Lecture 29 (12/3/21)

TODAY

•Reading: Ch7; 220-235

•Problems: Ch7; 1,2,3,5,9

NEXT

•Reading: Ch7; 236-241, 251-254, 258-260
Ch7; 241-250

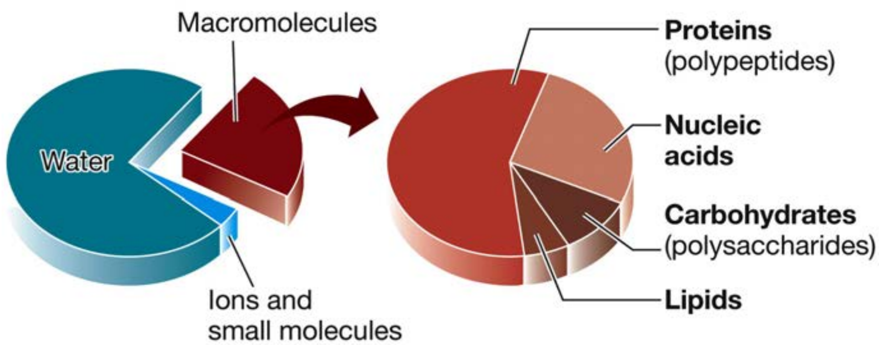
•Problems: Ch7; 4,6,7,8,13,14,15,18
Ch7; 16,17,25,27

Carbohydrates

A. Definition
B. Roles
C. Monosaccharides-Chemistry
   1. Chirality
      a. One or more asymmetric carbons
      b. Linear and ring forms
   2. Derivatives: the chemistry of carbohydrates
      a. Oxidation
         i. C1
         ii. C6
      b. Reduction
         i. C1/C2
         ii. Other carbons
      c. Ester formation
      d. Amino sugars
   3. Polymerization
      a. The Glycosidic Bond
      b. Non-covalent bonds in macro-molecular structure
D. Oligosaccharides
   1. Glycoproteins & glycolipids
   2. O-linked
   3. N-linked
   4. Sequence determination-ABO
E. Polysaccharides
   1. Polymers of glucose
   2. Polymers of disaccharides

Carbohydrates

Carbohydrates



Carbohydrates

Definition

- Carbo-Hydrate: have formula $C_n(H_2O)_n$ (for $n \geq 3$)
- The precursor-macromolecule relationship is:
  - Monosaccharide–polysaccharide (or oligosaccharide)
- Carbohydrates are everywhere (ubiquitous) and versatile in function; fulfill a variety of functions.
  - Can be covalently linked with proteins and lipids; are intimately involved in nucleic acids

	ROLES	Monosaccharide	Polysaccharide
1.	Energy source/storage	glucose, fructose, etc.	Starch, glycogen
2.	Structure	glucose, *glycerol*	Cellulose, chitin, lipids & membranes
3.	Information	ribose (nucleotides)	Nucleic acids
4.	Recognition	many	Glycolipids & glycoproteins

Carbohydrates

The 4 S's

Size — Range from as small as glyceraldehyde (M_w = 90 g/mol) to as large as amylopectin (M_w > 200,000,000 g/mol)

Shape — Depends on size and glycosidic bond

Solubility — Very polar, very soluble, until large polymers

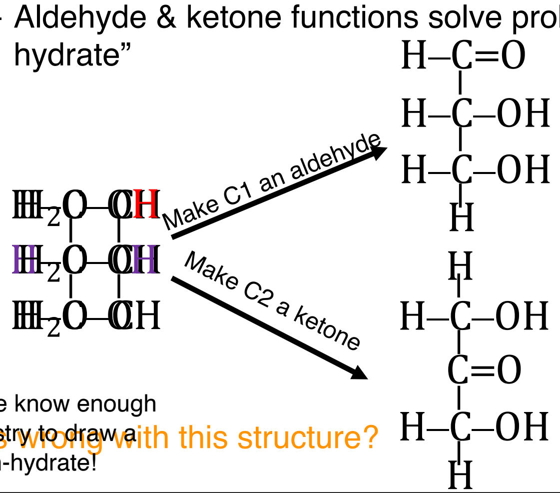
Stability — Stable due to glycosidic bond

Carbohydrates

Monosaccharides

$C_3(H_2O)_3$

- Basic nomenclature:
  - Use the suffix "-ose" — triose, tetrose, pentose, hexose
  - Aldehyde & ketone functions solve problem of a "carbo-hydrate"



= aldoses

aldotriose (triose), aldotetrose(tetrose), aldopentose, aldohexose

= ketose

Ketotriose (triulose), ketotetrose (tetrulose)… (pentulose, hexulose).

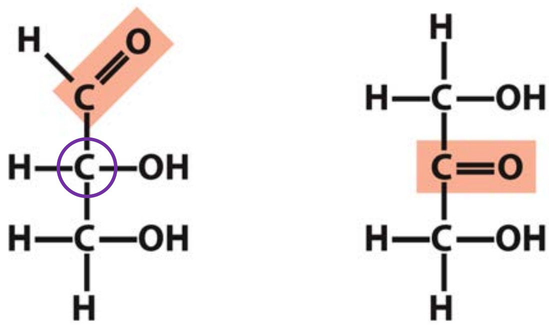
OK, we know enough chemistry to draw a carbon-hydrate!

What is wrong with this structure?

Carbohydrates

Monosaccharides

- An aldose is a carbohydrate with aldehyde functionality.
- A ketose is a carbohydrate with ketone functionality.



Glyceraldehyde, an aldotriose

Dihydroxyacetone, a ketotriose

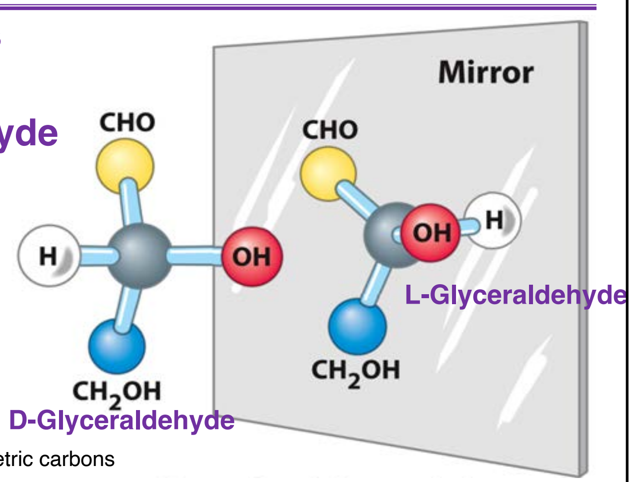
Figure 7-1a
Lehninger Principles of Biochemistry, Seventh Edition

Are there any chiral carbons?

Carbohydrates

Monosaccharides

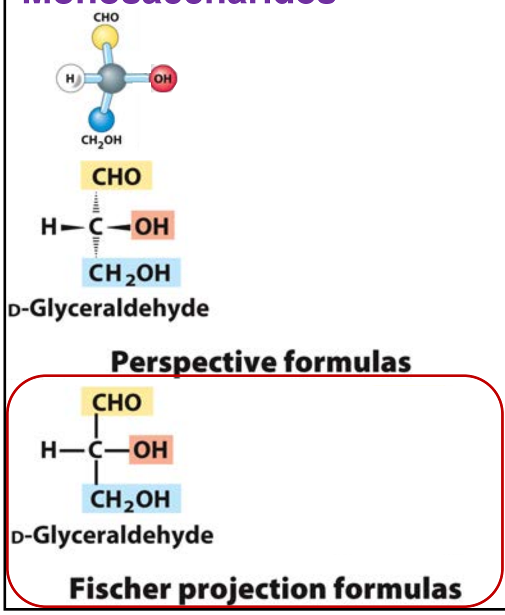
Glyceraldehyde



- Chemical Features:
  - Chirality
    - One or more asymmetric carbons
    - Linear and ring forms
  - Derivatives: the chemistry of carbohydrates
  - Polymerization
    - The Glycosidic Bond
    - Non-covalent bonds in macro-molecular structure

Carbohydrates

Monosaccharides



Fischer projections

- Vertical bonds are between carbons, with highest oxidation state at the top, AND project away from you.
- Horizontal bonds are pointing toward you.
- If hydroxyl is on the left; its **L**
- If hydroxyl is on the right; its **D**
- Here D=R & L=S

It turns out that the L form of glyceraldehyde is called L because it is "levorotary," meaning it will rotate plane-polarized light to the left, or counter-clockwise. D rotates "dextrorotary."

Carbohydrates

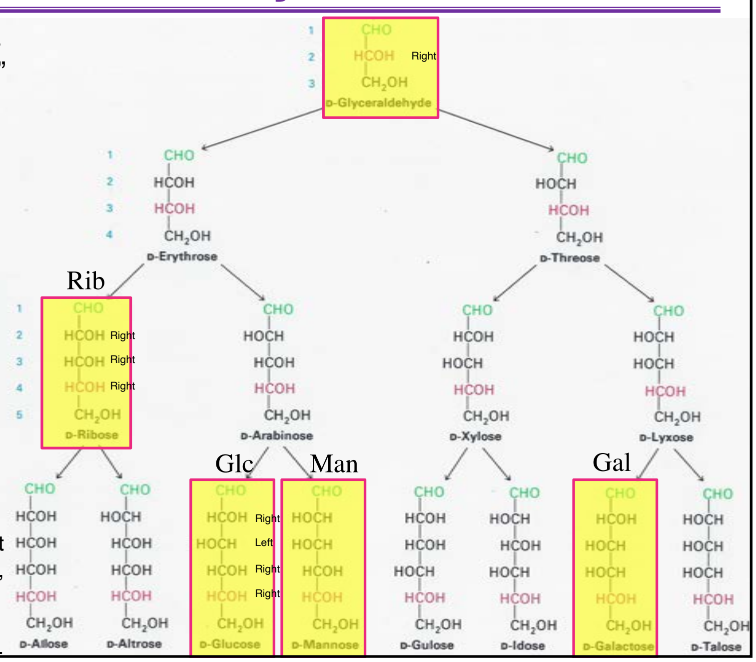
GREEN =functional group
RED=highest numbered chiral carbon

Nearly all sugars in biology are "D" (sort of like most amino acids are "L").

As you go to tetrose, pentose, etc., you are adding more chiral carbons.

A D- or L-sugar is defined by the chirality of the highest numbered carbon.

Another complete set of 15 L-aldoses exist, and are enantiomers of their D-aldose relatives shown here.



Carbohydrates

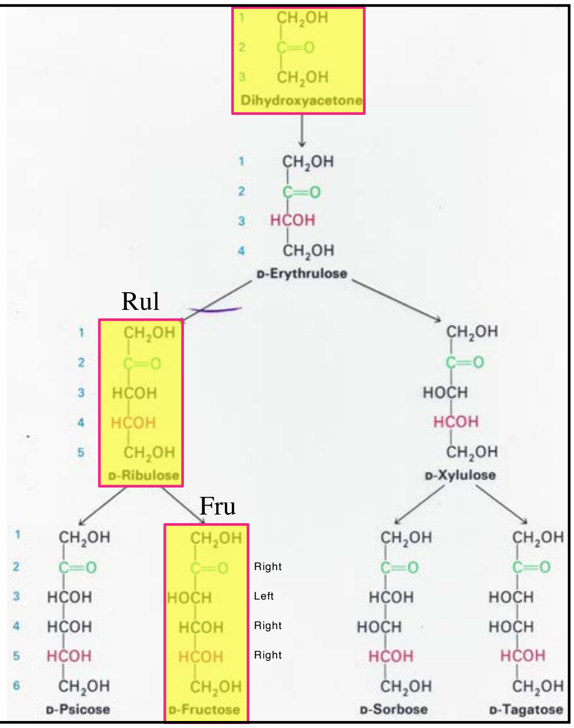
D-ketoses

The first chiral sugar is a tetrulose.

There is also another complete set of 7 L-ketoses exist, and are **enantiomers** of their D-ketose relatives shown here.

Fructose is the ketose form of glucose

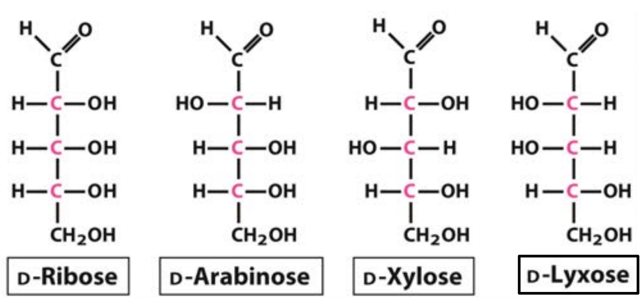
Ribulose is the ketose form of ribose



Carbohydrates

Monosaccharides: Stereoisomer Nomenclature

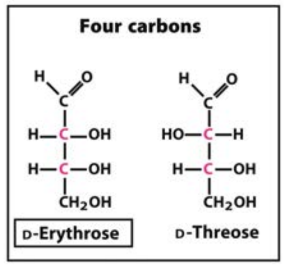
- Enantiomers
  - stereoisomers that are nonsuperimposable **complete** mirror images
  - Example: D-sugars & L-sugars
- Diastereomers
  - stereoisomers that are not complete mirror images
  - Diastereomers have different physical properties (e.g., water solubility)
  - Example:



Carbohydrates

Monosaccharides: Stereoisomer Nomenclature

- Epimers
  - Epimers are stereoisomers that differ at only **one** chiral center
  - Epimers are diastereomers; diastereomers have different physical properties (i.e., water solubility, melting temp)
  - Example:

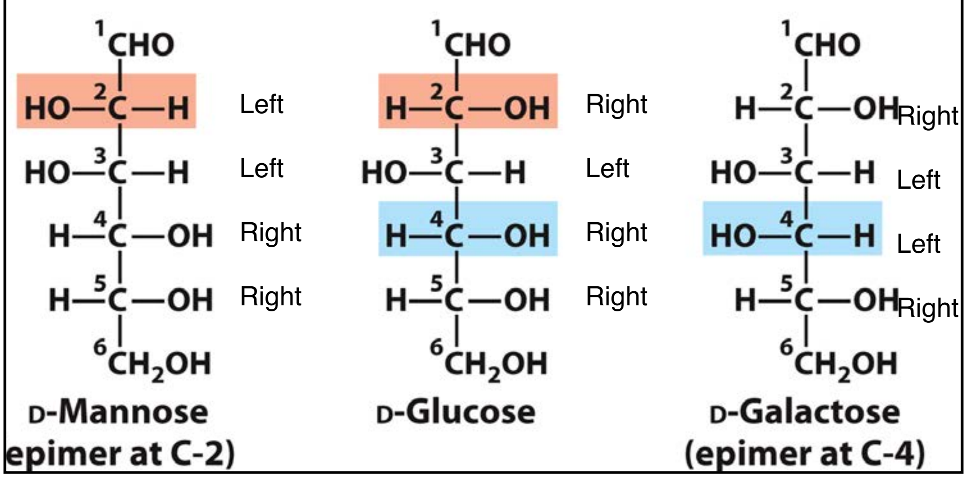


  - Glc & Man (2 epimer); Glc & Gal (4 epimer); Rib & Ara; Rib & Xyl
- Anomers
  - Anomers have different chirality at carbon involved in ring formation

Carbohydrates

Monosaccharides: Stereoisomer Nomenclature

- D-Mannose and D-galactose are both epimers of D-glucose.
- D-Mannose and D-galactose vary at more than one chiral center and are diastereomers, but <u>not</u> epimers.



Carbohydrates

Monosaccharides: The most important sugars

- Glyceraldehyde and dihydroxyacetone are the simplest (3 carbon) aldose and ketose, respectively.
- Ribose (Rib) is the standard five-carbon sugar.
- Glucose (Glc) is the standard six-carbon sugar.
- Galactose (Gal) is an C4-epimer of glucose.
- Mannose (Man) is an C2-epimer of glucose.
- Fructose (Fru) is the ketose form of glucose.
- Ribulose (Rul) is the ketose form of ribose.

Need to know, recognize, draw Fisher Projection, name, abbreviate

Carbohydrates

Monosaccharides: Stereoisomer Nomenclature

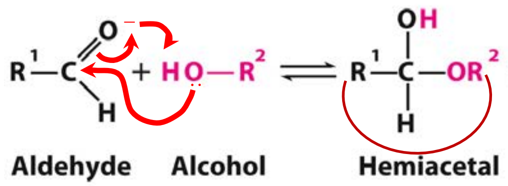
- Enantiomers
  - stereoisomers that are nonsuperimposable **complete** mirror images
  - Example: D-sugars & L-sugars
- Diastereomers
  - stereoisomers that are not complete mirror images
  - Diastereomers have different physical properties (e.g., water solubility)
  - Example: ribose & lyxose
- Epimers
  - Epimers are stereoisomers that differ at only **one** chiral center
  - Epimers are diastereomers; diastereomers have different physical properties (i.e., water solubility, melting temp)
  - Example:
  - Glc & Man (2 epimer); Glc & Gal (4 epimer); Rib & Ara; Rib & Xyl
- Anomers
  - Anomers have different chirality at carbon involved in ring formation

Carbohydrates

Monosaccharides: What are these “ring” forms?

- SUGARS WITH ≥5 CARBONS RAPIDLY AND STABLY FORM **RINGS** THROUGH HEMIACETAL (ALDOSES) AND HEMIKETAL (KETOSES) BONDS.

Hemiacetals

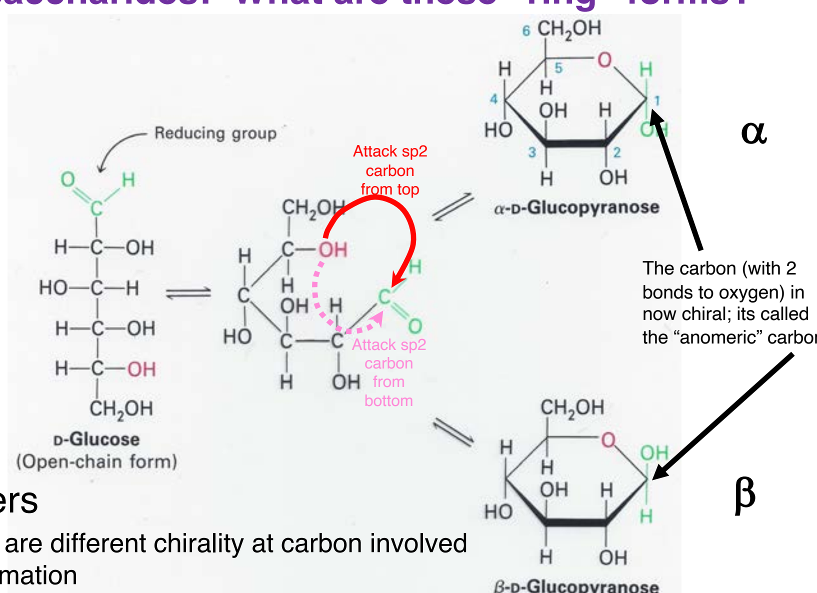


Not chiral   Chiral

- If the aldehyde (R^1) and the alcohol (R^2) are on the same molecule, you have a RING!
- Due to the oxygen, the ring is heterocyclic

Carbohydrates

Monosaccharides: What are these “ring” forms?



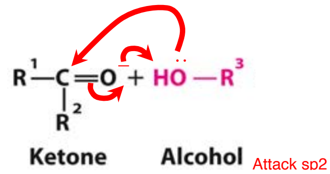
- Anomers
  - Anomers are different chirality at carbon involved in ring formation
  - These are designated α (OH down) or β (OH up)

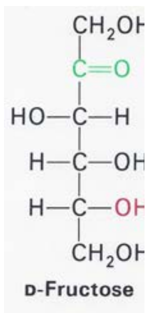
*for D-sugars

Carbohydrates

Monosaccharides: What are these “ring” forms?

Hemiketals





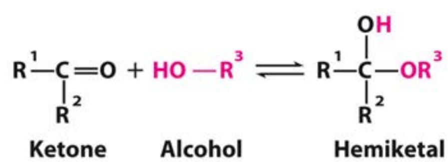
α (OH down) or β (OH up)

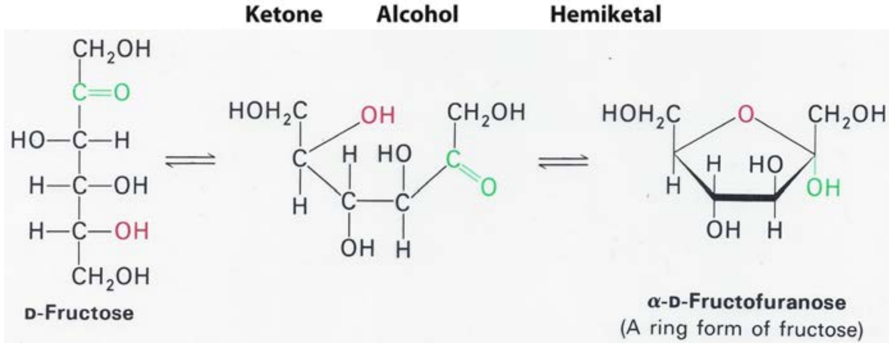
Besides the α & β, what is this pyran and furan?
Its all about which alcohols are used in these reactions.

Carbohydrates

Monosaccharides: What are these “ring” forms?

Hemiketals





α (OH down) or β (OH up)

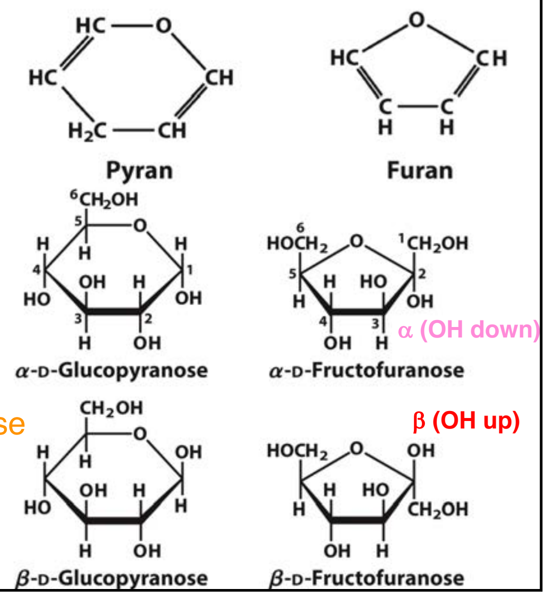
Besides the α & β, what is this pyran and furan?
Its all about which alcohols are used in these reactions.

Carbohydrates

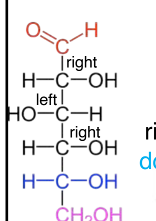
Monosaccharides: What are these "ring" forms?

- Six-membered oxygen-containing rings are called pyranoses after the pyran ring structure.
- Five-membered oxygen-containing rings are called furanoses after the furan ring structure.

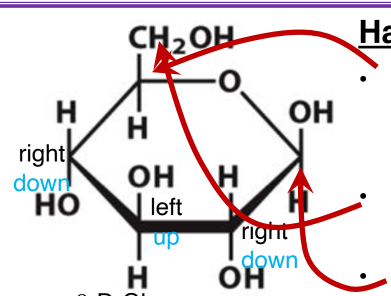
The way we are drawing these sugars is called a Haworth projection…..



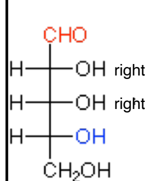
Carbohydrates



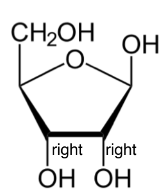
D-Glucose



β-D-Glucopyranose



D-ribose



β-D-Ribofuranose

Haworth projections

- Highest carbon with hemiacetal/hemiketal alcohol in back; oxygen to right.
- If chiral (as for D-sugars), next highest carbon up if D, or down if L.
- The anomeric carbon is usually drawn on the right side.
- Other chiral carbons are down if right in Fisher projection and up if left in Fisher
- β-D-Glc pyranose goes up, down, up down, up as you go from C5 to C1
- β-D-Rib furanose goes up, down, down, up as you go from C4 to C1

Carbohydrates

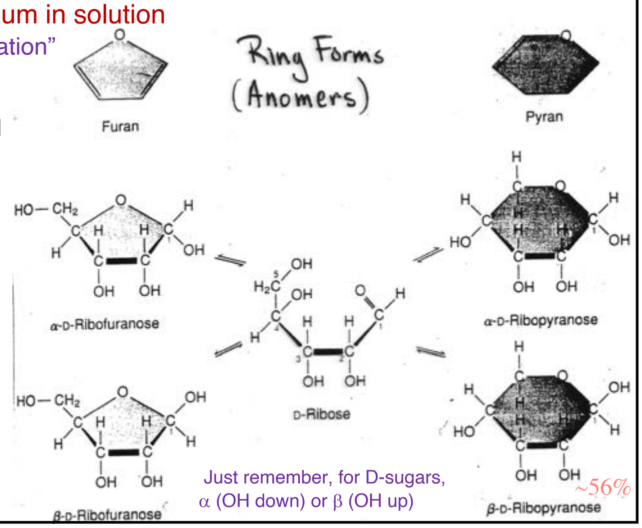
- Pentoses and hexoses readily undergo intramolecular cyclization.
- The former carbonyl carbon becomes a new chiral center, called the anomeric carbon.
- ALL forms are in equilibrium in solution

  Process is called "mutarotation"

  – When the former carbonyl oxygen becomes a hydroxyl group, the position of this group determines if the anomer is *α* or *β*.

  – If the hydroxyl group is on the opposite side (trans) of the ring as the CH_2OH moiety, the configuration is *α*.

  – If the hydroxyl group is on the same side (cis) of the ring as the CH_2OH moiety, the configuration is *β*.



Just remember, for D-sugars, α (OH down) or β (OH up)

Carbohydrates

Relative amounts of tautomeric forms for some monosaccharide sugars at equilibrium in water at 40°C[a]

Mono-saccharide	Relative Amount (%)				
	α-Pyranose	β-Pyranose	α-Furanose	β-Furanose	Total Furanose
➡ Ribose	20	56	6	18	24
Lyxose	71	29	b	b	<1
Altrose	27	40	20	13	33
➡ Glucose	36	64	b	b	<1
➡ Mannose	67	33	b	b	<1
➡ Fructose	3	57	9	31	40

[a] In all cases, the open-chain form is much less than 1%. For data on other sugars, see S. J. Angyal, The composition and conformation of sugars in solution, *Angew. Chem.* 8:157–226(1969).

[b] Much less than 1%.

Why is the β-Glc more stable than α-Glc, and *visa versa* for Man?

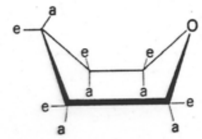
to answer this, we need to look at **ACTUAL** structures.

These Haworth Projections are not the actual conformation…. What is?

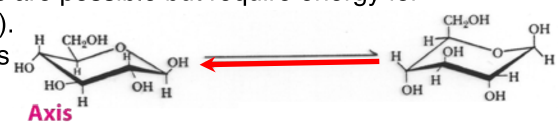
Carbohydrates

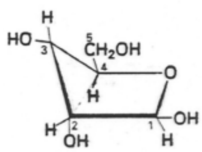
Actual Conformations of Cyclized Monosaccharides

- Cyclohexane rings have “chair” or “boat” conformations.

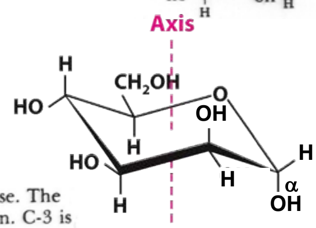


- Pyranose rings favor “chair” conformations.
- Multiple “chair” conformations are possible but require energy for interconversion (~46 kJ/mole).
- Furanose rings are envelopes





An envelope form of β-D-ribose. The C₃-*endo* conformation is shown. C-3 is out of plane on the same side as C-5.



We can understand why there is a 2:1 ratio of β:α glucose….. steric hindrance

AND why α–mannose is favored (2:1 ratio of α:β)

Two possible chair forms of β-D-glucopyranose

Lecture 30 (12/6/21)

TODAY

•Reading: Ch7; 236-241, 251-254, 258-260
Ch7; 241-250

•Problems: Ch7; 4,6,7,8,13,14,15,18
Ch7; 16,17,25,27

NEXT

•Reading: Ch4; 188-199
Ch6; 178
Ch8; 295
Ch10; 356-359
Ch14; 530-531,534-535
Ch16; 576, 590
Ch17; 613-615
Ch18; 629, 641-643

Carbohydrates

A. Definition
B. Roles
C. Monosaccharides-Chemistry
   1. Chirality
      a. One or more asymmetric carbons
      b. Linear and ring forms
   2. Derivatives: the chemistry of carbohydrates
      a. Oxidation
         i. C1
         ii. C6
      b. Reduction
         i. C1/C2
         ii. Other carbons
      c. Ester formation
      d. Amino sugars
   3. Polymerization
      a. The Glycosidic Bond
      b. Non-covalent bonds in macro-molecular structure
D. Oligosaccharides
   1. Glycoproteins & glycolipids
   2. O-linked
   3. N-linked
   4. Sequence determination-ABO
E. Polysaccharides
   1. Polymers of glucose
   2. Polymers of disaccharides

Carbohydrates

Monosaccharides: Chemistry

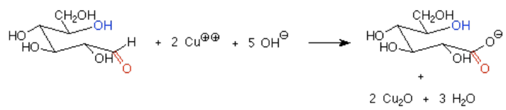
- **Chemical Features:**
  - Chirality
    - One or more asymmetric carbons
    - Linear and ring forms
  - Derivatives: the chemistry of carbohydrates
    - ① Oxidation
      - C1
      - C6
    - ② Reduction
      - C1/C2
      - Other carbons
    - ③ Ester formation
    - ④ Amino sugars
  - Polymerization
    - The Glycosidic Bond
    - Non-covalent bonds in macro-molecular structure

Carbohydrates ①

Monosaccharides: Derivatives

Oxidation: These make "sugar acids" or "acid sugars"

- Oxidation of aldehyde/ketone to acid (2e⁻ loss); reaction from the C1 of aldoses
  - named as "onic" acids ("onate" for conjugate base)
  - these sugars can reduce Cu^{2+} to Cu^{+} (Fehling's/Benedict's test) or Ag^{+} to Ag^{0} (Tollens' test)
  - Example: gluconic acid



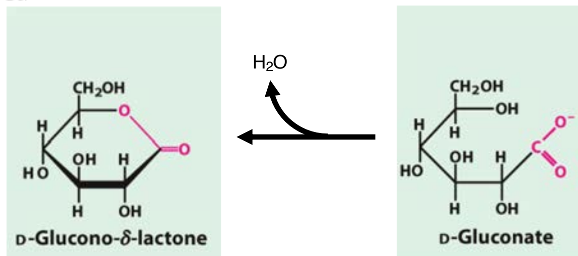
$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$
Blue

Cu^{2+} + Reducing sugar $\rightarrow Cu^{+}$

$Cu^{+} \rightarrow Cu_2O$
Red (ppt)

This reaction is called Benedict's test

The copper is reduced and the sugar is oxidized. So, the sugar is called a **Reducing Sugar**. Reducing sugars have a free anomeric carbon.

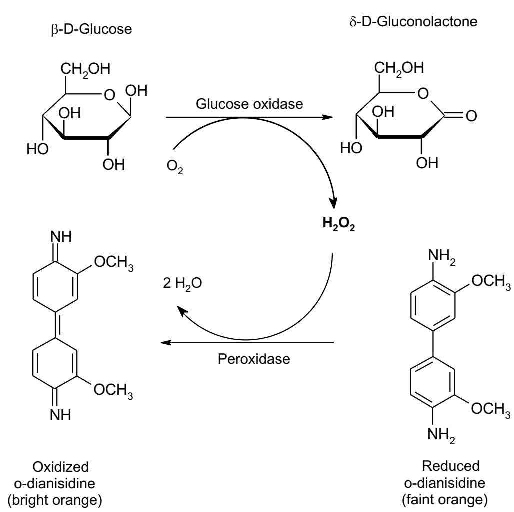


Carbohydrates ①

Monosaccharides: Derivatives

Oxidation: These make "sugar acids" or "acid sugars"

Colorimetric Glucose Analysis



- Enzymatic methods are used to quantify reducing sugars such as glucose.
  - The enzyme glucose oxidase catalyzes the conversion of glucose to glucono-δ-lactone and hydrogen peroxide.
  - Hydrogen peroxide oxidizes organic molecules into highly colored compounds.
  - Concentrations of such compounds is measured colorimetrically.
- Electrochemical detection is used in portable glucose sensors.

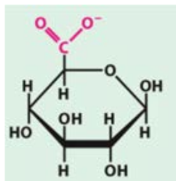
Carbohydrates ①

Monosaccharides: Derivatives

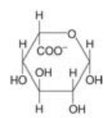
Oxidation: These make “sugar acids” or “acid sugars”

Oxidation of alcohol to acid (4e⁻ loss)

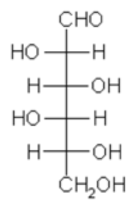
- Reaction for C6 groups; like C1 oxidation, normally on aldoses
- Named as **ur**onic acids (“uronate” for conjugate base)
- Many L-sugars are Uronic acids
- Examples: D-glucuronic acid, L-iduronic acid



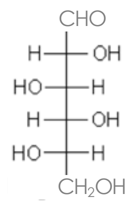
β-D-Glucuronate



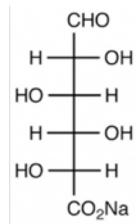
β-L-Iduronic acid (IdoA)



D-Idose



L-Idose



L-Iduronic acid

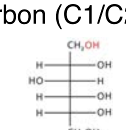
Carbohydrates ②

Monosaccharides: Derivatives

Reduction: These make “sugar alcohols” or “deoxysugars”

Reduction of aldehyde/ketone to alcohol (2e⁻ gain)

- Only carbon not already an alcohol is the anomeric carbon (C1/C2)
- Named as sugar **“ol”** or “itol”
- Examples: glycerol, mannitol, glucitol (sorbitol)

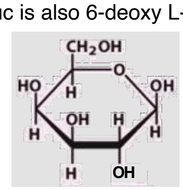


Sorbitol

Reduction of alcohol carbon to methyl/methylene (2e⁻ gain)

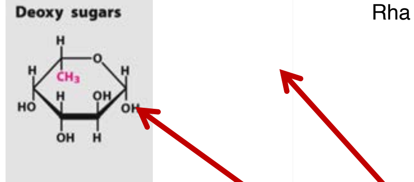
- Can react at any except the anomeric carbon
- Named as “x-deoxy” sugar with x being the reduced carbon
- Many are L-sugars, and have specific trivial names
- Examples: 2-deoxyribose, L-Fucose (Fuc) and L-Rhamnose (Rha)

Fuc is also 6-deoxy L-Gal



β-D-Gal

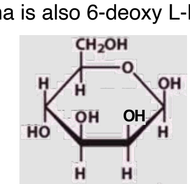
Deoxy sugars



β-L-Fucose

Notice that for L-sugars the β-anomer is **down** and α-anomer is **up**

Rha is also 6-deoxy L-Man



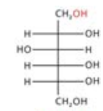
β-D-Man

Carbohydrates ②

Monosaccharides: Derivatives

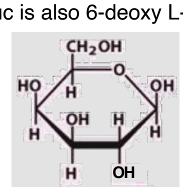
Reduction: These make "sugar alcohols" or "deoxysugars"

Reduction of aldehyde/ketone to alcohol (2e⁻ gain)
- Only carbon not already an alcohol is the anomeric carbon (C1/C2)
- Named as sugar **"ol"** or "itol"
- Examples: glycerol, mannitol, glucitol (sorbitol)

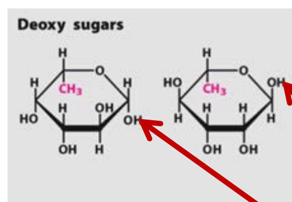


Reduction of alcohol carbon to methyl/methylene (2e⁻ gain)
- Can react at any except the anomeric carbon
- Named as "x-deoxy" sugar with x being the reduced carbon
- Many are L-sugars, and have specific trivial names
- Examples: 2-deoxyribose, L-Fucose (Fuc) and L-Rhamnose (Rha)

Fuc is also 6-deoxy L-Gal

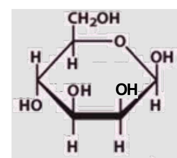


β-D-Gal



Notice that for L-sugars the β-anomer is **down** and α-anomer is **up**

Rha is also 6-deoxy L-Man



β-D-Man

Carbohydrates

Monosaccharides: Chemistry

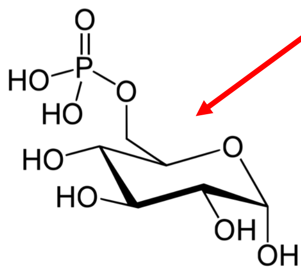
- **Chemical Features:**
  - Chirality
    - One or more asymmetric carbons
    - Linear and ring forms
  - Derivatives: the chemistry of carbohydrates
    - ① Oxidation
      - C1 -onic
      - C6 -uronic
    - ② Reduction
      - C1/C2 -tol
      - Other carbons deoxy-
    - ③ Ester formation
    - ④ Amino sugars
  - Polymerization
    - The Glycosidic Bond
    - Non-covalent bonds in macro-molecular structure

Carbohydrates ③

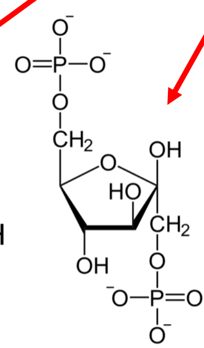
Monosaccharides: Derivatives

Esters: condensation of alcohol (sugar) and an acid

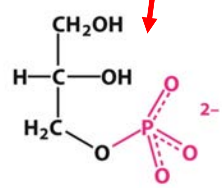
- Most important sugar esters use a phosphoric acid
  - These are called phospho-sugars or sugar phosphates
  - Examples: nucleotides, Glc 6-P, Fru 1,6-P_2, glycerol 3-phosphate



α–D–Glucose 6–phosphate



β–D–Fructose 1,6–bisphosphate



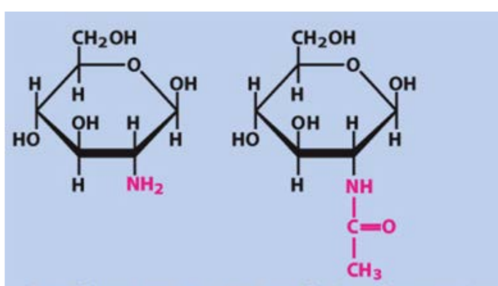
D-Glycerol 3-phosphate

Carbohydrates ④

Monosaccharides: Derivatives

Amines: condensation of alcohol (sugar) and ammonia

- These are called amino-sugars
- In biology, its ALWAYS at C2
- Often, the amino group will be further modified by an acetyl group (CH_3CO–) making an amide
- Named as sugar“amine” and when acetylated, the “N-acetyl” comes first. When abbreviation used “NAc” it comes after.
- Examples: glucosamine, N-acetyl-glucosamine (GlcNAc)



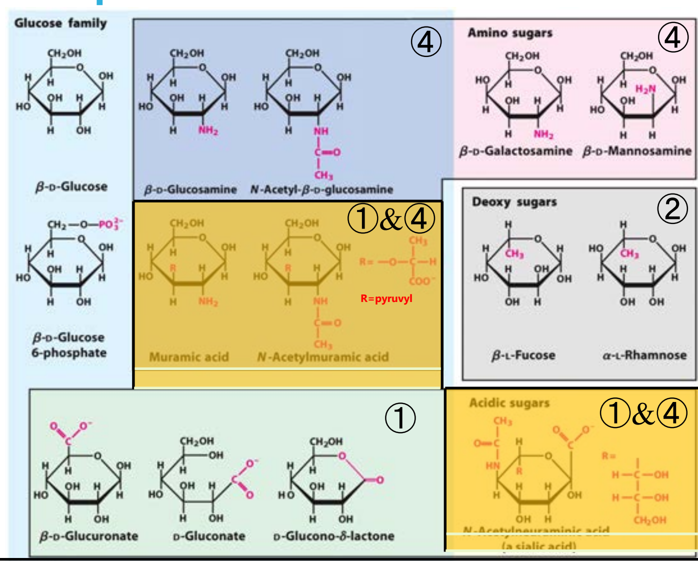
β-D-Glucosamine *N*-Acetyl-*β*-D-glucosamine (GlcNAc)

Carbohydrates

Monosaccharides: Derivatives

Important Hexose Derivatives

③



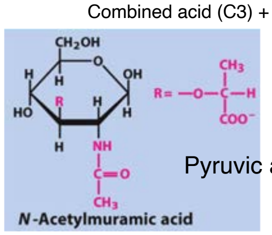
Carbohydrates

①&④

Monosaccharides: Derivatives

Muramic acid

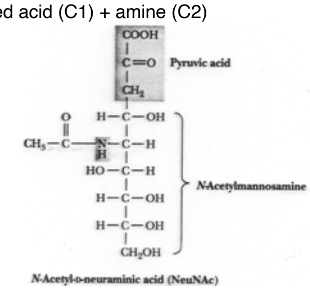
Combined acid (C3) + amine (C2)

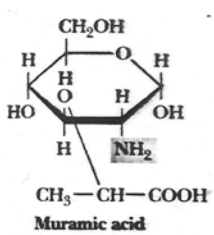


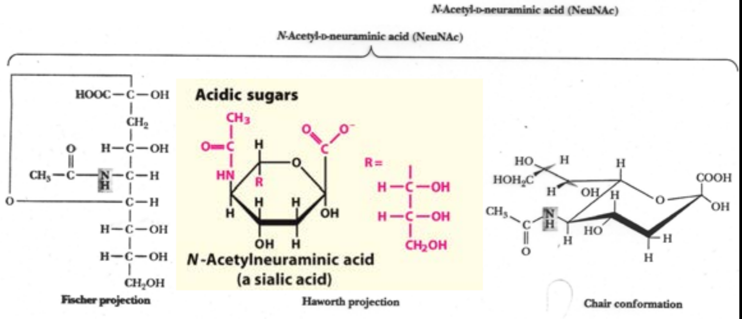
Pyruvic acid = $H_3C\text{-}\overset{\overset{O}{\|}}{C}\text{-}COO^-$

Sialic Acid (Sia) (aka NeuNAc)

Combined acid (C1) + amine (C2)







Carbohydrates

Monosaccharides: Chemistry

- **Chemical Features:**
  - Chirality
    - One or more asymmetric carbons
    - Linear and ring forms
  - Derivatives: the chemistry of carbohydrates
    - Oxidation
      - C1
      - C6
    - Reduction
      - C1/C2
      - Other carbons
    - Ester formation
    - Amino sugars
  - Polymerization
    - The Glycosidic Bond
    - Non-covalent bonds in macro-molecular structure

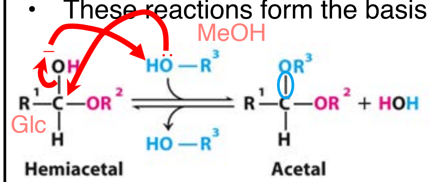
Carbohydrates

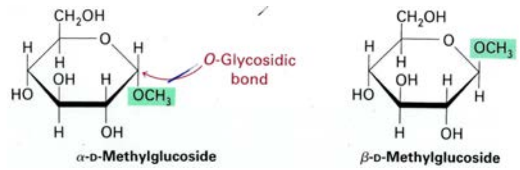
The Glycosidic Bond

Carbohydrates

Hemiacetals and Hemiketals are reactive to alcohols in condensation reactions

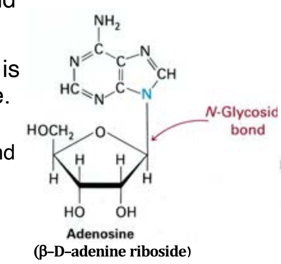
- Hemiacetals condense with alcohols to form Acetals.
- Hemiketals condense with alcohols to form Ketals.
- These reactions form the basis of the GLYCOSIDIC BOND.

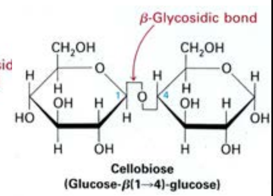




- Two sugar molecules can be joined via a glycosidic bond between an anomeric carbon (the hemiacetal/hemiketal) and a hydroxyl carbon (the other sugar).
- The glycosidic bond between sugars is stable and does not readily hydrolyze.
  - The anomeric carbon involved in the glycosidic linkage is fixed in its chirality and is therefore nonreducing.
  - The second monomer, with its unreacted hemiacetal, is still reducing.

The Glycosidic Bond

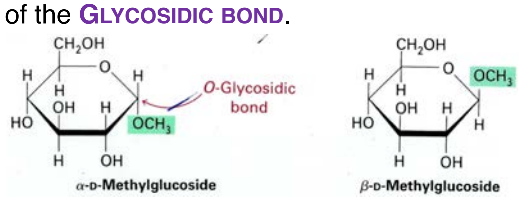




Carbohydrates

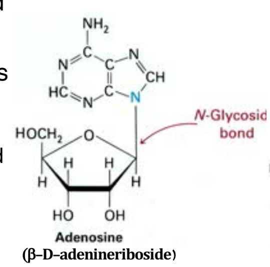
Hemiacetals and Hemiketals are reactive to alcohols in CONDENSATION reactions

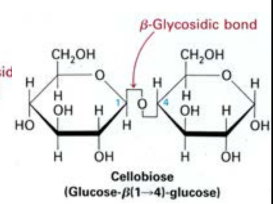
- Hemiacetals condense with alcohols to form Acetals.
- Hemiketals condense with alcohols to form Ketals.
- These reactions form the basis of the GLYCOSIDIC BOND.



- Two sugar molecules can be joined via a glycosidic bond between an anomeric carbon (the hemiacetal/hemiketal) and a hydroxyl carbon (the other sugar).
- The glycosidic bond between sugars is stable and does not readily hydrolyze.
  - The anomeric carbon involved in the glycosidic linkage is fixed in its chirality and is therefore nonreducing.
  - The second monomer, with its unreacted hemiacetal, is still reducing.

The Glycosidic Bond





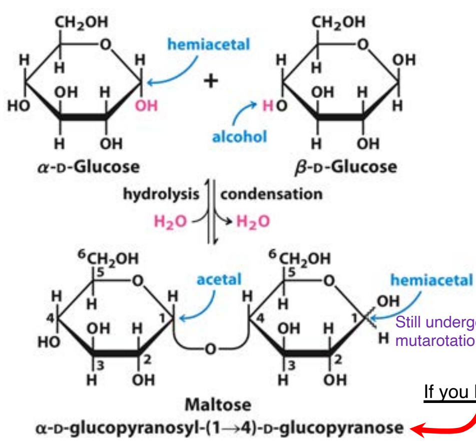
Carbohydrates

Disaccharides

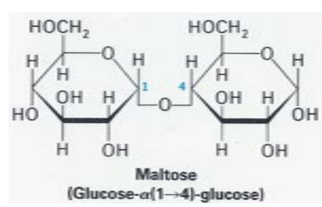
Carbohydrates

Disaccharides:

- Disaccharides can be named by the organization and linkage or a common name.
  - The disaccharide formed upon condensation of two glucose molecules via a 1 → 4 bond is described as α-D-glucopyranosyl-(1→4)-D-glucopyranose.
  - The common name for this disaccharide is maltose.



Still undergoing mutarotation



If you only know the sugar and the linkage

Non-reducing → reducing

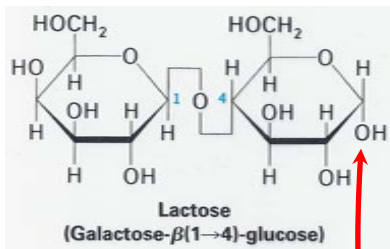
If you know the exact structure of the sugar

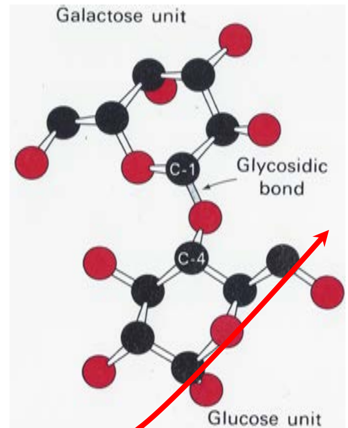
As we make sugar-polymers, the convention is to have the non-reducing sugar to the LEFT and the reducing end at the RIGHT.

Carbohydrates

Disaccharides:

Here is likely the first disaccharide you encountered in your life:
Lactose.





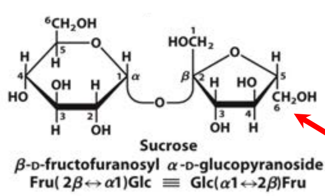
Non-reducing → reducing

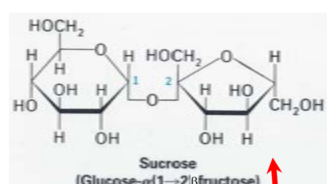
Still undergoing mutarotation

Carbohydrates

Disaccharides:

Here is likely the disaccharide you ingest the most:
Sucrose.





Notice that these are drawn upside down

Trehalose

Nonreducing Disaccharides

- Two sugar molecules can be also joined in a glycosidic bond between two anomeric carbons.
- The product has two acetal groups and no hemiacetals or hemiketals.
- There are no reducing ends; this is a nonreducing sugar.

Carbohydrates

Polysaccharides

- The majority of natural carbohydrates are usually found as large polymers.
- These polysaccharides can be:
  – homopolysaccharides (one monomer unit)
  – heteropolysaccharides (multiple monomer units)
  – linear (one type of glycosidic bond)
  – branched (multiple types of glycosidic bonds)
- Polysaccharides do not have a defined molecular weight.
  – This is in contrast to proteins because, unlike proteins, no template is used to make polysaccharides.
  – Polysaccharides are often in a state of flux; monomer units are added and removed as needed by the organism.

Carbohydrates

Polysaccharides: Polymers of Glucose

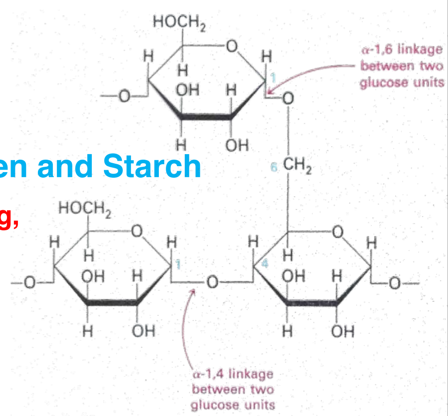
Homopolymers of Glucose:

- Starch
- Glycogen
- Cellulose
- Chitin

- Glycogen and Starch are the main storage polysaccharides for energy.
  – Glycogen and starch are insoluble due to their high molecular weight and often form granules in cells.
  – Molecular weight reaches several millions (~200 x 10^6)(can see in microscope).
- Glycogen is a branched homopolysaccharide of glucose.
  – Glucose monomers form $\alpha(1 \rightarrow 4)$ linked chains.
  – There are branch points with $\alpha(1 \rightarrow 6)$ linkers every 8–12 residues.
- Starch is a mixture of two homopolysaccharides of glucose.
  – Amylopectin is like glycogen, but the branch points ($\alpha(1 \rightarrow 6)$ linkages) occur every 24–30 residues.
  – Amylose is an unbranched polymer of $\alpha(1 \rightarrow 4)$ linked residues.

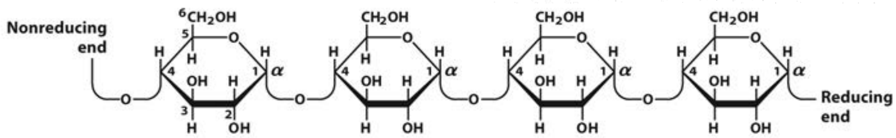
Carbohydrates

Polysaccharides: Glycogen & Starch



Glycosidic Linkages in Glycogen and Starch

(Glc-α(1→4)Glc)$_n$ with α(1→6) branching, where n≈10^6



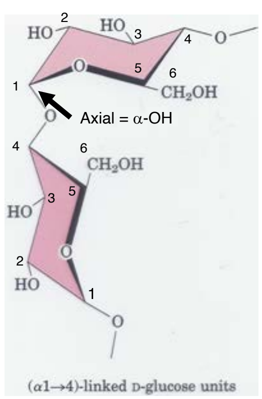
Non-reducing → reducing

Haworth projections are not good to show the actual shape, which is helical!

Carbohydrates

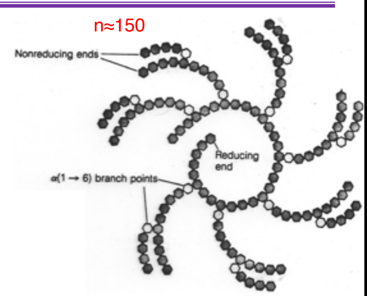
Polysaccharides: Glycogen & Starch

I_2



- Granules contain enzymes that synthesize and degrade these polymers.
- Glycogen and amylopectin have one reducing end but many nonreducing ends.
- Enzymatic processing occurs simultaneously in many nonreducing ends.

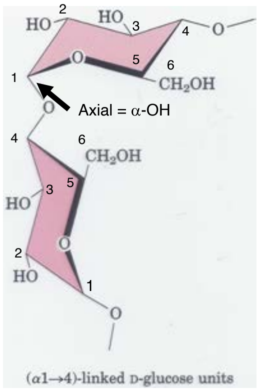
n≈150

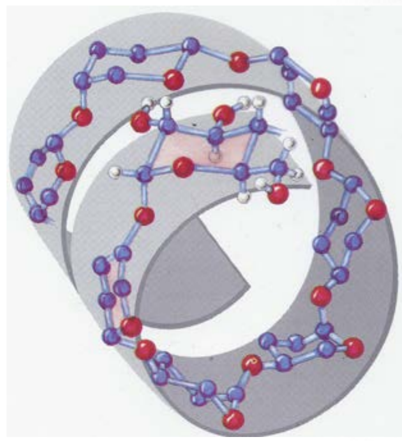


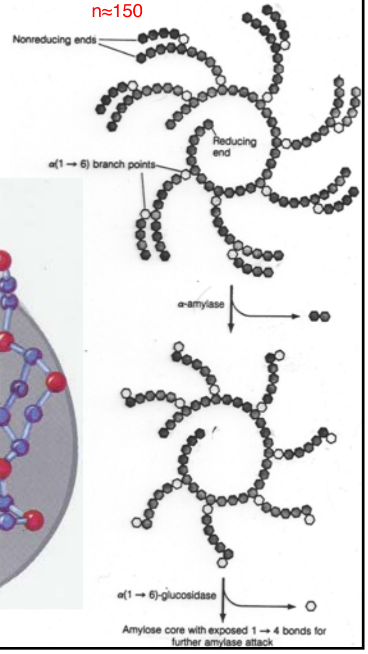
Carbohydrates

Polysaccharides: Glycogen & Starch

I_2

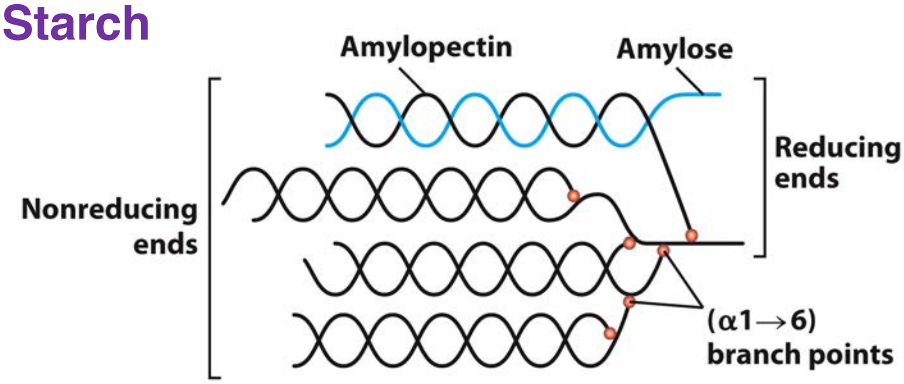






Carbohydrates

Polysaccharides: Glycogen & Starch



Mixture of Amylose and Amylopectin in Starch

Carbohydrates

Polysaccharides:

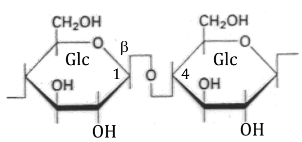
Homopolymers of Glucose:

- Starch
- Glycogen
- Cellulose
- Chitin

- Cellulose is a linear homopolysaccharide of glucose.
  - Glucose monomers form $\beta(1 \rightarrow 4)$ linked chains.
  - Hydrogen bonds form between adjacent monomers.
  - There are additional H-bonds between chains.
  - Structure is now tough and water insoluble.
  - It makes up almost 50% of plant mass; in cell walls.
  - Cotton is nearly pure fibrous cellulose.
- Chitin is a linear homopolysaccharide of *N*-acetylglucosamine (GlcNAc).
  - *N*-acetylglucosamine monomers form $\beta(1 \rightarrow 4)$-linked chains.
  - forms extended fibers that are similar to those of cellulose
  - hard, insoluble, cannot be digested by vertebrates
  - structure is tough but flexible, and water insoluble
  - found in cell walls in mushrooms and in exoskeletons of insects, spiders, crabs, and other arthropods

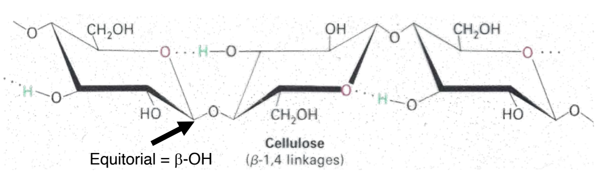
Carbohydrates

Polysaccharides:
Cellulose & Chitin

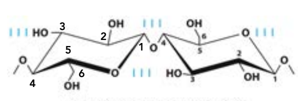


Glycosidic Linkages in Cellulose & Chitin

$(Glc\text{-}\beta(1\rightarrow4)Glc)_n$ with NO branching, $n \approx 10^4$



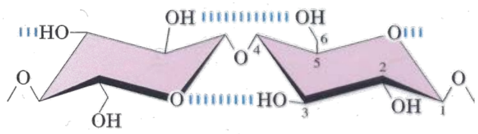
Notice that each chair is alternatively flipped



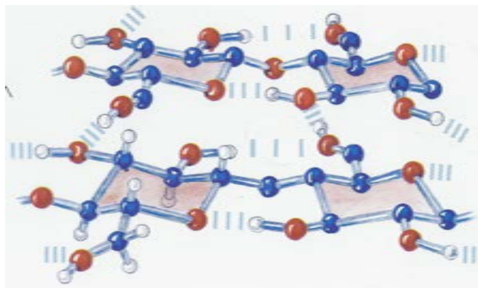
THE most abundant biological molecule in the world: ~300 trillion kg

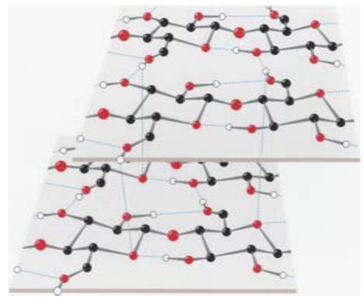
Carbohydrates

Polysaccharides: Cellulose & Chitin

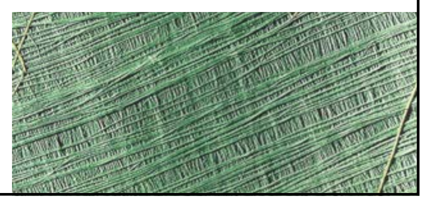


(β1→4)-linked D-glucose units





- The fibrous structure and water insolubility make cellulose a difficult substrate to act upon.
- Most animals cannot use cellulose as a fuel source because they lack the enzyme to hydrolyze β(1→4) linkages (β-Amylase or cellulase).
- Fungi, bacteria, and protozoa secrete cellulase, which allows them to use wood as source of glucose.
- Ruminants and termites live symbiotically with microorganisms that produce cellulase and are able to absorb the freed glucose into their bloodstreams.
- Cellulases hold promise in the fermentation of biomass into biofuels.

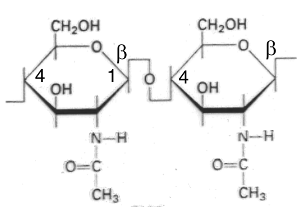


Carbohydrates

Polysaccharides: Cellulose & Chitin

A Sally lightfoot crab. The exoskeleton of this arthropod is rich in chitin, one of the most abundant biopolymers on earth.

Paul Whitten/Science Source



Chitin

(GlcNAc–β(1→4)–GlcNAc)$_n$