The Chemistry of Food
Lecture 1

Chemistry in Context
06525/06529/06509

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Topics in Food Chemistry

Physical and chemical properties of:

- Carbohydrates
  - saccharides (mono-, di-, oligo- and poly-)
- Proteins
  - amino acids and polypeptides
- Lipids
  - oils and fats
- Colourings
- Flavour chemicals
- Vitamins
- Minerals
- Water
- Preservatives

Carbohydrates - general

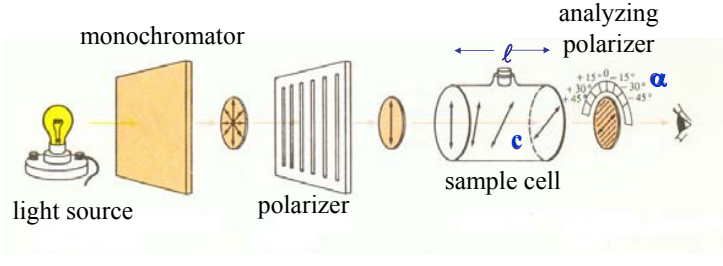
- Source of energy and sweetness (see later)

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{ENERGY}$$
$$C_6H_{12}O_6 + 6O_2 \longleftarrow 6CO_2 + 6H_2O + \text{SUNLIGHT}$$

- Carbohydrates consist of single units known as monosaccharides or multiple units thereof.
- Simple sugars (mono- and disaccharides)
- Oligo- and polysaccharides (sugar polymers)

- Many stereoisomers possible

Polarimetry



Observer rotates analyzing polarizer to view maximum / minimum light and records angle α

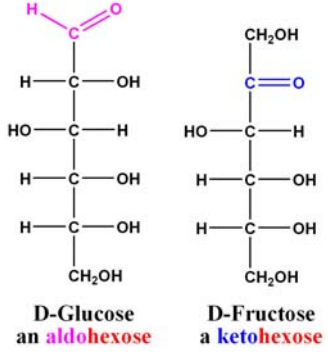
Length of sample cell ℓ (dm) is known, concentration c ($g.cm^{-3}$) may be known or unknown

Simple Sugars

- Glucose
  - also known as *grape sugar*, *corn sugar* or *dextrose*
  - dextrorotatory (+)
  - made commercially by hydrolyzing starch
- Fructose
  - also known as *fruit sugar* or *laevulose*
  - laevorotatory (-) (but in the D-sugar series!)
  - made by hydrolyzing starch and isomerizing the glucose from the corn syrup

Monosaccharides

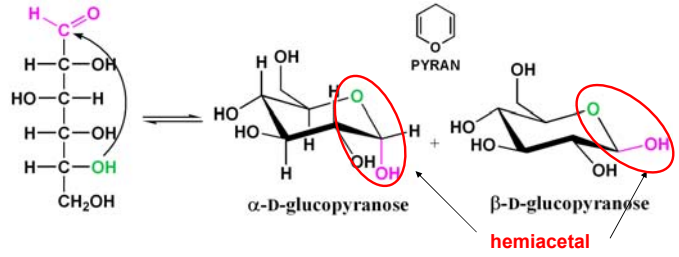
- General Formula $(CH_2O)_n$
- Polyhydroxy carbonyl compounds, e.g. aldoses (aldehyde based) and ketoses (ketone based)
- Carbon content can vary (typically 3-8) for each type of saccharide, e.g. pentoses (C_5) and hexoses (C_6)



FISCHER PROJECTIONS

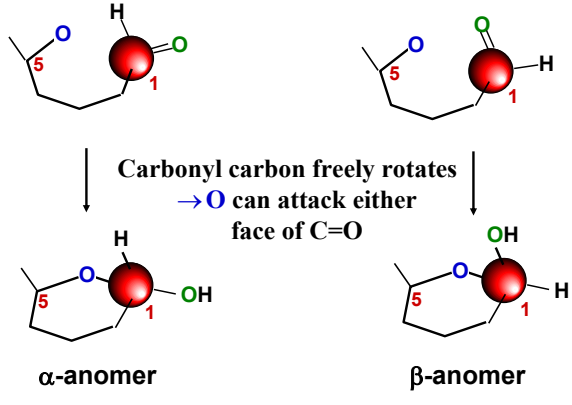
Monosaccharides

- Monosaccharides mainly exist as cyclic hemiacetals
- Attributed names on the basis of the *ring size*, e.g. furanose (5-ring, c.f. furan) and pyranose (6 ring, c.f. pyran)



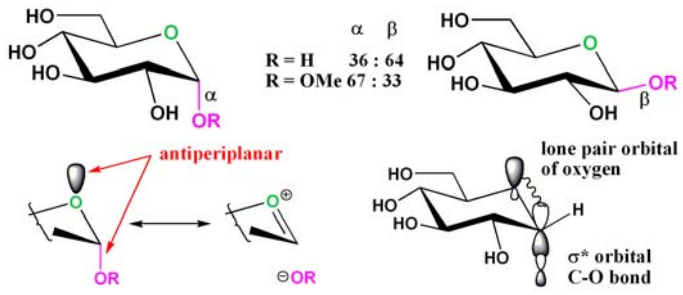
- α- and β- anomers of the cyclic forms exist

Cyclisation of linear sugars



The anomeric effect

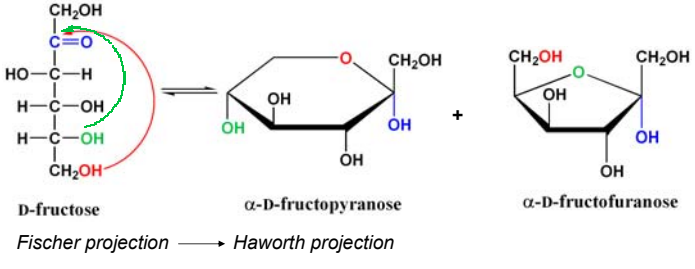
- When compared to the β-anomer, the α-anomer is often much more stable than expected so that in many cases [α-anomer] > [β-anomer].



- There is a stereoelectronic preference for conformations in which the best donor lone pair, or bond, is antiperiplanar to the best acceptor bond.

Monosaccharides

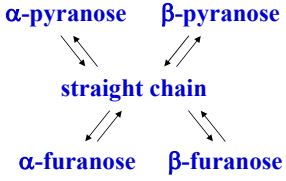
- Fructose



- Conversion of either anomer into the equilibrium mixture is called mutarotation

Mutarotation

- Single molecule *in solution* can interchange between
  - straight chain and ring
  - different ring sizes
  - α and β anomers



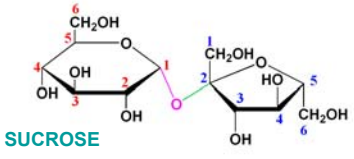
- Mutarotation is
  - a dynamic equilibrium
  - all isomers can potentially exist in solution
  - energy / stability of different forms vary

Sucrose and Lactose: disaccharides

- Sucrose
  - Also known as *cane sugar* or *beet sugar*
  - Obtained commercially from sugar beet or sugar cane
  - Only one isomer present in solution
  - Easily crystallized
- Lactose
  - Also known as *milk sugar*
  - Primary sugar in mammalian milk (human > cow)
  - Also is a by-product of cheese manufacture
  - Not very sweet (relative intensity ≤ 0.3 cf sucrose)
  - Hydrolyzed by enzyme β-galactosidase. Many adults lack this enzyme and are therefore *lactose intolerant*

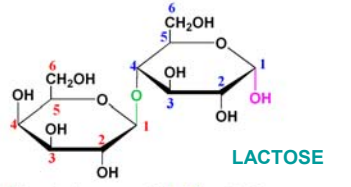
Glycosidic linkages

- Disaccharides are formed by linking two monosaccharides *via* a glycosidic link (acetal).



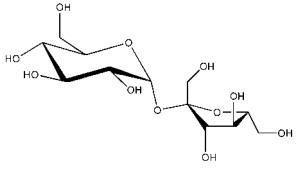
SUCROSE

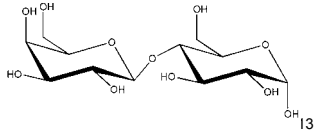
α-D-glucopyranosyl-(1→2)-β-D-fructofuranose



LACTOSE

β-D-galactopyranosyl-(1→4)-α-D-glucopyranose





Invert sugars

- Invert sugar is produced by acid hydrolysis of sucrose
- Produces a mixture of glucose and fructose

$$H_2O + \text{sucrose} \longrightarrow \text{glucose} + \text{fructose}$$

$$[\alpha]_D \quad +66.5^\circ \qquad +52.7^\circ \qquad -92.4^\circ$$

  - Rotation of solution goes from *dextrorotatory* to *laevorotatory* overall
  - Process is called "inversion" of sucrose - producing "invert sugar"

Tri- and tetrasaccharides

Raffinose

α-D-galactopyranosyl-(1→6)-α-D-glucopyranosyl-(1→2)-β-D-fructofuranose

Stachyose

α-D-galactopyranosyl-(1→6)- α-D-galactopyranosyl-(1→6)-α-D-glucopyranosyl-(1→2)-β-D-fructofuranose

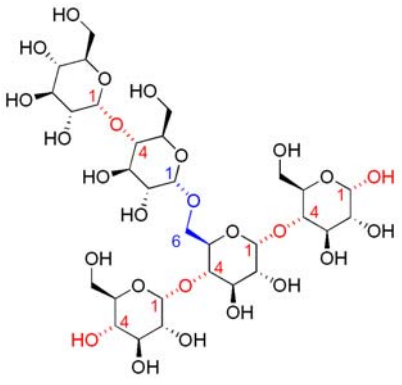
- Both found in legumes (peas, beans, soya)
- But neither hydrolysed nor digested by humans……
- providing "a feast" for bacteria (e.g. *E. coli*) in the gut which produce H_2 and CO_2 causing flatulence.

Polysaccharides

- *Digestible*
  - Starches (glycogen / amylose / amylopectin)
- *Indigestible* (dietary fibre / roughage)
  - Cellulose
  - Pectin
  - Seaweed polysaccharides (agarose / carageenan)
  - Xanthan and gellan (gums)

Glycogen

- Glycogen is the major carbohydrate storage molecule in animals.
- It is a homopolymer of glucose (a *glucan*) with α-(1,4)-linkages.
- It is also highly branched, with α-(1,6) branch linkages occurring every 8-10 residues.



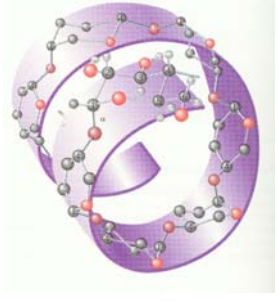
Starches: amylose and amylopectin

- Starch is the major form of stored carbohydrate in plant cells e.g. grains, potatoes etc.
- *Unbranched* starch is called amylose and *branched* starch is called amylopectin.
  - Amylose: linear glucan with α-(1,4)-glycosidic linkages and ~10^4 subunits
  - Amylopectin: branched glucan with α–(1,4) and α-(1,6) linkages with ~10^6 subunits: more compact than amylose for same MW
    - Structure is identical to glycogen, except for a much lower degree of branching (about every 20-30 residues).

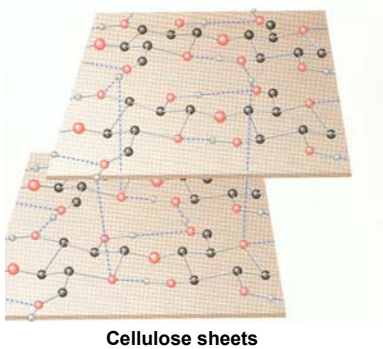
Cellulose

- Cellulose is a a linear glucan with β-(1,4)-glycosidic linkages
  - Humans lack *cellulase* enzymes, so cellulose is indigestible for us
- Different stereochemistry of glycosidic bond compared to starches [i.e. β–(1,4)- *vs.* α-(1,4)-]
  - results in very different molecular shape in solution

Amylose *vs.* Cellulose



Amylose helix

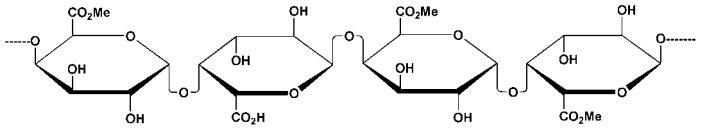


Cellulose sheets

(Solomons and Fryhle, 2000; © John Wiley & Sons, Inc.)

Pectin

- Polysaccharide of D-galacturonic acid (and derivatives) joined by α-(1,4)-linkages



  - can contain up to 20% neutral sugars
  - found naturally in fruits, vegetables
  - charged at higher pH
  - can form gels - used in the making of jams / preserves

Other food polysaccharides

Polysaccharide	Subunits	Linkages	Characteristics
Alginate	D-mannuronic + L-guluronic	α–(1,4) + β–(1,4)	Charged, linear
Agarose	D-galactose	α–(1,3) + β–(1,4)	Neutral, linear
Carrageenan	sulphonated D-galactose	α–(1,3) + β-(1,4)	Charged (-SO_3^-), linear
Guar Gum	D-mannose & D-galactose	α–(1,6) + β–(1,4)	Neutral, branched