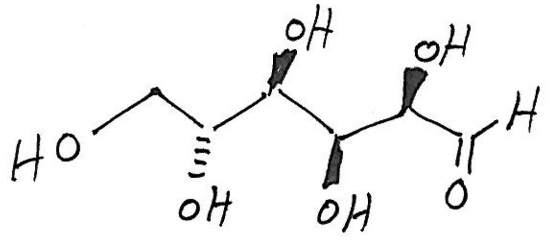
Chapter 23: Structure and Reactivity in Biological Molecules

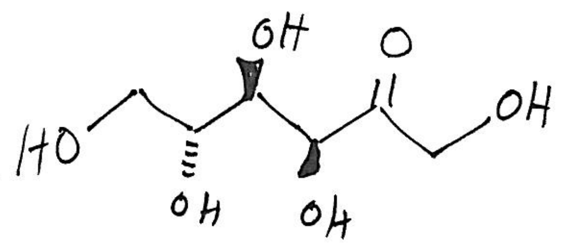
Carbohydrates: polyhydroxy aldehydes or ketones and compounds that hydrolyze to them

→ term arose because most sugars have molecular formulas of $C_n(H_2O)_n$

ex:



glucose - open chain form
- an aldohexose
  - ald (aldehyde)
  - hex (6-carbons in the chain)
  - ose (a sugar)



fructose - open chain form
- a ketohexose
  - keto (ketone)
  - hex (6-carbons in the chain)
  - ose (a sugar)

Definitions:

Monosaccharides - carbohydrates that can not be hydrolyzed to simpler cmpds

disaccharides - 2 monosaccharide units linked together

oligosaccharides - made up of about 3-10 monosaccharide units

lysaccharides - MANY monosaccharides linked together
↓
are biopolymers

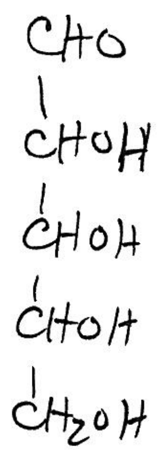
ex: starch $\xrightarrow[\Delta]{H_3O^+}$ glucose (<1000)

cellulose $\xrightarrow[\Delta]{H_3O^+}$ glucose (>1000)

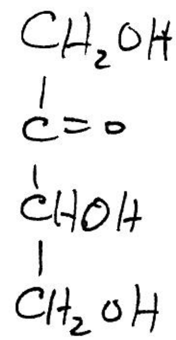
Classification of Monosaccharides

1) Whether sugar has a ketone or aldehyde
2) The # of carbon atoms in the carbon chain
3) The stereochemical configuration of the carbon atom furthest from the carbonyl group (we will talk more about later)

ex.



an aldopentose

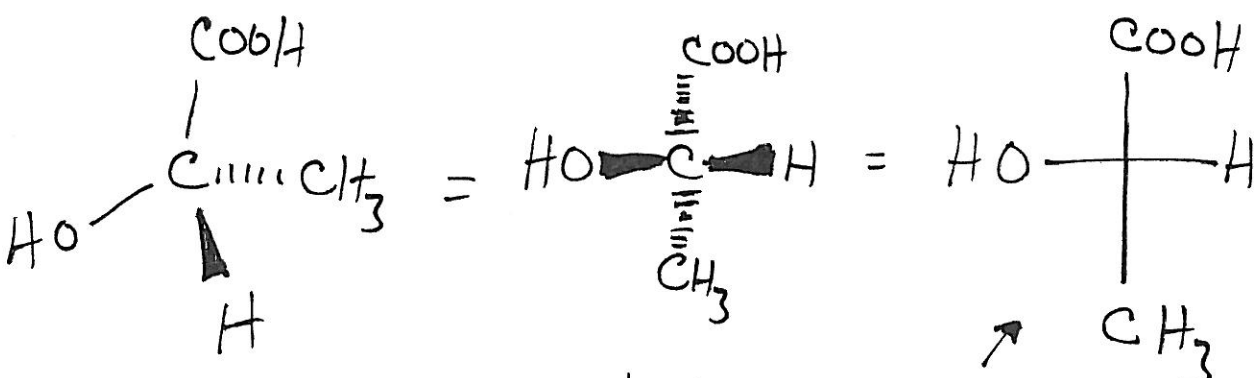


a ketotetrose

Fischer Projections

"Bowtie" convention

looks like cross, with chiral carbon at the point where the lines cross



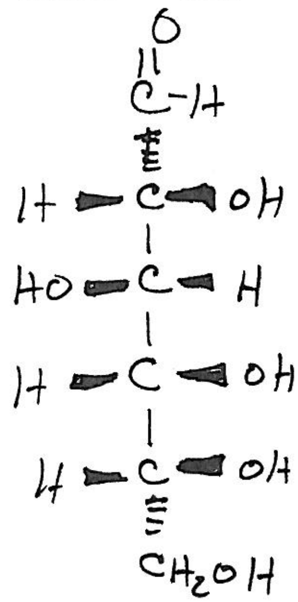
S-lactic acid

- horizontal lines taken as wedges;
- vertical lines taken as dashes (project away from viewer)

- A Fischer projection must be kept in the plane of the paper and can only be rotated by 180°. (can <u>not</u> rotate them 90° or turn them over)

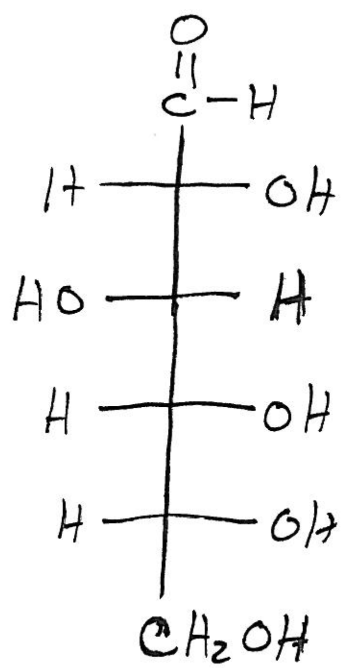
- The carbon chain of a Fischer projection is drawn <u>along</u> <u>the</u> <u>vertical</u> <u>line</u> with the most highly oxidized carbon at the top (or nearest the top).

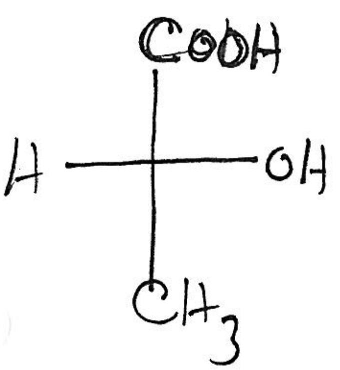
Glucose



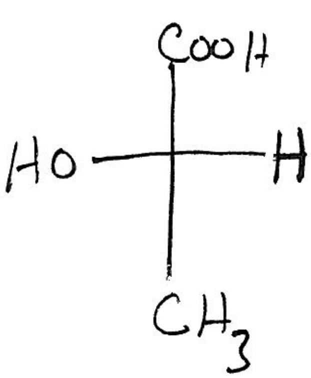
≡

Fischer Projection of Glucose



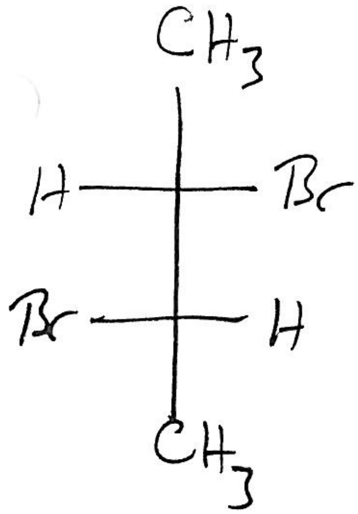


R-lactic acid



S-lactic acid

- When a mirror image of a Fischer projection is drawn, the image <u>can</u> <u>be</u> an enantiomer of the original



Draw the mirror image

Are these molecules enantiomers?

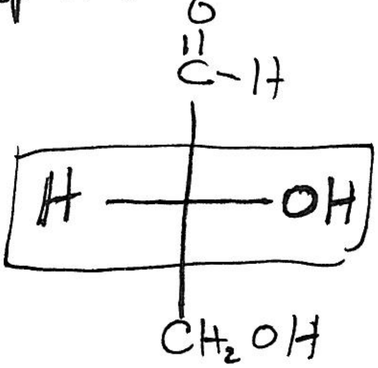
rotate 180°

- rotate mirror image 180°. Does it superimpose?

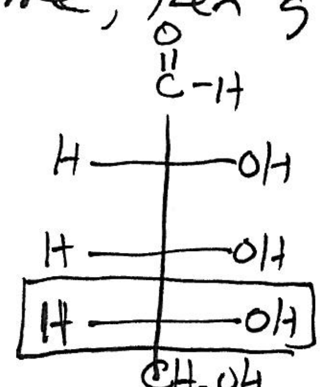
- Can assign R or S configuration to chiral centers in Fischer projections (remember, horizontal lines – groups sticking out; vertical lines – groups sticking back)

- **Designations of Chiral Compounds as D or L**
  - only used for carbohydrates and amino acids
  - last chiral center in carbohydrate chain compared with configuration of D-(+)-glyceraldehyde if the same, then given D-configuration name

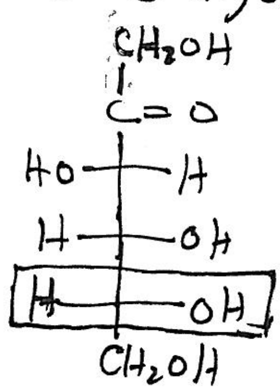
ex: (p978)



D-(+)-glyceraldehyde

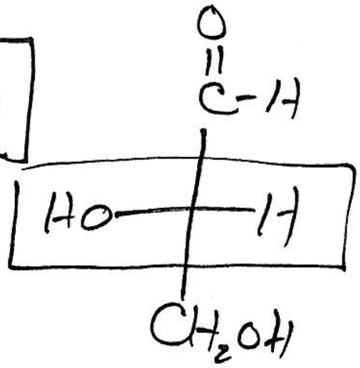


D-(-)-ribose

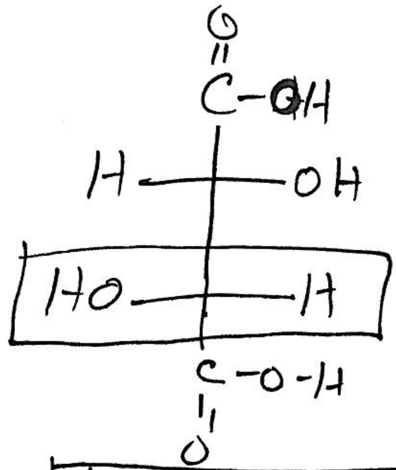


D-(-)-fructose

L-family



L-(-)-glyceraldehyde

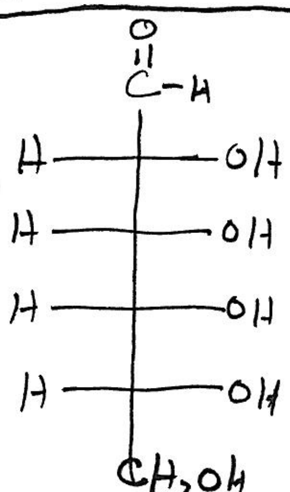


L-(+)-tartaric acid

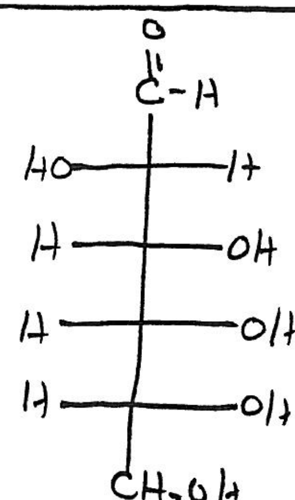
Nomenclature of Monosaccharides

→ need to know The D-hexose family (but nothing else in This section 23.2 D)

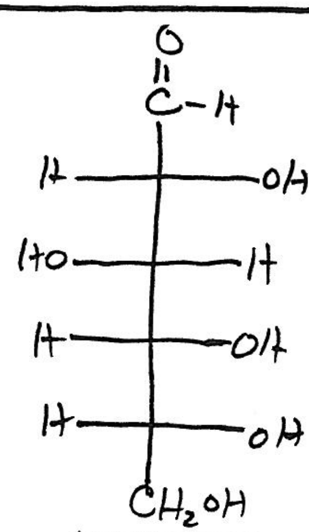
All Altruists Gladly Make Gum In Gallon Tanks



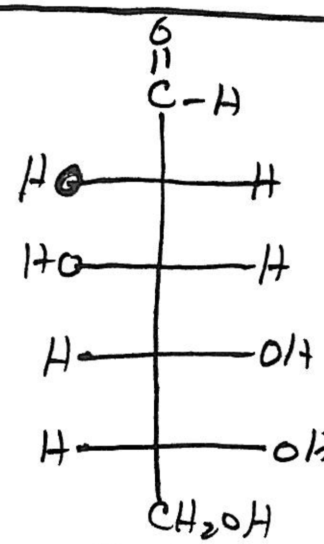
D-allose (All)



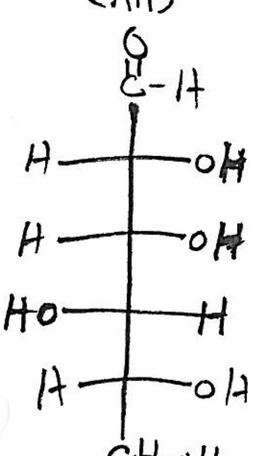
D-altrose (Altruists)



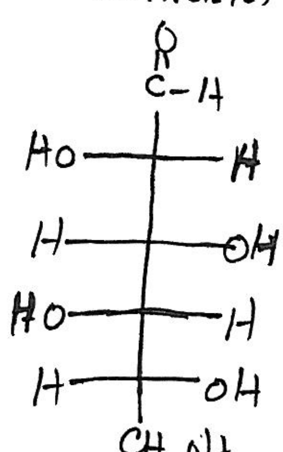
D-glucose (Gladly)



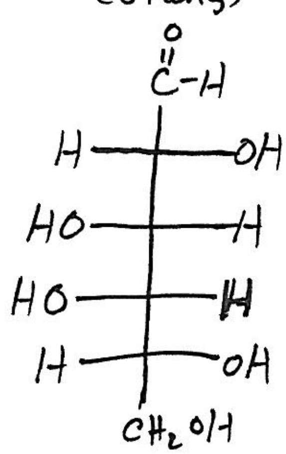
D-mannose (make)



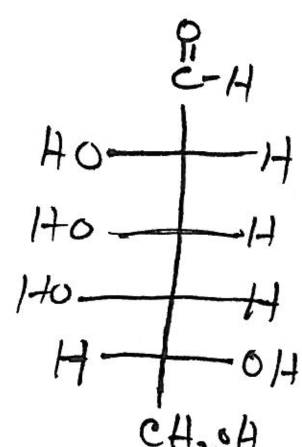
D-gulose gum



D-idose in



D-galactose gallon



D-talose tanks

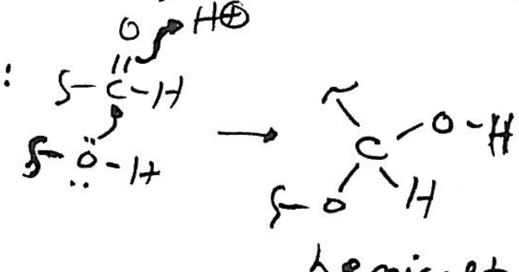
- Let's practice drawing the D-hexose family Fischer projections.

Haworth Projection Formulas. The Cyclic Hemiacetal Forms of Glucose

Glucose → an aldohexose (contains an aldehyde + five O-H groups)

→ remember that glucose can form a number of different cyclic hemiacetals

(hemiacetals:



)

- α + β-D-glucopyranose; α + β-D-glucofuranose (See p 567 in text; Ch. 14 section 8)

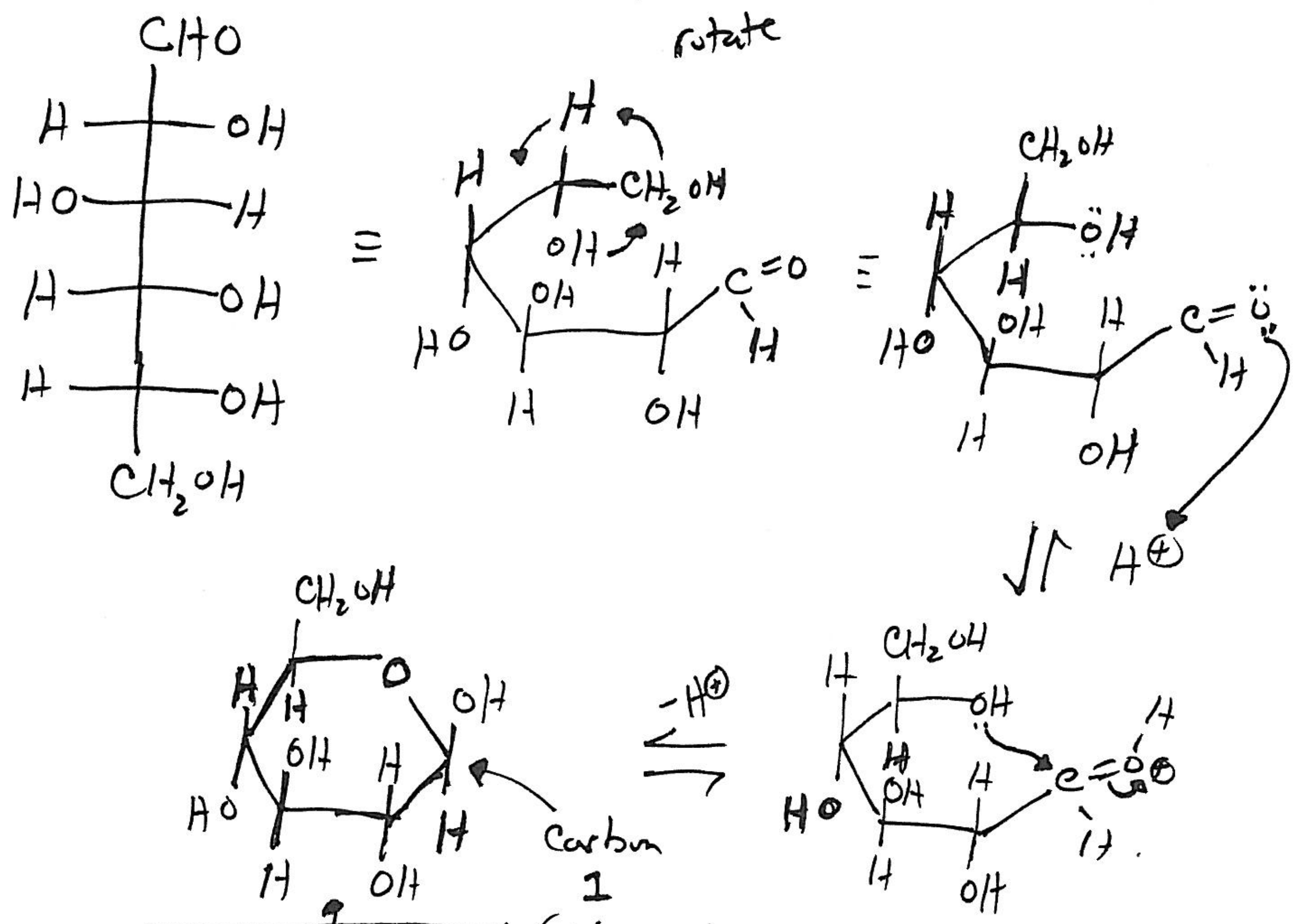
- We can draw the chair form of pyranose rings or use the line-wedge-dash convention for 5-membered furanose rings. However, we can also draw the cyclic hemiacetal forms of D-hexoses with **HAWORTH PROJECTIONS**

1. Lay the Fischer projection on its right side. (Groups on the right side are down + groups on the left are up).

2. C5 + C6 curl away back from you. The C4–C5 bond must be rotated so that the C5 hydroxyl group can form part of the ring. (Put C-6 in glucose + other D-series sugars upward).

Fischer Projection of Open Chain form of D-Glucose

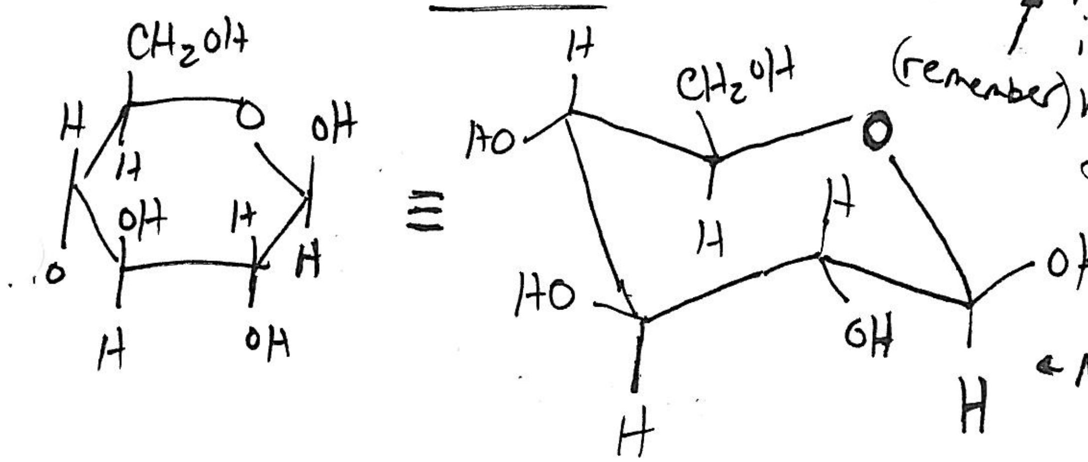
• Lay Fischer projection on its right side; C5-C6 curl away back from you. Rotate so that C6 $-CH_2OH$ is up.



Haworth Projection of D-Glucose

O-H group can be up or down at C1

Pyranose form



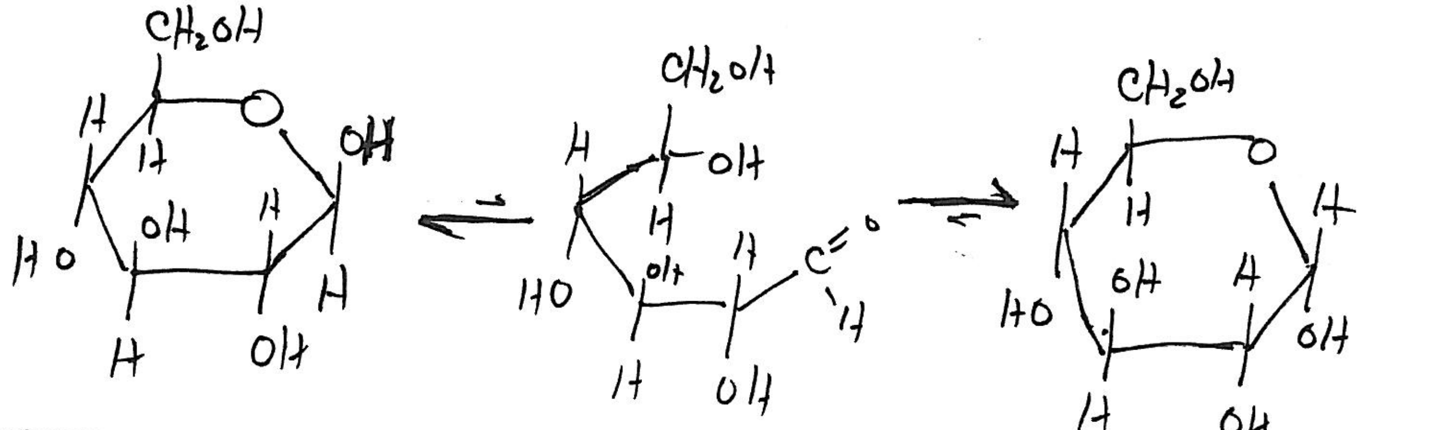
• A monosaccharide (remember) in its 6-membered ring cyclic hemiacetal form is called a **PYRANOSE**

← Note: all OH groups equatorial

- Remember:

If the C1 OH group is UP on a Haworth Projection it is a β-pyranose; if the C1 O-H group is DOWN its a α-Pyranose.

(6-membered ring — Haworth)

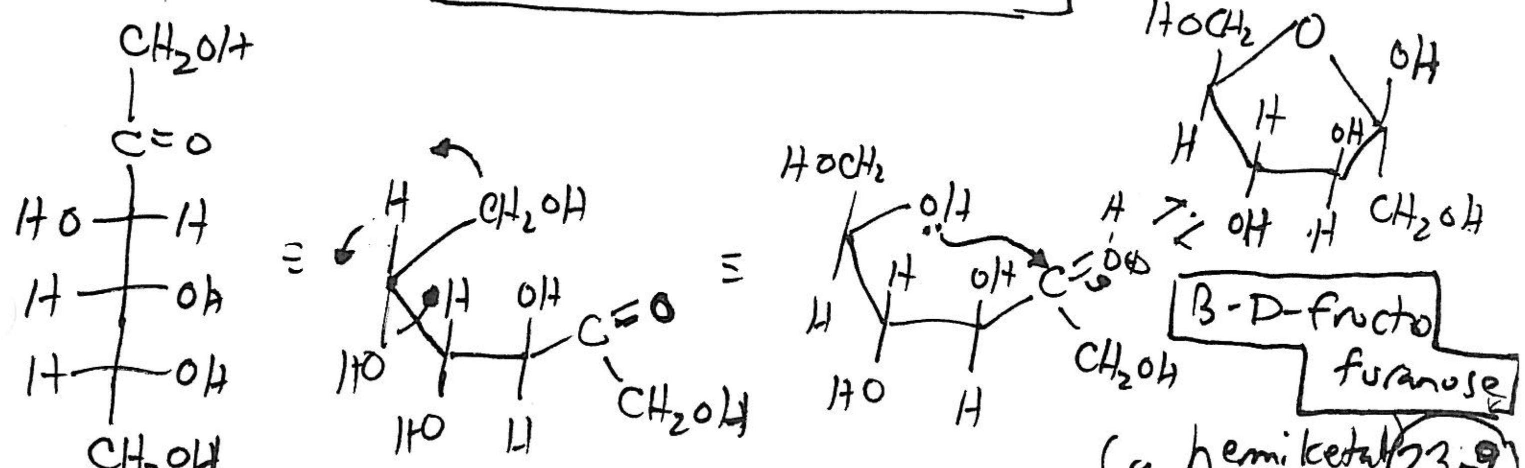


β-D-glucopyranose | open chain form of glucose | α-D-glucopyranose

- α & β-D-glucopyranose and open chain glucose forms are in equilibrium in soln (majority is in closed ring forms)

Recall: A 5-membered ring cyclic hemiacetal is called a **FURANOSE**

D-Furanose Form of Fructose



D-Fructose

β-D-fructofuranose

(a hemiketal)

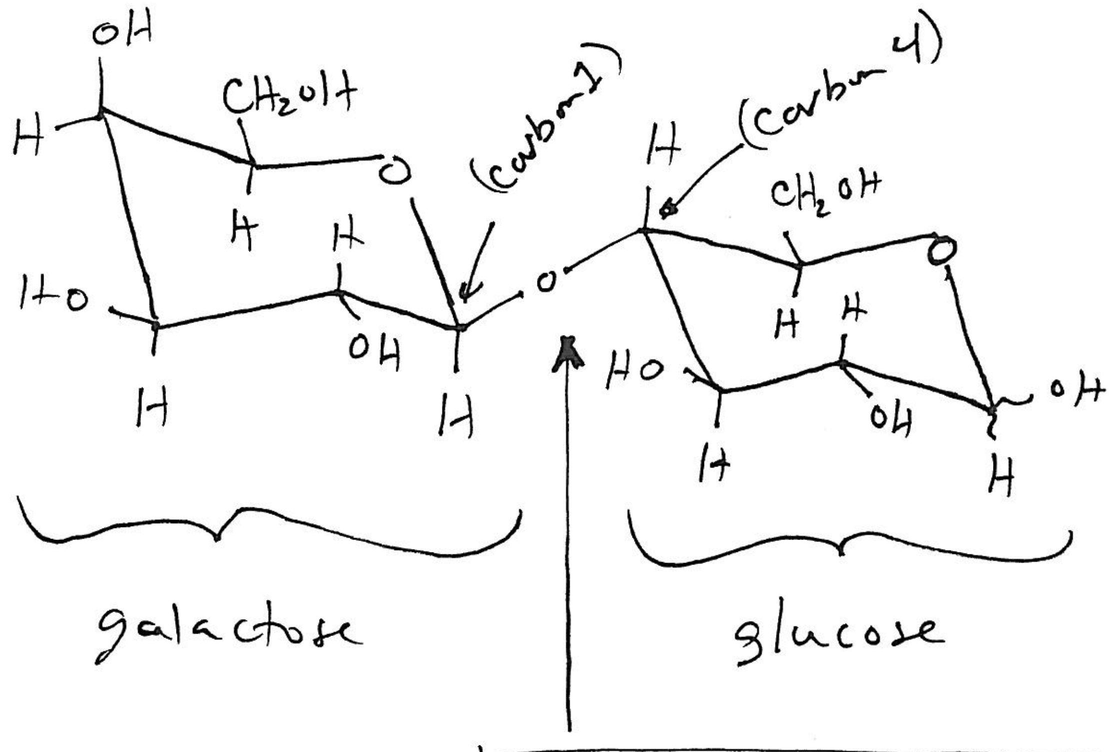
- Draw the Haworth projection of α-D-galactopyranose

- Draw the Haworth projection of β-D-glucofuranose

23.5 Oligosaccharides

(A) Lactose

- found in milk
- made from glucose and galactose with monosaccharides linked together by a glycosidic linkage



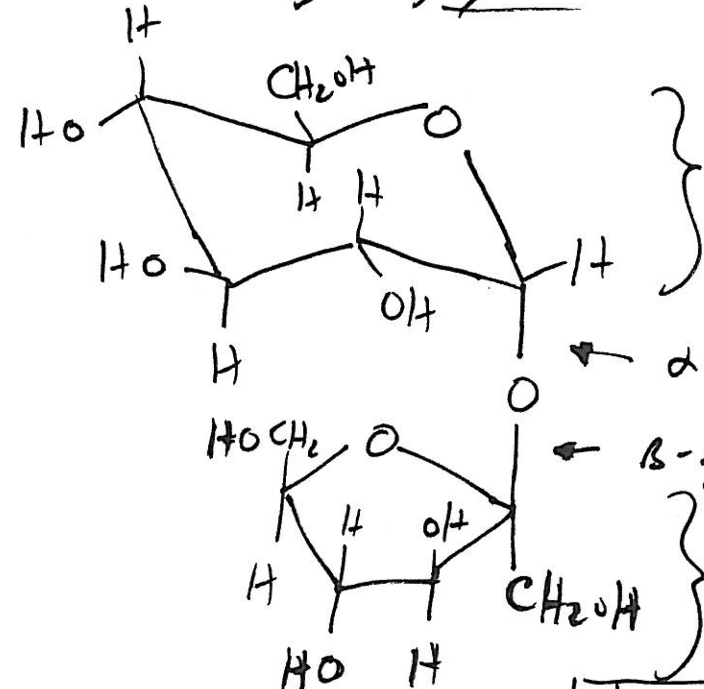
β-glycosidic linkage from C1 of galactose to C4 of OH group of glucose

- need β-galactosidase enzyme (also called "lactase") to hydrolyze lactose into glucose + galactose

23.5 • Skip - maltose + cellobiose (23.5 (B))

(C) **Sucrose** - found in plants

- made from glucose and fructose with monosaccharides held together by a glycosidic linkage.



23.7

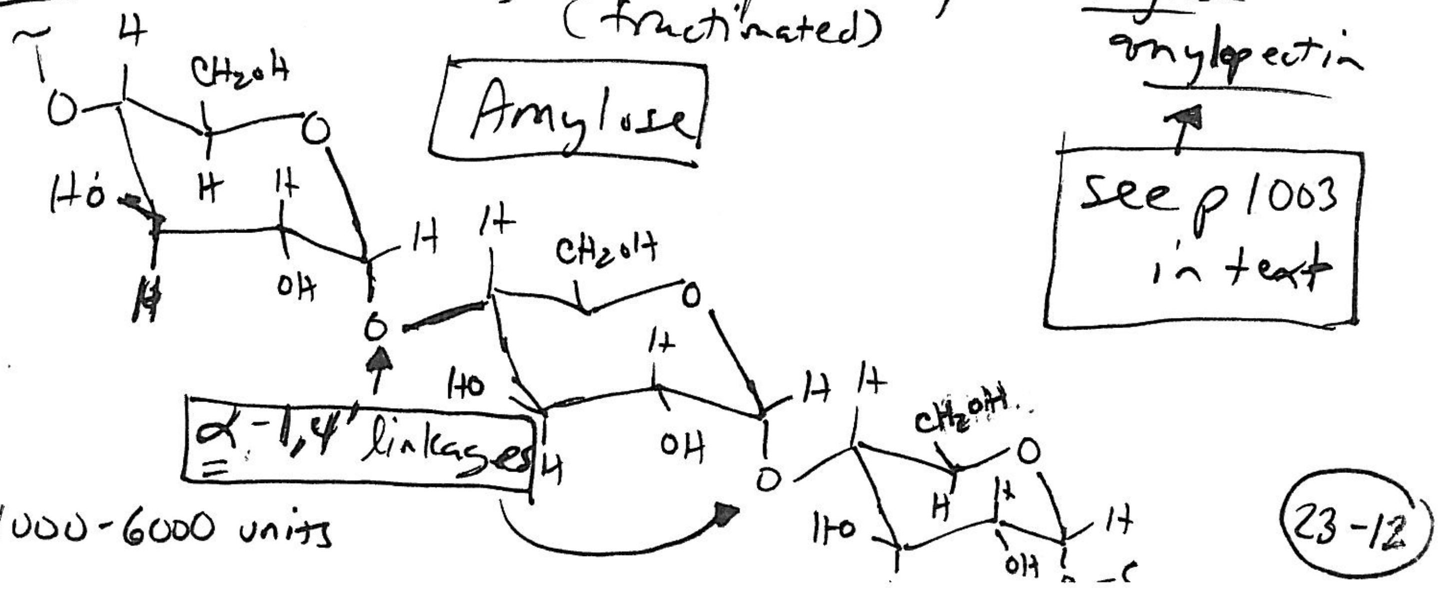
Polysaccharides

• when sucrose is hydrolyzed, resulting glucose/fructose mixture is sweeter because fructose sweeter than sucrose

(A) **Starch** - found in plants (how plants store energy)

made up of D-glucose

- can be hydrolyzed partially to amylose + amylopectin (fractionated)



Amylose

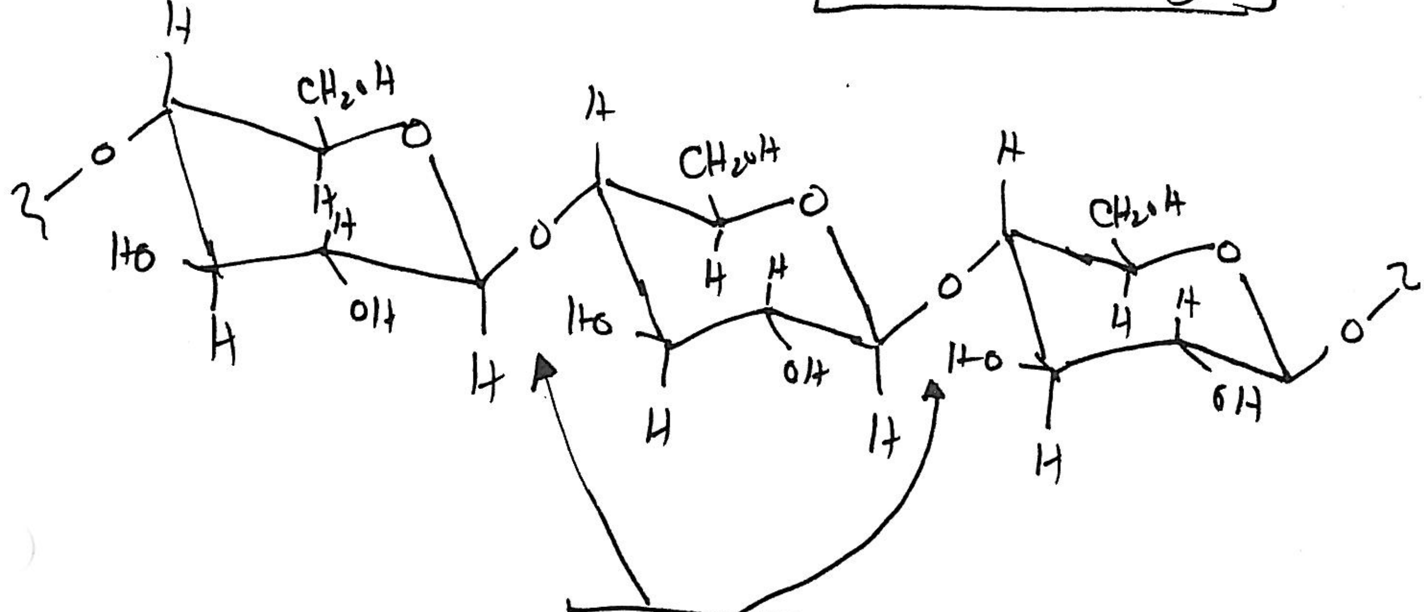
see p 1003 in text

• 1000-6000 units

23.7(B)

Cellulose

- most abundant organic material
- found in trees and cotton
- Composed of D-glucose linked together by **β-1,4' linkages**



β-1,4' linkages

- Humans and other mammals lack enzyme needed to hydrolyze cellulose, therefore they can not use it for food.

- Some animals (termites + cows, for instance) maintain colonies of bacteria in their stomachs + intestines that can hydrolyze cellulose → so these animals can get energy from cellulose containing materials (like hay)