CLASSIFICATION OF CARBOHYDRATES

• most abundant organic molecules in plants and animals.
• made by photosynthesis.

\[ n\text{CO}_2 + n\text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O})_n + n\text{O}_2 \]

• Carbohydrate = hydrates of carbon.
  eg., glucose \( C_6H_{12}O_6 \) can also be written \( C_6(\text{H}_2\text{O})_6 \)
Not all carbohydrates can be written this way but the general name of carbohydrate has been retained.

Saccharides (or sugars) is also used as simplest members have a sweet taste

• There are 3 main types of carbohydrates
  (i) monosaccharides
  (ii) oligosaccharides
  (iii) polysaccharides

• Monosaccharides are the simplest carbohydrate or sugar that cannot be hydrolyzed to simpler compounds.

• generally represented as Fisher projections.
  eg.

D-glucose (α-D-glucose) and D-fructose (α-D-fructose) are constitutional isomers.
• may contain one or more stereogenic centres!

• naturally occurring sugars have the **D-configuration** at the chiral carbon farthest from the carbonyl group.

\[
\text{L-Glyceraldehyde (not naturally occurring)}
\]

\[
\text{D-Glyceraldehyde}
\]

\[
\text{L-Glucose (not naturally occurring)}
\]

\[
\text{D-Glucose}
\]

**ENANTIOMERS**

**EVERY STEREOGENIC CENTRE HAS THE OPPOSITE CONFIGURATION**
Figure 25.3
Configurations of D aldoses

3 C's
1 stereogenic centre
2\textsuperscript{1} stereoisomers

4 C's

5 C's

6 C's

D-Glyceraldehyde

D-Erythrose

D-Threose

D-Ribose

D-Arabinose

D-Xylose

D-Lyxose

D-Alloose

D-Altrose

D-Glucose

D-Mannose

D-Gulose

D-Idose

D-Galactose

D-Talose
Sugars form Rings

In solution (i.e. in cells etc.) they flop around and prefer to cyclise.

Compare:

6-membered ring form of a sugar = pyranose
5-membered ring form of a sugar = furanose
GLUCOSE: AN IMPORTANT HEMIACETAL

open-chain form of D-glucose

alcohol that attacks carbonyl

hydrogens on carbon omitted for clarity

rotate about C-4 and C-5 σ-bond so C-5 hydroxyl is positioned so it can attack aldehyde group from above or below

carbonyl carbon becomes the anomeric carbon (a new stereogenic centre)

hemiacetal formation by attack by hydroxyl on top face of aldehyde

hemiacetal formation by attack by hydroxyl on bottom face of aldehyde

α-D-glucopyranose 36% α-anomer

β-D-glucopyranose 64% β-anomer

HEMiacETALS
FISCHER AND HAWORTH STRUCTURES

D-glucose

\[
\begin{align*}
\text{CHO} & \\
\text{CH}_2\text{OH} & \\
\end{align*}
\]

α-D-glucopyranose

\[
\begin{align*}
\text{C}_1 & \\
\text{O} & \\
\text{C}_5 & \\
\end{align*}
\]

β-D-ribofuranose

\[
\begin{align*}
\text{C}_1 & \\
\text{O} & \\
\text{C}_4 & \\
\end{align*}
\]

For the remaining stereocentres:
- OH on RHS in Fischer structure → down in Haworth
- OH on LHS in Fischer structure → up in Haworth

α-anomer: CH\textsubscript{2}OH and anomeric OH are \textit{trans}

β-anomer: CH\textsubscript{2}OH and anomeric OH are \textit{cis}

D-ribose

\[
\begin{align*}
\text{CHO} & \\
\text{CH}_2\text{OH} & \\
\end{align*}
\]

D-fructose

\[
\begin{align*}
\text{CHO} & \\
\text{CH}_2\text{OH} & \\
\text{C}=\text{O} & \\
\text{CH}_2\text{OH} & \\
\end{align*}
\]

α-D-fructofuranose
Anomers can be isolated under certain conditions (e.g. crystallisation)

\[ \alpha \text{-D-glucopyranose} \]

- crystallises from ethanol/water at 30° C
- m.p. = 146° C, \([\alpha]_D = +112°\)

\[ \beta \text{-D-glucopyranose} \]

- crystallises from ethanol/water at >90° C
- m.p. = 150° C, \([\alpha]_D = +18.7°\)

Dissolve in water

Final \([\alpha]_D = +52.5°\)

Equilibration (\(\alpha \Leftrightarrow \beta\)) and resulting change in specific or optical rotation in solution is called MUTAROTATION

\[ \alpha \text{-anomer} \quad \leftrightarrow \quad \text{open-chain sugar} \quad \leftrightarrow \quad \beta \text{-anomer} \]

REATIONS OF MONOSACCHARIDES

- the hemiacetals are in equilibrium with small amount of the open-chain aldehyde:

**Oxidation**

\[ \alpha \text{-D-glucopyranose} \quad \text{and/or} \quad \beta \text{-D-glucopyranose} \]

(hemiacetals)

\[ \begin{align*}
\text{CHO} & \\
\text{H} & \text{OH} \\
\text{HO} & \text{H} \\
\text{H} & \text{OH} \\
\text{H} & \text{OH} \\
\text{CH}_2\text{OH}
\end{align*} \]

\[ \begin{align*}
\text{CO}_2^- & \\
\text{H} & \text{OH} \\
\text{HO} & \text{H} \\
\text{H} & \text{OH} \\
\text{H} & \text{OH} \\
\text{CH}_2\text{OH}
\end{align*} \]

\[ [\text{Ag(NH}_3\text{)}_2]^- \quad \text{+ Ag (s)} \]

Carbohydrates which can be oxidised by Tollens' reagent are called reducing sugars.

**Reduction**

\[ \alpha \text{-D-glucopyranose} \quad \text{and/or} \quad \beta \text{-D-glucopyranose} \]

(hemiacetals)

\[ \begin{align*}
\text{CHO} & \\
\text{H} & \text{OH} \\
\text{HO} & \text{H} \\
\text{H} & \text{OH} \\
\text{H} & \text{OH} \\
\text{CH}_2\text{OH}
\end{align*} \]

\[ \begin{align*}
\text{CH}_2\text{OH} & \\
\text{H} & \text{OH} \\
\text{HO} & \text{H} \\
\text{H} & \text{OH} \\
\text{H} & \text{OH} \\
\text{CH}_2\text{OH}
\end{align*} \]

\[ \text{NaBH}_4 \]
Recall:

\[
\begin{align*}
\text{aldehyde} & \quad \xrightarrow{\text{excess } R_3^3OH / H^+ \text{cat.} / \text{heat}} \quad \text{acetal} \\
\text{or ketone} & \quad \xrightarrow{\text{dilute } H^+ / H_2O / \text{heat}} \quad \text{acetal}
\end{align*}
\]

For cyclic hemiacetals:

\[
\begin{align*}
\text{HO} & \quad \xrightarrow{\text{excess } R_3^3OH / H^+ \text{cat.} / \text{heat}} \quad \text{cyclic acetal} \\
\text{CH} & \quad \xrightarrow{\text{dilute } H^+ / H_2O / \text{heat}} \quad \text{cyclic acetal}
\end{align*}
\]

GLYCOSIDE FORMATION

\[
\begin{align*}
\alpha-D-\text{glucopyranose} & \quad \text{and/or} \quad \beta-D-\text{glucopyranose} \\
& \quad \xrightarrow{\text{excess CH}_3OH / \text{cat. } H_2SO_4 / \text{heat}} \\
\text{methyl } \alpha-D-\text{glucopyranoside} & \quad \text{+} \quad \text{methyl } \beta-D-\text{glucopyranoside}
\end{align*}
\]

These are methyl glycosides of D-glucose. These acetals or glycosides are not in equilibrium with open-chain aldehydes.
DISACCHARIDES

- are acetals formed if a monosaccharide reacts with an alcohol that is another sugar:

LACTOSE

β-D-galactopyranose  α-D-glucopyranose

(hydrogens on carbon omitted for clarity)

4-O-(β-D-galactopyranosyl)-α-D-glucopyranose (LACTOSE)

4-O-(β-D-galactopyranosyl)-β-D-glucopyranose
**SUCROSE** (hydrogens on carbon omitted for clarity)

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{O} \\
\text{OH} & \quad \text{OH} \\
\alpha\text{-D-glucopyranose} & \quad \text{H} \\
\text{HOH}_2\text{C} & \quad \text{O} \\
\text{O} & \quad \text{OH} \\
\beta\text{-D-fructofuranose} & \quad \text{H} \\
\end{align*}
\]

**In Summary:**

- Hemiacetal present $\rightarrow$ reducing sugar
  $\rightarrow$ mutarotates

- No hemiacetal present $\rightarrow$ non-reducing sugar
  $\rightarrow$ cannot mutarotate

**Hydrolysis of glycosides:**

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{OH} & \quad \text{OH} \\
\text{H} & \quad \text{OCH}_3 \\
methyl \alpha\text{-D-glucopyranoside} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{dilute H}^+ / \text{H}_2\text{O} & \quad \text{heat} \\
\text{CH}_2\text{OH} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{OH} & \quad \text{OH} \\
\text{H} & \quad \text{CH}_2\text{OH} \\
+ & \quad \text{CH}_3\text{OH} \\
\text{OH} & \quad \text{O} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{OH} \\
\text{H} & \quad \text{H} \\
\text{OH} & \quad \text{OH} \\
\end{align*}
\]
DISACCHARIDES

The most common oligosaccharides are disaccharides. In a disaccharide, two monosaccharides are linked by a glycosidic bond between the anomeric carbon of one monosaccharide unit and a hydroxyl group on the other unit. The glycoside bond to the anomeric carbon can be either alpha or beta.

(i) Maltose

- obtained by partial hydrolysis of starch
- further hydrolysis of maltose gives only D-glucose
- anomeric carbon on the right glucose in maltose is a hemiacetal, therefore maltose is a reducing sugar

(ii) Cellobiose

- obtained by partial hydrolysis of cellulose
- further hydrolysis of cellobiose gives only D-glucose
- cellobiose differs from maltose only in having the β-configuration at C1 of the left glucose unit
- anomeric carbon on the right glucose in cellobiose is a hemiacetal, therefore cellobiose is a reducing sugar
(iii) Lactose

- major sugar in human and cow’s milk
- hydrolysis of lactose gives equimolar amounts of D-galactose and D-glucose
- anomic carbon on the right glucose in lactose is a hemiacetal, therefore lactose is a reducing sugar

(iv) Sucrose

- most important commercial disaccharide, table sugar.
- hydrolysis of sucrose gives equimolar amounts of D-glucose and the ketose D-fructose
- sucrose differs from the other disaccharides(i)-(iii) in that the anomic carbons of both units are involved in the glycoside link.
- sucrose does not contain a hemiacetal group and is therefore a non-reducing sugar and cannot mutarotate
POLYSACCHARIDES

Polysaccharides are carbohydrates in which tens, hundreds or even thousands of simple sugars are linked together through glycoside bonds. Since they have no free anomeric hydroxyls (except for the one at the end of the chain), polysaccharides are not reducing sugars and do not show mutarotation.

(i) Cellulose

- consists of several thousand D-glucose units linked by 1,4'-β-glycoside bonds
- wood, leaves, grasses and cotton are primarily cellulose

Cellulose, a 1,4'-O-(β-D-glucopyranoside) polymer

(ii) Starch

- polymer of D-glucose in which monosaccharides are linked by 1,4'-α-glycoside bonds
- contains two fractions  - amylpectin (water soluble)
- amylose (water insoluble)

Amylose, a 1,4'-O-(α-D-glucopyranoside) polymer

- amylpectin (~80% starch) contains branches which results in a complex 3-dimensional structure.
- nature uses starch as a means by which plants store energy for later use (potatoes, corn, cereal grains).
- when eaten, starch is digested by enzymes called glycosidases, which specifically catalyze the hydrolysis of α-glycosides; hence humans can eat potatoes and grains but not grass and wood which contain β-glycosides.
Sucrose, α-D-glucopyranosyl-β-D-fructofuranoside, is table sugar. Its structure is shown on the right.

Does sucrose display "mutarotation"? Justify your answer.

Draw the Fischer projection of the open chain form of D-fructose.

D-Fructose, on treatment with acidified methanol, gives two furanosides. Draw the Haworth structures of these.

Draw the Haworth structure of the disaccharide 2-O-(β-D-glucopyranosyl)-β-D-glucopyranose.