Carbohydrates
Real world food nonsense
Carbohydrates (sugars)

• Source
  – Many foods including fruits and vegetables
  – Commercial source of sucrose is sugar cane and sugar beets
Functions in foods

• Sweetening agents

• Texturizer in baked goods

• Required for “normal” pectin gel (fruit jelly) formation

• Principal ingredient in candy
Aldoses and ketoses

- Carbohydrates are polyhydroxy aldehydes and ketones

D-glucose

D-fructose

1 2 3 4 5 6
<table>
<thead>
<tr>
<th>No. of carbon atoms</th>
<th>Aldehyde</th>
<th>Ketone</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Triose</td>
<td>Triulose</td>
</tr>
<tr>
<td>4</td>
<td>Tetrose</td>
<td>Tetrulose</td>
</tr>
<tr>
<td>5</td>
<td>Pentose</td>
<td>Pentulose</td>
</tr>
<tr>
<td>6</td>
<td>Hexose</td>
<td>Hexulose</td>
</tr>
<tr>
<td>7</td>
<td>Heptose</td>
<td>Heptulose</td>
</tr>
</tbody>
</table>
D-glyceraldehyde

This is a chiral carbon (it is bonded to 4 different groups)

Because of the chirality of this molecule we can have two sets of structures, D-glyceraldehyde (shown here) and its mirror image, L-glyceraldehyde.

Emil Fischer, 1852-1919
D- and L-sugars

D-glyceraldehyde    L-glyceraldehyde
D and L sugars are always mirror images!
Determination of D or L in other sugars

- Draw the Fischer projection with the carbonyl group at the top
Determination of D or L in other sugars

- Locate the chiral carbon atom farthest from the carbonyl group
Determination of D or L in other sugars

- If the OH group on this carbon points to the right, it is a D-sugar

- If the OH group on this carbon points to the left, it is an L-sugar
Rosanoff structures

D-glyceraldehyde

D-erythrose

D-threose
The D-pentoses
(Fischer projection)

D-ribose
D-arabinose
D-xylose
D-lyxose
Rosanoff structures

• In similar fashion one could construct the D-hexoses (see page number 144, Lecture Notes)

• Mnemonic for remembering the names of the D-hexoses
  - “All altruists gladly make gum in gallon tanks”
  - Allose, altrose, glucose, mannose, gulose, idose, galactose, talose
Generating the D-hexoses

Generating the D-hexoses

D-glyceraldehyde
Isomerization

D-glucose

D-fructose

D-mannose

Trans-enediol

Cis-enediol

Lobry de Bruyn-Alberda van Ekenstein transformation
Isomerization

• Enzymatically mediated reaction of this type is used today to produce high fructose corn syrup (HFCS) used in soft drinks

• Efforts by the Corn Refiners Association to rename HFCS as “corn sugar” were denied by the FDA on May 31, 2012
HFCS ridiculousity
Acetal formation

But what happens when the alcohol is part of the aldehyde structure to begin with?
Ring formation

D-glucose (open chain)

D-glucopyranose (Haworth projection)
Ring size--reference compounds

pyran
tetrahydrofuran
Ring size

alpha-D-glucopyranose

beta-D-fructofuranose
Ring representations

beta-D-glucopyranose

(Haworth projection)

4C1 chair conformation of beta-D-glucopyranose

Ring hydrogens are not shown here for purposes of clarity.
Ring structures

This is a special type of isomer called ANOMERS.
Anomeric carbon determination

- Find the ring oxygen atom

alpha-D-glucopyranose
Anomeric carbon determination

- Locate the attached carbon atoms

alpha-D-glucopyranose
Anomeric carbon determination

• Whichever of these two carbons has another directly attached oxygen is the anomeric carbon.

alpha-D-glucopyranose

The anomeric carbon atom or anomeric center
Reducing sugars

• If this attached oxygen is part of an OH (hydroxyl) group, this is a reducing sugar

alpha-D-glucopyranose
Non-reducing sugars

- If the oxygen atom bears any group other than H (such as alkyl, aryl, etc.), then it is a non-reducing sugar

methyl alpha-D-glucopyranoside
Ring equilibriums

α-D-glucopyranose

β-D-glucopyranose

α-D-glucofuranose

β-D-glucofuranose

open chain

Image courtesy of Engelsen (newton.foodsci.kvl.dk/engelsen/poster/mgms_poly.html#Disordered)
Carbohydrate classes

• Monosaccharides
  – One sugar ring
• Disaccharides
  – Two sugar rings combined
• Oligosaccharides
  – A few sugar rings combined
• Polysaccharides
  – Many sugar rings combined
Monosaccharides

alpha-D-glucopyranose

beta-D-fructofuranose
Disaccharides

Sucrose
(glucose (α1→2) fructose)

Lactose
(Galactose (β1→4) Glucose)

Images courtesy of MIT Biology Hypertextbook (esg-www.mit.edu:8001/esgbio/lm/sugars/sugar.html)
Sucrose (another view)

D-glucose

D-fructose
Invert sugar

\[ \text{H}^+ \text{ Acid catalyst} \]

Glu-O-Fru

Protonation of the glycosidic oxygen weakens this bond.
Invert sugar

Glu-O   Fru$^+$
Invert sugar

```
H
/
| Glu-O  Fru
|     O^+
|     H
|     H
```

Food Chemistry 45300
Invert sugar

This 1:1 mixture of glucose and fructose is invert sugar.

Regenerated catalyst
Oligosaccharides

• 3-10 monosaccharide units (an arbitrary number)
  – Raffinose = D-fructose, D-glucose, D-galactose
  – Stachyose
  – Verbascose
Polysaccharides

- More than 10 monosaccharide units (usually hundreds or thousands)
  - Cellulose and plant gums
    - Structure, texture
  - Starch (amylose, amylopectin)
    - Energy storage (plants)
  - Glycogen
    - Energy storage (animals)
Amylose

Alpha-1,4-linkage
Amylopectin

Image courtesy of Dept. of Biological Science, Western Michigan Univ. (www.wmich.edu/bios150/osmosis.html)
Cellulose

Cellulose
poly (1,4′-O-β-D-glucopyranoside)

Beta-1,4 linkage

Occurrence of common sugars

• Glucose
  – Most abundant in foods. Also called grape sugar or dextrose.

• Fructose
  – Occurs in many fruits. The major sugar in honey. Also called fruit sugar or levulose.

• Galactose
  – Constituent of lactose (milk sugar).
Reducing and non-reducing sugars

**Non-reducing**

- **Sucrose**
  - (glucose (α1→2) fructose)

**Reducing**

- **Lactose**
  - (Galactose (β1→4) Glucose)
Fehling’s test

- $2\text{Cu(OH)}_2 + \text{RCHO} \rightarrow \text{RCOOH} + \text{Cu}_2\text{O} + \text{H}_2\text{O}$

Blue solution

Reducing sugar

Red precipitate
Fehlings vs Benedicts

Fehling’s Test (After Water Bath)

H₂O = blue soln
Glucose = red ppt
Fructose = brick red ppt
Sucrose = blue soln
Starch = blue soln

Starch & Sucrose show no reducing property

Note precipitate
The Tollens’s test and other reducing sugar oxidations

(a) \[ R-C=O + \text{KMnO}_4 + \text{OH}^- \rightarrow R-C=O + 2\text{H}_3O^+ \]

(b) \[ R-C=O + \text{Ag}_2O + \text{OH}^- \rightarrow R-C=O + 2\text{H}_3O^+ \]

(c) \[ R-C=O + \text{Ag(NH}_3\text{)}_2\text{OH}^- \rightarrow R-C=O + \text{Ag(s)} \]

Fig 10 - Oxidation of Aldehydes

Silver mirror