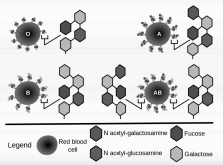
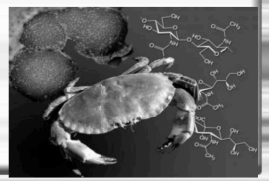
Carbohydrates
Saccharides
Sugars

Carbohydrates: $C_n(H_2O)_n$

- Energy storage
  - Energy stored in the chemical bonds of 1 mol of glucose (180 g): 720 kcal
- Molecular recognition
  - Blood groups
  - ECM-receptors
- Structural role
  - Plant cell wall
  - Arthropods exoskeleton





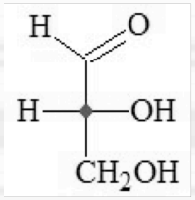
Classification

- Monosaccharides: aldehydes or ketones with 3-9 C
- Disaccharides: 2 units of monosaccharides
- Oligosaccharides: 3-20 units of monosaccharides
- Polysaccharides: >20 units of monosaccharides

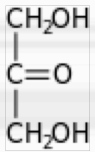
- The polymerization occurs by the formation of a glycosidic bond between the units

Monosaccharides

- Aka poly-hydroxy-aldehydes or poly-hydroxy-ketones
- The most important ones in the metabolism of mammals are those with 3, 5, 6 Carbon atoms
- The earliest example of the aldose family is glyceraldehyde, that of the ketones family is di-hydroxy-acetone



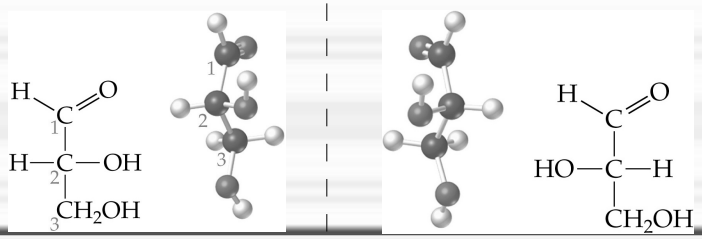
2,3 di-hydroxy-propanale



1,3 di-hydroxy-propanone

Fischer convention of optical isomerism

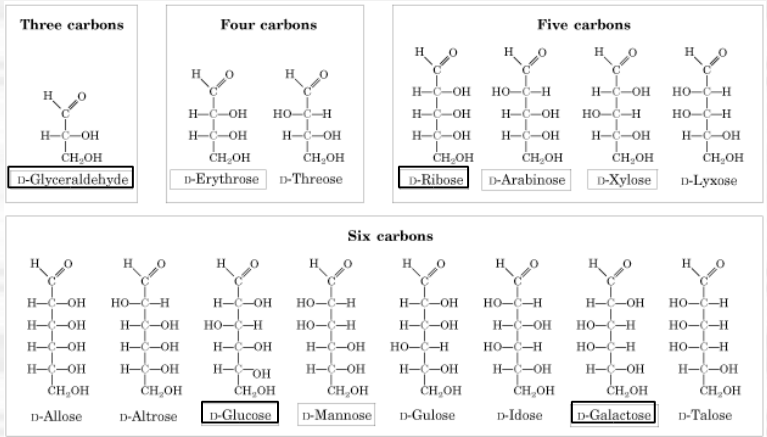
- Whenever there is a C atom linked to 4 different residual groups optical isomerism arises
- Sugars are optically active compounds with the possibility to have D or L spatial configuration
- In the Fisher convention the asymmetric C is placed in the centre, the aldehyde (or the ketone) is placed on the top, therefore one H and one OH are coming off the plane in the horizontal position.
- **D** is when a substituent is on the right side with respect to the H; **L** is the mirror image



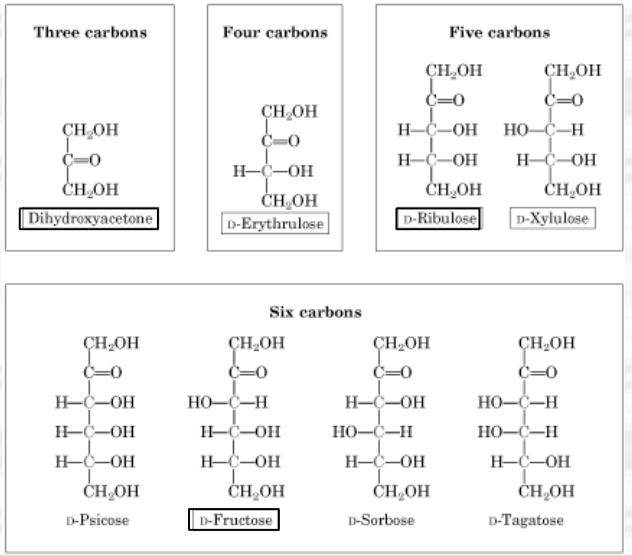
Name conventions

- **Enantiomers** are two mirror image molecules (chiral molecules):
  - D-Glyceraldehyde *vs* L-Glyceraldehyde
  - D-Alanine *vs* L-Alanine
- **Epimers** are molecules with >1 chiral C and only one of those is a mirror image of the other molecule
  - D-Glucose *vs* D-Galactose
  - D-threose *vs* D-erythrose
- **Anomers** are the cyclic form of monosaccharides in which the carbonyl atom has become a new chiral centre
  - α-D-glucose *vs* β-D-glucose
- **Diastereomers**: epimers and anomers, i.e. molecules with more than 1 chiral C

Aldose series of D sugars



Ketose series of D sugars



Sugars in our body

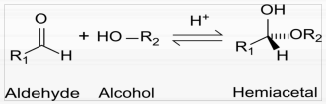
- All the mammals produce and use only sugars of the D series, either/both aldose and ketones
- The most common are:
  - Glyceraldehyde
  - Ribose
  - Glucose
  - Galactose
  - Dihydroxyacetone
  - Ribulose
  - Fructose

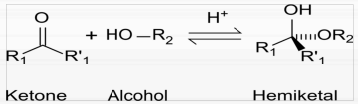
Reaction of sugars

- Reactions with R-OH (hemiacetals, glycosidic bonds)
- Oxidations
- Modifications

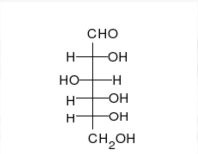
Cyclic sugars

- Carbonyl groups (R-CHO and R-CO-R) can react with alcoholic groups (R-OH) to form hemiacetals /hemiketals
- The reaction is an acid catalysed electrophile addition to the double bond



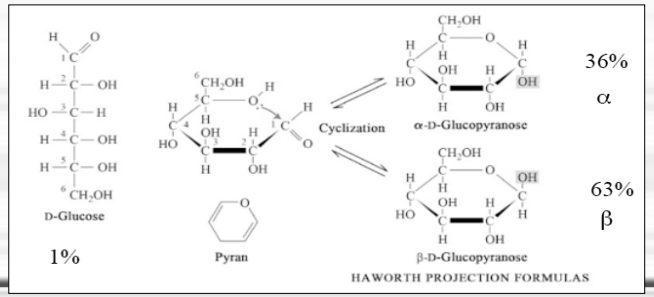


- When this reaction involves the internal -OH groups, the sugar can become cyclic and add one more asymmetric C to the molecule



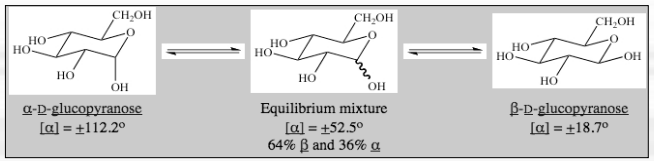
Cyclic sugars

- Usually hemiacetals and hemiketals are unstable, but cyclic sugars are indeed stable in water solutions
- 6-C aldoses form hexatomic rings (α-D-glucose and β-D-glucose) resembling pyran
- 5-C aldoses and 6-C ketones form pentatomic rings, resembling furan



Mutarotation

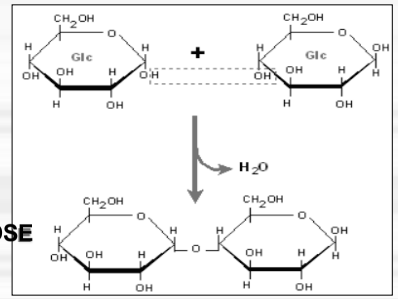
- Chiral centres can rotate the plane of polarised light either clockwise or counterclockwise
- Linear sugars in water solution can become cyclic, producing different amounts of α and β anomers
- The change in polarization with time is a proof of this dynamic equilibrium



Disaccharides, oligosaccharides and polysaccharides

- The anomeric hemicetal/hemiketal can attack another -OH group of a close-by sugar ring to produce multimers linked by acetals, ketals → glycosidic bonds

$$R\text{-}OH + HO\text{-}R' \rightarrow R\text{-}O\text{-}R' + H_2O$$



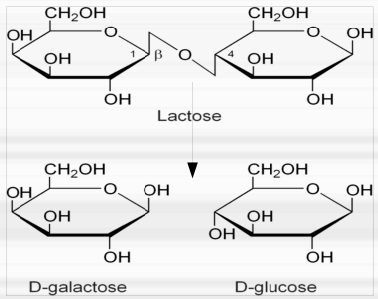
MALTOSE

α-1,4glycosidic bond

Disaccharides, oligosaccharides and polysaccharides

- The anomeric hemicetal/hemiketal can attack another -OH group of a close-by sugar ring to produce multimers linked by acetals, ketals → glycosidic bonds

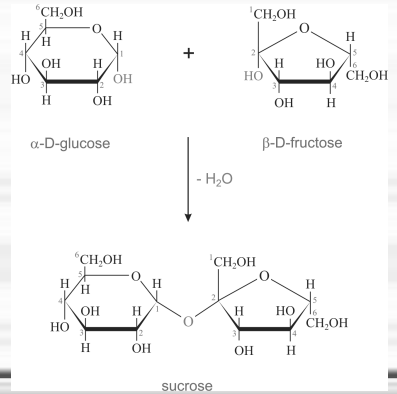
LACTOSE



β-1,α-4glycosidic bond

Disaccharides, oligosaccharides and polysaccharides

- The anomeric hemicetal/hemiketal can attack another -OH group of a close-by sugar ring to produce multimers linked by acetals, ketals → glycosidic bonds

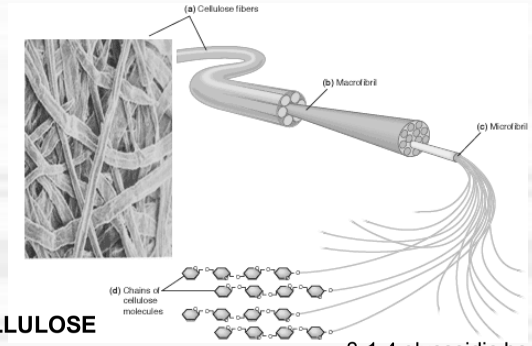


SUCROSE

α-1,β-2 glycosidic bond

Disaccharides, oligosaccharides and polysaccharides

- The anomeric hemicetal/hemiketal can attack another -OH group of a close-by sugar ring to produce multimers linked by acetals, ketals → glycosidic bonds

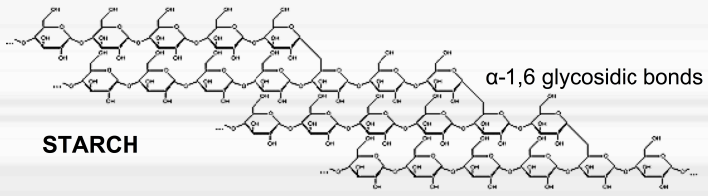


CELLULOSE

β-1,4 glycosidic bonds

Disaccharides, oligosaccharides and polysaccharides

- The anomeric hemicetal/hemiketal can attack another -OH group of a close-by sugar ring to produce multimers linked by acetals, ketals → glycosidic bonds



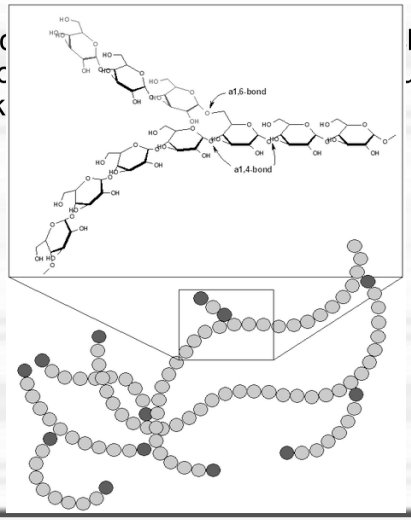
STARCH

α-1,6 glycosidic bonds

α-1,4 glycosidic bonds

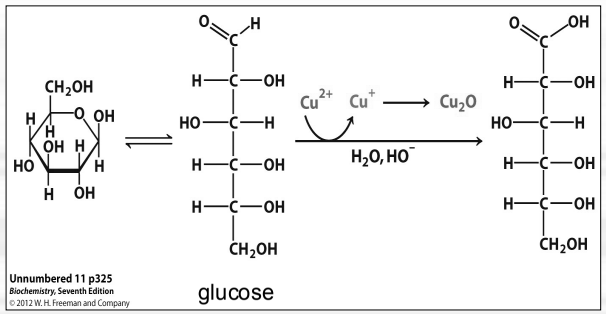
Disaccharides, oligosaccharides and polysaccharides

- The anomeric hemicetal/hemiketal can attack another -OH group of a close-by sugar ring to produce multimers linked by acetals, k



GLYCOGEN

Reaction of sugars

- Reactions with R-OH (hemiacetals, glycosidic bonds)
- Oxidations
- 

glucose

Glucuronic acid

Reaction of sugars

- Modifications: acetylation, phosphorylation, sulfation

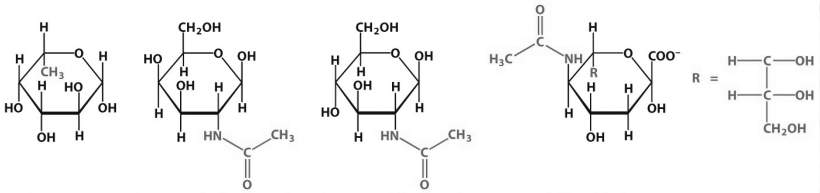
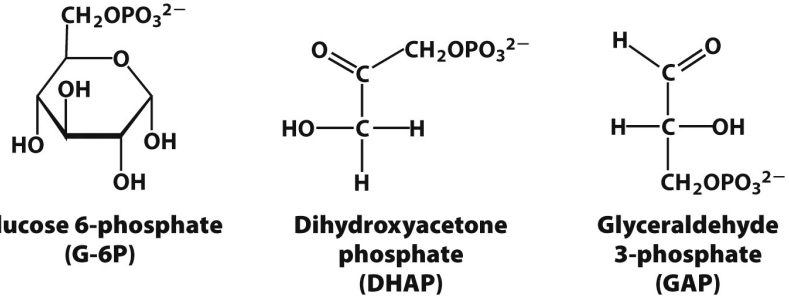


Figure 11.9
***Biochemistry,* Seventh Edition**

Reaction of sugars

- Modifications: acetylation, phosphorylation, sulfation



Unnumbered 11 p326
***Biochemistry,* Seventh Edition**

Reaction of sugars

- Modifications: acetylation, phosphorylation, sulfation

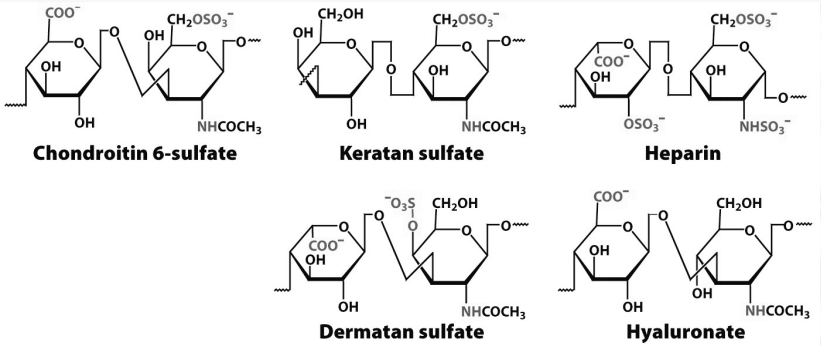


Figure 11.18
***Biochemistry,* Seventh Edition**