Carbohydrates - Monomers

Monday, 12 March 2018 9:18 am

- Carbohydrates are produced from CO_2 and H_2O via photosynthesis
  - Occur in the form $C_n(H_2O)_n$
- Can be linked covalently with proteins and lipids
- Are highly polar

Function

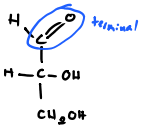
- Energy source and storage
- Structural component of cell walls and exoskeletons
- Informational molecules (cell-cell signalling)

Classification

- # carbons + "-ose"
  - E.g. pentose, hexose, triose
- All carbohydrates have a carbonyl group

Aldose

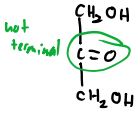
Carbonyl group is on the terminal carbon



Aldotriose

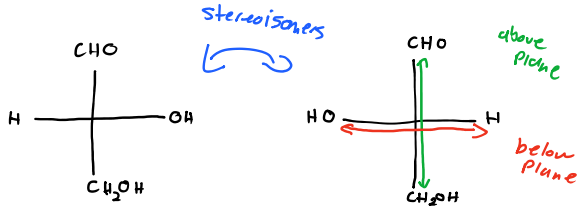
Ketose

Carbonyl group is within the carbon chain



Ketotriose

Fischer Projection



D-Glyceraldehyde L-Glyceraldehyde

- If the prefix is different, but the name is the same
  - Enantiomers - mirror images of each other
- If the prefix is the same, but the name is different
  - Diastereoisomers - non mirror images

Rotation of light

When linear polarised light is passed through a sample of homogeneous carbohydrate, the light will get rotated. This can be used as a classification, based on the direction of the rotation

Dextrorotatory - "D" forms - Light rotates clockwise through sample
Laevorotatory - "L" forms - Light rotates counter-clockwise through the sample.

Typical Carbohydrates

- Glucose - most common hexose
- Ribose - common pentose
- Galactose - epimer of glucose
- Mannose - epimer of glucose

Not epimers of each other

- Fructose - ketose form of glucose

Chemical Properties

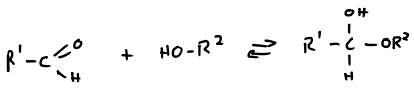
Aldehydes are strong reductants

- Therefore, ketoses and aldoses should be too, right?
  - They are, but not as strong as expected

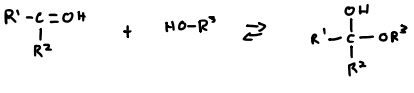
Carbonyl groups absorb UV and IR light,

- Carbohydrates, not so much...

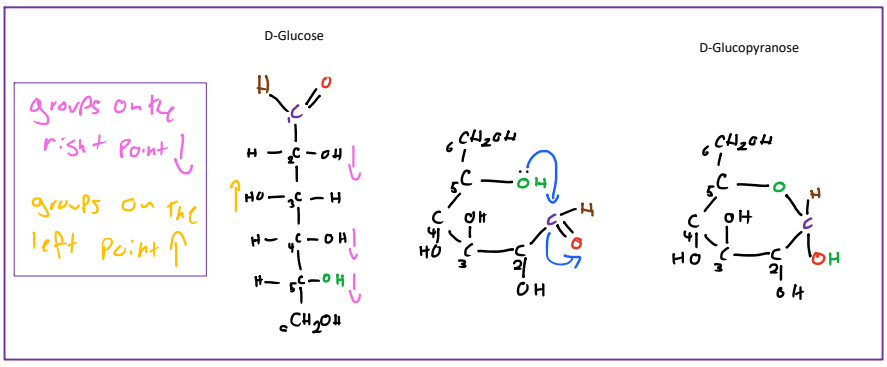
Aldehydes and alcohols can react with themselves to form rings.



Aldehyde + Alcohol ⇄ Hemiacetal



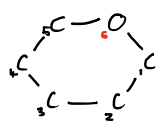
Ketone + Alcohol ⇄ Hemiketal



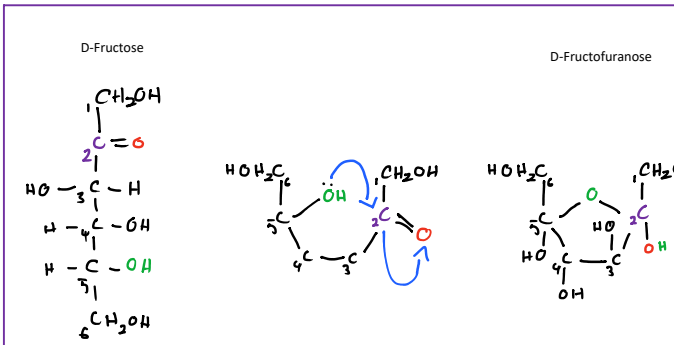
Pyranose and Furanose

As you can see from the examples on the right, hexoses can form into cyclic form with either five or six atoms.
We have to specify how these fold, which can be denoted by the prefixes pyranose and furanose

Pyranose - cyclohex...



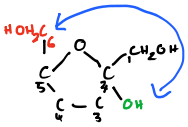
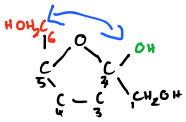
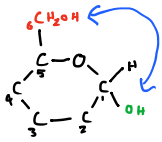
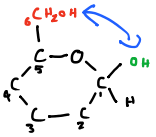
Furanose - cyclopent...



Animers

Animers

Animers are stereoisomers that differ specifically at the chiral centre of the hemiketal/hemiacetal.
α and β forms of pyranose and furanose refer to the location of the OH group on c_1, in realtion to the CH_2OH on C_6

	α - Opposite Side	β - same side
Ketose		
Aldose		

Conformations

Various conformations of carbohydrates exist, with varying energy levels

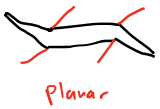
Chair

Boat

- Favourable in pyranoses
- Multiple chair conformations possible

Direction of Bulky Groups

Equatorial



Axial

Carbohydrates - Polymers

Monday, 12 March 2018 8:57 pm

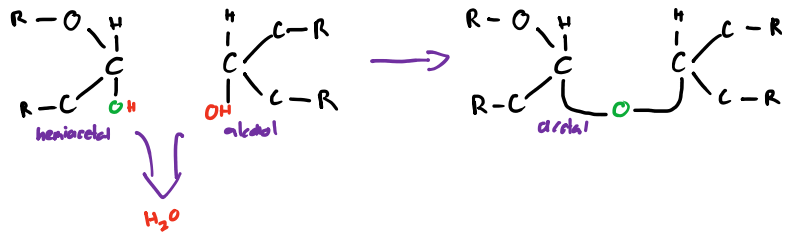
Types

- One carbohydrate monomer - monosaccharide
- Two carbohydrate monomers - disaccharide
- Polymer chain - polysaccharide
- Short polymer chain - oligosaccharide

Glycosidic Bond

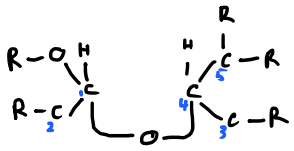
The hemiacetal or hemiketal reacts with an alcohol group in a dehydration reaction to form a "glycosidic bond"

- When a carbohydrate forms a glycosidic bond, it cannot linearise, change configuration or reduce
  - Sugars can only reduce if they have a free carbonyl group.

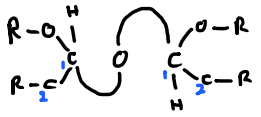


E.g. Bond Types

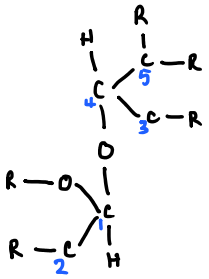
$(\alpha 1 \rightarrow 4)$



$(\alpha 1 \rightarrow 1)$



$(\beta 1 \rightarrow 4)$



Naming Sugars - Systematic

Reducing

- Anomeric prefix
  - E.g. α or β
- Prefix indicating the non reducing monosaccharide
  - E.g. D-gluco, D-lacto, L-fructo
- Descriptor of ring form changed to "-yl" suffix
  - E.g. pryranosyl, furanosyl
- Numbers to indicate linked carbon from monosaccharide one to two
  - E.g. $(1 \rightarrow 4)$
- Systemic name of the second monosaccharide with "-ose" suffix

E.g. Maltose Non-Reducing-Bond-Reducing

α-D-glucopyranosyl-$(1 \rightarrow 4)$-D-glucypyranose

Non-Reducing

- Naming similar to reducing sugars
- No reducing sugar means order of monosaccharides is not important
- Anomeric form must be included in both monosaccharide names
- Whichever is named second gets "-ide" suffix

E.g. Sucrose Non-Reducing-Bond-Non-Reducing

α-D-glucopyranosyl-$(\alpha 1 \rightarrow 2\beta)$-$\beta$-D-fructofuranoside

Polysaccharide Types

- Homopolysaccharides - single monomer subunit type
- Heteropolysaccharides - different monomer subunit types
- Can be linear or branched
- No molecular weight because of undefined length
- Typically in a state of flux. Can shrink and grow as needed

Starch

- Amylose $(\alpha 1 \rightarrow 4)$ glucose, unbranched
- Amylopectin $(\alpha 1 \rightarrow 6)$ glucose, branched every ~24-30 subunits
- Energy storage in plants

Glycogen

- $(\alpha 1 \rightarrow 4)$ linked glucose
- Branched $(\alpha 1 \rightarrow 6)$ every 8-12 subunits
- Energy storage in animals

Cellulose

- Linear, $(\beta 1 \rightarrow 4)$ linked
- h-bonds link adjacent monomers to each other linearly
- Parallel strands link with h-bonds to each other
- Insoluble in water

- Highly networked/strong.
- Used for structure in plants
- Difficult to metabolise (most animals cannot break $(\beta 1 \rightarrow 4)$ bonds. Ruminants require cellulase secreting bacteria to do it for them

Chitin

- $(\beta 1 \rightarrow 4)$ linked
- Similar to cellulose
- Hard, insoluble, difficult to digest

Agar

- Branched heteropolysaccharide
- Agrose and agaropectin