

Chapter 8 - Carbohydrates

Hydrates of Carbon: $C_m(H_2O)_n$

Saccharides: Latin: *Saccharum* = Sugar

1. Energy transport and storage.
2. Structural *e.g.* bacterial cell walls, cellulose.
3. Information *e.g.* signals on proteins and membranes.

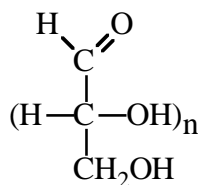
Naming: Monosaccharide, 1 unit; disaccharide, 2 units ...

Oligosaccharides: several sugar units.

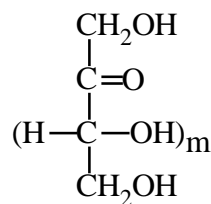
Polysaccharides: long chains of 100s – 1000s.

Triose, tetrose, pentose refers to the # of C in 1 unit.

2 Families

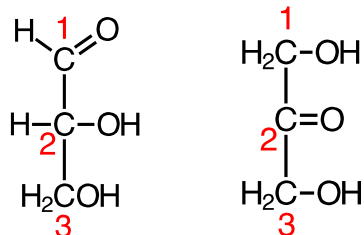


Aldose
n = 1 - 4



Ketose
m = 0 - 3

The **Aldoses** derive from *D*-Glyceraldehyde, the **Ketoses** from Dihydroxyacetone:



The **carbon numbering** starts with the end of the molecule nearest the carbonyl carbon.

Aldotrioses and ketotrioses have 3 C's in the backbone.

Aldotetroses and ketotetroses have 4 C's.

Pentoses and hexoses have 5 and 6 C's.

Fig. 8.3 shows the family of *D*-aldoses.

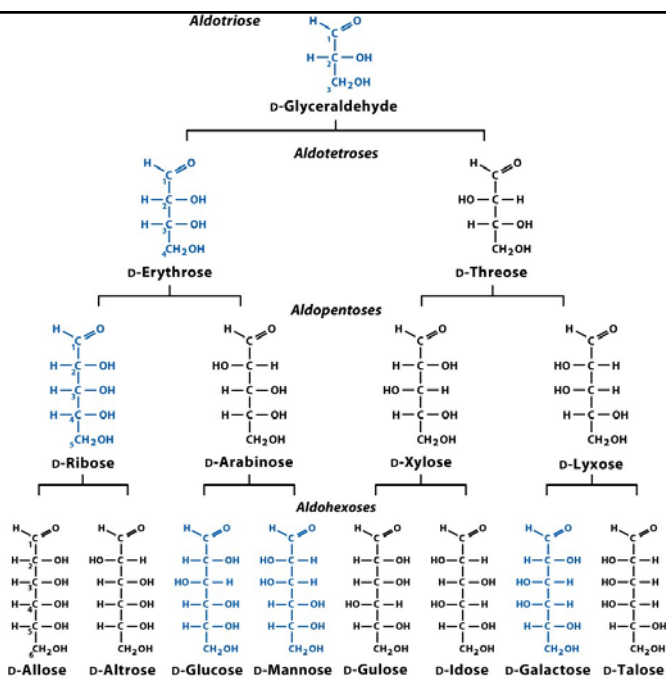


Figure 8-3 Principles of Biochemistry, 4/e
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Fig. 8-5 shows
the family of *D*-ketoses.

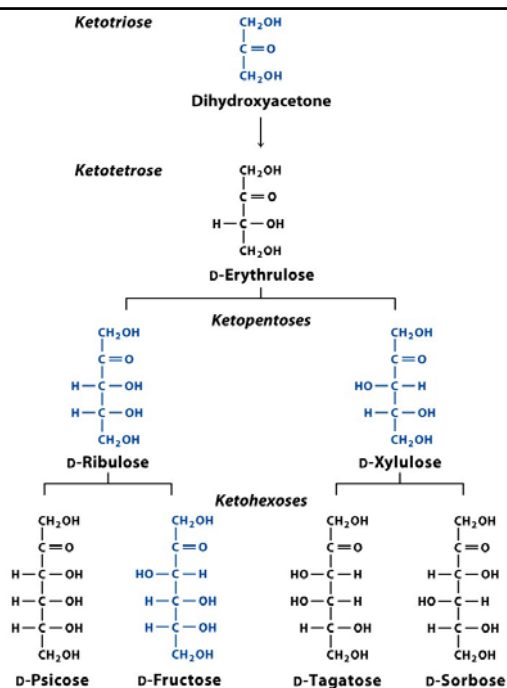


Figure 8-5 Principles of Biochemistry, 4/e
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The 4C and 5C ketoses are named after the aldoses with the
addition of - ul - Ribose \rightarrow Ribulose Xylose \rightarrow Xylulose

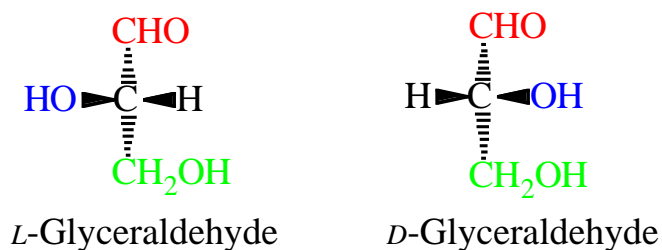
Abbreviations

Glucose	Glc
Glucosamine	GlcN
Glucuronic Acid	GlcA
Fructose	Fru
Galactose	Gal
Galactosamine	GalN
N-Acetylglucosamine	GlcNAc
Mannose	Man
Ribose	Rib

Except for dihydroxyacetone, all the aldoses and ketoses have **asymmetric = chiral** carbons.

In nature, most sugars are *D*- most AA are *L*-.

D- and *L*-glyceraldehyde are reference molecules for assignment of stereochemistry (absolute configuration).

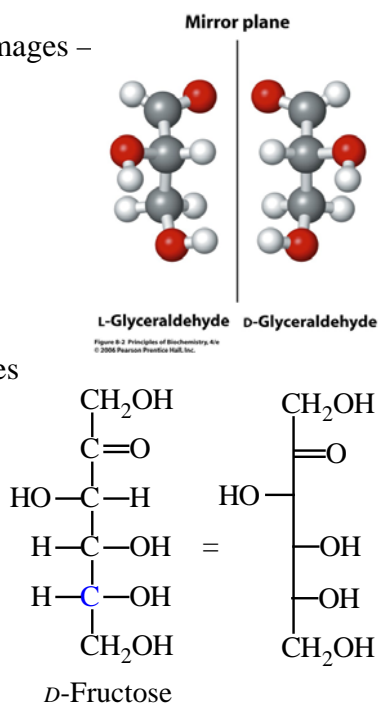


These are nonsuperimposable mirror images – **enantiomers**.

The diagrams above are called “**perspective formulae**”.

Fisher projection formulae retain the stereochemical information but use lines for the bonds. See fructose below:

Why *D*-? The **chiral C** furthest from the C=O has the same configuration as *D*-glyceraldehyde.



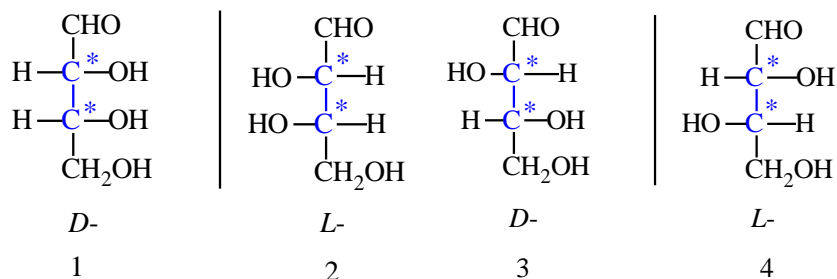
These molecules are optically active: they rotate the plane of monochromatic plane-polarized light in opposite directions. dextrorotatory (+) or levorotatory (-). For example,

D-(+)-glucose (dextrose)

D-(-)-fructose (levulose)

Erythrose

Threose



1 & 2 are enantiomers. 3 & 4 are enantiomers.

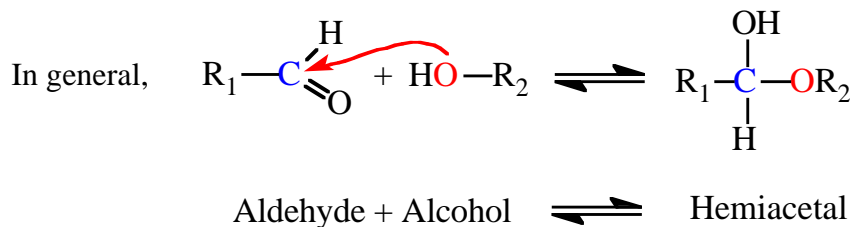
Diastereomers: Non-mirror image stereoisomers.

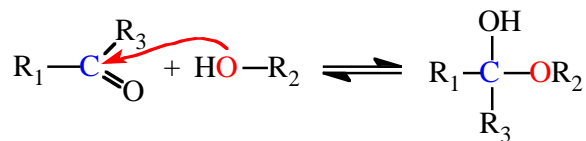
1 & 3 1 & 4 2 & 3 2 & 4

Epimers: Diastereomers that differ in configuration at 1 C.

1 & 3 @ C2 1 & 4 @ C3 2 & 3 @ C3 2 & 4 @ C2

Cyclic Forms:

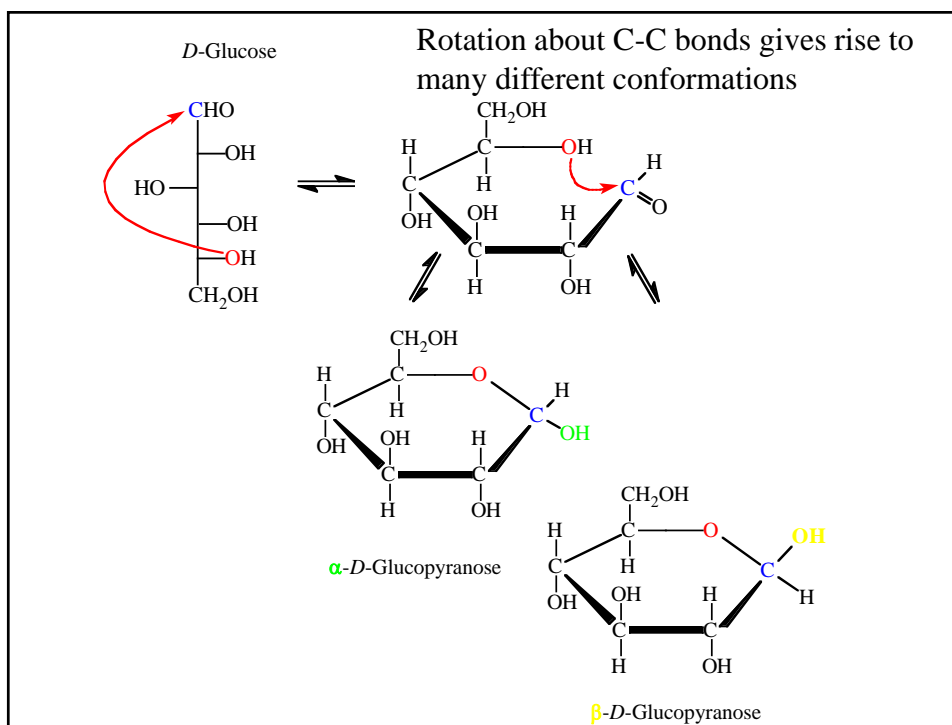




A second alcohol can add to form an Acetal / Ketal, respectively.

Notes:

1. New chiral centres have been created.
2. The above reactions are **intermolecular**.
3. In aldoses and ketoses **intramolecular** hemiketals / hemiacetals form in solution.



These are called “**Haworth**” diagrams. They illustrate some aspects of the stereochemistry of these molecules.

4. The 6-membered ring is much more stable than the 5-membered ring.

5. They are called pyranoses because of pyran:



6. **C1** is a new asymmetric C: Isomers that differ only at the hemiacetal or hemiketal C are called **anomers** and the C is the **anomeric C**.

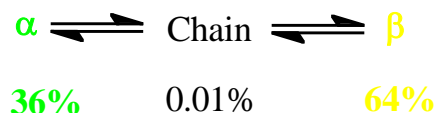
7. α -anomer: **OH** on C1 is on the **opposite** side of the ring to C6.

β -anomer: **OH** on C1 is on the **same** side of the ring as the C6.

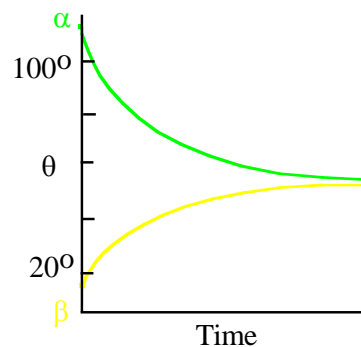
8. OH on asymmetric C on the “**right**” in the Fisher diagrams are “**down**” in the Haworth Diagrams.

9. Fisher diagrams (straight chain) are correct for sugars with 3 or 4 C, otherwise ring structures are more stable.

10. In water all three forms of glucose exist in equilibrium:



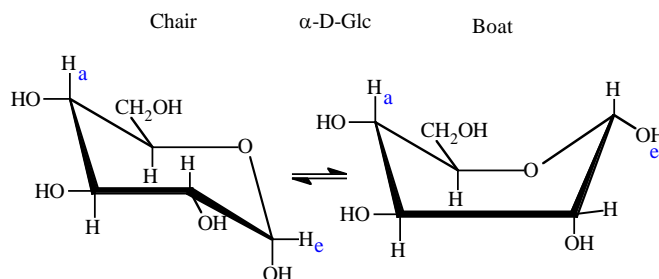
The interconversion is called **Mutarotation** and can be measured by the rotation of plane-polarized light.



Pure α -D-Glc rotates light $+112^\circ$, pure β -D-Glc rotates $+19^\circ$, and at equilibrium the mixture rotates light $+53^\circ$.

$$36\% (112^\circ) + 64\% (19^\circ) = +53^\circ$$

The pyranose rings are not entirely planar. Each configuration (α , β) can exist in 2 “puckered” **conformations**:



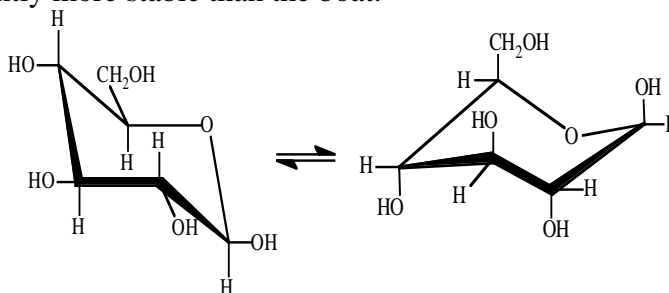
e = equatorial - The group is in the plane, or parallel to, the planar part of the ring.

There is less steric hindrance if bulky groups go in the e positions.

a = axial – The group is perpendicular to the planar part of the ring.

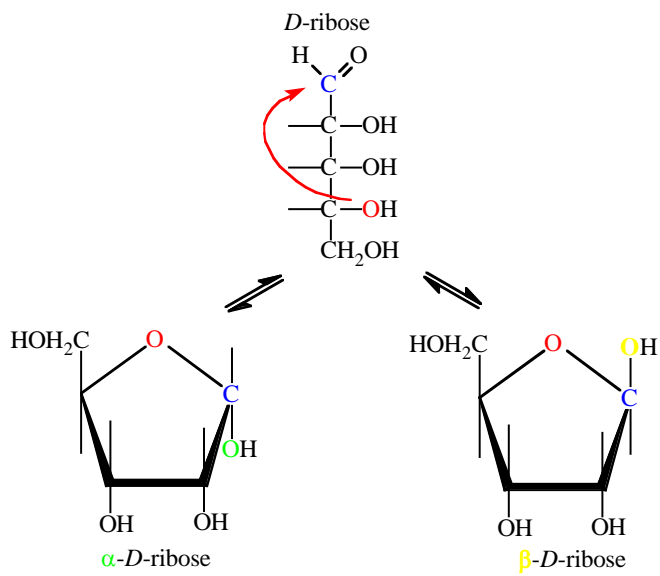
The chair is slightly more stable than the boat.

Here are two possible chair conformations of β -D-Glc.



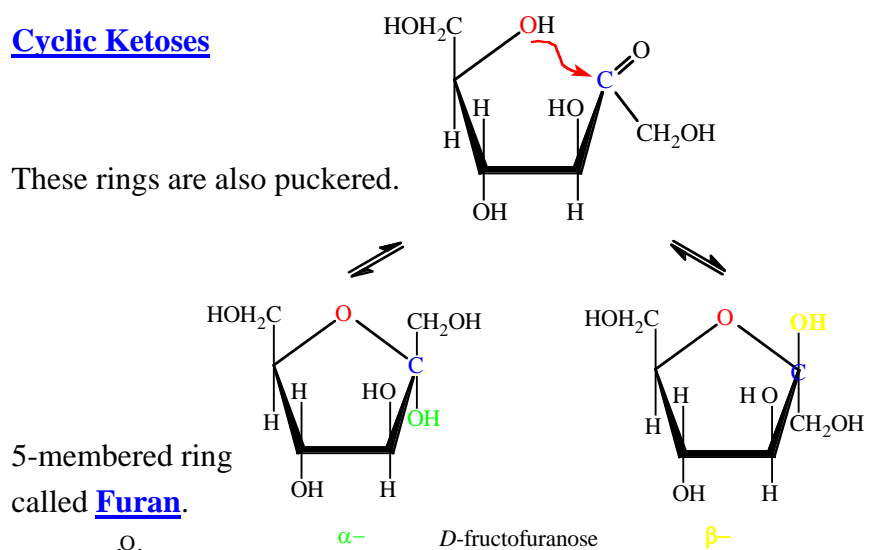
Only β -D-Glc can put all bulky substituents in the equatorial position so it is a very stable and abundant molecule.

The pentoses also form hemiacetals:

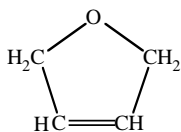


Cyclic Ketoses

These rings are also puckered.

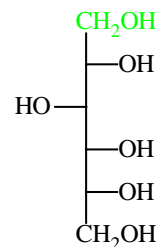


5-membered ring
called Furan.



Sugar Derivatives

1. Reduction of *D*-glyceraldehyde yields glycerol, an alcohol.

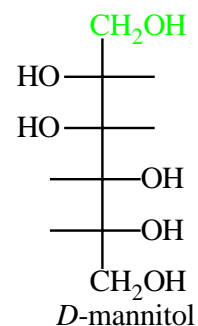
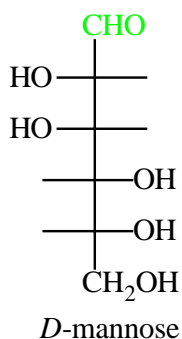


Glucitol

Reduction of *D*-glucose yields *D*-glucitol (Sorbitol).

Reduction of mannose yields mannitol.

Note that Glc and Man are epimers at C2.



Mannitol and sorbitol are used as low calorie sweeteners. They are only very slowly metabolized to glucose and stimulate little insulin secretion, a property helpful to diabetics.

They have a positive heat of solution giving them a “cool” sensation.

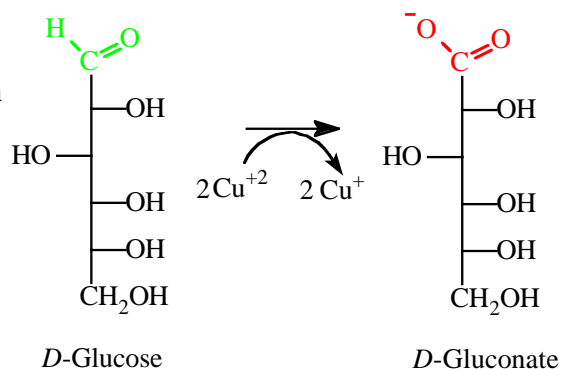
Any excess, unabsorbed sugar alcohols have a laxative effect as they prevent absorption of water.

2. Monosaccharides are reducing agents.

They give up electrons and are themselves oxidized. Oxidation of aldols yields the Aldonic acid family. This can be detected in an alkaline solution of Copper.

Cu^+ is insoluble and precipitates from solution as brick-red Cu_2O .

“Benedict’s Test”
Experiment 4.

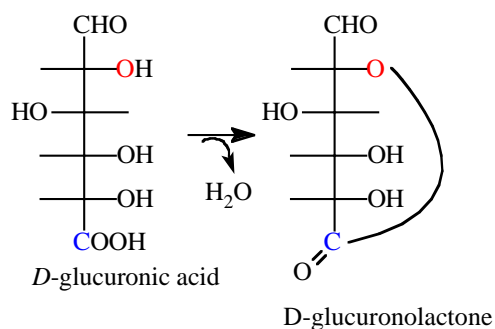


Only the straight chain forms of the sugars are reactive.

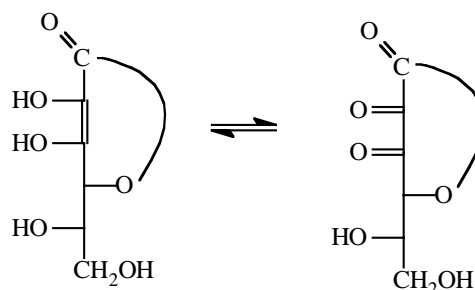
The ketoses will react slowly because they must isomerize to the aldehyde.

Oxidation at C6 produces the [Uronic acid](#) family. *E.g.* *D*-glucuronic acid.

3. Aldonic and uronic acids form stable intramolecular esters called [sugar lactones](#):



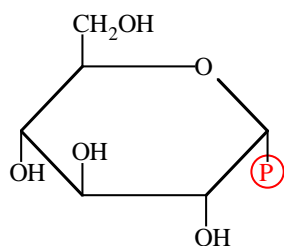
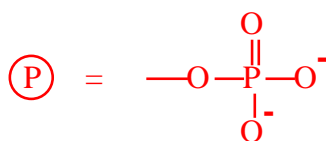
Vitamin C = *L*-ascorbic acid
a sugar acid lactone:



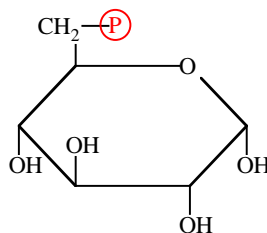
Primates and fruit bats have lost the ability to make Vitamin C so it is an **essential nutrient**.

Humans have also lost the ability to oxidise uric acid so some of the antioxidant function of Vitamin C may have been taken over by uric acid. The ancient DNA encoding *L*-glucuronolactone oxidase is still present in the human genome.

4. Sugar Phosphate esters are intermediates in sugar synthesis that prevent transport of the sugar across hydrophobic membranes.

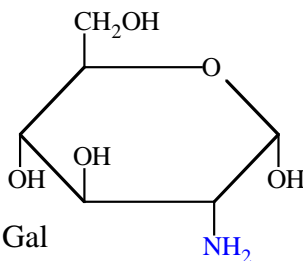
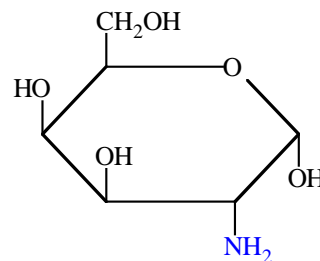


Glc-1-P



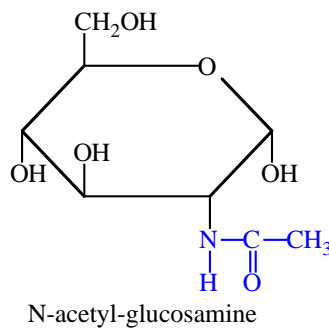
Glc-6-P

5. Amino Sugars

 α -D-glucosamine α -D-galactosamine

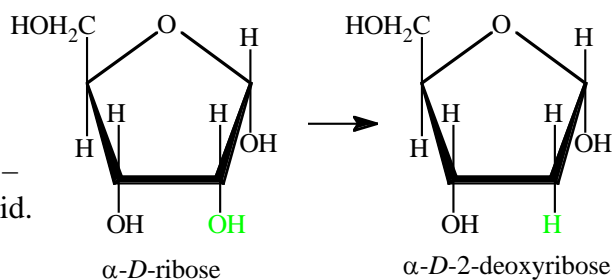
Note that Glc and Gal are epimers at C4.

6. Sugar Amides



7. Deoxy-sugars

This is the sugar component of DNA – deoxyribonucleic acid.

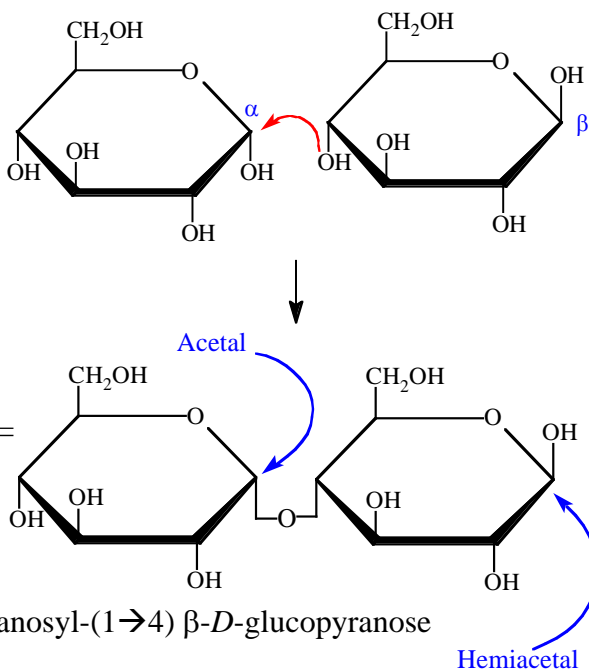
DisaccharidesMaltose

A reducing sugar.



Maltose (β -form) =
Glc(α 1 \rightarrow 4)Glc

= O- α -D-glucopyranosyl-(1 \rightarrow 4) β -D-glucopyranose



It is made from starch by the enzyme *amylase*.

Notes: 1. The left Glc is an acetal. It is non-reducing and non-mutarotating.

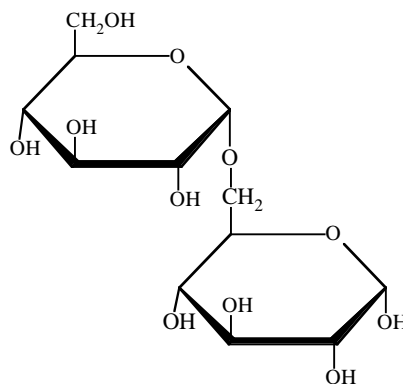
2. The right glucose is a hemiacetal. It has a reducing end and mutarotates.

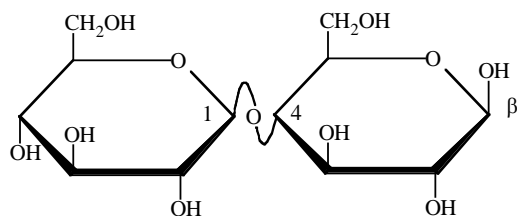
3. **Glycosidic bonds** join sugars.

3. **Glycosidic bonds** join sugars.

Iso-maltose is Glc ($\alpha 1 \rightarrow 6$) Glc. It is a reducing sugar.

Made from hydrolysis of dextrans.



CellobioseGlc ($\beta 1 \rightarrow 4$) Glc

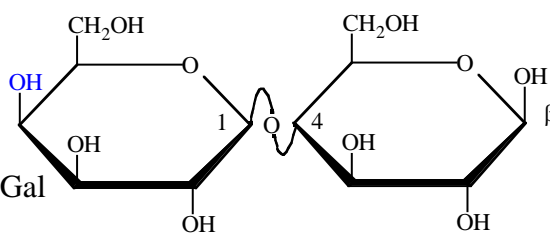
A reducing sugar, produced by acid hydrolysis of cellulose.

Lactose

Milk sugar.

A reducing sugar.

Remember, Glc and Gal are epimers at C4.

Gal ($\beta 1 \rightarrow 4$) Glc

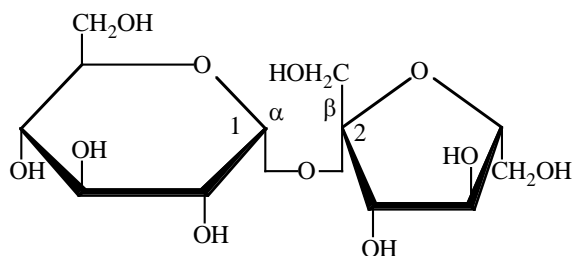
Adults without the enzyme *lactase* cannot digest lactose and are **Lactose Intolerant**.

In the small intestine, bacteria switch their metabolism to digest lactose (fermentation) producing large amounts of gas and cramping.

Sucrose: A **non-reducing sugar**.

Table Sugar.

Made by plants.

Glc ($\alpha 1 \leftrightarrow \beta 2$) FruFru ($\beta 2 \leftrightarrow \alpha 1$) Glc

Sucrose rotates light by $+66^\circ$. Hydrolysis of sucrose results in a mixture that rotates light at -39° , called “invert sugar”.
 ~ 2x sweeter than “sugar”. A popular food additive.

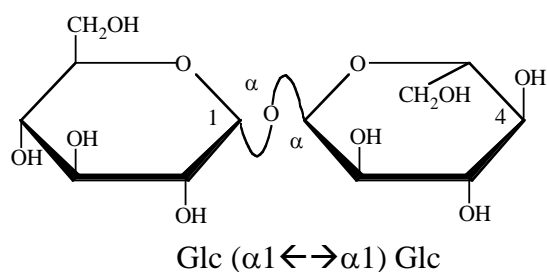
$\alpha + \beta$ -D-Glc are $+53^\circ$ and $\alpha + \beta$ -D Fru are -92° .
 Honey is essentially invert sugar. Here is a picture of crystals of honey viewed with polarized light.



Trehalose

A **non-reducing sugar**.

Energy storage in insects.



Most sugars are stored as **Polysaccharides** = **Glycans**

They may be branched or unbranched.

Starch: Storage of D-Glc in plants; 2 types:

Amylose: Unbranched chains of $\alpha 1 \rightarrow 4$ linked Glc *i.e.* Maltose; up to 4,000 Glc in one chain.

It forms a tightly coiled **helical** structure stabilized by H-bonding with 6 residues per turn.

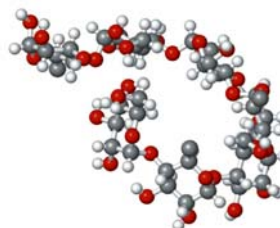
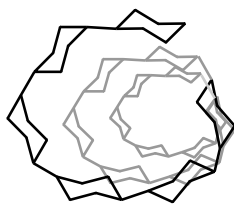
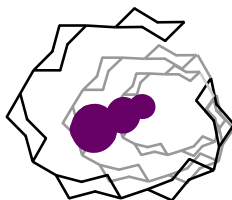


Figure 4.28 Structure of Amylose (1979) © 1979 McGraw-Hill Education

Iodine can insert into the middle of the helix giving starch a **blue** colour in a potato (right). Apples (left) contain very little starch.



<http://www.webexhibits.org/causesofcolor/image/content/emerald/DSC03426Z.jpg>

Amylopectin: Up to 200 amylose chains linked $\alpha 1 \rightarrow 6$ at “Branch Points”.

So just like iso-maltose.

This cannot form the helical structure.

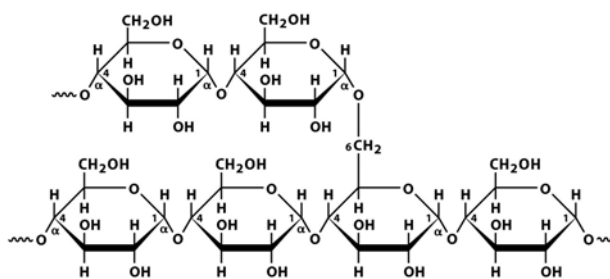


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So starch has Maltose and isomaltose units with one reducing end and many non-reducing ends.

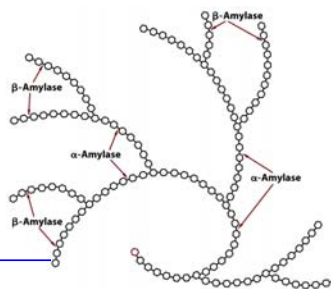
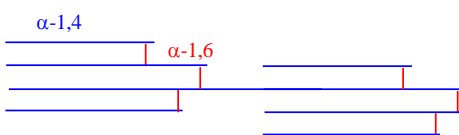


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Saliva and pancreas secrete α -amylase that randomly cleaves α -1,4 bonds. Plants and bacteria secrete β -amylase that removes maltose units starting at the non-reducing end. Debranching enzymes hydrolyse the α -1,6 bonds.

Glycogen: Animal cell storage of Glc.

Similar to amylopectin but more branched. ~15-30 sugars per branch.

Dextrans: Bacterial polysaccharides with $\alpha 1 \rightarrow 6$ links and some $\alpha 1 \rightarrow 2$ and $\alpha 1 \rightarrow 4$ glucose links.

Fructans or **Levans** are fructose storage forms found in plants.

These are all used for reversible energy storage.

Cellulose: $(\text{Glc } \beta 1 \rightarrow 4 \text{ Glc})_n$

Linear chain of 10,000 - 15,000 Glc. See cellobiose.

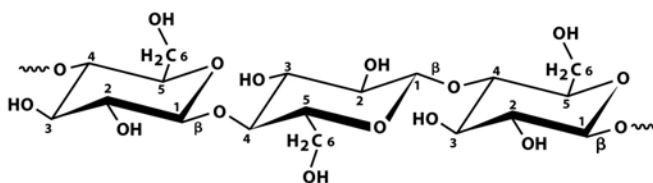


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This is a structural polysaccharide. A strong rod-like structure of parallel chains packed side-by-side is formed.

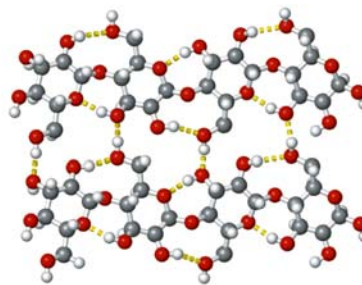
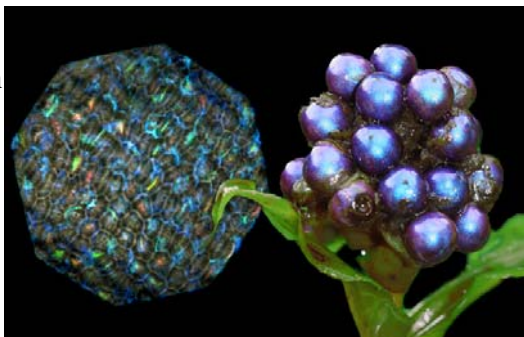


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In *Pollia condensata* the iridescent blue color comes from the interaction of light with the helical rods of cellulose in the outer skin. There is no pigment.



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Chitin: arthropod exoskeleton, shells of crustaceans, & peacock feathers.



[www.davidlnelson.md/ Cazadero/Bugs.htm](http://www.davidlnelson.md/Cazadero/Bugs.htm)

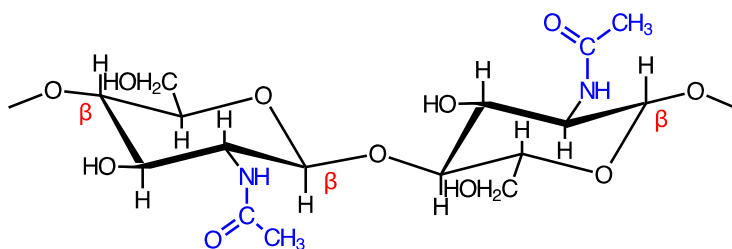
<http://faculty.clintoncc.suny.edu/faculty/michael.gregory/>



<http://www.photobiology.info/Ball.html>

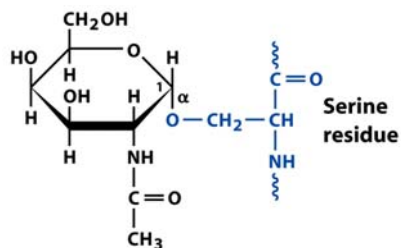
N-acetylglucosamines linked $\beta 1 \rightarrow 4$ in a linear chain.

It is cellulose with a C2 N-acetyl.



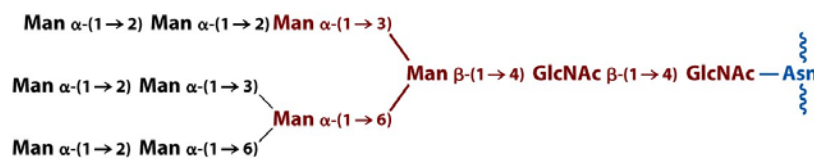
Glycoproteins:

Sugars may be O-linked to Ser/Thr/Tyr.



Or N-linked to Asn/Gln.

(a)



A great variety of sequence, branching, and linkage.

α / β ; 1 \rightarrow 2, 1 \rightarrow 3, 1 \rightarrow 4 ...

The cell walls of bacteria contain a cross-linked network of short peptides and sugars called **peptidoglycan**.

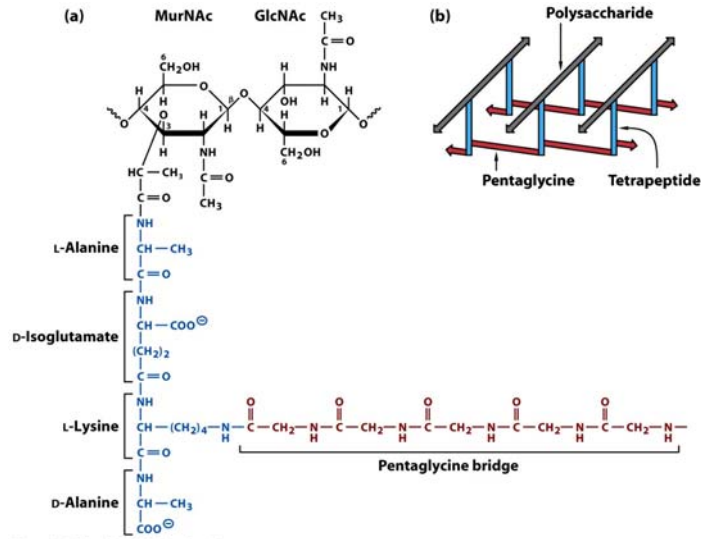


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In animals, extracellular matrix, cartilage, tendons, and skin contain **proteoglycans**. Proteins with large amounts of carbohydrate.

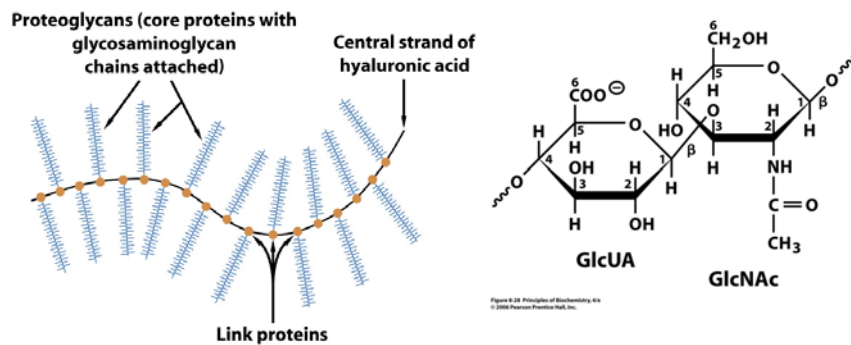


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