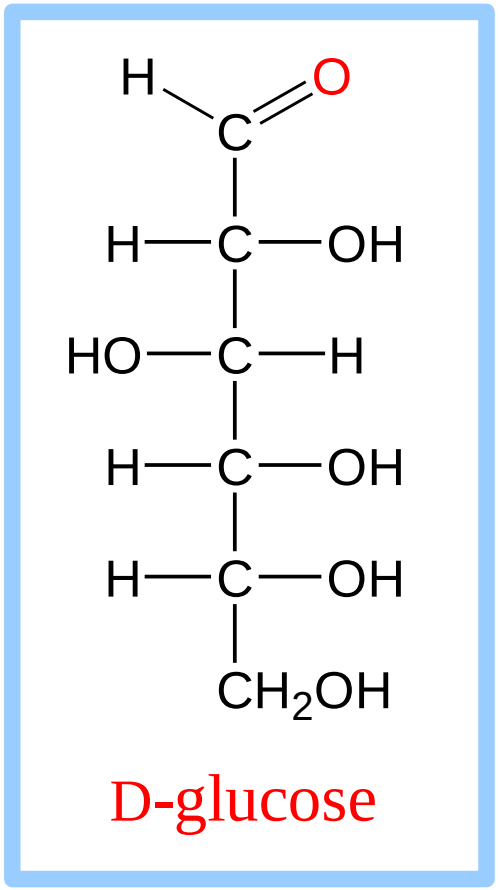
Carbohydrates (glycans) have the following basic composition:

$(CH_2O)_n$ or $H-\overset{|}{\underset{|}{C}}-OH$

- Monosaccharides - simple sugars with multiple OH groups. Based on number of carbons (3, 4, 5, 6), a monosaccharide is a triose, tetrose, pentose or hexose.
- Disaccharides - 2 monosaccharides covalently linked.
- Oligosaccharides - a few monosaccharides covalently linked.
- Polysaccharides - polymers consisting of chains of monosaccharide or disaccharide units.

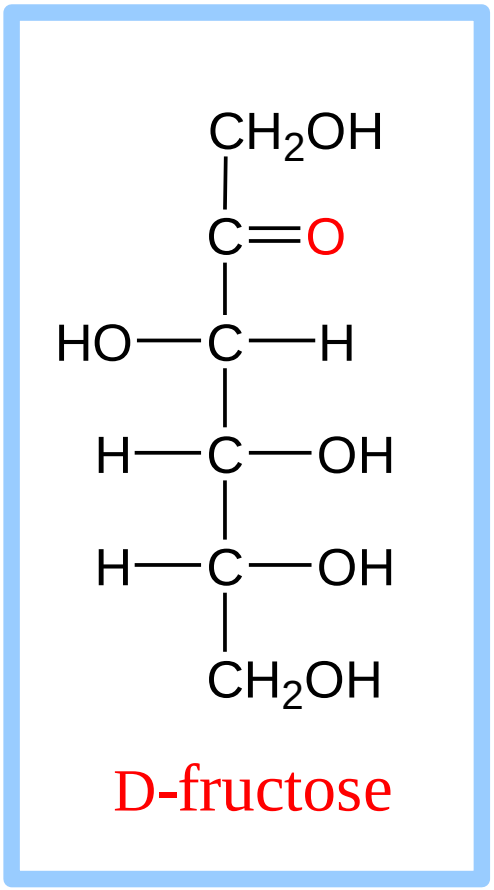
Monosaccharides

Aldoses (e.g., glucose) have an aldehyde group at one end.



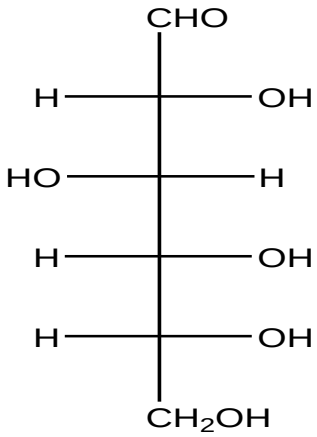
D-glucose

Ketoses (e.g., fructose) have a keto group, usually at C2.

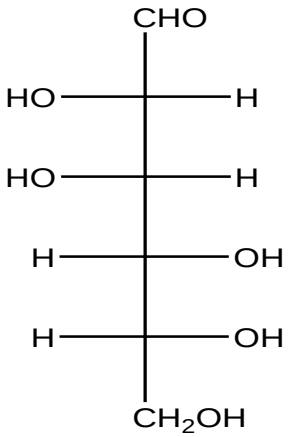


D-fructose

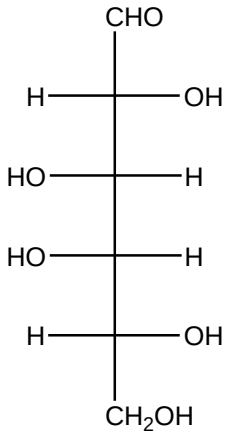
D-
Glucose

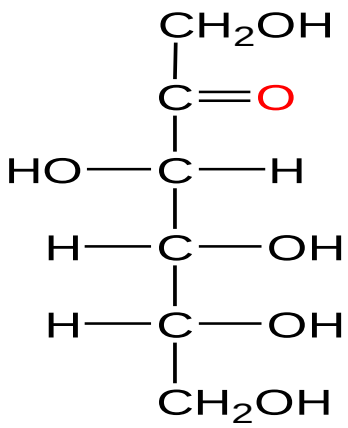


D-
Mannose



D-
Galactose



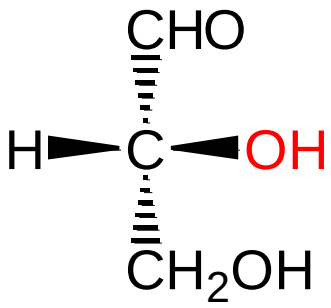


D-fructose

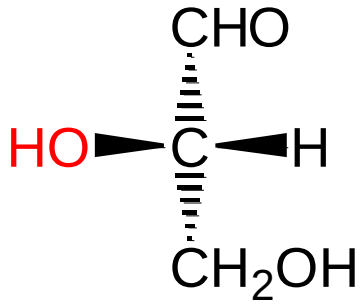
D vs L Designation

D & L designations are based on the configuration about the single asymmetric C in glyceraldehyde.

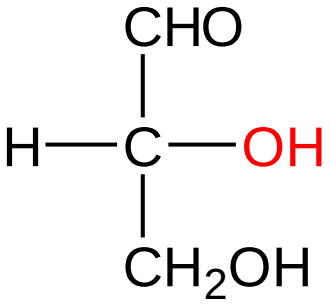
The lower representations are Fischer Projections.



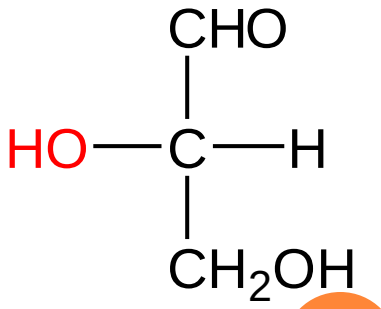
D-glyceraldehyde



L-glyceraldehyde



D-glyceraldehyde

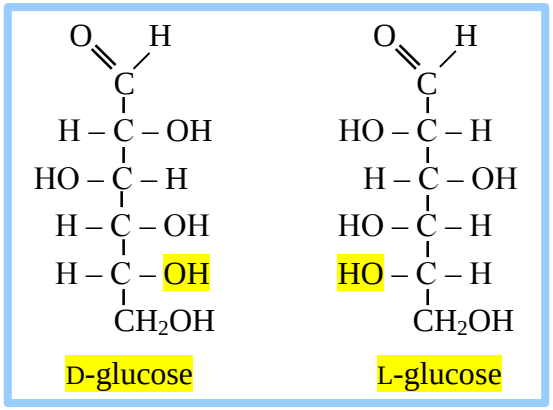


L-glyceraldehyde

Sugar Nomenclature

For sugars with more than one chiral center, **D** or **L** refers to the asymmetric **C** farthest from the aldehyde or keto group.

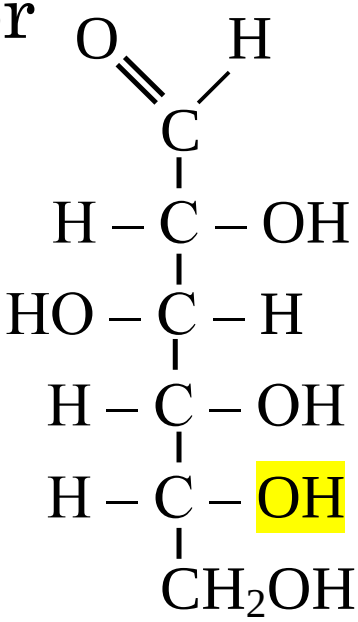
Most naturally occurring sugars are D isomers.



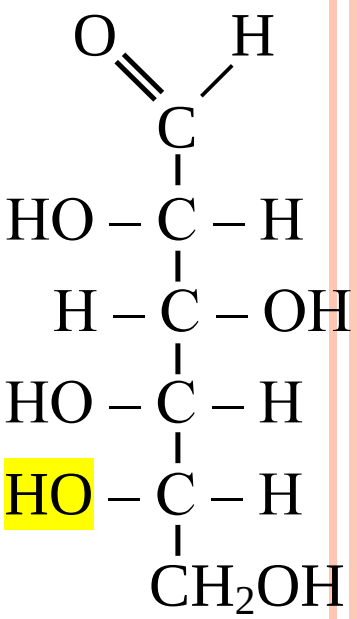
D & L sugars are mirror images of one another.

They have the same name, e.g., D-glucose & L-glucose.

Other stereoisomers have unique names, e.g., glucose, mannose, galactose, etc.



D-glucose



L-glucose

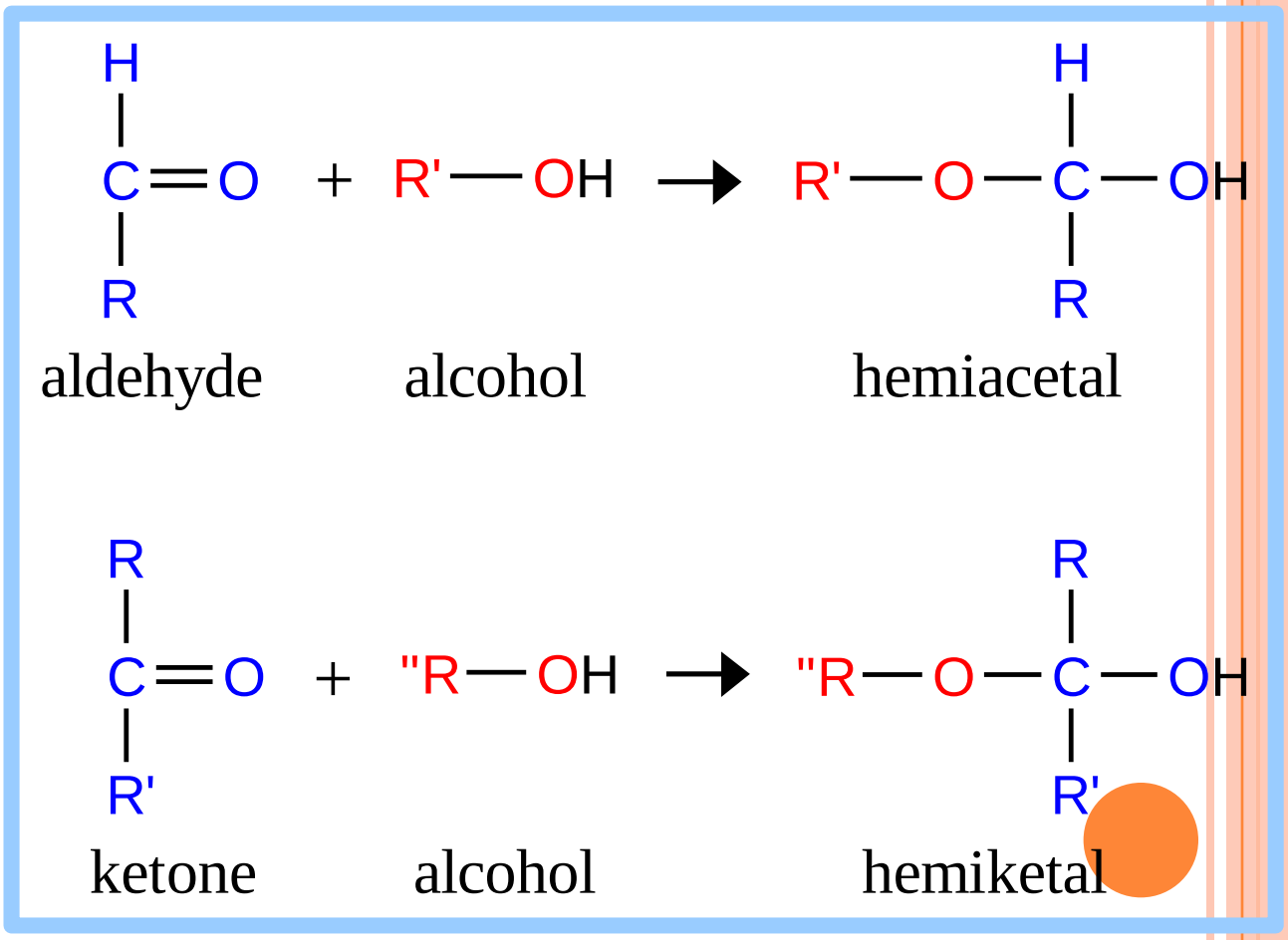
The number of stereoisomers is 2^n, where n is the number of asymmetric centers.

The 6-C aldoses have 4 asymmetric centers. Thus there are 16 stereoisomers (8 D-sugars and 8 L-sugars).

Hemiacetal & hemiketal formation

An aldehyde can react with an alcohol to form a hemiacetal.

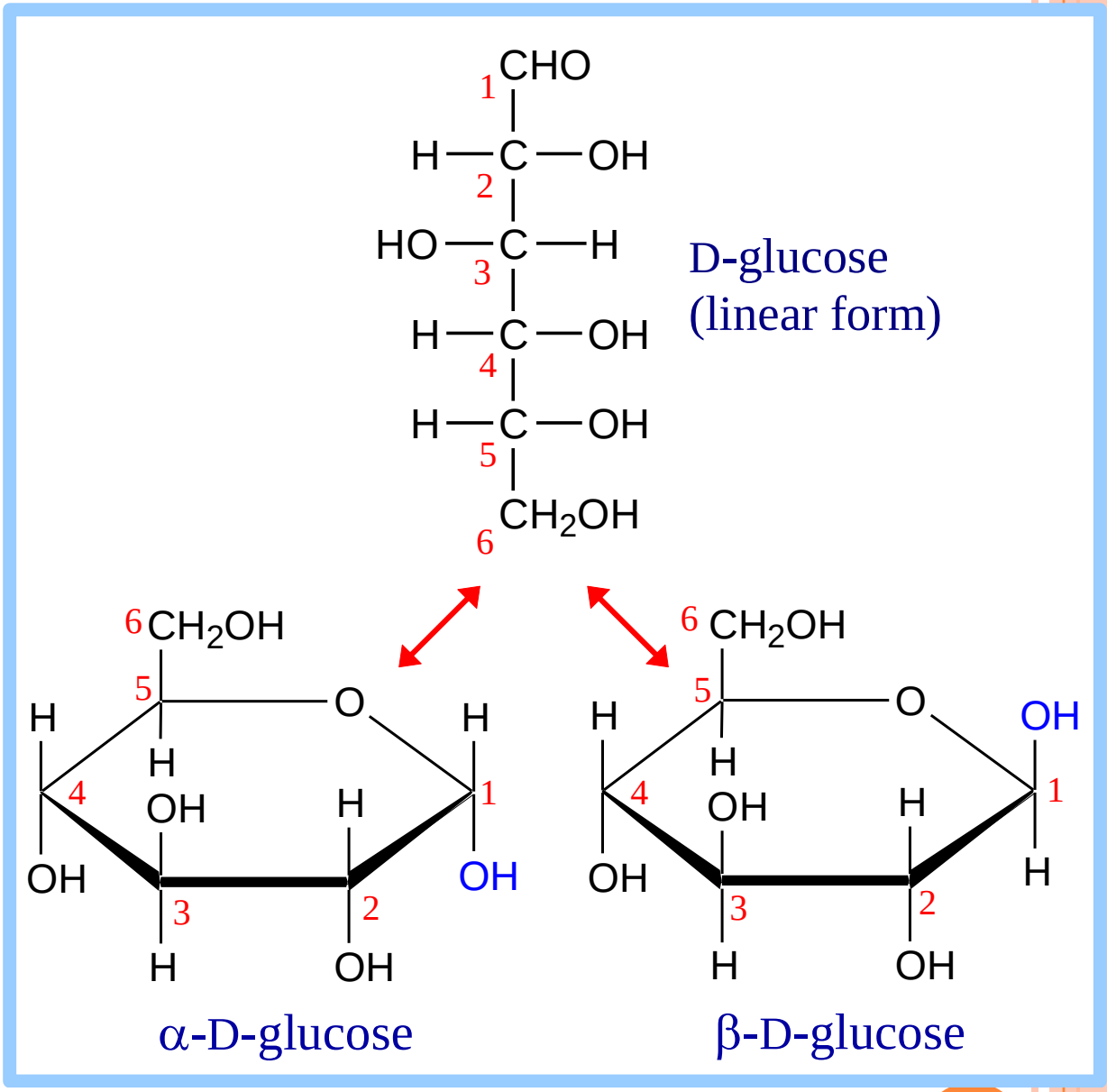
A ketone can react with an alcohol to form a hemiketal.



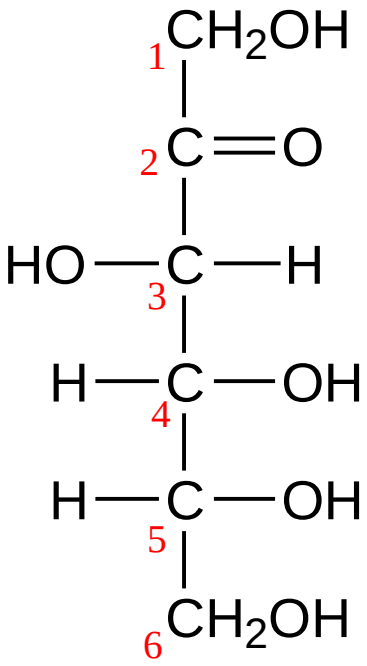
- Monosaccharides have hydroxyl and carbonyl groups in the same molecule and those with five or more carbons exist almost entirely as five- and six-membered cyclic hemiacetals.
  - **Anomeric carbon:** The new stereocenter created as a result of cyclic hemiacetal formation.
  - **Anomers:** Carbohydrates that differ in configuration at their anomeric carbons named α and β.

Pentoses and hexoses can cyclize as the ketone or aldehyde reacts with a distal OH.

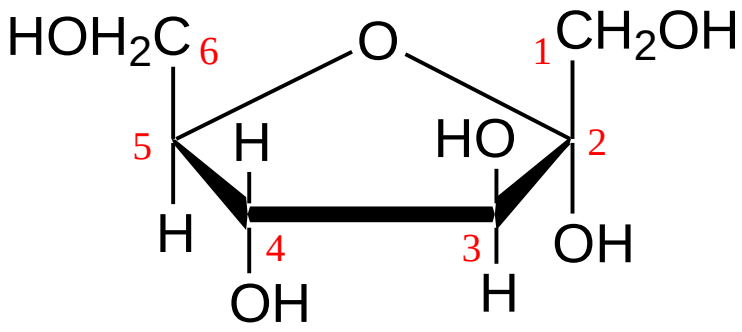
Glucose forms an intra-molecular hemiacetal, as the C1 aldehyde & C5 OH react, to form a 6-member pyranose ring, named after pyran.



These representations of the cyclic sugars are called Haworth projections.



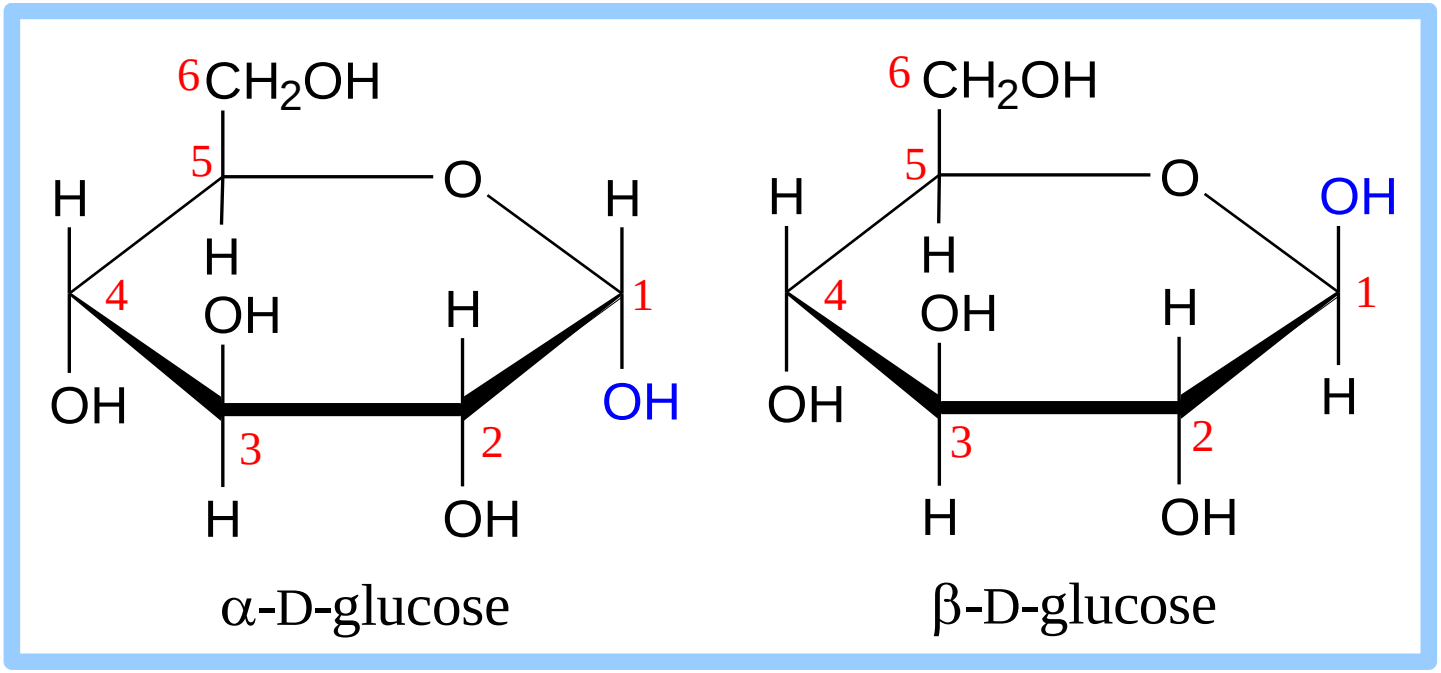
D-fructose (linear)



α-D-fructofuranose

Fructose forms either

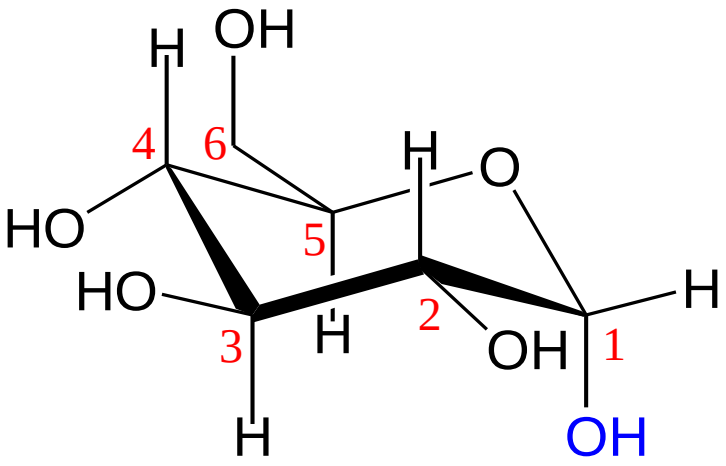
- a 6-member pyranose ring, by reaction of the C2 keto group with the OH on C6, or
- a 5-member furanose ring, by reaction of the C2 keto group with the OH on C5.



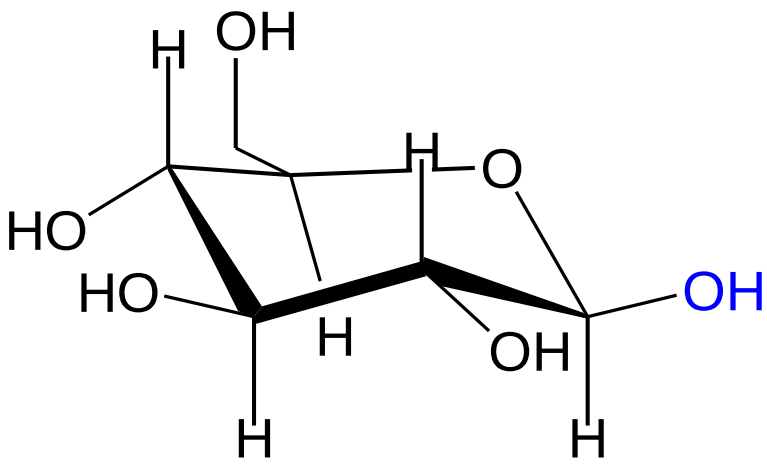
Cyclization of glucose produces a new asymmetric center at C1. The 2 stereoisomers are called anomers, α & β.

Haworth projections represent the cyclic sugars as having essentially planar rings, with the OH at the anomeric C1:

- α (OH below the ring)
- β (OH above the ring).



α-D-glucopyranose

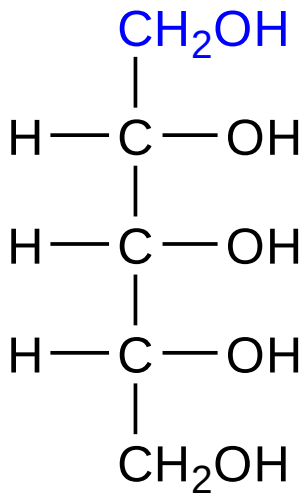


β-D-glucopyranose

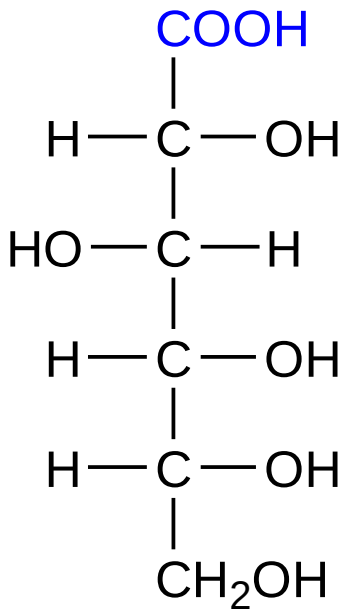
Because of the tetrahedral nature of carbon bonds, pyranose sugars actually assume a "chair" or "boat" configuration, depending on the sugar.

The representation above reflects the chair configuration of the glucopyranose ring more accurately than the Haworth projection.

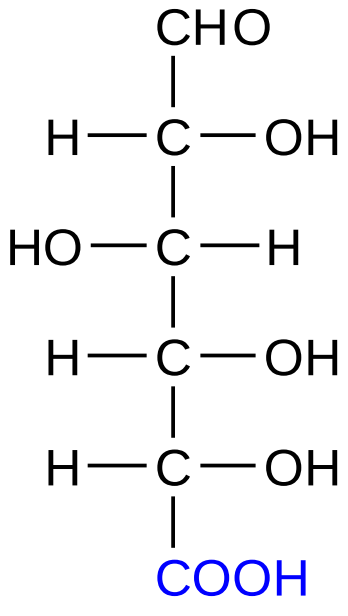
Sugar derivatives



D-ribitol



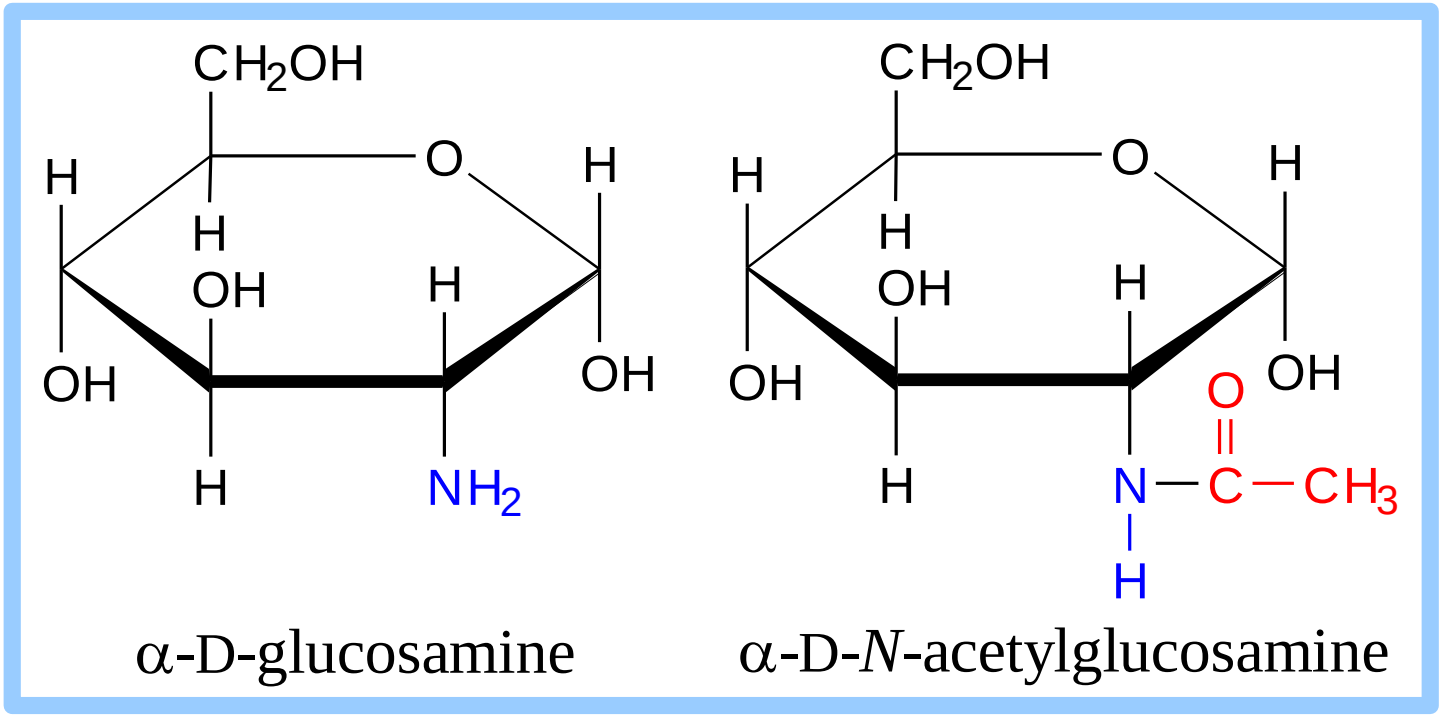
D-gluconic acid



D-glucuronic acid

- sugar alcohol - lacks an aldehyde or ketone; e.g., ribitol.
- sugar acid - the aldehyde at C1, or OH at C6, is oxidized to a carboxylic acid; e.g., gluconic acid, glucuronic acid.

Sugar derivatives



α-D-glucosamine

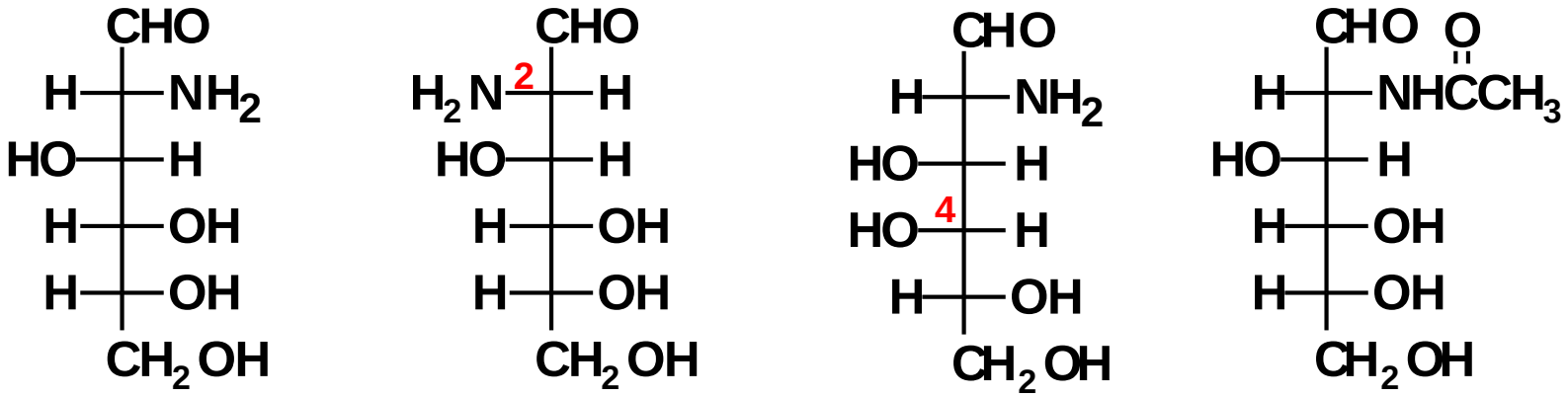
α-D-*N*-acetylglucosamine

amino sugar - an amino group substitutes for a hydroxyl. An example is glucosamine.

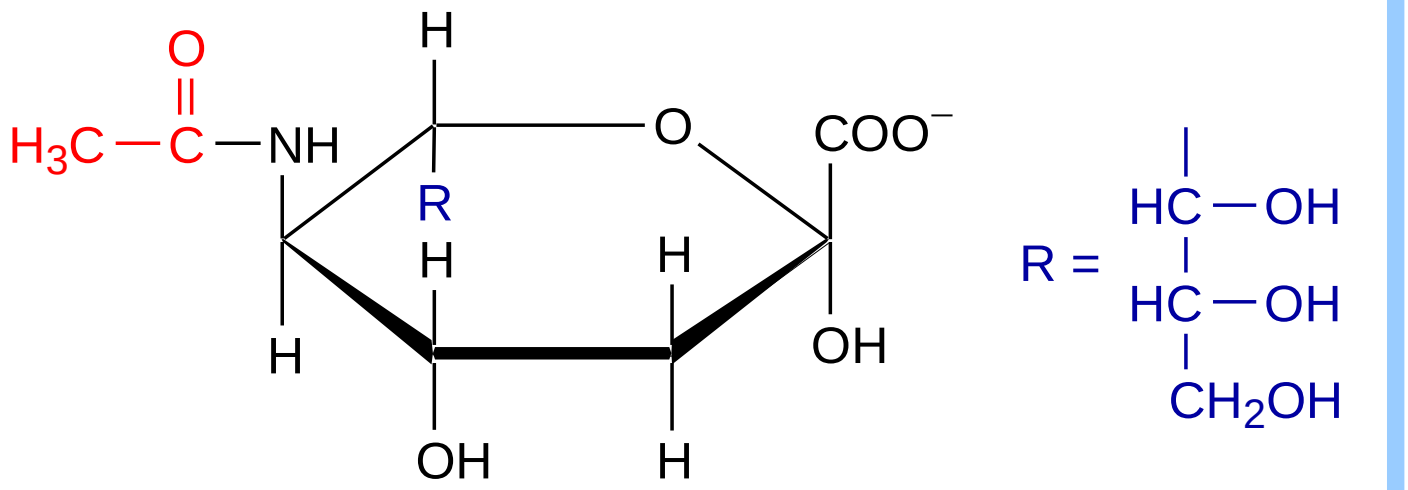
The amino group may be acetylated, as in *N*-acetylglucosamine.

Amino Sugars

- **Amino sugar:** A sugar that contains an -NH_2 group in place of an -OH group.
  - Only three amino sugars are common in nature
  - *N*-Acetyl-D-glucosamine is a derivative of D-glucosamine.



D-Glucosamine **D-Mannosamine** **D-Galactosamine** ***N*-Acetyl-D-glucosamine**

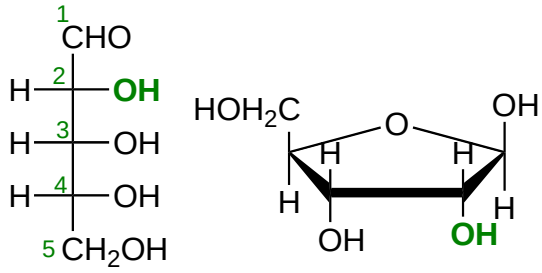


N-acetylneuraminate (sialic acid)

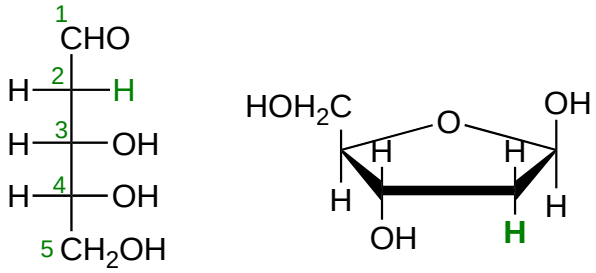
N-acetylneuraminate (N-acetylneuraminic acid, also called sialic acid) is often found as a terminal residue of oligosaccharide chains of glycoproteins.

Sialic acid imparts negative charge to glycoproteins, because its carboxyl group tends to dissociate a proton at physiological pH, as shown here.

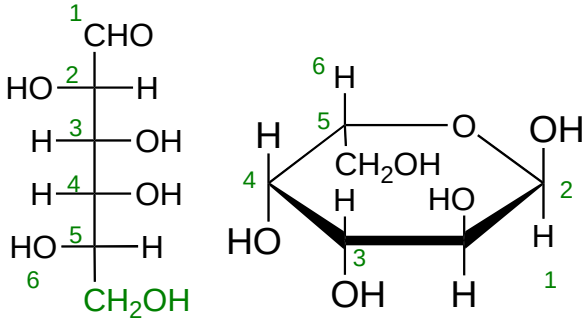
Deoxy Sugars. Carbohydrates that are missing a hydroxy group.



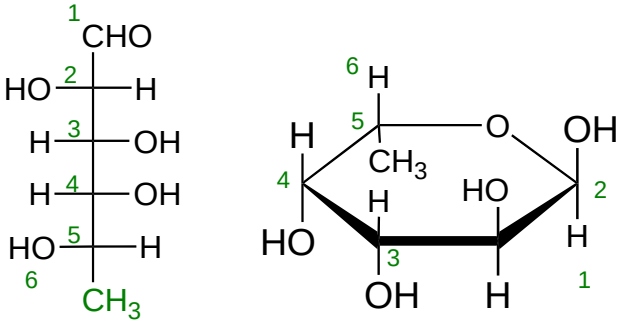
D-ribose



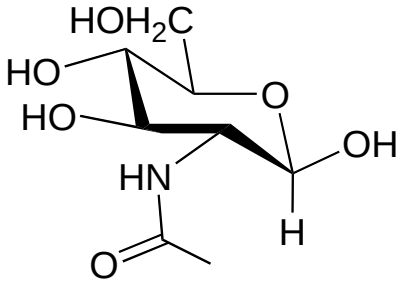
2-Deoxy-D-ribose



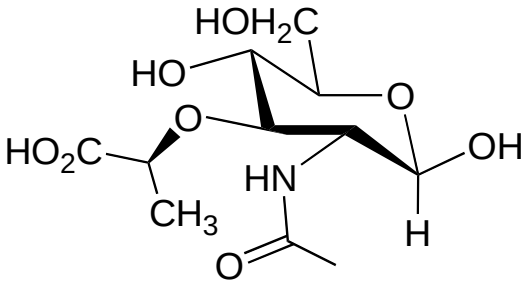
L-Galactose



6-Deoxy-L-Galactose (fucose)



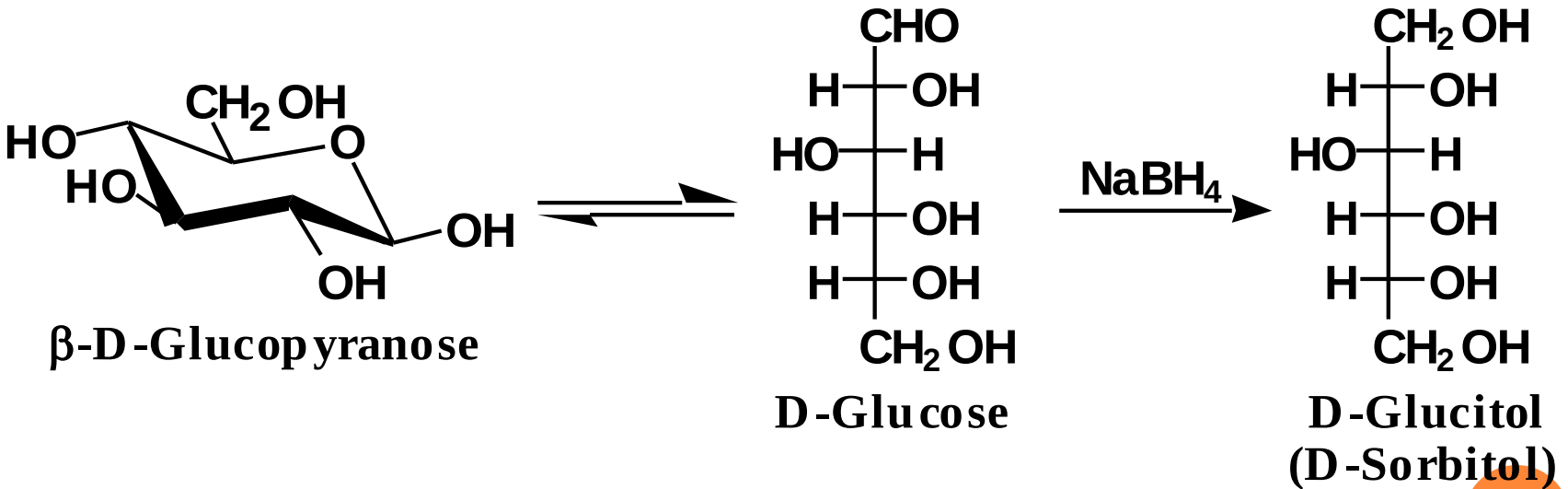
N-acetyl-D-glucosamine
(GlcNAc or NAG)



N-Acetylmuramic acid
(MurNAc)

Reduction to Alditols, aldehyde → alcohol

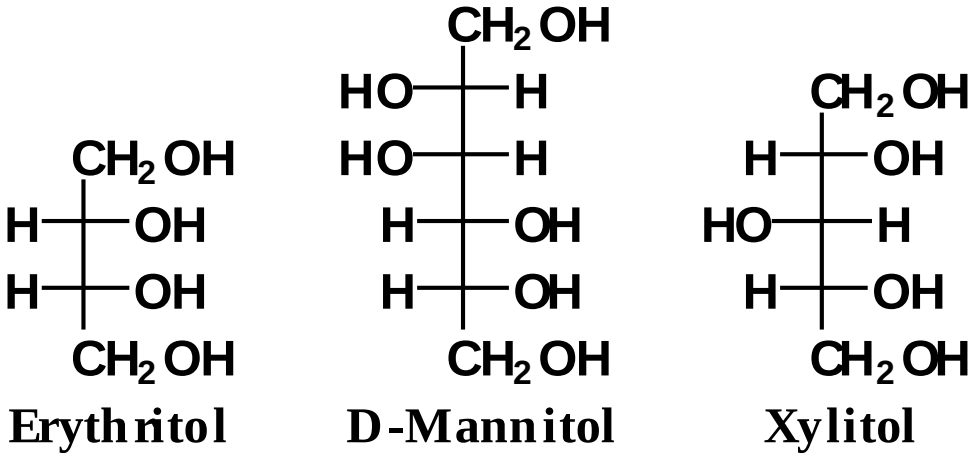
- The carbonyl group of a monosaccharide can be reduced to an hydroxyl group by a variety of reducing agents, including $NaBH_4$ and H_2/M.



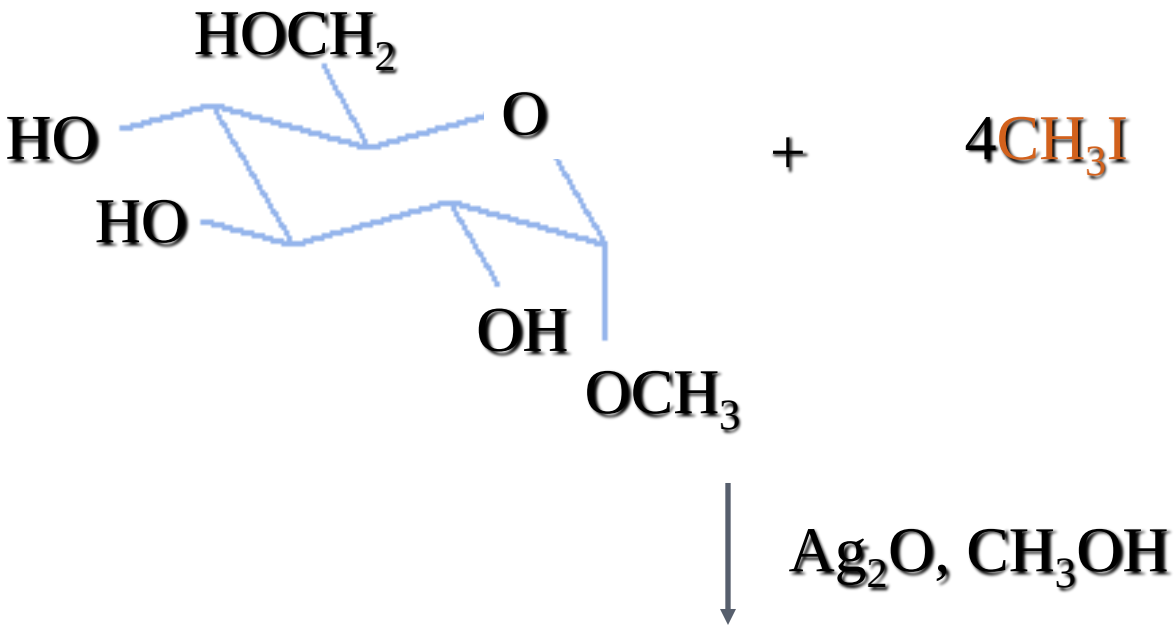
An alditol

Other alditols

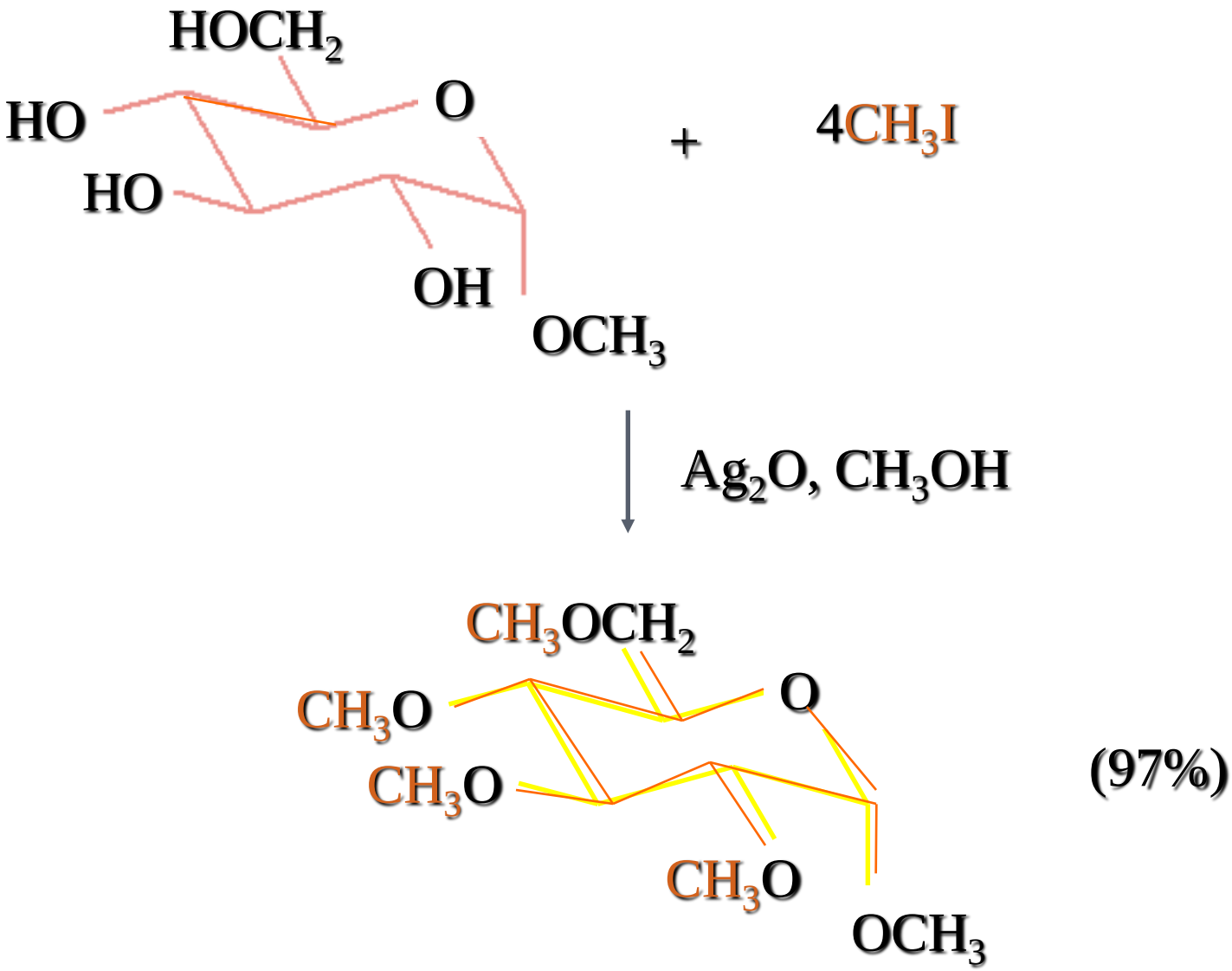
- Other alditols common in the biological world are:



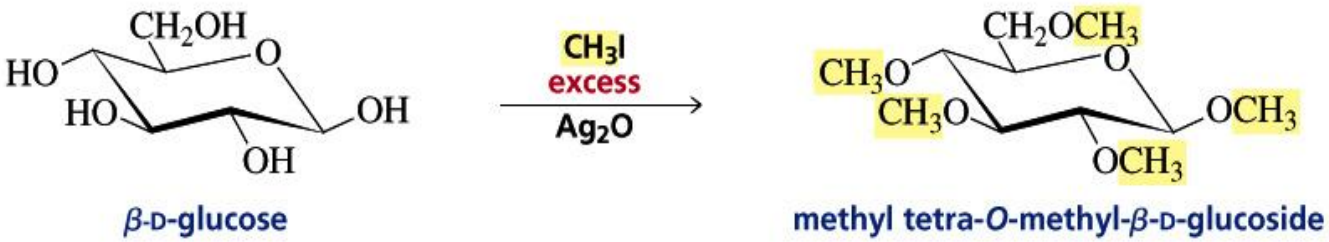
Example: Alkylation of methyl a-D-glucopyranoside



Example: Alkylation of methyl a-D-glucopyranoside



Alkylation of the OH Groups



Oxidations

Oxidation can be done in several ways.

Tollens reagent ($Ag^{+}(NH_3)_2$ or Benedict's solution (Cu^{2+} tartrate complex). Not synthetically useful due to side reactions.

Bromine water oxidizes aldoses (not ketoses) to monocarboxylic acids (Aldonic Acids).

Nitric Acid oxidizes aldoses to dicarboxylic acids (Aldaric acids).

Enzyme catalyzed oxidation of terminal OH to carboxylic acid (Uronic Acid)

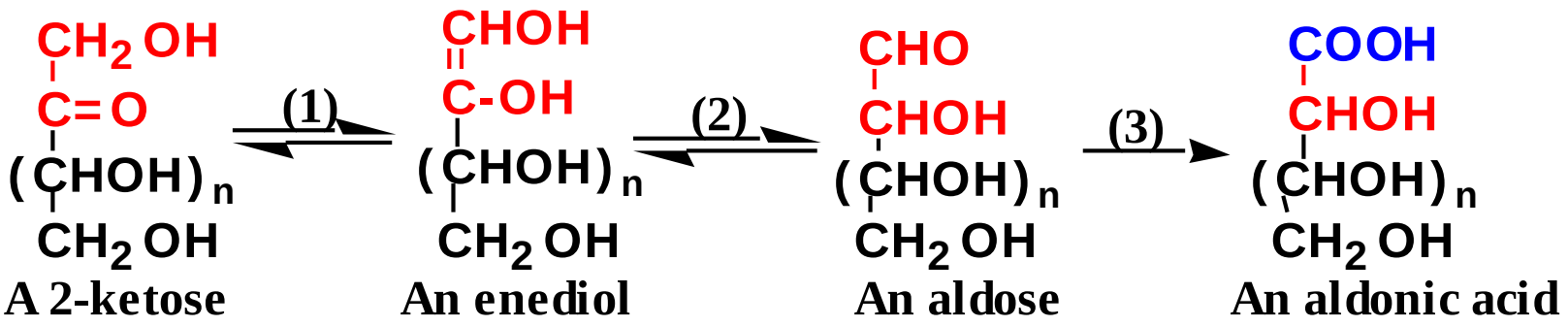
Periodic Acid oxidizes and breaks C C bonds. Later for that.

Reducing Sugars

- Sugars with aldehyde (or ketone group) in solution. The group can be oxidized and is detected with Tollens or Benedicts solution. Ketone groups converted to aldehyde via tautomeric shifts

Problem with Tollens

- 2-Ketoses are also oxidized to aldonic acids in basic solution (Tollens).



Ketose to aldose conversion via keto enol tautomerism

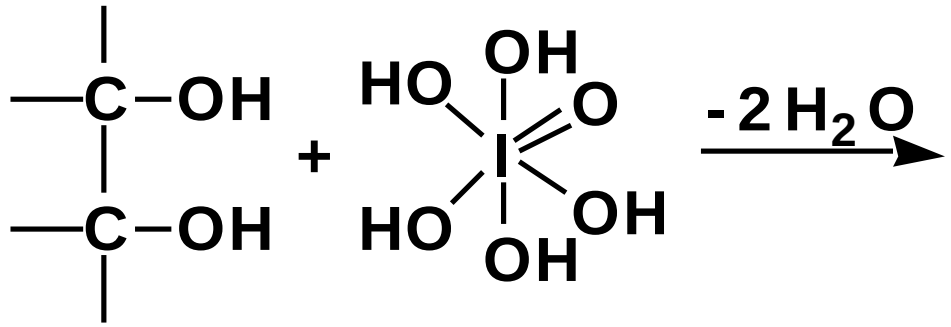
Oxidation

Reducing sugar

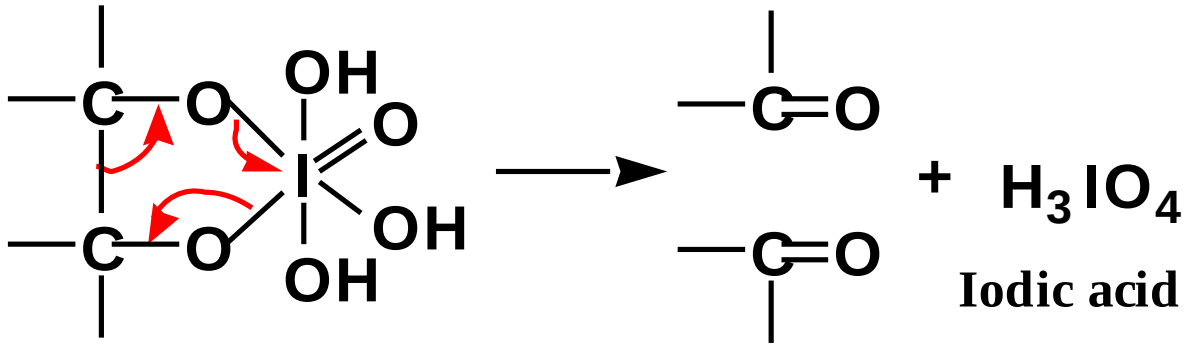
Oxidation to carboxylic acids

Oxidation by periodic acid, HIO_4 or H_5IO_6

- Periodic acid cleaves the C-C bond of a glycol.



A 1,2-diol **Periodic acid**

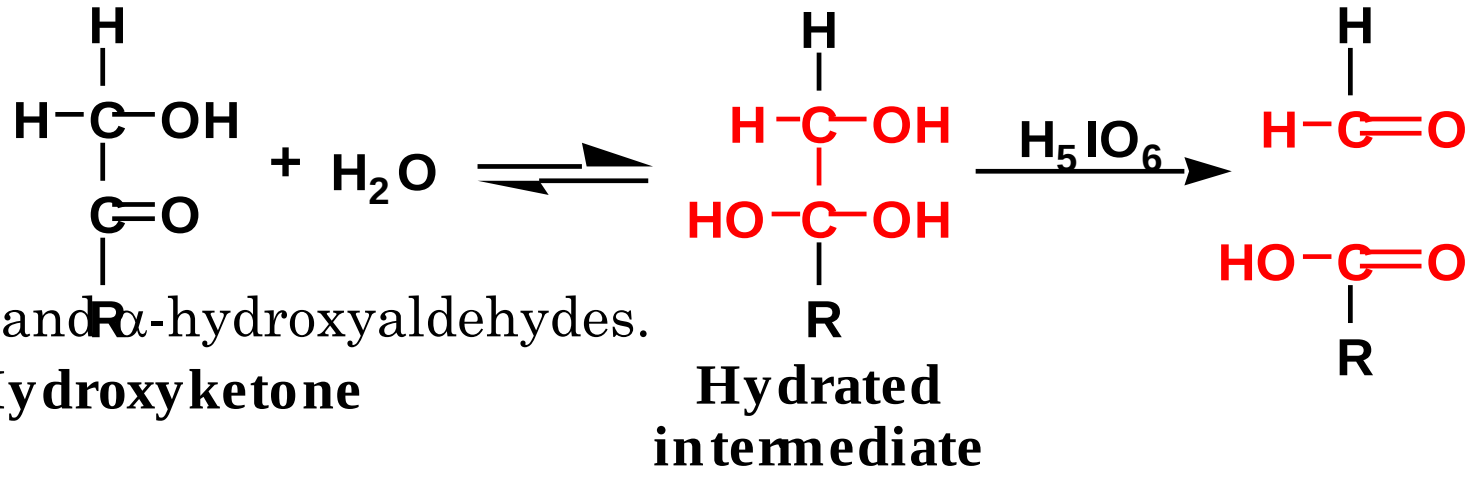


A cyclic periodic ester

Iodic acid

Oxidation by HIO_4

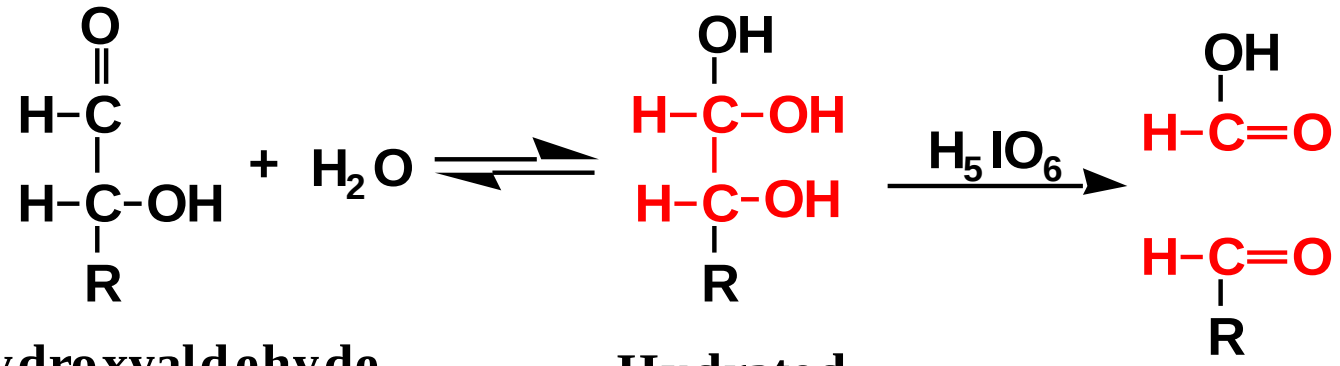
- It also cleaves α-hydroxyketones



and α-hydroxyaldehydes.

α-Hydroxyketone

Hydrated intermediate



α-Hydroxyaldehyde

Hydrated intermediate

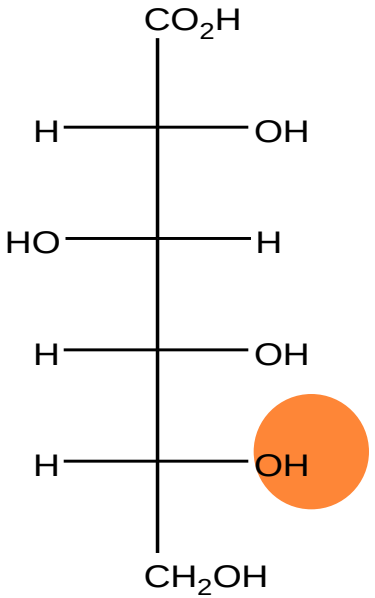
Examples. Identify each of the glucose derivatives.

A + 4 HIO_4 yielded 3 HCO_2H + HCHO + OHC-CO_2H

B + 5 HIO_4 yielded 4 HCO_2H + 2 HCHO

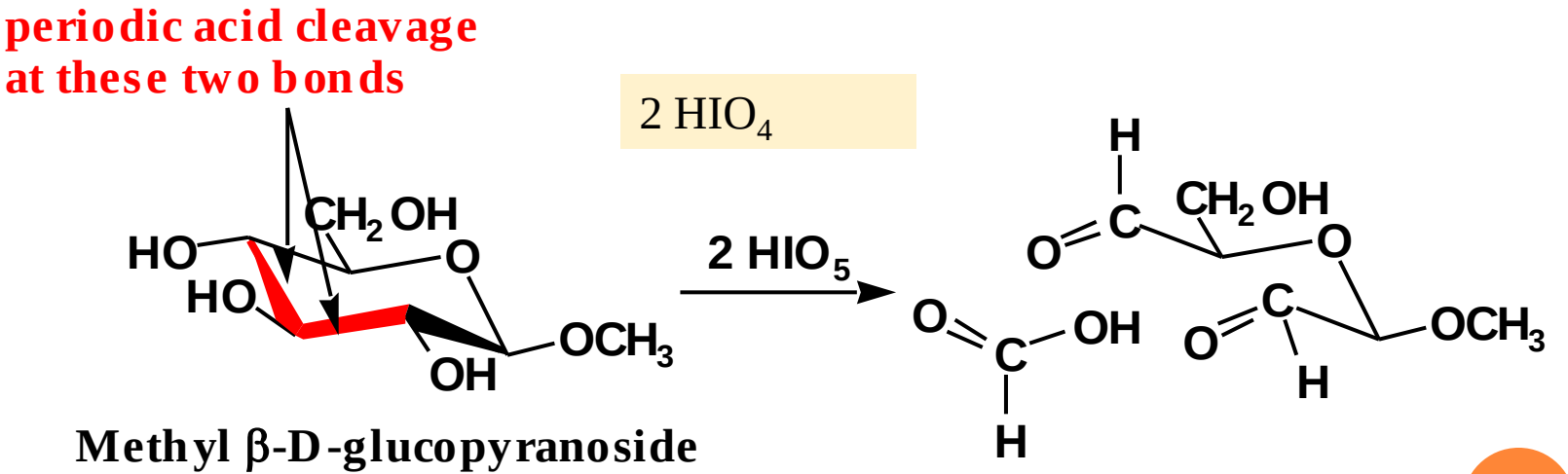
C + 3 HIO_4 yielded 2 HCO_2H + 2 OHC-CO_2H

Analysis of A:
4 moles of periodic acid used. 4 bonds broken.
Products:
Formic acid from –CHOH- or CHO-.
Formaldehyde from CH_2OH-
OHC-CO_2H from –CHOH-CO_2H

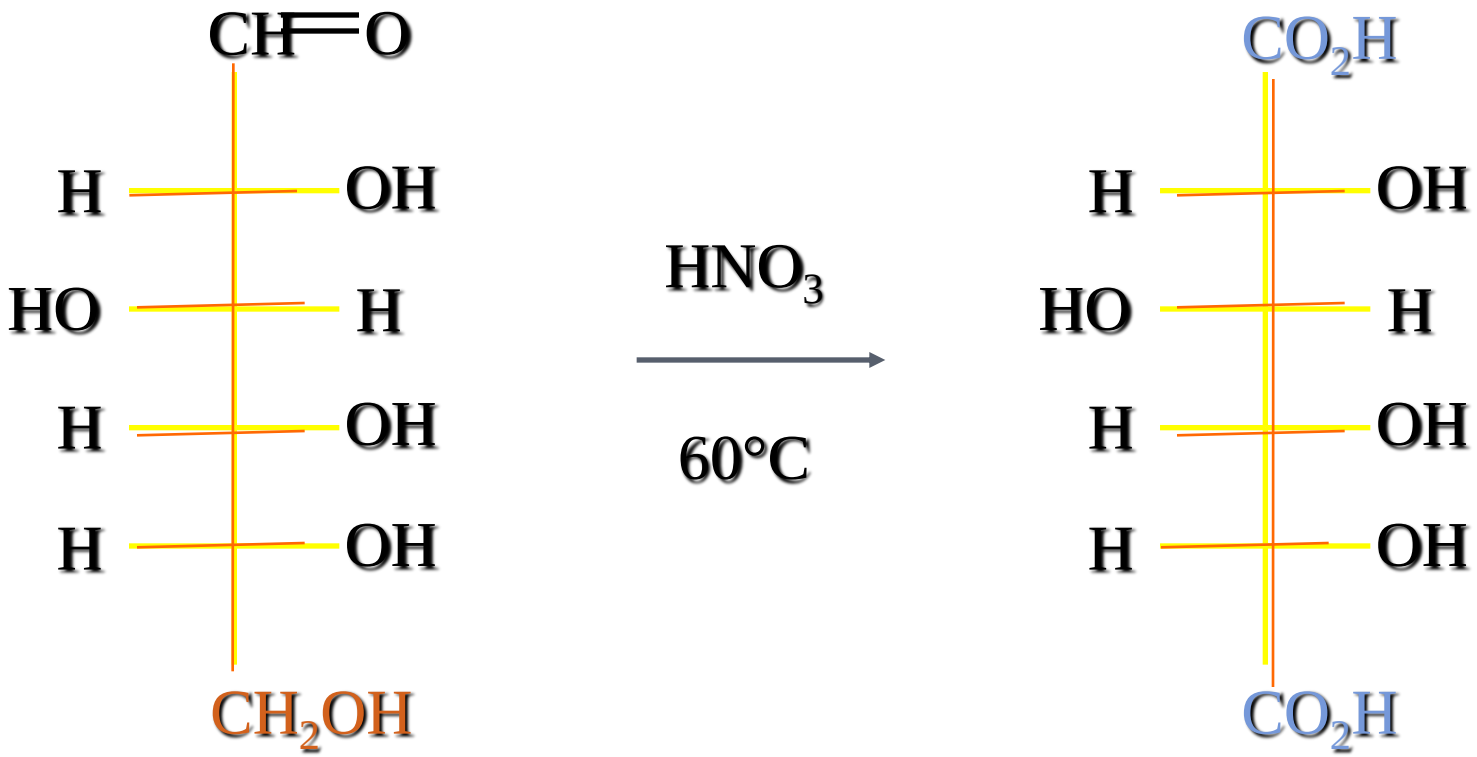


Another example

- Oxidation of methyl β-D-glucoside consumes two moles of HIO_4 and produces one mole of formic acid, which indicates three adjacent C-OH groups.



Nitric Acid Oxidation

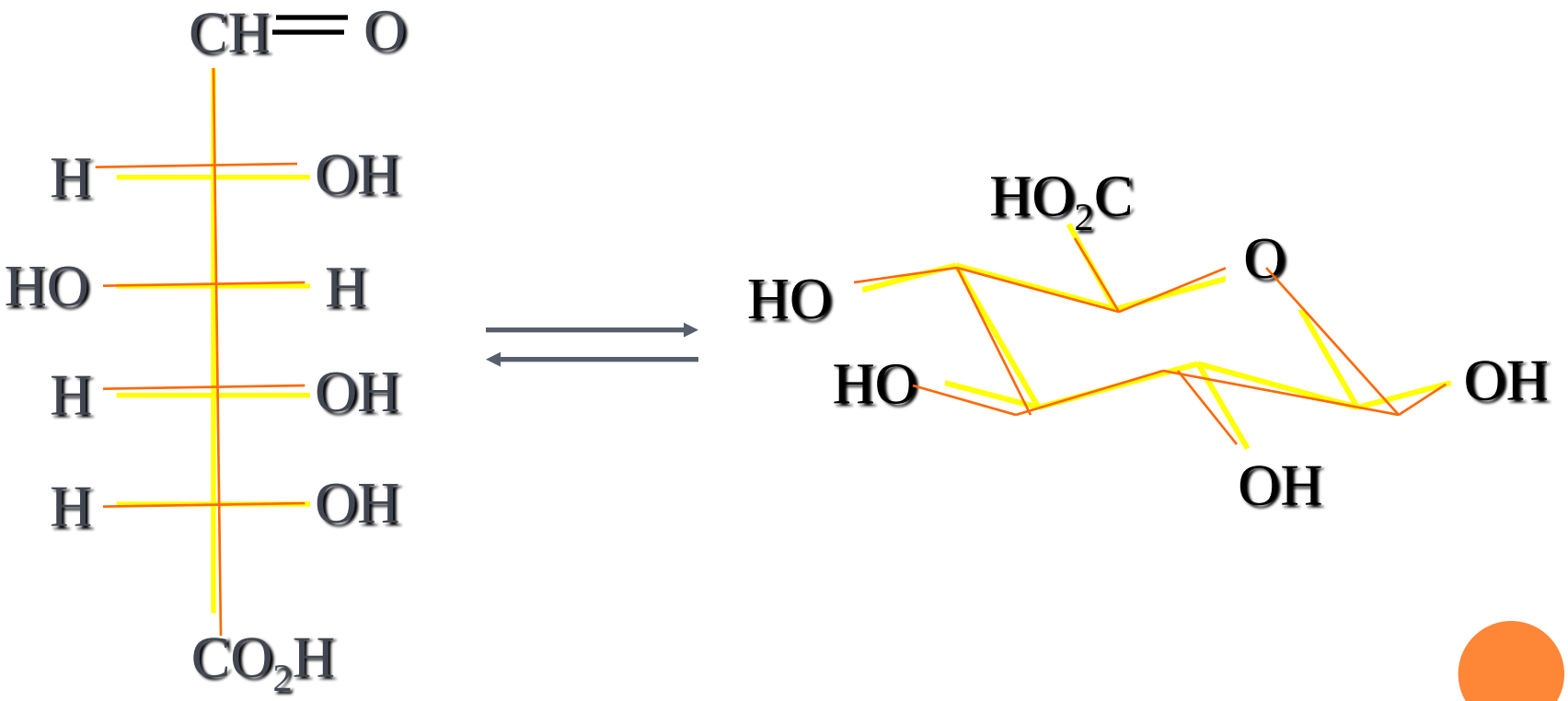


D-Glucose

D-Glucaric acid (41%)

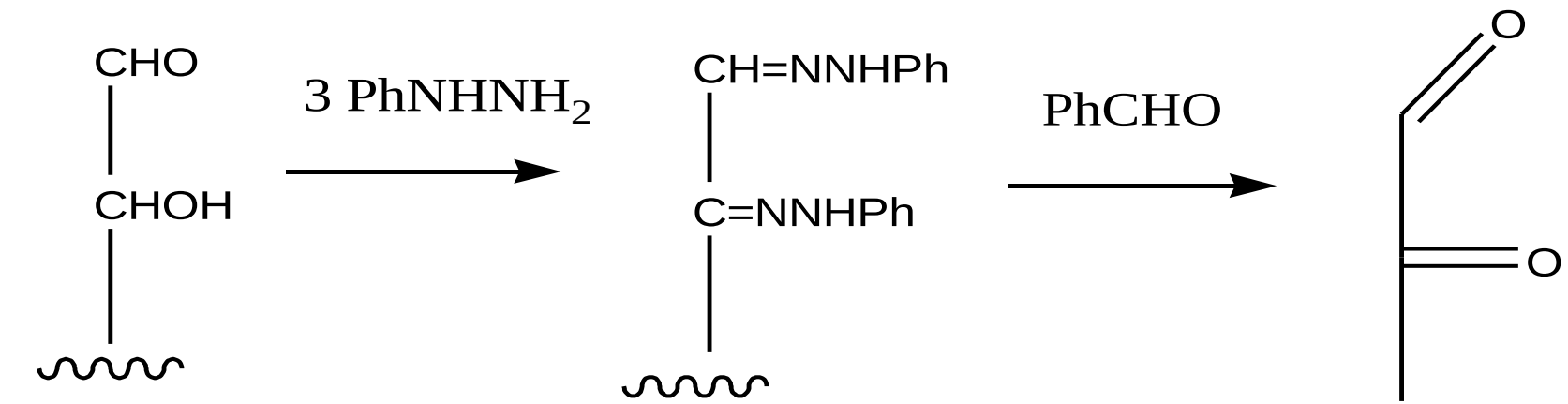
Uronic Acids

Uronic acids contain both an aldehyde and a terminal CO_2H function.



D-Glucuronic acid

Osazones, Epimers



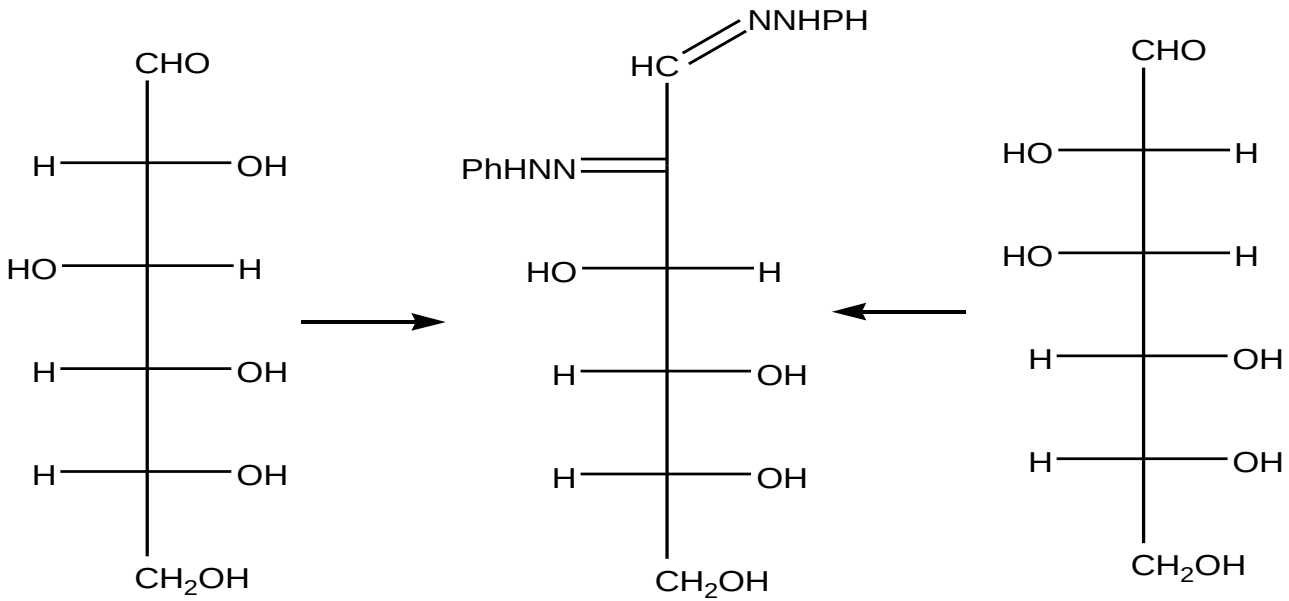
aldose

osazone

osone

Use of osazone in structure determination

Fischer found that (+) glucose and (+) mannose yielded the same osazone indicating that they differed only at the C2 configuration. Hence, if we know the configuration of (+) glucose we immediately have that of (+) mannose. Stereoisomers that differ in configuration at only one stereogenic center are called epimers. D-glucose and D-mannose are epimers.

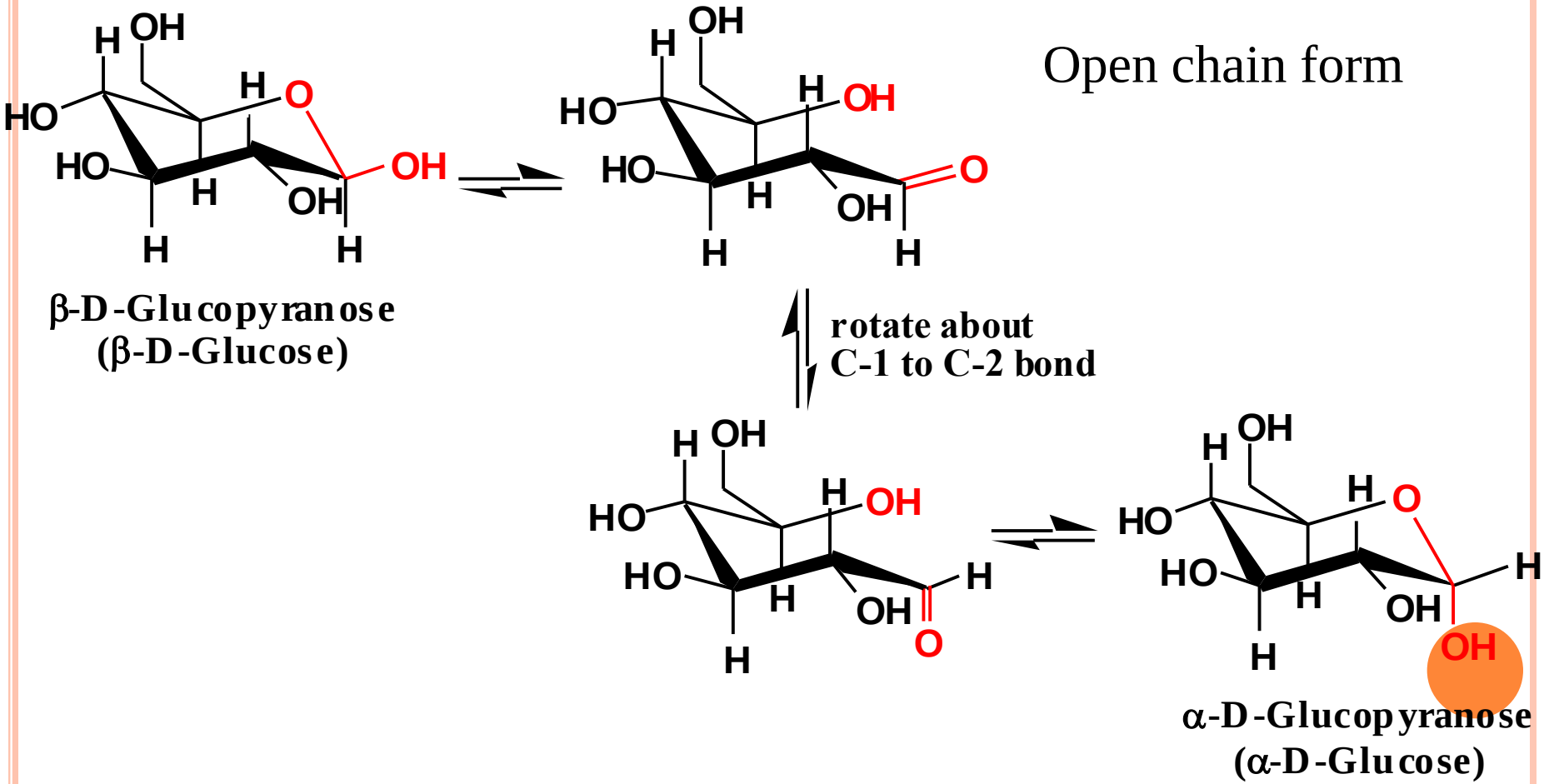


D glucose

D mannose

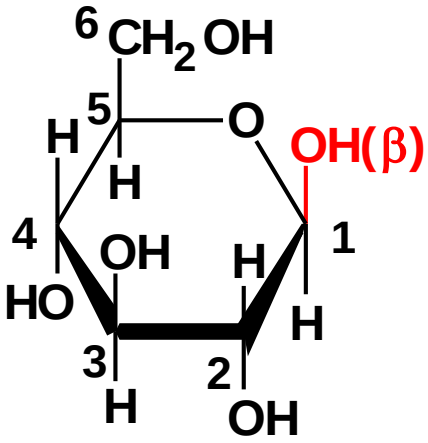
Conformational Formulas; β to α Conversion

- For pyranoses, the six-membered ring is more accurately represented as a chair conformation.

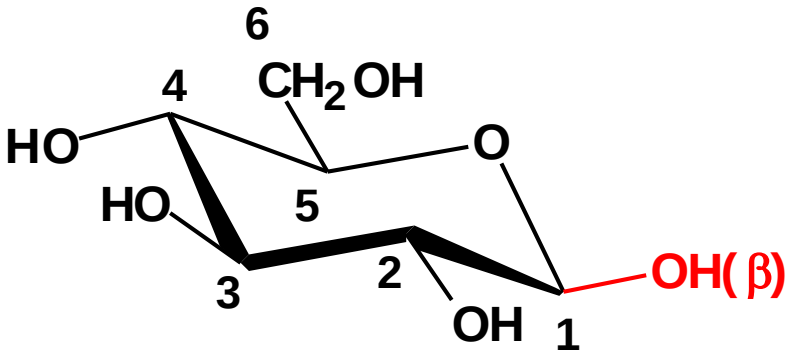


Conformational Formulas

- The orientations of groups on carbons 1-5 in the Haworth and chair projections of β-D-glucopyranose are up-down-up-down-up.



β-D-Glucopyranose
(Haworth projection)



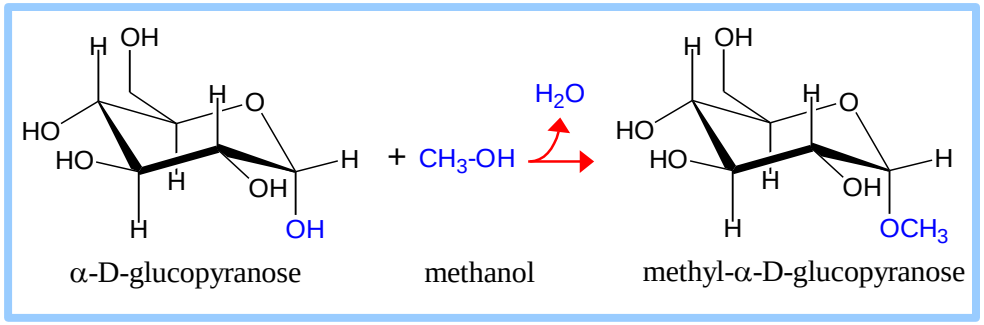
β-D-Glucopyranose
(chair conformation)

Glycosidic Bonds

The anomeric hydroxyl and a hydroxyl of another sugar or some other compound can join together, splitting out water to form a glycosidic bond:

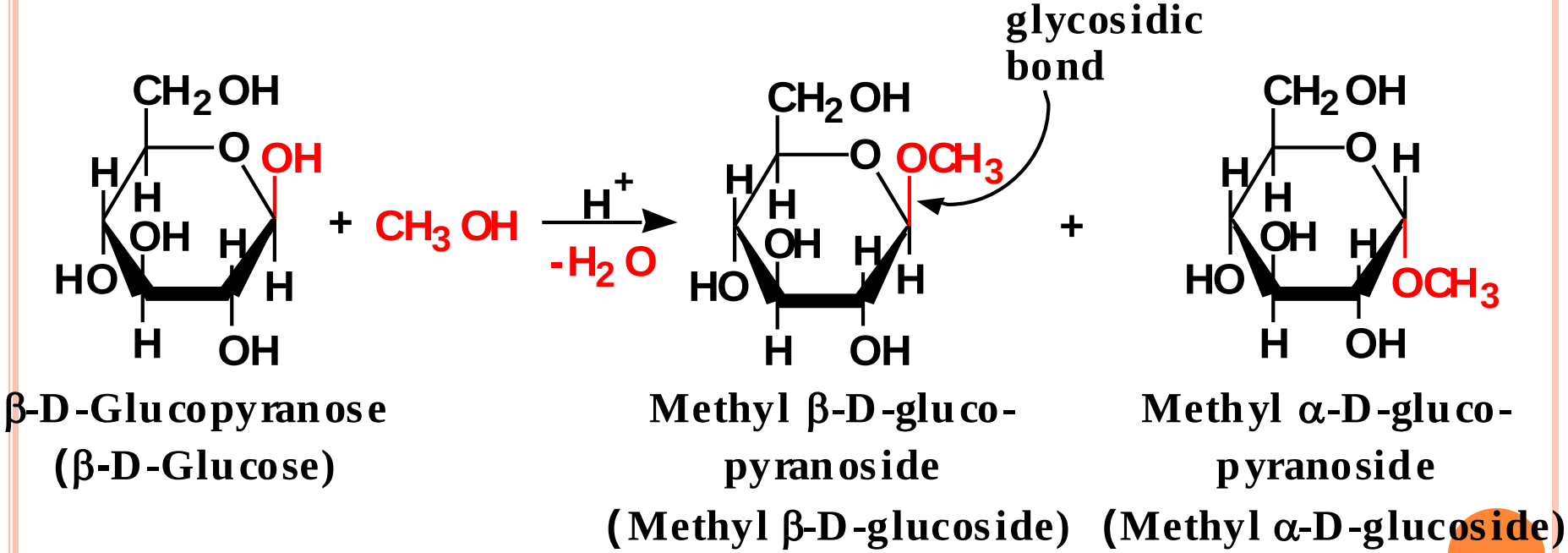
R-OH + HO-R' → R-O-R' + H_2O

E.g., methanol reacts with the anomeric OH on glucose to form methyl glucoside (methyl-glucopyranose).



Glycosides, anomeric OH becomes OR, acetal formation.

- **Glycoside:** A carbohydrate in which the -OH of the anomeric carbon is replaced by -OR.
  - methyl β-D-glucopyranoside (methyl β-D-glucoside)



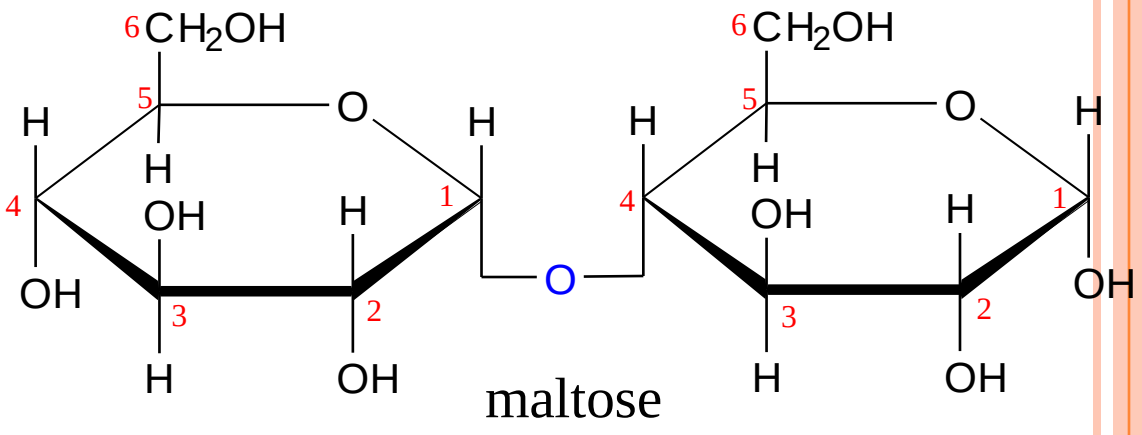
Disaccharide

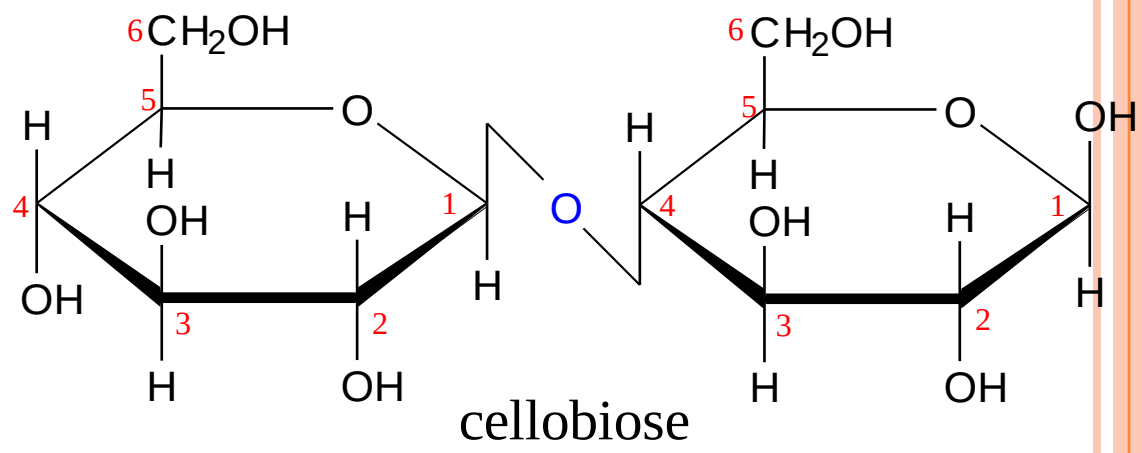
- A **disaccharide** is formed when a dehydration reaction joins two monosaccharides
- This covalent bond is called a **glycosidic bond**
- **Lactose = Glu + Gal**
- **Maltose = Glu + Glu**
- **Sucrose = Glu + Fru**

Disaccharides:

Maltose, a cleavage product of starch (e.g., amylose), is a disaccharide with an $\alpha(1\rightarrow 4)$ glycosidic link between C1 - C4 OH of 2 glucoses.

It is the **α** anomer (C1 O points down).





Cellobiose, a product of cellulose breakdown, is the otherwise equivalent **β** anomer (O on C1 points up).

The $\beta(1\rightarrow 4)$ glycosidic linkage is represented as a zig-zag, but one glucose is actually **flipped over** relative to the other.

Other **disaccharides** include:

- **Sucrose**, common table sugar, has a glycosidic bond linking the anomeric hydroxyls of glucose & fructose.

  Because the configuration at the anomeric C of glucose is α (O points down from ring), the linkage is α(1→2).

  The full name of sucrose is α-D-glucopyranosyl-(1→2)-β-D-fructopyranose.)

- **Lactose**, milk sugar, is composed of galactose & glucose, with β(1→4) linkage from the anomeric OH of galactose. Its full name is β-D-galactopyranosyl-(1→ 4)-α-D-glucopyranose

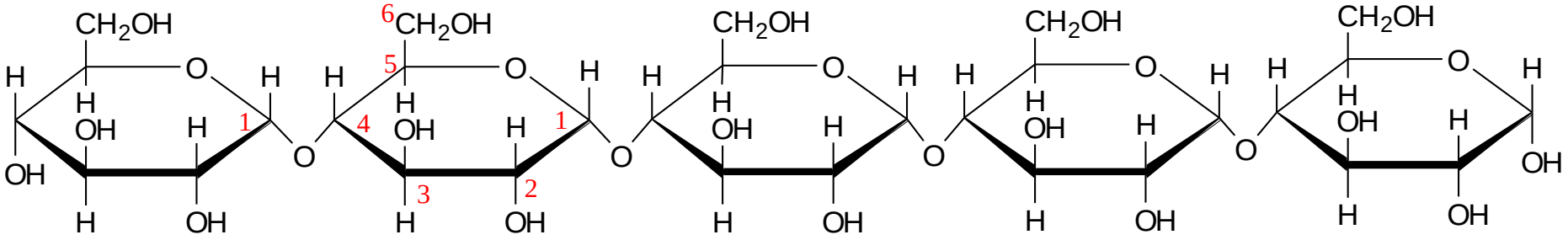
Polysaccharides

- **Polysaccharides**, the polymers of sugars, have **storage** and **structural** roles
- The structure and function of a polysaccharide are determined by its sugar monomers and the positions of **glycosidic linkages**

Storage Polysaccharides

- **Starch**, a storage polysaccharide of plants, consists entirely of glucose monomers
- Plants store surplus starch as granules within **chloroplasts** and other **plastids**

- **Glycogen** is a storage polysaccharide in animals
- Humans and other vertebrates store glycogen mainly in **liver** and **muscle cells**



amylose

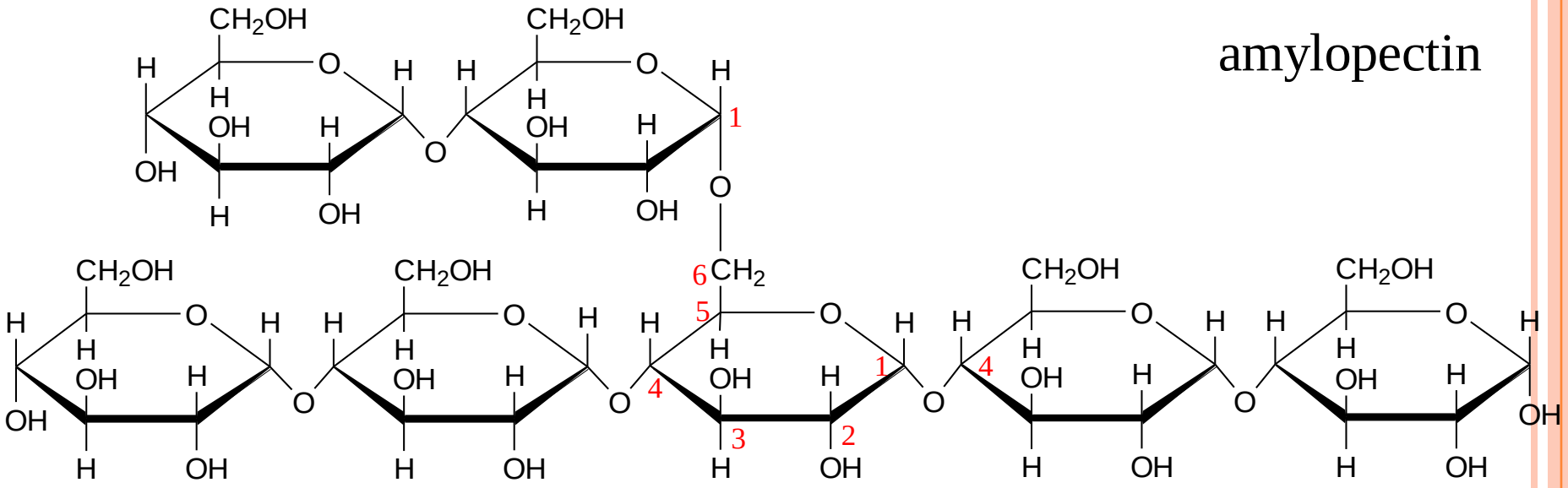
Polysaccharides:

Plants store glucose as **amylose** or **amylopectin**, glucose polymers collectively called starch.

Glucose storage in **polymeric** form **minimizes osmotic effects**.

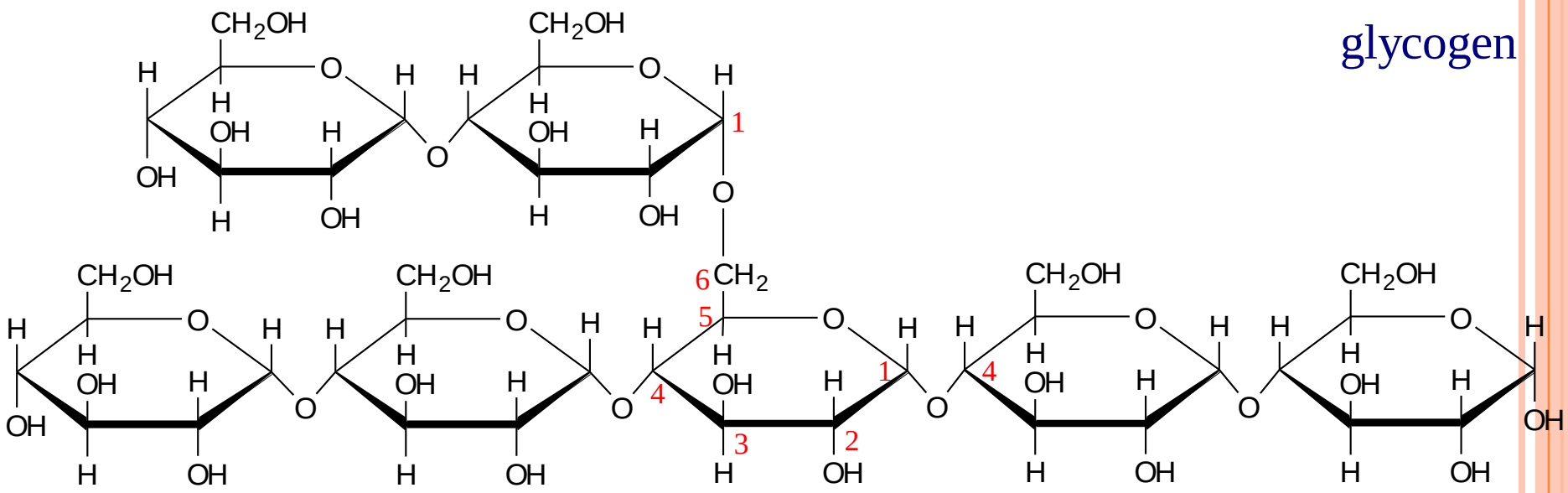
Amylose is a glucose polymer with **α(1→4)** linkages.

The end of the polysaccharide with an anomeric C1 not involved in a glycosidic bond is called the **reducing end**.



Amylopectin is a glucose polymer with mainly α(1→4) linkages, but it also has **branches** formed by α(1→6) linkages. (Branched sugars) Branches are generally longer than shown above.

The branches produce a compact structure & provide multiple chain ends at which enzymatic cleavage can occur.

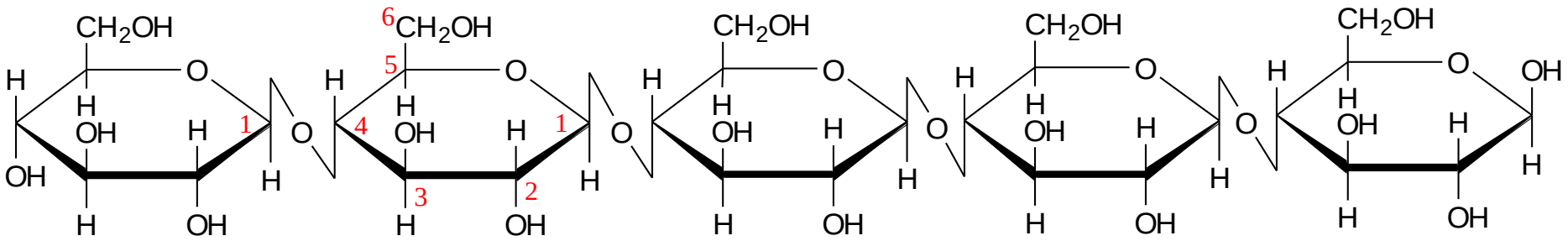


Glycogen, the glucose storage polymer in **animals**, is similar in structure to amylopectin.

But glycogen has **more** α(1→6) **branches**.

The highly branched structure permits rapid glucose release from glycogen stores, e.g., in muscle during exercise.

The ability to rapidly mobilize glucose is more essential to animals than to plants.

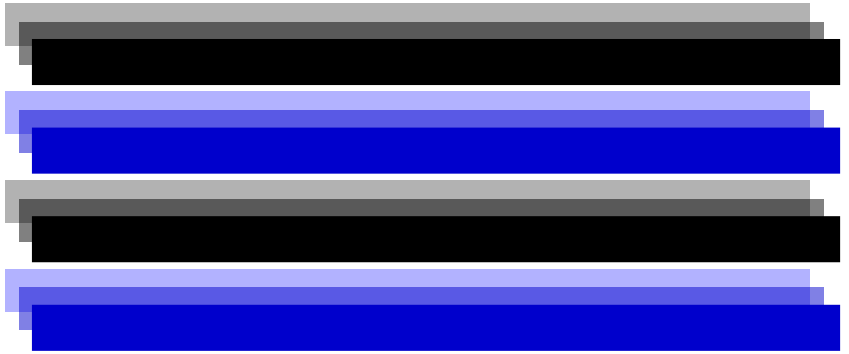


cellulose

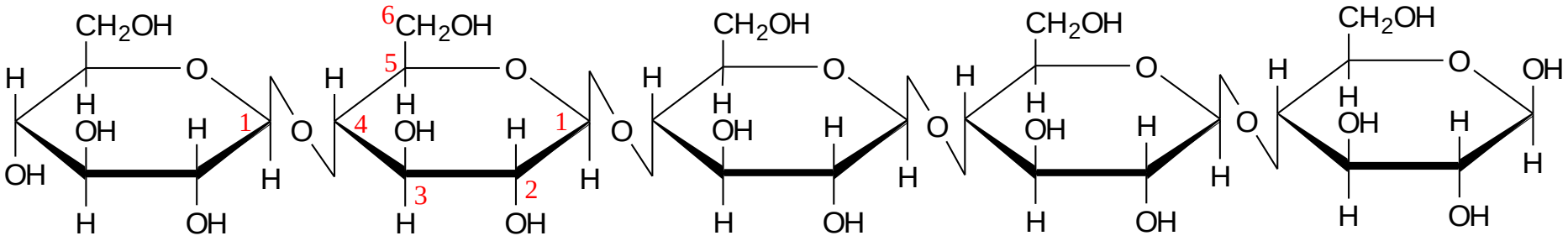
Cellulose, a major constituent of plant cell walls, consists of long linear chains of glucose with β(1→4) linkages.

Every other glucose is flipped over, due to β linkages. This promotes intra-chain and inter-chain H-bonds and

van der Waals interactions, that cause cellulose chains to be straight & rigid, and pack with a crystalline arrangement in thick bundles - microfibrils.



Schematic of arrangement of cellulose chains in a microfibril.



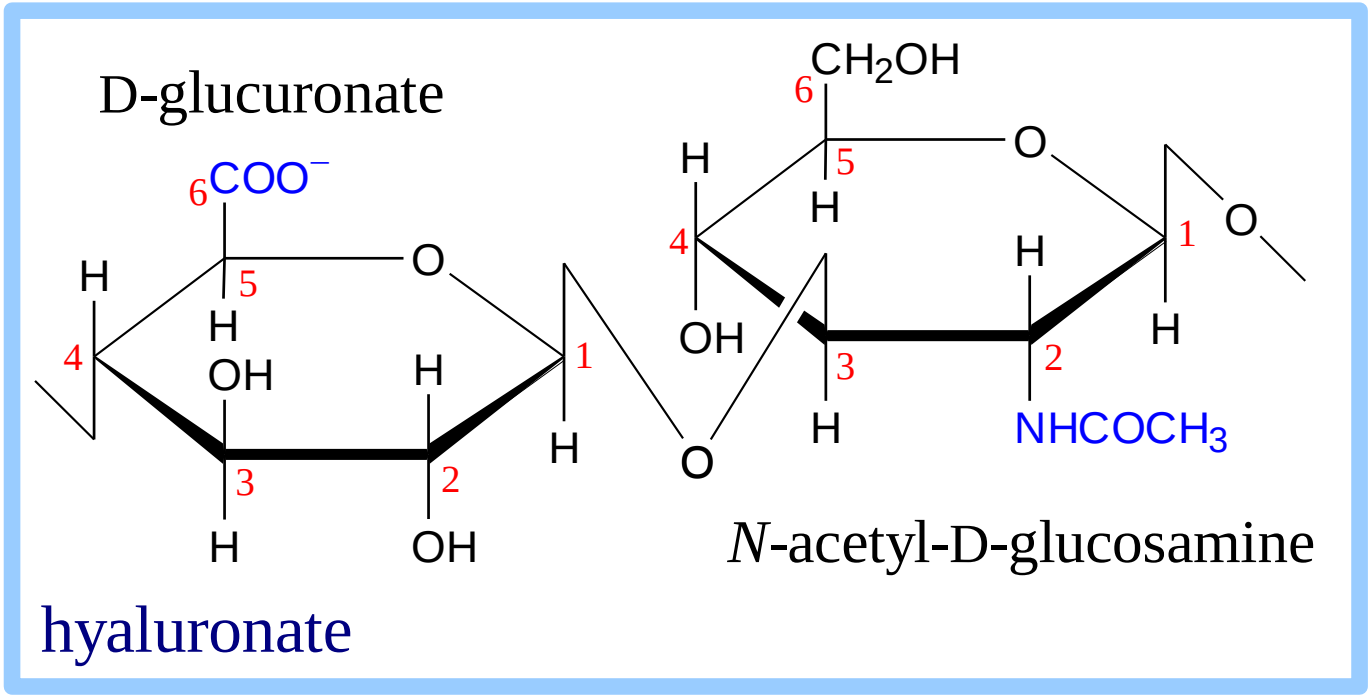
cellulose

Multisubunit **Cellulose Synthase** complexes in the plasma membrane spin out from the cell surface microfibrils consisting of 36 parallel, interacting cellulose chains.

These **microfibrils** are very **strong**.

The **role** of cellulose is to impart strength and rigidity to plant cell walls, which can withstand high hydrostatic pressure gradients. Osmotic swelling is prevented.

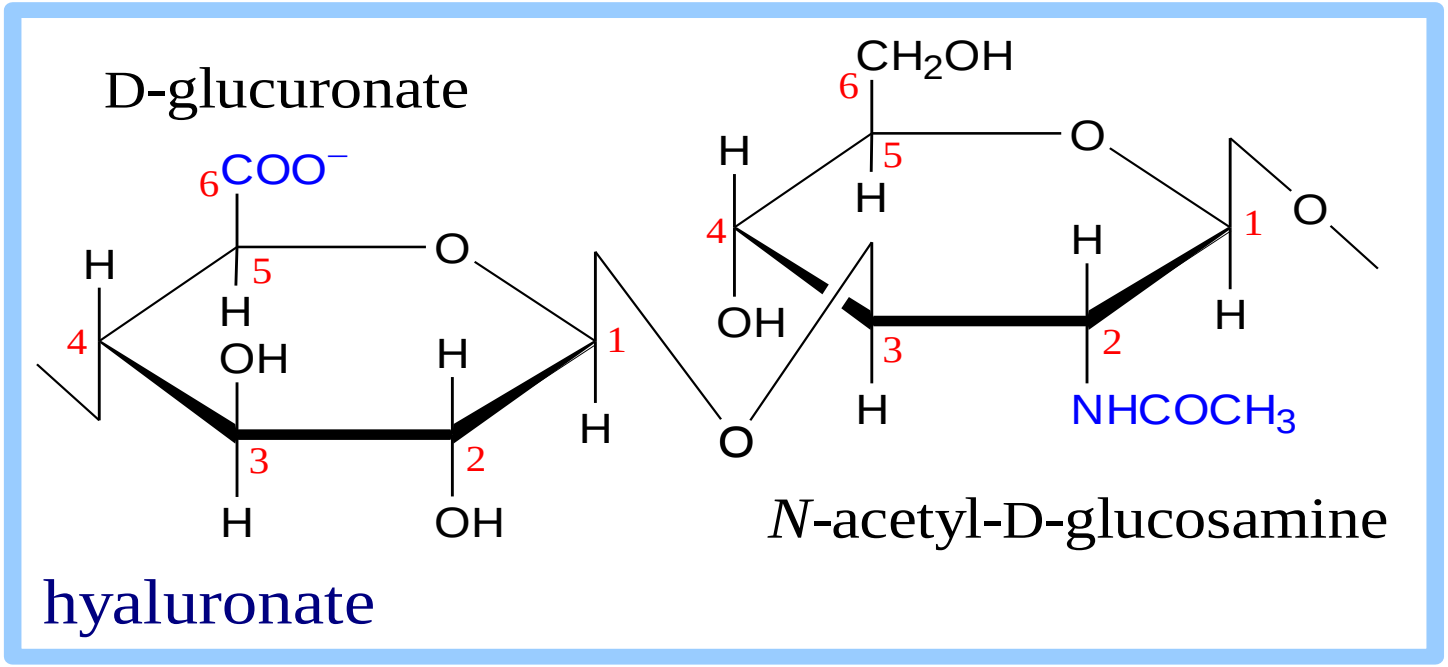
Explore and compare structures of amylose & cellulose using Chime.



Glycosaminoglycans (mucopolysaccharides) are linear polymers of **repeating disaccharides**.

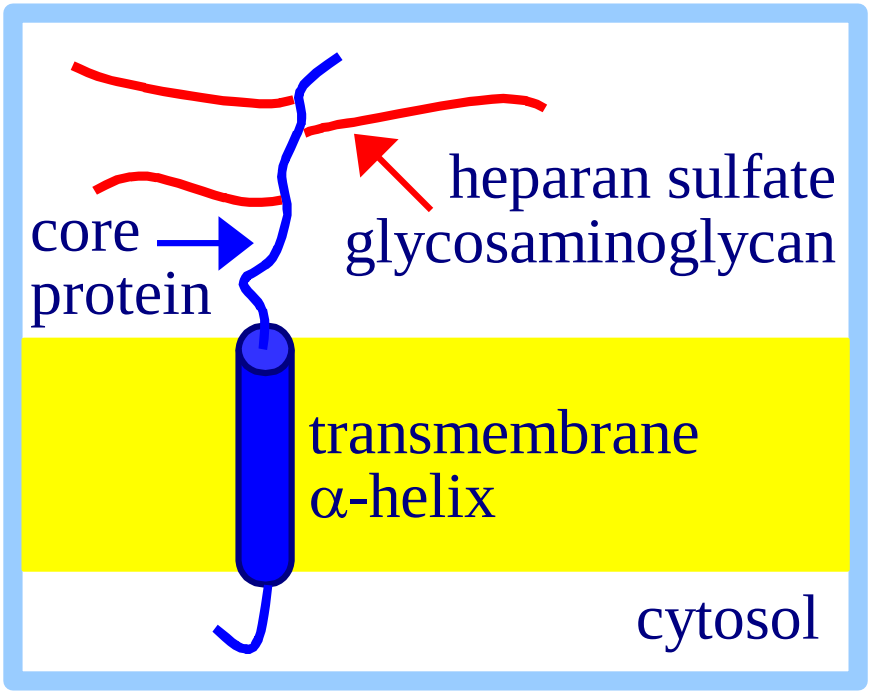
The constituent monosaccharides tend to be **modified**, with acidic groups, amino groups, sulfated hydroxyl and amino groups, etc.

Glycosaminoglycans tend to be **negatively charged**, because of the prevalence of acidic groups.



Hyaluronate (hyaluronan) is a **glycosaminoglycan** with a repeating disaccharide consisting of 2 glucose derivatives, glucuronate (glucuronic acid) & *N*-acetyl-glucosamine.

The glycosidic linkages are β(1→3) & β(1→4).



Proteoglycans are **glycosaminoglycans** that are covalently linked to serine residues of specific **core proteins**.

The glycosaminoglycan chain is synthesized by sequential addition of sugar residues to the core protein.

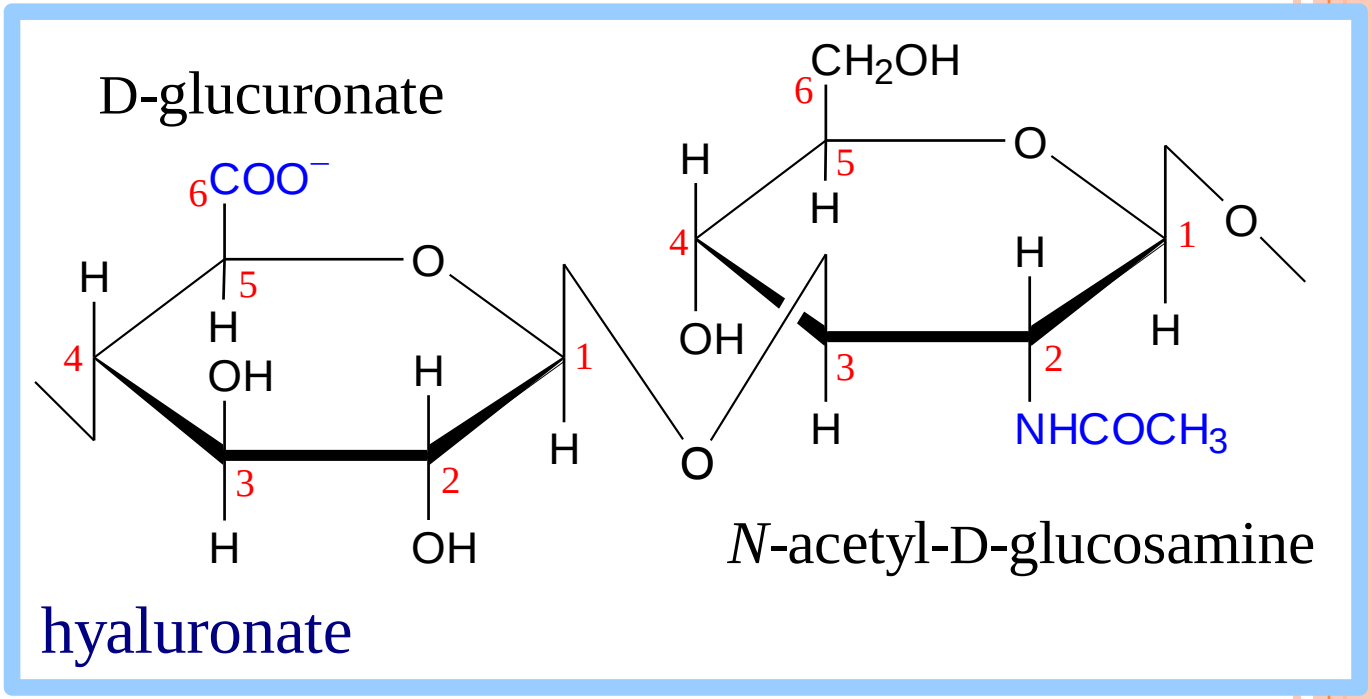
Some proteoglycans of the extracellular matrix **bind** non-covalently to **hyaluronate** via protein domains called **link modules**. E.g.:

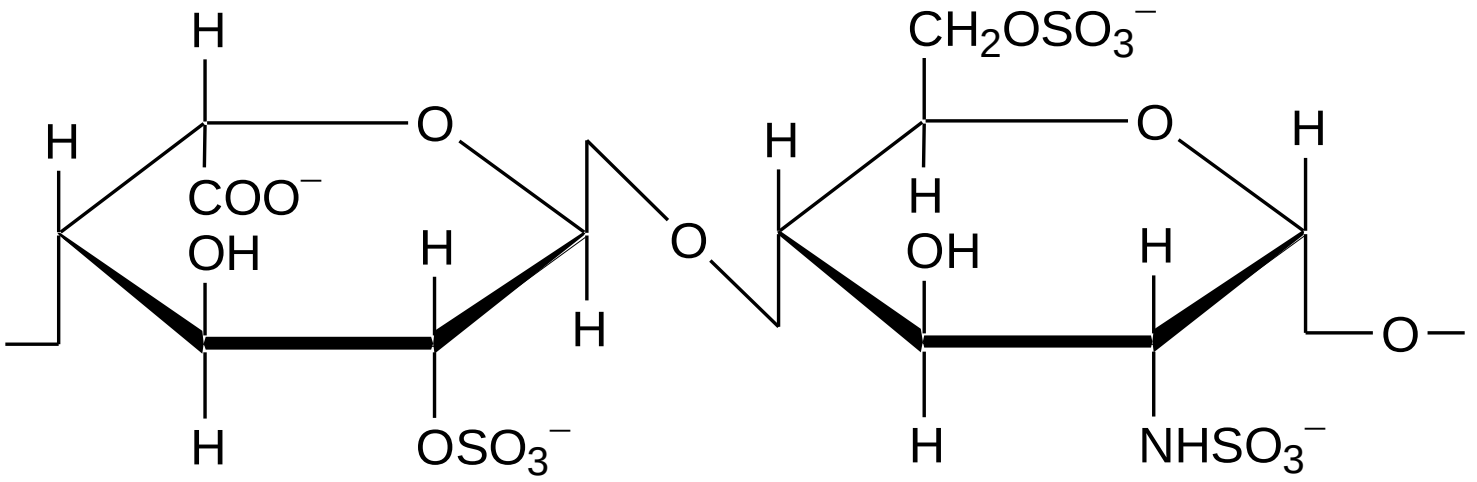
- Multiple copies of the **aggrecan** proteoglycan associate with hyaluronate in cartilage to form large complexes.
- **Versican**, another proteoglycan, binds hyaluronate in the extracellular matrix of loose connective tissues.

Websites on:

Aggrecan

Aggrecan & versican.





heparin or heparan sulfate - examples of residues

Heparan sulfate is initially synthesized on a membrane-embedded core protein as a polymer of alternating ***N*-acetylglucosamine** and **glucuronate** residues.

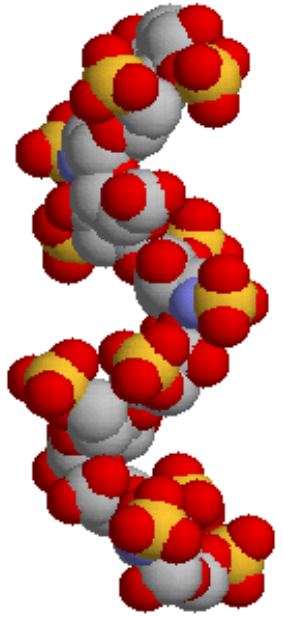
Later, in segments of the polymer, glucuronate residues may be converted to the sulfated sugar **iduronic acid**, while *N*-acetylglucosamine residues may be deacetylated and/or sulfated.

Heparin, a soluble glycosaminoglycan found in granules of mast cells, has a structure similar to that of heparan sulfates, but is more **highly sulfated**.

When released into the blood, it inhibits clot formation by interacting with the protein antithrombin.

Heparin has an **extended helical conformation**.

PDB 1RID



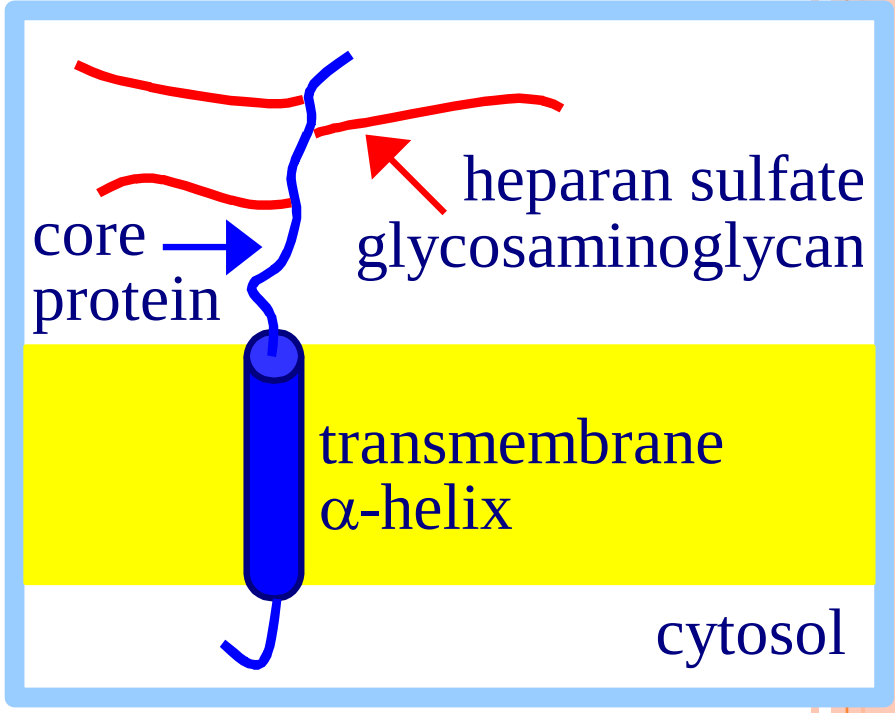
heparin: $(IDS\text{-}SGN)_5$

C O N S

Charge repulsion by the many negatively charged groups may contribute to this conformation.

Heparin shown has 10 residues, alternating IDS (iduronate-2-sulfate) & SGN (N-sulfo-glucosamine-6-sulfate).

Some **cell surface heparan sulfate** glycosaminoglycans remain covalently linked to core proteins embedded in the plasma membrane.



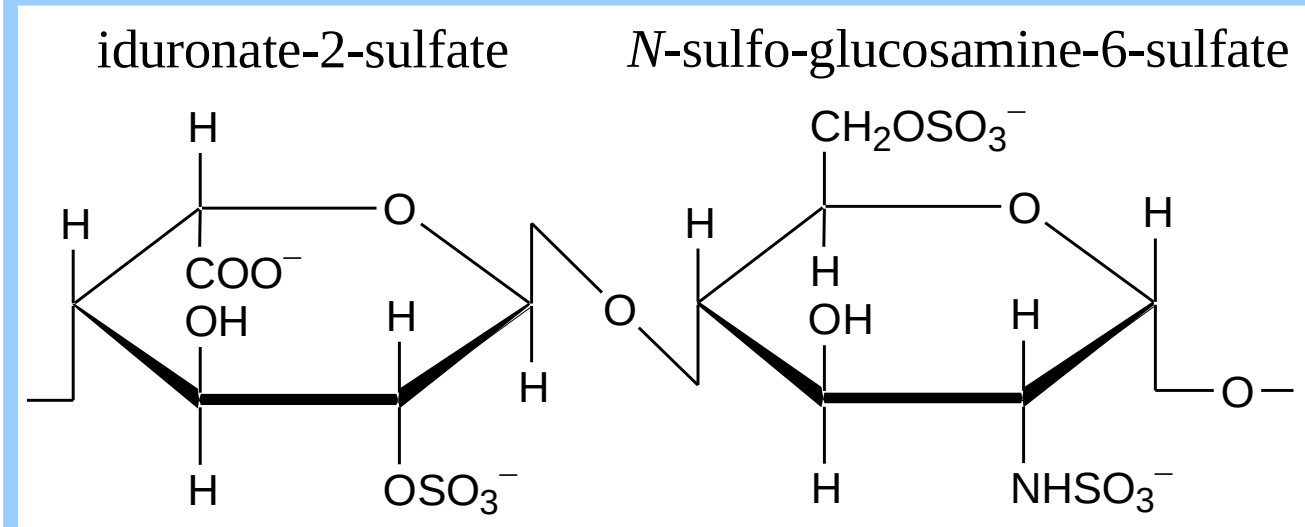
- The core protein of a **syndecan** heparan sulfate proteoglycan includes a single **transmembrane α-helix**, as in the simplified diagram above.
- The core protein of a **glypican** heparan sulfate proteoglycan is attached to the outer surface of the plasma membrane via covalent **linkage to** a modified phosphatidylinositol **lipid**.

Proteins involved in **signaling** & **adhesion** at the cell surface recognize & bind heparan sulfate chains.

E.g., binding of some **growth factors** (small proteins) to cell surface receptors is enhanced by their binding also to heparan sulfates.

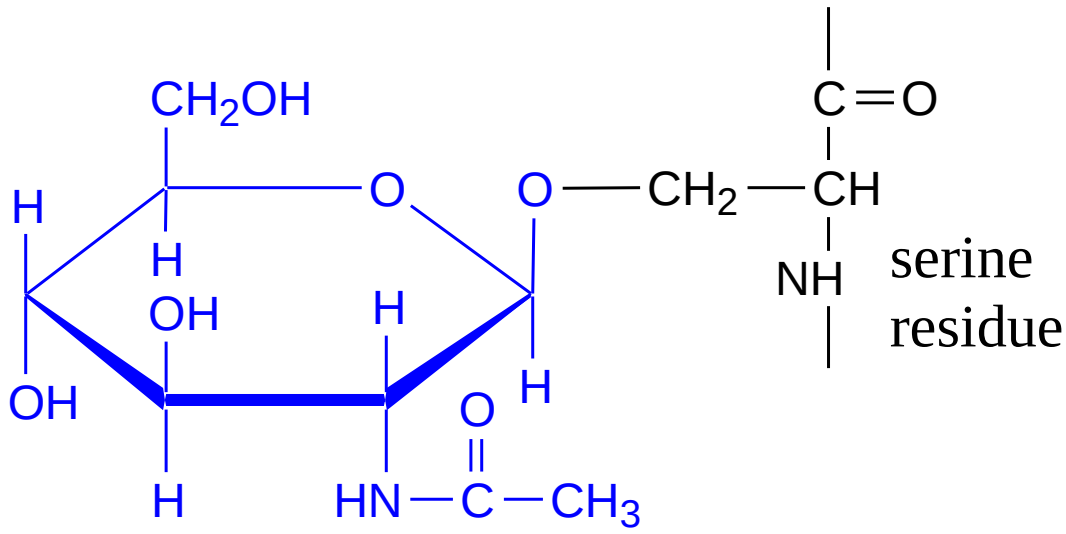
Regulated cell surface **Sulf** enzymes may **remove sulfate** groups at particular locations on heparan sulfate chains to **alter affinity** for signal proteins, e.g., growth factors.

Diagram by Kirkpatrick & Selleck.



heparin or heparan sulfate - examples of residues

Oligosaccharides that are covalently attached to proteins or to membrane lipids may be linear or branched chains.

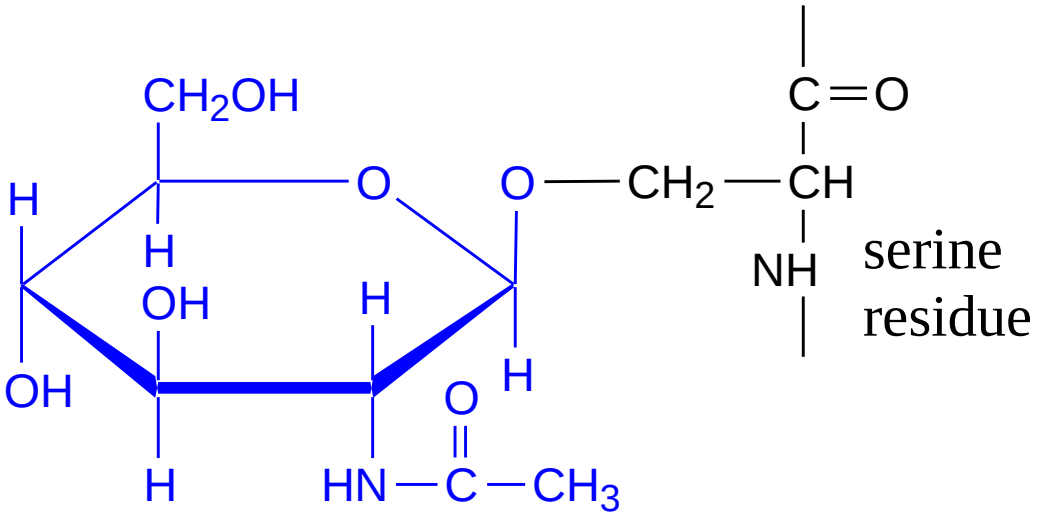


β-D-*N*-acetylglucosamine

O-linked oligosaccharide chains of glycoproteins vary in complexity.

They link to a protein via a glycosidic bond between a sugar residue & a **serine or threonine OH**.

O-linked oligosaccharides have roles in **recognition**, **interaction**, and **enzyme regulation**.

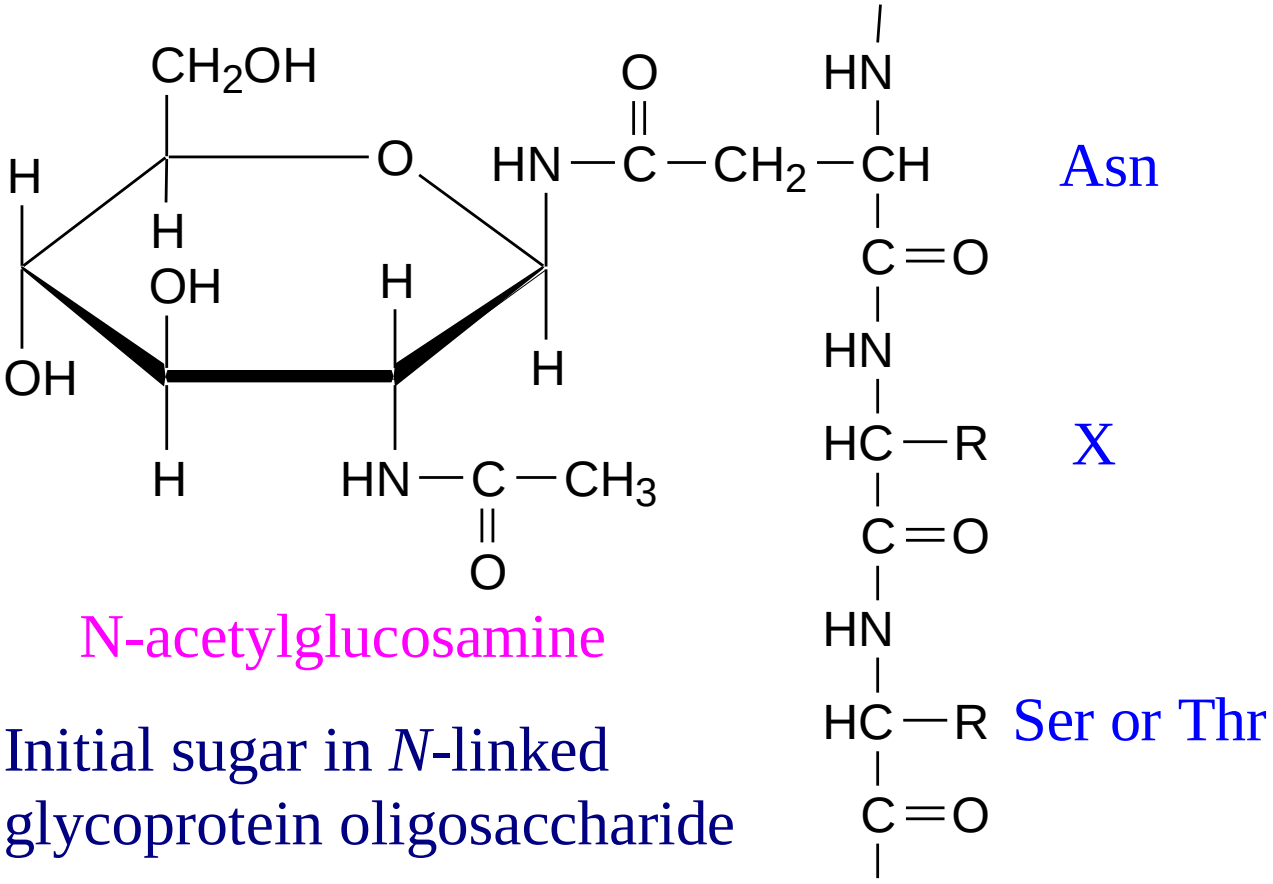


β-D-*N*-acetylglucosamine

***N*-acetylglucosamine** (**GlcNAc**) is a common O-linked glycosylation of protein serine or threonine residues.

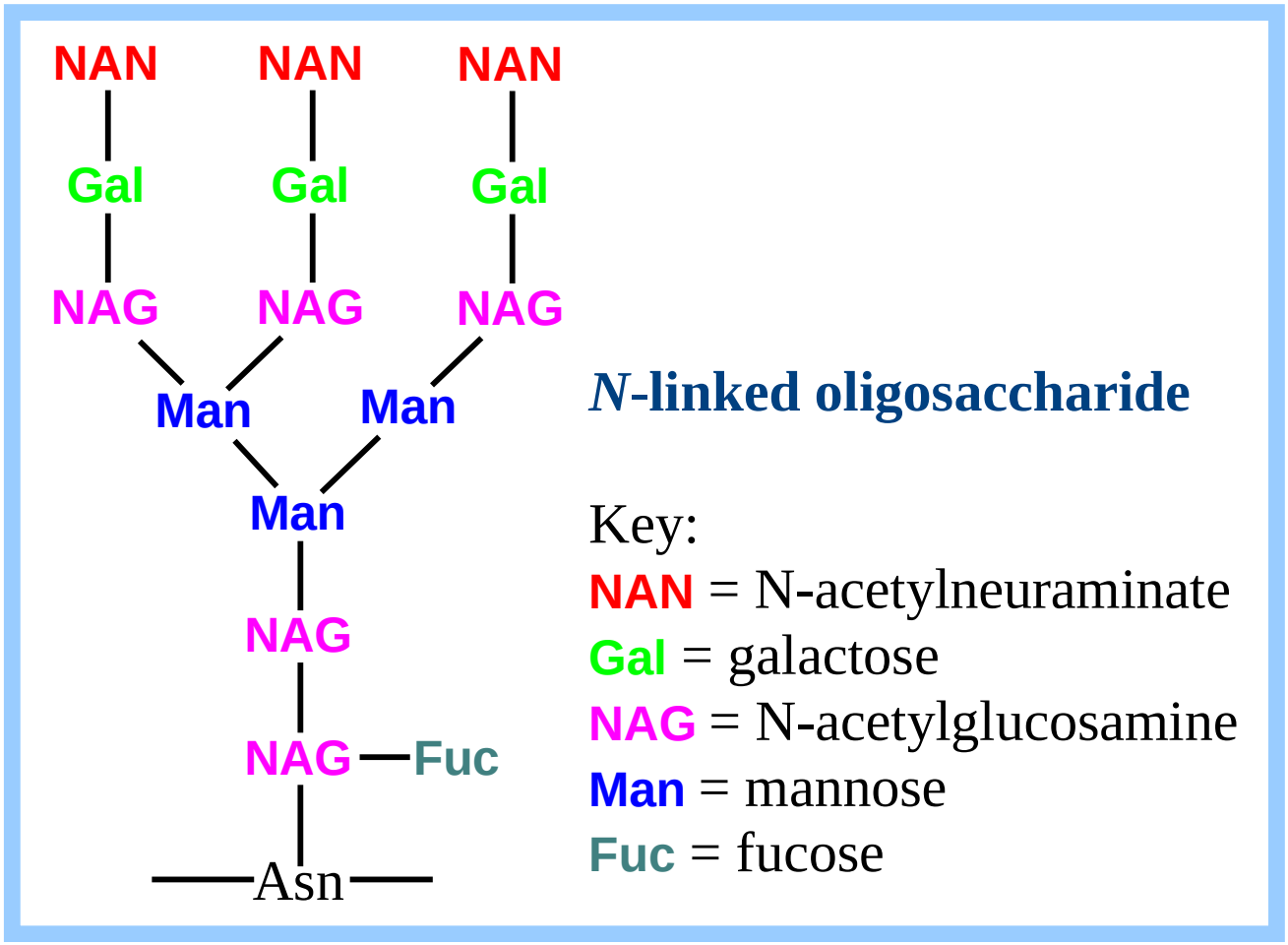
Many cellular proteins, including enzymes & transcription factors, are **regulated** by reversible GlcNAc attachment.

Often attachment of GlcNAc to a protein OH **alternates with phosphorylation**, with these 2 modifications having opposite regulatory effects (stimulation or inhibition).



***N*-linked oligosaccharides** of glycoproteins tend to be complex and branched.

First ***N*-acetylglucosamine** is linked to a protein via the side-chain N of an asparagine residue in a particular 3-amino acid sequence.



Additional monosaccharides are added, and the *N*-linked oligosaccharide chain is modified by removal and addition of residues, to yield a characteristic branched structure.

Many proteins secreted by cells have attached N-linked oligosaccharide chains.

Genetic diseases have been attributed to deficiency of particular enzymes involved in synthesizing or modifying oligosaccharide chains of these glycoproteins.

Such diseases, and gene knockout studies in mice, have been used to define pathways of modification of oligosaccharide chains of glycoproteins and glycolipids.

Carbohydrate chains of plasma membrane glycoproteins and glycolipids usually face the outside of the cell.

They have roles in cell-cell interaction and signaling, and in forming a protective layer on the surface of some cells.

Lectins are glycoproteins that **recognize** and **bind** to specific **oligosaccharides**.

Concanavalin A & **wheat germ agglutinin** are plant lectins that have been useful research tools.

The **C-type lectin-like domain** is a **Ca^{++}-binding** carbohydrate recognition domain in many **animal lectins**.

Recognition/binding of CHO moieties of glycoproteins, glycolipids & proteoglycans **by** animal **lectins** is a factor in:

- cell-cell recognition
- adhesion of cells to the extracellular matrix
- interaction of cells with chemokines and growth factors
- recognition of disease-causing microorganisms
- initiation and control of inflammation.

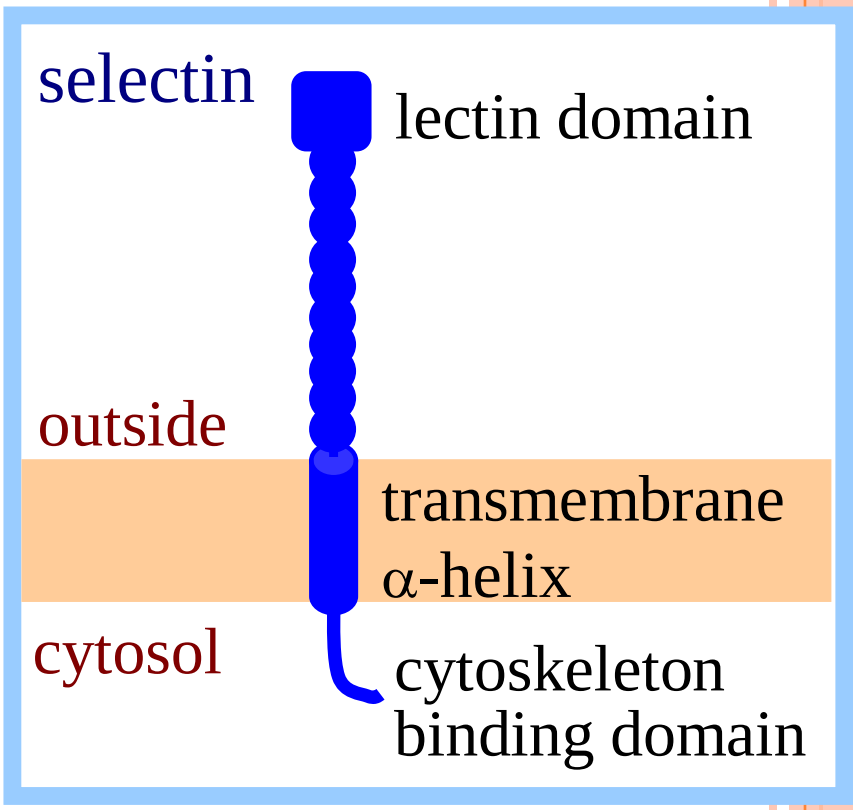
Examples of animal lectins:

Mannan-binding lectin (**MBL**) is a glycoprotein found in blood plasma.

It binds cell surface carbohydrates of **disease-causing microorganisms** & promotes phagocytosis of these organisms as part of the immune response.

Selectins are integral proteins of mammalian cell plasma membranes with roles in **cell-cell recognition** & binding.

The C-type **lectin-like domain** is at the end of a multi-domain extracellular segment extending out from the cell surface.



A **cleavage site** just outside the transmembrane α-helix provides a mechanism for regulated release of some lectins from the cell surface.

A **cytosolic domain** participates in regulated interaction with the actin cytoskeleton.

Disaccharides

- Sucrose, table sugar

(1-α-D-glucopyranosyl-ß-D-fructofuranoside)

- Maltose, from barley

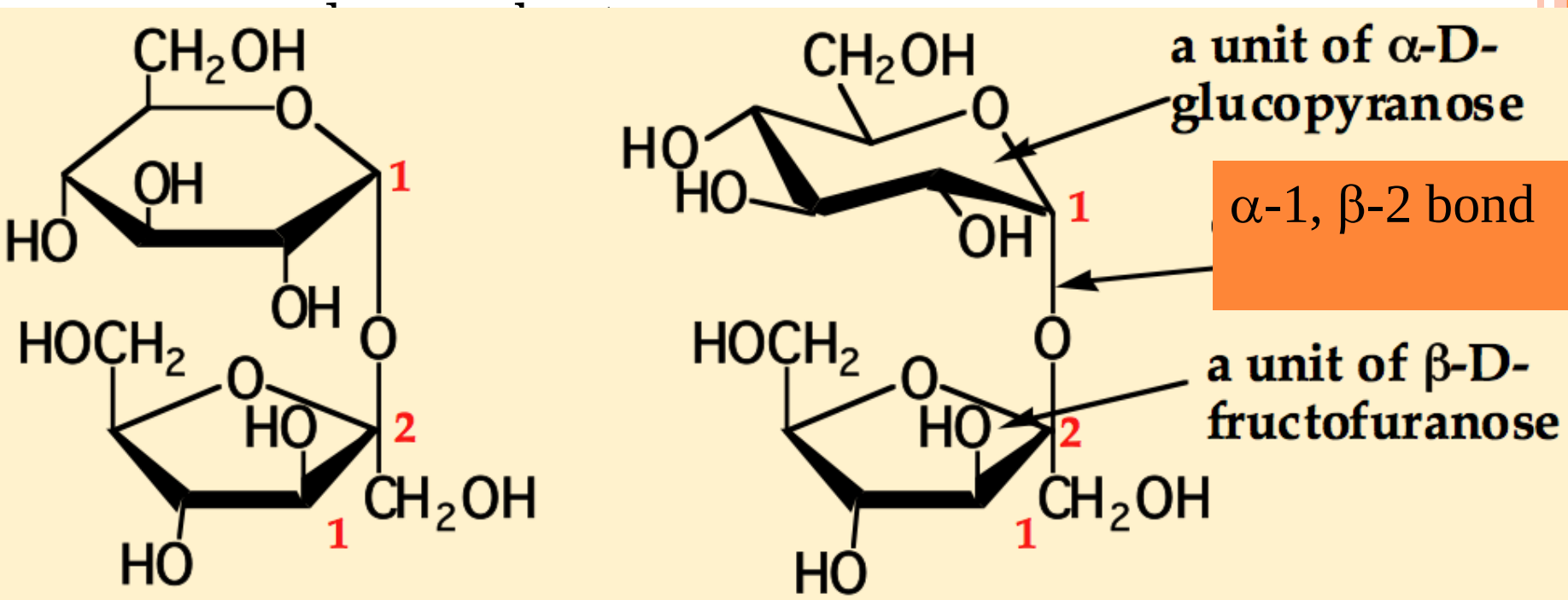
(4-α –D-glucopyranosyl α or ß D-glucopyranose)

- Lactose, milk sugar

(4- ß-D-Galactopyranosyl-D-glucopyranose)

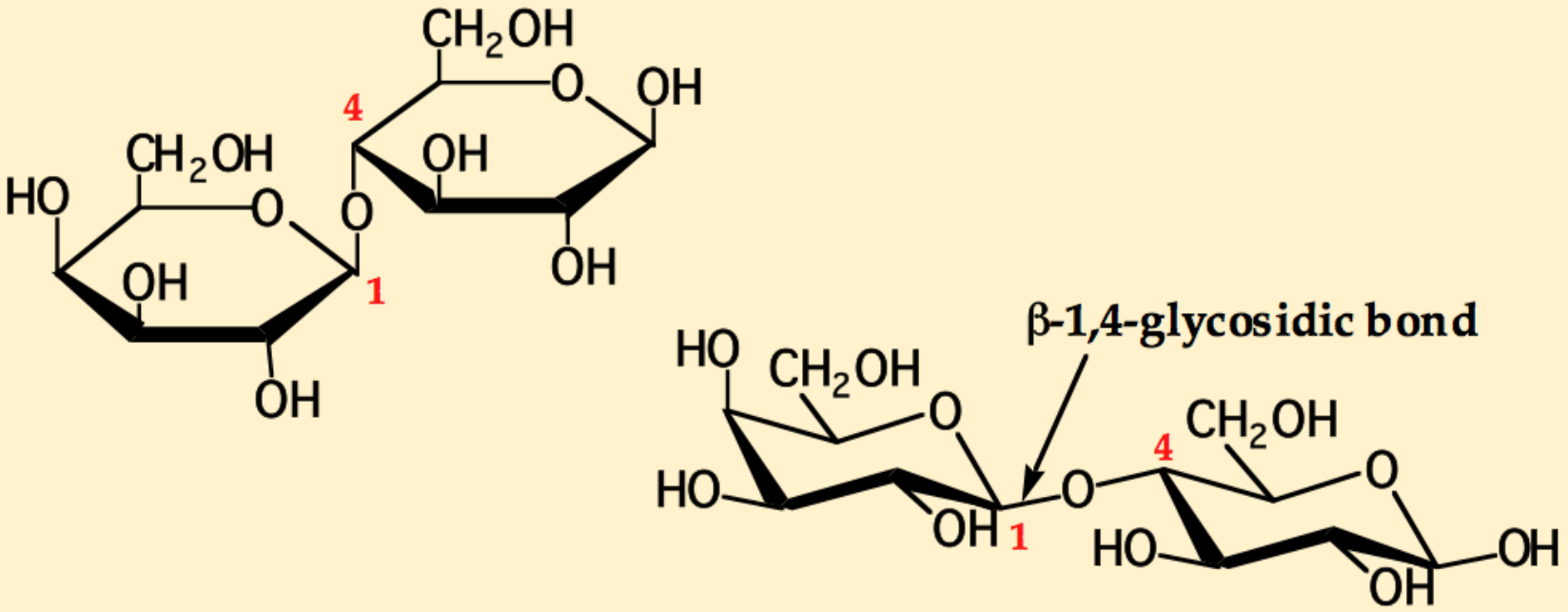
Sucrose, table sugar

- Table sugar, obtained from the juice of sugar



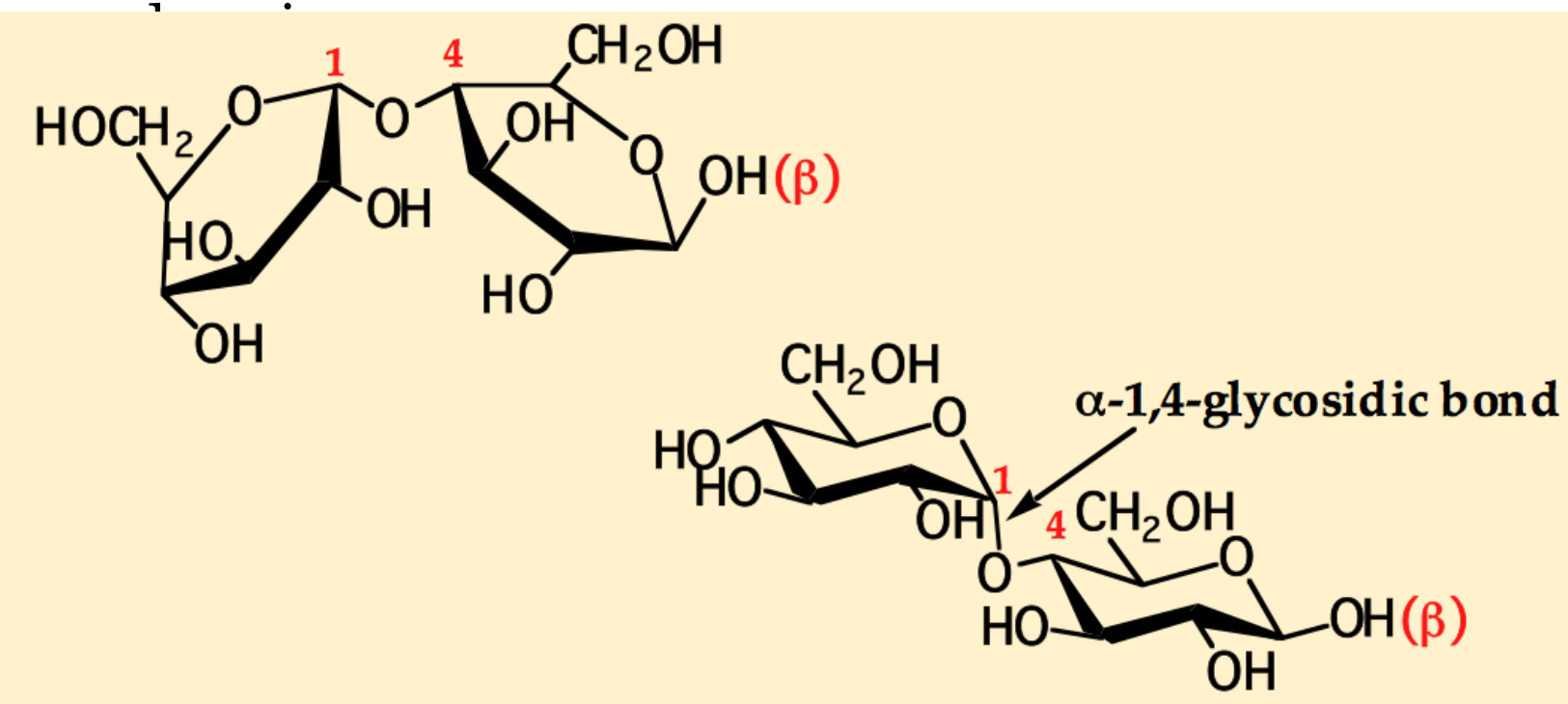
Lactose

- The principle sugar present in milk, 5 – 10%.



Maltose

- From malt, the juice of sprouted barley and other



Determination of Structure

- General steps involved can be summarized as follows.

1. Determination whether the disaccharide is reducing or not.
2. Acid hydrolysis of disaccharide yields two monosaccharide's which are then identified.

3. The determination of glycosidic bond , α or ß often rest on enzyme with known specificities.

e.g yeast maltase attacks only α –glycosides while almond emulsion is specific for ß - glucosides

4. Next step is to ascertain which hydroxyl group of the molecule acting as alcohol is involved in formation of glycosidic linkage.

This is done by completely methylating disaccharide.

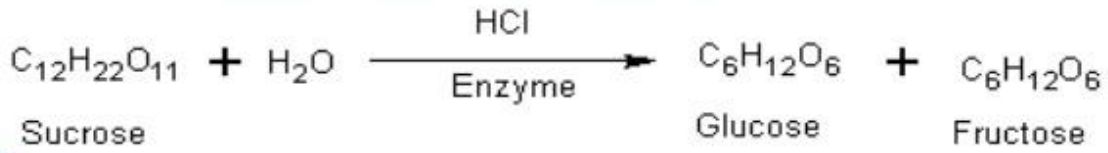
Methylated disaccharide is then hydrolyzed to yield methyleted monosaccharide's which are then identified by oxidation method

An alternative method for determining the position of glycosidic linkage is periodate oxidation.

5. Finally the structure is established by synthesis

STRUCTURAL ELUCIDATION OF SUCROSE

- Sucrose is the commonest sugar known. The most common sources are sugar cane and sugar beets and other sources are maple saps, honey and fruit juices.
- The use of sugar is as food in various forms.
- The molecular formula is $C_{12}H_{22}O_{11}$
- On hydrolysis with acids or enzymes, sucrose gives equal parts of glucose and fructose; which thus constitute the two monosaccharides units of sucrose.

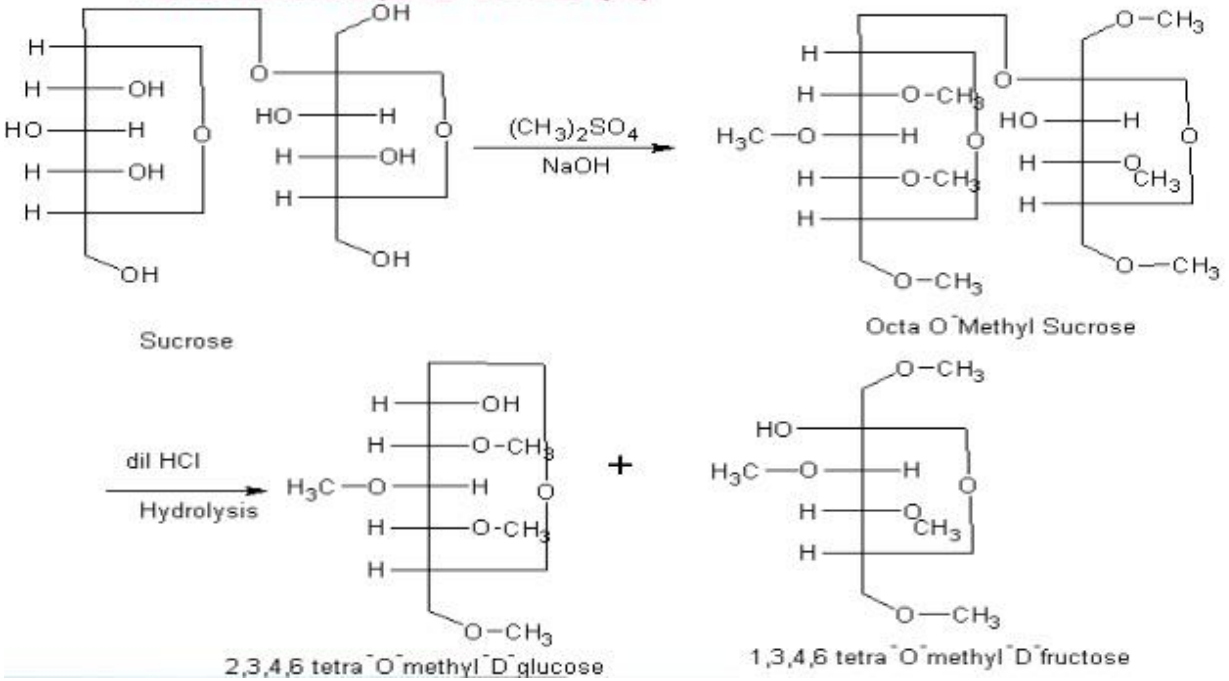


$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Enzyme}]{\text{HCl}} C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose — Glucose — Fructose

- Sucrose neither reacts with phenylhydrazine nor reduce Fehling's solution indicating that the carbonyl group of the both monosaccharides involved in linkage.
- The glucose linked via its C_1(-CHOH) to the C_2(OH)CH_2-C(OH) of fructose.
- Sucrose is hydrolysed by maltase but not by emulsin , thus indicating an alfa-D -glucose unit.
- Sucrose is also hydrolysed by an enzyme takainvertase thus indicates the beta-D-fructofuranose unit in sucrose.

- The identities of these products demonstrate that the glucose portion is a pyranoside(1:5 linkage) and that the fructose portion is a furanoside(2:5 linkage)

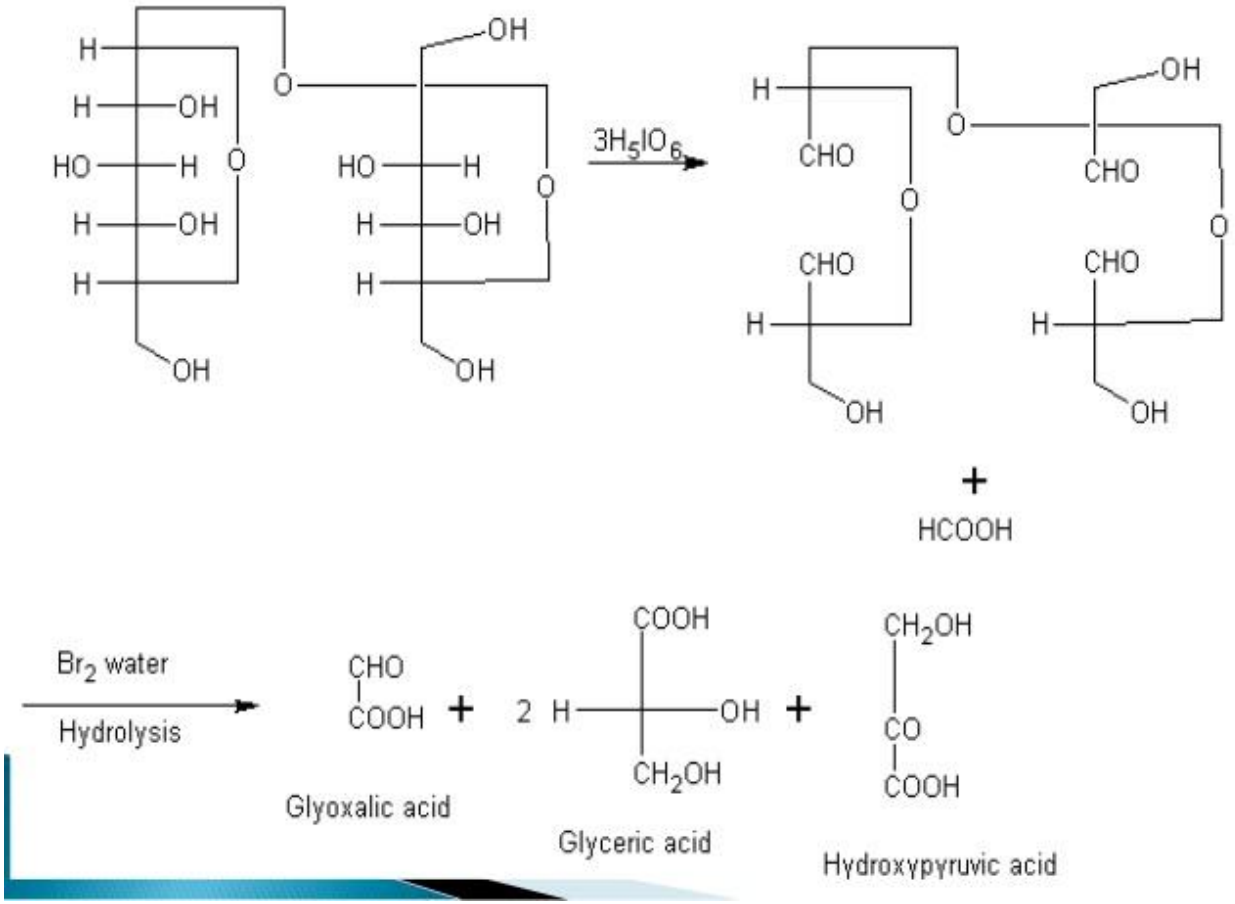


Periodic acid method :

- Periodate oxidation conforms the structure of sucrose by following reaction.

- When sucrose is treated with three moles of periodic acid , one mole of formic acid and one mole of a tetra-aldehydes are formed .

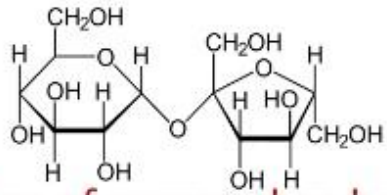
- The Latter compound on oxidation with bromine water follwed by acid hydrolysis yields a mixture of glyoxylic , glyceric and hydroxypyruvic acids.


$3H_5IO_6$
HCOOH
Br_2 water
Hydrolysis
Glyoxalic acid
Glyceric acid
Hydroxypyruvic acid

Confirmation of Sucrose

- The structure of sucrose has been confirmed by several physical and chemical evidences.

- Determination of stereochemistry of D-glucoside and D-fructoside linkage is complicated by the fact that both linkages are hydrolyzed at the same time.



- The structure of sucrose has been confirmed by X-ray analysis
- The X-ray analysis of susrose sodium bromide dihydrate confirmed the stereochecal configuration found chemically ,and also the five membered ring of fructose.

Structure Determinatin of (+) Maltose

- Experimental Facts
- $C_{12}H_{22}O_{11}$
- Positive for Tollens and Fehlings solution, reducing sugar
- Reacts with phenylhydrazine to yield osazone, $C_{12}H_{20}O_9(NNHC_6H_5)_2$
- Oxidizes by bromine water to monocaboxylic acid.
- Exists in two forms which undergo mutarotation.

Consistent with two aldoses linked together with one hemiacetal group.

More data…..

- Maltose undergoes hydrolysis with aq. acid or maltase to yield two D (+) glucose units. Two glucose units joined together: glucose – acetal linkage (glucoside) – glucose – hemiacetal.
- Maltase hydrolysis is characteristic of α glucosides. Conclude something like

CH_2O

How to proceed…..

Label the rings and label the free OH groups.

Next Slide

Hydrolysis products

Point of attachment to the other glucose unit.

Used in hemiacetal link.

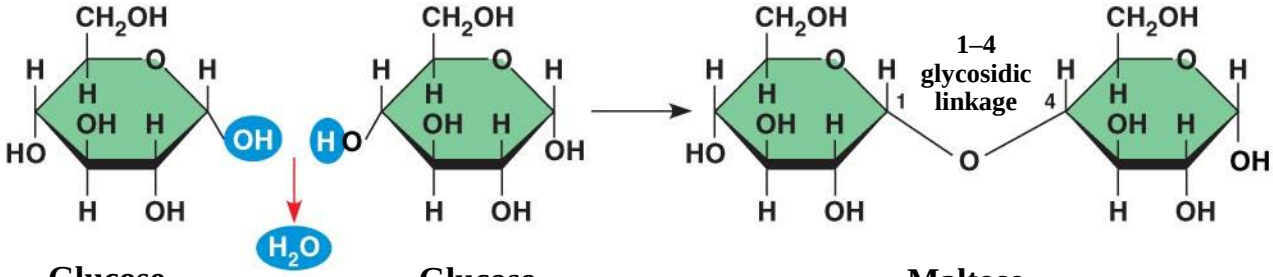
Not the reducing aldohexose unit (not the carboxylic acid).

This glucose derivative was the “free” CHO unit, the reducing sugar.

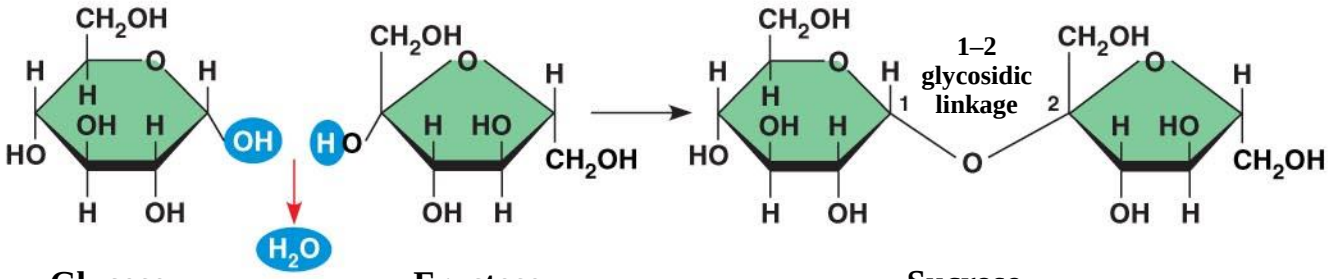
Structure on next slide.

Maltose

(a) Dehydration reaction in the synthesis of maltose

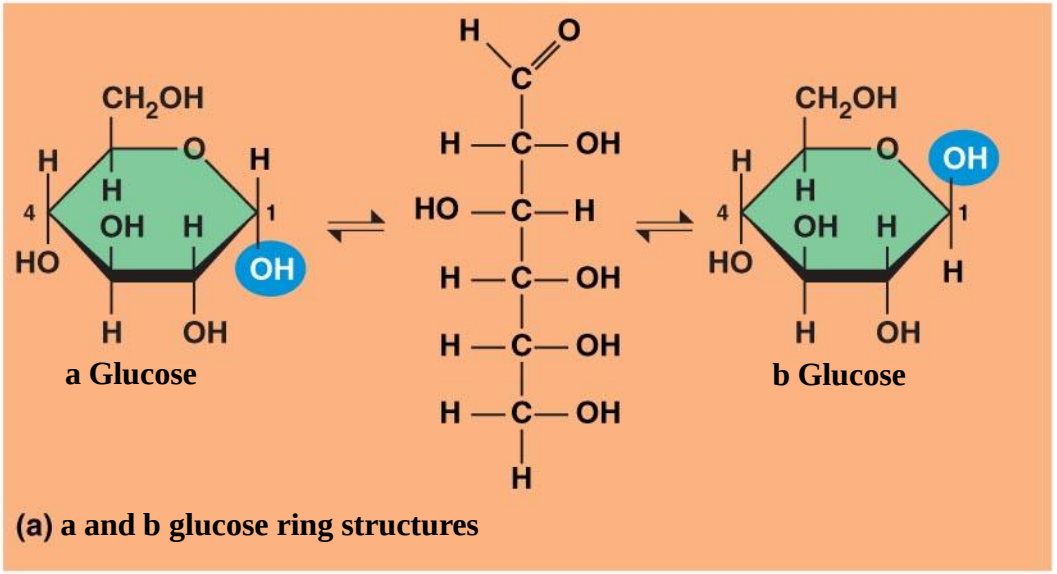


(b) Dehydration reaction in the synthesis of sucrose

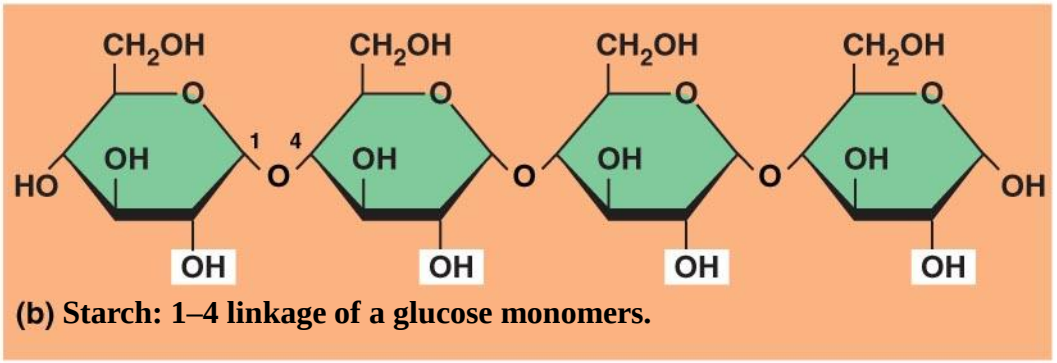


Starch

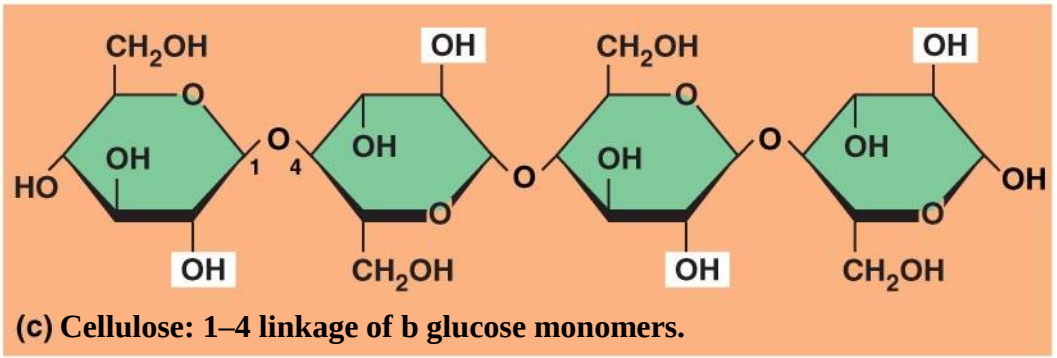
- Starch is used for energy storage in plants
  - It can be separated into two fractions; amylose and amylopectin; each on complete hydrolysis gives only D-glucose.
  - **Amylose**: A polysaccharide composed of continuous, unbranched chains of up to 4000 D-glucose units joined by α-1,4-glycosidic bonds.
  - **Amylopectin**: A highly branched polymer of D-glucose; chains consist of 24-30 units of D-glucose joined by α-1,4-glycosidic bonds and branches created by α-1,6-glycosidic bonds.



(a) a and b glucose ring structures



(b) Starch: 1–4 linkage of a glucose monomers.



(c) Cellulose: 1–4 linkage of b glucose monomers.

Glycogen

- Glycogen is the reserve carbohydrate for animals.
  - Like amylopectin, glycogen is a nonlinear polymer of D-glucose units joined by α-1,4- and α-1,6-glycosidic bonds bonds.
  - The total amount of glycogen in the body of a well-nourished adult is about 350 g (about 3/4 of a pound) divided almost equally between liver and muscle.

Cellulose

- Cellulose: A linear polymer of D-glucose units joined by β-1,4-glycosidic bonds.
  - It has an average molecular weight of 400,000 g/mol, corresponding to approximately 2800 D-glucose units per molecule.
  - Both rayon and acetate rayon are made from chemically modified cellulose.

Thank You