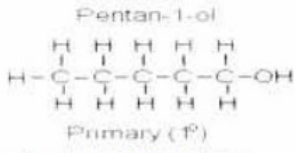
Alcohols, Aldehydes and Ketones

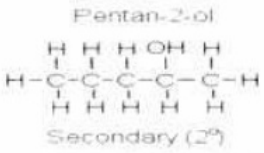
Classifying and Reactions

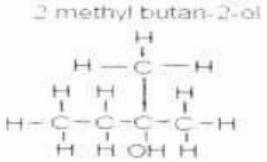
Alcohols: RCOH

Classification:

Alcohols are classified based on number of carbon atoms bonded to the hydroxyl group.







Common name :
PC as a branch followed by alcohol

Alcohols can also be classified based on the number of hydroxyl groups attached.

1 –OH monohydric 2 –OH dihydric 3 –OH trihydric

more than one –OH can be referred to as polyhydric

Physical Properties:

Alcohols are a polar molecule due to the polar hydroxyl group and the polar carbon to oxygen bond. Alcohols in solution will form hydrogen bonds with each other. This increased intermolecular bonding causes alcohols to have higher boiling points than similar aliphatic compounds.

Reactions:

1. Combustion – burning in the presence of O_2 (g) producing water and carbon dioxide.
   $C_2H_5OH + 3\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + 3\ H_2O$

2. Dehydration – loss of water adds a bond. The hydroxyl bonds to an adjacent hydrogen to form a water molecule and a double bond. This reaction generally requires acid and heat as catalysts.

   $$C_2H_5OH \xrightarrow[180^\circ C]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

3. Hydrolysis – addition of water results in the deletion of a bond. A water molecule is used to add a hydroxyl group and a hydrogen forming an alcohol.
   $CH_2{=}CH_2 + H_2O \rightarrow C_2H_5OH$

4. Oxidation – partial oxidation of an alcohol can yield either an aldehyde or a ketone and water.

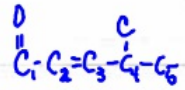
   $$2\ C_2H_5OH + O_2\ (g) \xrightarrow[H_2SO_4]{K_2Cr_2O_7} C_2H_4O + 2\ H_2O$$

5. Reactions with alcohol and an organic acid will form an ester.

Aldehydes: RC=O (carbonyl group)

Classification:

1. Aldehydes are generally named based on the carboxylic acid the form when oxidized. For example: acetaldehyde forms acetic acid.
2. Aldehydes can also be named based on the longest carbon chain followed by –al. For example: C_2H_4O is ethanal



4-methyl-2-pentenal

Reactions:

Aldehydes are good reducing reagents and are also used to polymerize (uniting to form polymers). An important example of the reducing action of an aldehyde is using Benedict's Solution to determine simple sugar concentrations.

Ketones are generally good solvents. Ketones can be found in excessive amounts in the blood and urine of untreated diabetics.

Tollen's Reagent can be used to identify aldehydes and ketones. Tollen's Reagent will oxidize the aldehydes forming carboxylic acids. Ketones will resist oxidation and remain unaffected by Tollen's Reagent.

Carbohydrates:

Classification:

Carbohydrates occur in all plants and animals and are essential to life. Carbohydrates can be divided into several categories:

1. Polyhydroxyaldehydes and polyydroxyketones. Carbohydrates contain both hydroxyl groups and carbonyl groups. The location of the carbonyl group determines whether a carbohydrate is a polyhydroxyaldehyde or a polyhydroxyketone.

2. Monosaccharides, oligosaccharides (meaning a few saccharides), disaccharides and polysaccharides based on their hydrolysis possibilities.

$$\text{Polysaccharides} \xrightarrow[H^+]{H_2O} \text{Oligosaccharides (Disaccharides)} \xrightarrow[H^+]{H_2O} \text{Monosaccharides}$$

Monosaccharides:

Monosaccharides - (simple sugars) carbohydrates that can not be hydrolyzed to simpler compounds.

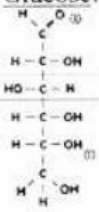
Physical Properties:

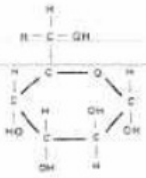
Monosaccharides are typically white crystalline solids, that are sweet and soluble in water.

Important Monosaccharides:

Pentoses (5C) $C_5H_{10}O_5$ – arabinose, xylose, ribose and deoxyribose
Hexoses (6C) $C_6H_{12}O_6$ – glucose, galactose and fructose

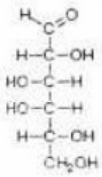
Glucose: (dextrose) aldose – found in fruits and honey. Also found in the bloodstream. Glucose is commercially prepared from the acid hydrolysis of cornstarch.



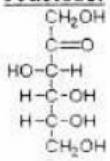


The first illustration shows glucose in its aliphatic form. The second shows the hemiacetal form of glucose.

Galactose: aldose - is not found in its free state in nature. It is found in the disaccharide lactose and in the polysaccharide pectin. Galactose is less sweet and less soluble than glucose.



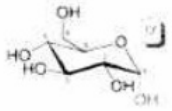
Fructose: (levulose) ketose – occurs with glucose in fruits and honey. Fructose is the most soluble and the sweetest of all the sugars.



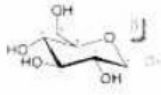
Hemiacetals:

When monosaccharides form heterocyclic hemiacetals the new stereo center formed is called an anomeric carbon. (the carbon bonded to one –OH and –OR)

- six membered: pyranose
- five membered: furanose

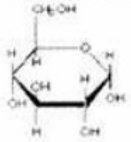


alpha (α) orientation

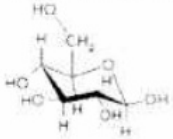


beta (β) orientation

Haworth Projections:

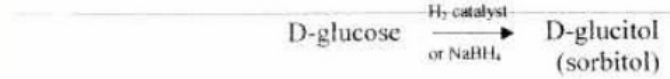


Chair Formation:

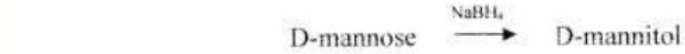


Reactions of Monosaccharides:

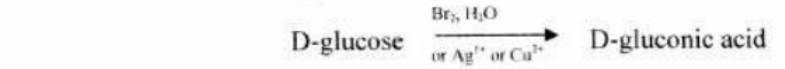
1. Reductions – When aldoses and ketoses are reduced they yield polyols, called alditols.



* Sorbitol is used as a sweetner or sugar substitute.



2. Oxidation – aldehyde groups can be oxidized to form acids, called aldonic acids.



Strong oxidizers will produce dicarboxylic acids called aldaric acids.

Examples of oxidizers to know:
- ✓ Tollen's Reagent: Ag^{1+} in aqueous ammonia - positive silver mirror test
- ✓ Fehling's Reagent: Cu^{2+} with tartrate – positive red (copper) precipitate
- ✓ Benedict's Reagent: Cu^{2+} with citrate – positive red (copper) precipitate

3. Formation of Glycosides – Reaction of a hemiacetal with alcohol yield an acetal, forming a glycosidic bond. (the bond from the anomeric carbon of a glycoside to an –OR group)

4. Dehydration Synthesis – When two monosaccharides undergo dehydration synthesis the molecules are linked forming a disaccharide, releasing a water molecule.

5. Fermentation – Monosaccharides (except galactose and lactose) are fermented by enzymes to produce alcohol and carbon dioxide.

Disaccharides

Disaccharides are carbohydrate molecules containing two monosaccharides linked by a glycosidic bond between the anomeric carbon of one molecule and the hydroxyl group of the other molecule.

Important Disaccharides:

Sucrose – (glucose + fructose) common table sugar. Prepared commercially from sugar cane or sugar beets. Sucrose is sweeter than glucose but not as sweet as fructose. It is very soluble.

Maltose – (glucose + ~~galactose~~ glucose) often called *malt sugar*, found in germinating grains and in malt. Maltose is less soluble and less sweet than sucrose.

Lactose – (glucose + ~~glucose~~ galactose) milk sugar. Lactose is the least soluble and least sweet of all common sugars.

Reactions of Disaccharides:

1. Hydrolysis – hydrolysis of disaccharides yield two molecules of monosaccharides.

Polysaccharides

Polysaccharides are chains of monosaccharides joined together by glycosidic bonds.

Physical Properties:

Polysaccharides are generally amorphous in appearance, with little or no flavor. They are generally insoluble or form colloidal dispersions.

Important Polysaccharides:

Starch – (amylase and amylopectin) Starch is the reserve food of plants. It is also used in laundering and in the manufacture of paste, sizing, alcohols, glucose and corn syrup.

Glycogen – Glycogen is the reserve starch of animals. When blood glucose levels rise glucose is converted to glycogen by the liver. This process is referred to as glycogenesis. The energy required form this process is derived by converting ATP to ADP.
The reverse of glycogenesis is called glycogenolysis. This process converts glycogen back into glucose (occurs in the liver).

Cellulose – Cellulose is the main constituent of the cell membranes of plants. Used to manufacture paper, rayon, cellophane, cellulose, acetate, and other similar products.

Other notable polysaccharides: chitin, pectin, dexitrin

Important modified polysaccharides: Ascorbic acid (vitamin C) and heparin.

Metabolism of Carbohydrates

Dietary Sources of Carbohydrates:

1. Starches: plant material. Plants synthesize carbohydrates through carbon fixation methods (like photosynthesis).
2. Disaccharides: sucrose from refined sugars and milk lactose.
3. Glycogen: animal tissue (small quantity)

Carbohydrate Digestion (human):

1. Salivary glands: secrete amylase which begins the digestion of starches.
2. Small intestine:
   - ✓ Further degradation of carbohydrates
   - ✓ Produces amino acids, hexose sugars, fatty acids and glycerol
   - ✓ Moves materials into blood for transport to cells

Important Metabolic Pathways:

1. Carbon fixation: CO_2 is reduced to a carbohydrate
2. Glycolysis: breakdown of glucose to ATP and pyruvate. Pyruvate will then enter the Kreb's cycle.

$$\text{Glucose} + 2\ \text{ATP} + 2\ \text{ADP} + 2\ PO_4^{-} + 2\ NAD^{+} \xrightarrow{\text{10 enzymes}} 2\ \text{pyruvate} + 2\ \text{NADH} + 2H_2O + 4\ \text{ATP}$$

3. Pentose Phosphate Pathway: hexose is converted into pentose to regenerate NADPH.
4. Glycogenesis: excess glucose is converted into glycogen in the liver. (promoted by insulin)
5. Glycogenolysis: glycogen is converted into glucose in order to maintain proper glucose levels in the bloodstream. (promoted by glucagon)

Hormone	Source	Target Tissue	Action
Glucagon	Pancreas	Liver	Stimulate glycogen breakdown
Adrenaline	Adrenals	Muscle	Stimulate glycogen breakdown
Insulin	Pancreas	Liver and muscle	Stimulate glycogen synthesis, and stimulates uptake of glucose into liver and muscle

Links:
http://ull.chemistry.uakron.edu/genobc/Chapter_23/

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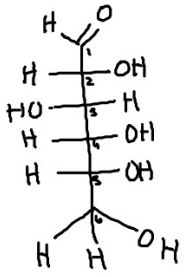
Monosaccharides

glucose

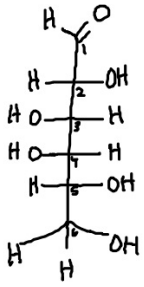


aldose

found in fruits, veggies & honey

Sweet & Soluble in H_2O

galactose

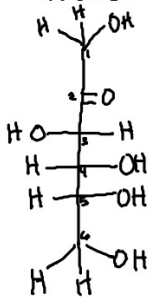


aldose

Not found in nature in its free state

less sweet & less Soluble than glucose

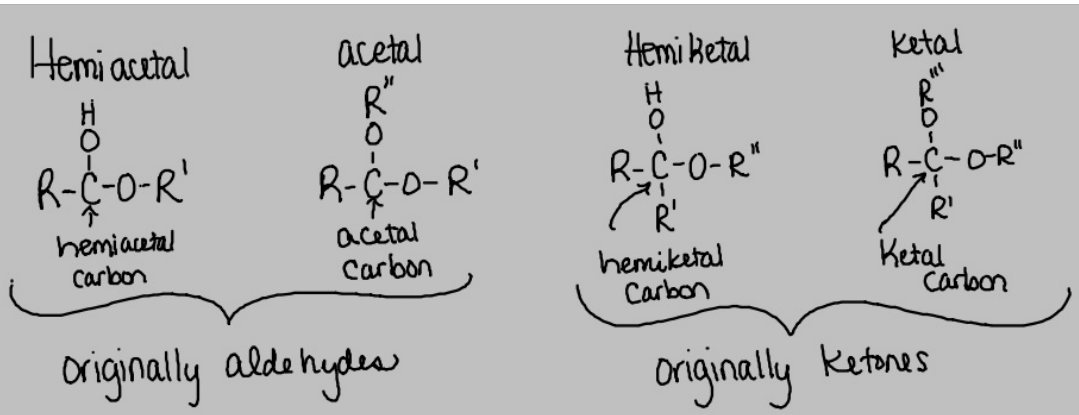
fructose



Ketose

found in fruits, veggies & honey

most sweet & most Soluble



Hemiacetals & Hemiketals are intermediates of a reversable reaction.

Aldehydes + alcohol → hemiacetal + alcohol → acetal

Ketone + alcohol → hemiketal + alcohol → Ketal

Formation of a hemiacetal