ELEC6205
BioNanotechnology

Carbohydrates
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- Most abundant molecules on earth
- Photosynthesis converts 100 billion metric tons CO$_2$ and H$_2$O into cellulose and other plant products.
- Oxidation of carbohydrates is the main source of energy in non-photosynthesising organisms.
- Carbohydrates are responsible for molecular recognition and adhesion between cells.
- Insoluble carbohydrates are structural polymers.

- Three classes:
  - Monosaccharides – simple sugars, e.g. glucose
  - Oligosaccharides – short chains of monosaccharides,
  - Polysaccharides – > 20 monosaccharide units, e.g. cellulose
Monosaccharides

Soluble, colourless and dissolve in polar liquids.

Two or more hydroxyl groups

D-glucose

D-fructose
Nature is right handed (mostly)

- Molecules come in two forms – right and left handed depending on the way they rotate plane-polarised light. Called CHIRAL
  - Right handed $D$ (dexter)
  - Left handed $L$ (laevus)
- Nearly all monosaccharides occur in optically active isomers
  (isomer- molecule of same Mw but different structural shape)
- Glucose is made in plants by photosynthesis but only the \textit{D}-isomer is made.
- \textit{L}-glucose is not metabolised by animals.
- However only the \textit{L}-isomers of amino acids are used in enzymes and proteins.
In aqueous solution all monosaccharides are cyclic (ring) structures. Reaction between C1 and C5.

Two stereo-isomers exist in solution (correct name is $\alpha$-$D$-Glucopyranose)
Two ends of the linear molecules form covalent bond.
Oxidation of glucose - metabolism

- Glucose is used in a myriad of reactions in biology
- It “carries” a lot of energy
- e.g. oxidation (with enzymes) gives:
  - Glucose + 6O₂ → 6CO₂ + 6H₂O
- Free energy released ΔG = -2840 kJ/mol
- This is used as ‘fuel’ for many other reactions
  (Hydrolysis of ATP to ADP is 30kJ/mole)
Oligosaccharides and Polysaccharides

- Starch, Cellulose, Glycogen, are all examples of **polysaccharides** – polymer chains of saccharides
- Polysaccharides are polymers made from individual sugar monomers
- Many proteins are glycosylated – have sugar molecules on the side chains.
- Glycosylation is the attachment of a carbohydrate (sugar) group to a protein
- Human blood groups are determined by the different oligosaccharides attached to glycoproteins
• **Storage polysaccharides** (homopolysaccharides).
• Multi-branched, assembled from repeating (same) sugar units.
  – Starch in plant cells
  – Glycogen in animal cells (liver)
  – Plant cell walls and exoskeletons
• Heavily hydrated – many exposed hydroxyl groups hydrogen bond with water
• Enzymes “chop off” sugar units (glucose) one at a time which are then metabolised
Glycogen
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Glycogen - a highly branched polymer (dendrimer) of 60,000 glucose residues. Mw = around $10^6$ to $10^7$. Every glucose in $\alpha$-conformation.

Why not store glucose directly in the cells? Glycogen is stored at a concentration of 0.01mM in hepatocytes - insoluble and makes little difference to the osmolality. This is equivalent to a concentration of 0.6M glucose!

If glucose was stored at this high level, the cell would be unable to cope with the osmotic pressure from the entry of water. Outside the cell, the glucose concentration in blood is 5mM.
Osmosis and osmotic stress

(a) Cell in isotonic solution; no net water movement.

(b) Cell in hypertonic solution; water moves out and cell shrinks.

(c) Cell in hypotonic solution; water moves in, creating outward pressure; cell swells, may eventually burst.
Structural polysaccharides

**Cellulose** is a major constituent of plant cell walls. It consists of long linear chains of D-glucose, approx. 10,000 to 15,000 of them. Water insoluble.

Glucose are all β-configuration. Every other glucose in cellulose is flipped over. Animals cannot use cellulose as a food source because they lack an enzyme to hydrolyse the linkages.

Termites use a symbiotic organisms that lives in their gut and breaks down wood using an enzyme called **cellulase**. So do fungi and bacteria found in ruminants’ stomach.
This flipping of every other molecule promotes intra-chain and inter-chain hydrogen bonds, as well as van der Waals interactions. The cellulose chains become straight and rigid, and pack with a crystalline arrangement in thick bundles called microfibrils. The water content is very low, because of the inter-chain H-bonding.
Chitin

- Similar to cellulose, but one of the alcohols $R – \text{OH}$ (in the glucose monomer) is replaced with (an acetylated amino acid):

$$R - \text{NH} - \text{C} - \text{CH}_3$$

Another long multi-branched polymer

Principle component of the exo-skeleton of a million species of arthropod: insects, lobsters, crabs and the second most abundant polysaccharide after cellulose
Bacterial cell walls

- Bacteria have a cell wall protecting the fragile lipid membrane.
- This is made from a hetero-polysaccharide, cross-linked by peptides.
- The enzyme lysozyme breaks bacterial cell walls (kills it) by hydrolysing (breaking) the bond between two of the mono-saccharides (next slide).
- Lysozyme is found in tears (and egg white) – good antibacterial agent (also in viruses).
Cell wall of \textit{S. aureus}.

Peptides link together the polysaccharide chains.

Penicillin kills bacteria by preventing the synthesis of the cross-links, so that the cell dies by osmotic lysis.

\begin{itemize}
\item Peptides
\end{itemize}
Lipopolysaccharides (LPS)

- Many bacteria have an outer membrane made from lipid molecules with polysaccharides attached to the lipid head groups.
- The polysaccharides are prime targets for the immune system and are determinants of the serotype of the bacteria, i.e. strains that are determined on the basis of their antigenic properties.
- Many LPS are extremely toxic – responsible for toxic shock from gram-negative bacteria.
Lipopolysaccharide (LPS) contains different carbohydrates. The 3-D model of LPS indicates that this is only on the outer leaflet of the bilayer. The inner leaflet is normal lipid, half a bilayer thick.
Polysaccharides and nanotechnology

• Major uses in:
(a) As artificial scaffolding material for cell engineering – repair and growth of new tissue constructs, cartilage, organs..
(b) Smart capsules for drug release, MRI contrast agents