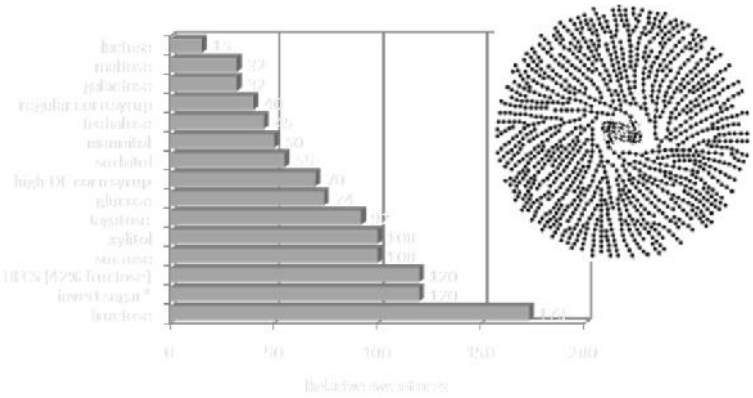
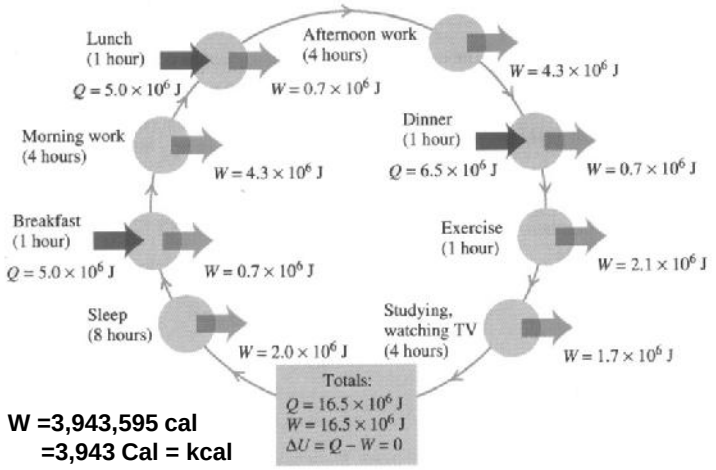
LECTURE 6
Oligo- and Polysaccharides



Lactose, a disaccharide found in milk,. is composed of a molecule of D-galactose and a molecule of D-glucose bonded by a β-1-4 glycosidic linkage.

How much energy you need everyday



W =3,943,595 cal
=3,943 Cal = kcal

http://firstyear.chem.usyd.edu.au/calculators/food_energy.shtml

LECTURE OUTCOMES

After completing this lecture and mastering the lecture materials, students are expected to be able

1. to compare and contrast monosaccharides, disaccharides, oligosaccharides, and polysaccharides.
2. to describe the structure of an oligosaccharide and polysaccharide
3. to identify the glycosidic bond (s) and characterize the glycosidic linkage by the bonding pattern [for example: β (1 ⟶ 4)].
4. to describe the Haworth structures of two monosaccharides, and to draw the disaccharide that is formed when they are connected by a glycosidic bond

5. to explain the difference between homopolysaccharides and heteropolysaccharides .
6. to compare and contrast the two components of starch.
7. to compare and contrast amylopectin and glycogen.
8. to identify acetal and hemiacetal bonding patterns in carbohydrates.
9. to describe several major oligosaccharides and polysaccharides produced by plants
10. to explain polysaccharides that function as structural and stored carbohydrates

LECTURE OUTLINE

QUESTIONS

1. OLIGOSACCHARIDES

Number of C Atoms

- disaccharides,
- trisaccharides,
- tetrasaccharides

Examples

- Sucrose
- Lactose
- Maltose
- Lactulose etc

2. POLYSACCHARIDES

- Starch
- Cellulose
- Glycogen
- Inulin and Oligofructose
- Agar and Carregeenan
- Pectins
- Glucomannan
- Resin
- Dextrans
- **Dextrins**
- Chitin
- Bacterial cell wall

QUESTIONS

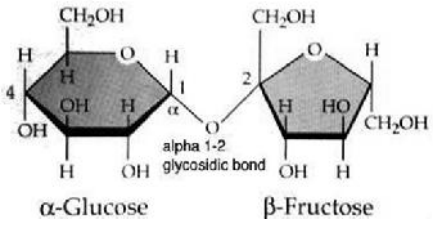
1. What are oligosaccharides?
2. What is glycosidic linkage?
3. What are the most common disaccharides?
4. What are the products resulting from the hydrolysis of sucrose?
5. What is the carbohydrate used as a medium to peoduce penicillin?
6. What is the carbohydrate produced by plants causing flatulence?
7. What are the carbohydrates as components of honeydew?
8. How many groups are carbohydrates classified as polysaccharides?
9. What are the components of starch?
10. What is the difference between amylose and amylopectin?

QUESTIONS

11. What is the color of amylose reacting with iodine?
12. What is the difference between starch and cellulose in term of each glucose constituent?
13. What is the product resulting from the partial and complete hydrolysis of cellulose?
14. What is the cellulose product used for plastic?
15. What is the animal starch?
16. What are the products of the reaction of glucose and the enzyme transglucosidase?
17. What carbohydrate is the components of dental plaques?
18. What is the carbohydrate used for glues?
19. What is the heteropolysaccharides found in the pulp of fruits (citrus, apples)?
20. What is the polysaccharide found some plants that function as an alternative stored carbohydrate?

Oligosaccharides

1. Oligosaccharides are compounds in which monosaccharide units are joined by **glycosidic linkages.** Carbohydrates consisting of 2-10 simple sugars joined by **glycosidic linkages** are called *oligosaccharides*,
2. **Glycosidic bonds** are covalent chemical bonds that hold together a **glycoside** which is simply a ring-shaped sugar molecule that is attached to another molecule.



Sucrose

Oligosaccharides

3. The condensation of two (or more) monosaccharides is an extremely important biochemical reaction producing oligosaccharides and polysaccharides .
4. The reaction occurs, most commonly, between the **OH** on **C1** of one monosaccharide and **OH** on **C4** of the second one to form 1- **4 GLYCOSIDIC** linkage.
5. Because the reaction involves C1, which can exist in either α- or β- forms, we can obtain either an α (1- 4) or a β (1- 4) **glycoside.**

6. According to the number of units, oligosaccharides are called
   - Disaccharides (2 monosaccharides)
   - Trisaccharides (3 monosaccharides)
   - Tetrasaccharides (4 monosaccharides)
   - Pentasaccharides (5 monosaccharides) etc.
7. The borderline with polysaccharides cannot be drawn strictly.

   However the term 'oligosaccharide' is commonly used to refer to **a defined structure** as opposed to **a polymer of unspecified length** or a homologous mixture. When the linkages are of other types, the compounds are regarded as oligosaccharide analogues.

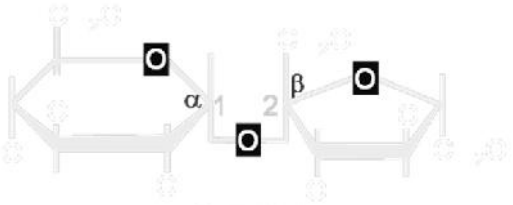
8. Most common Oligosaccharides (oligo- "several")
   - disaccharides: Sucrose, lactose, and maltose
   - Trisaccharide: **raffinose** (glucose, galactose and fructose)
   - Tetrasaccharide: **stachyose** (2 galactoses, glucose and fructose)
   - Pentasaccharide: **verbascose** (3 galactoses, glucose and fructose)
   - Hexasaccharide: **ajugose (4 galactoses, glucose and fructose)**

Disaccharide	Unit 1	Unit 2	Bond	Disaccha-ridase
Sucrose	glucose	fructose	$\alpha(1 \rightarrow 2)$	sucrase
Lactose	galactose	glucose	$\beta(1 \rightarrow 4)$	lactase
Maltose	glucose	glucose	$\alpha(1 \rightarrow 4)$	maltase
Trehalose	glucose	glucose	$\alpha(1 \rightarrow 1)$	trehalase
Cellobiose	glucose	glucose	$\beta(1 \rightarrow 4)$	cellobiase

Sucrose

- Sucrose ($C_{12}H_{22}O_{11}$), also called sugar (table sugar) and saccharose with a molar mass of 342.30 g/mol, is the type of carbohydrates transported around the plant
- Sugarcane and sugar beet are the main source of sucrose.

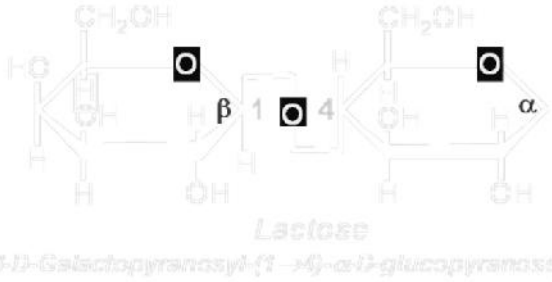
Sugar cane



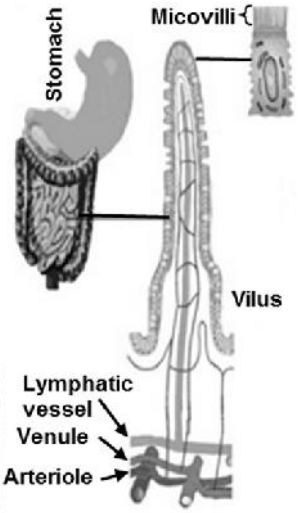
Sugar beet

- Sucrose consists of glucose (left) and fructose (right) joined by an α,β-1,2-glycosidic bond. Hydrolysis yield glucose and fructose (invert sugar) (sucrose: +66.5^{o} ; glucose +52.5^{o}; fructose –92^{o}) Hydrolysis yield glucose and fructose (invert sugar) (sucrose: +66.5^{o} ; glucose +52.5^{o}; fructose –92^{o})

- **Lactose**, milk sugar, consists of galactose joined to glucose by a β-1,4-glycosidic linkage. Milk contains the α and β-anomers in a 2:3 ratio, and β-lactose is sweeter and more soluble than ordinary α-lactose, and used in infant formulations, medium for penicillin production and as a diluent in pharmaceuticals.
- Lactose is hydrolyzed to these monosaccharides by *lactase* in human beings and by *β-galactosidase* in bacteria.

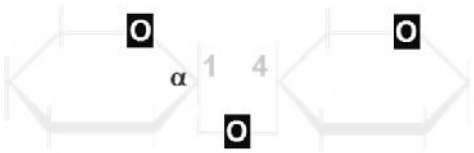


- Lactase and other enzymes that hydrolyze carbohydrates are present on microvilli that project from the outer face of the plasma membrane of intestinal epithelial cells.
- Lactase is found most abundantly in the jejunum (at the beginning of the small intestine) especially at the tip of the intestinal villi, and it specifically only hydrolyses lactose. The gene coding for lactase is located on chromosome 2



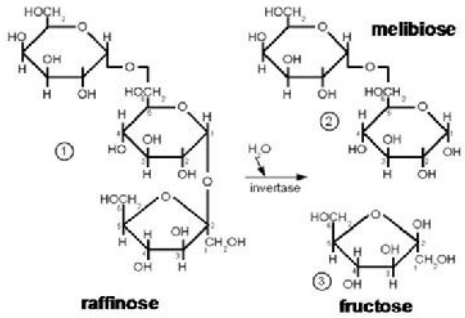
[From M. S. Mooseker and L. G. Tilney, *J. Cell. Biol.* 67(1975):725.]

- **Maltose,** known as malt sugar**,** consists of 2-glucose molecules joined via α (1,4) linkage
- It is produced by the partial hydrolysis of starch (either salivary amylase or pancreatic amylase), and used as a nutrient (malt extract; *Hordeum vulgare*); as a sweetener and as a fermentative reagent.



Trisaccharide

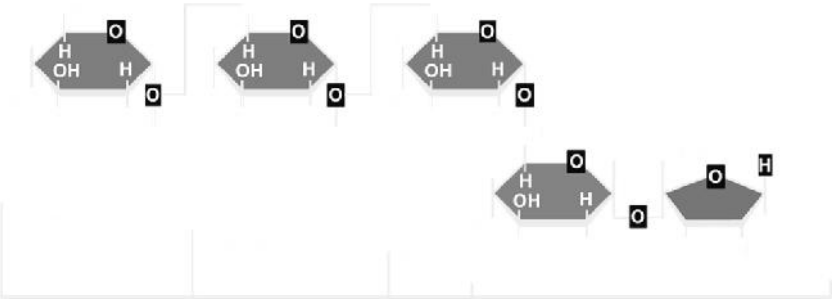
- Sweet potato contains raffinose, one of the sugars responsible for flatulence.
  - Raffinose consists of glactose, glucose and fructose (from the top). The enzyme invertase can split the bond between glucose and fructose to create (2) melibiose and (3) fructose

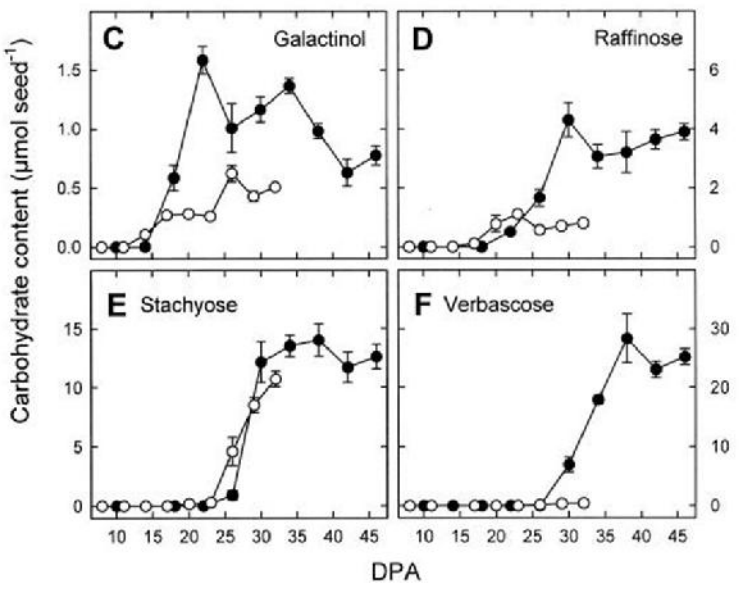


- Three of the sugars which occur in plant tissues, raffinose, stachyose and verbascose are not digested in the upper digestive tract, and so are fermented by colon bacteria to yield the flatus gases, hydrogen and carbon dioxide.

Tetrasaccharide

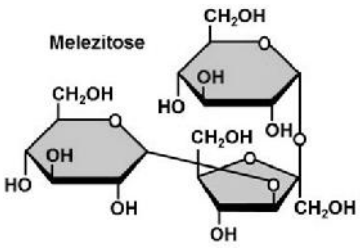
Stachyose (2 galactoses, glucose and fructose) is a constituent of many plants: white jasmine, yellow lupine, soybeans, lentils, etc; causes flatulence since humans cannot digest it). An enzymatic product (**Beano**) can be used to prevent the flatulence



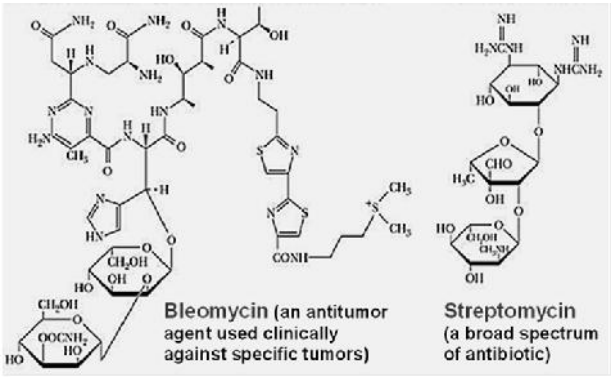


DPA = days after post anthesis. *Pisum sativum*: Peterbauer et al. (2001)

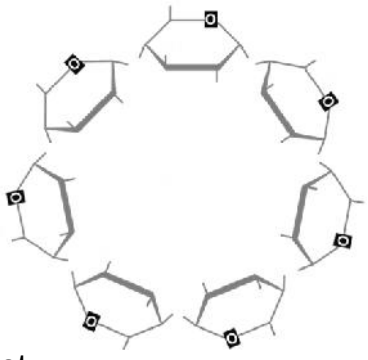
Honey also contains glucose and fructose along with some volatile oils



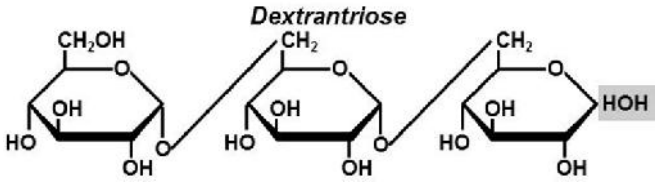
Oligosaccharides occur widely as components of antibiotics derived from various sources



Cycloheptaamylose is a breakdown product of starch with enzyme *cyclodextrin glycosyl transferase*, useful in chromatographic separation



Dextratriose is a constituent of sake and honeydew

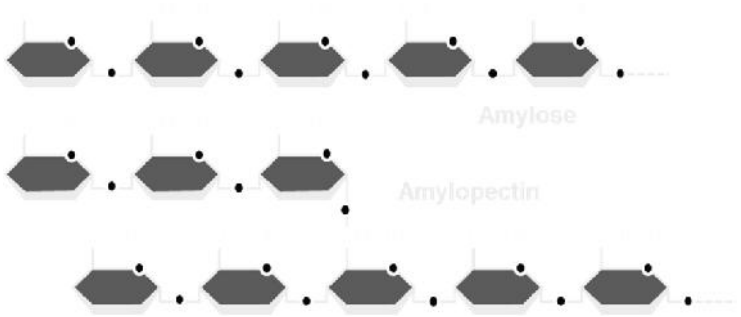


2. POLYSACCHARIDES

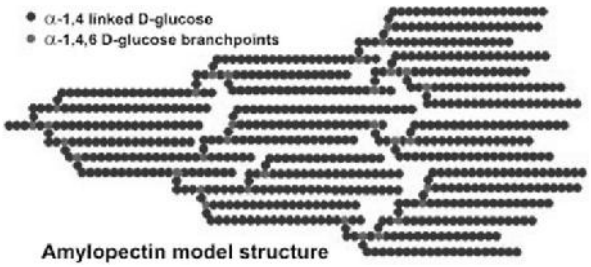
1. Polysaccharide (glycan) is a macromolecule consisting of a large number of monosaccharide (glycose) residues joined to each other by glycosidic linkages.
2. Polysaccharides can be divided into the
   a. **Structural polysaccharides** (e.g. cellulose, pectins)
   b. **Storage polysaccharides** (e.g. starch, fructosans)
   or
   a. **Homopolysaccharides (h**omoglycans) that are composed of only one kind of monosaccharide (starch, cellulose, glycogen, inulin)
   b. **Homopolysaccharides** (heteroglycans) that are composed of two or more different kinds of monosaccharide (gums, mucopolysaccharides)
3. The most important compounds in this class are **starch**, **glycogen** and **cellulose**

Starch

1. Starch, the most common storage polysaccharide in plants, is composed of ~**-amylose** (10-30%) and **amylopectin** (70-90%) depending on the source.
2. Amylose, the unbranched type of starch, consists of glucose residues in α-1,4 linkage. Amylopectin, the branched form, has about one α-1,6 linkage per 30 α-1,4 linkages.

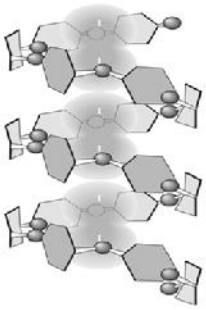


3. Both amylopectin and amylose are rapidly hydrolyzed by *α-amylase,* an enzyme secreted by the salivary glands and the pancreas.
4. Rice starch, present in the endosperm, is mainly composed of starch (90%) that consists of about 20-30% amylose and 70-80% amylopectin.
5. Amylose is more resistant to digestion than other starch molecules due to its tightly packed structure.
6. Rice types with a high amylose content cook dry with firm and separate grain, while low amylose types are tender, glossy and cohesive after cooking.
7. Starchy foods with high amylose levels are associated with lower blood glucose levels, and slower emptying of the human gastrointestinal tract compared to those with low levels of amylose.



Amylopectin model structure

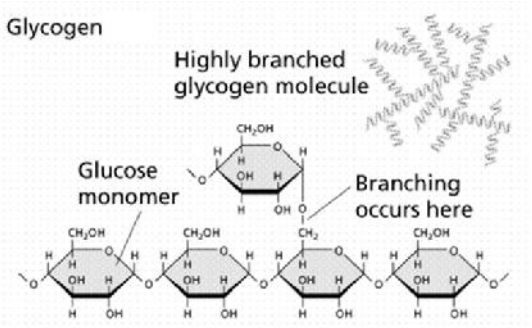
8. Suspensions of amylose in water adopt a helical conformation, and Iodine (I_2) can insert in the middle of the amylose helix to give a blue color that is characteristic and diagnostic for starch



Glycogen

1. Glycogen is the storage form of glucose in animals and humans which is analogous to the starch in plants.
2. Glycogen is synthesized and stored mainly in the liver and the muscles.
3. Structurally, glycogen is very similar to amylopectin with alpha acetal linkages, however, it has even more branching, and more glucose units than in amylopectin does.
4. Various samples of glycogen have been measured at 1,700-600,000 units of glucose.
5. Glycogen contains both α(1,4) links and α(1,6) branches at every 8 to 12 glucose unit

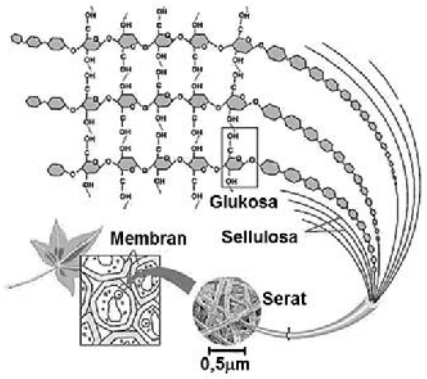
6. Glycogen and iodine gives a red-violet color, and hydrolyzed by both α and β-amylases and by glycogen phosphorylase. A complete hydrolysis of glycogen yields glucose



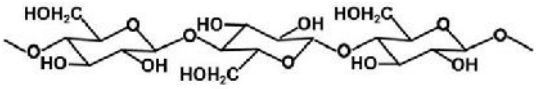
Glycogen

Cellulose

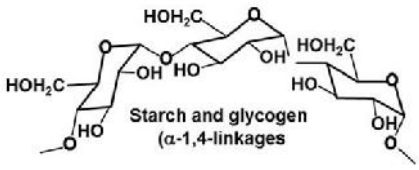
1. Cellulose, the other major polysaccharide found in plants, is an unbranched polymer of glucose residues joined by β-1,4 linkages. The β configuration allows cellulose to form very long, straight chains.
2. Fibrils are formed by parallel chains that interact with one another through hydrogen bonds.
3. Cellulose as a component of cell wall serves a structural rather than a nutritional role.



4. The α-1,4 linkages in glycogen and starch produce a very different molecular architecture from that of cellulose.
5. In the β-1,4 linkages of cellulose, a hollow helix is formed instead of a straight chain. These differing consequences of the α and β linkages are biologically important.
6. Cellulose is one of the most abundant organic compounds in the biosphere, and synthesized and degraded on Earth each year at a rate of ~ 10^{15} kg/year.



Cellulose (β-1,4-linkages)

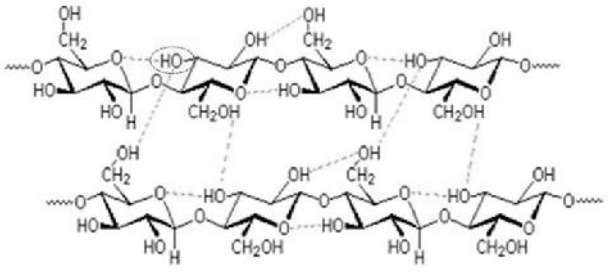


Starch and glycogen (α-1,4-linkages

a (-OH group below the ring) &
b (-OH group above the ring)

7. The straight chain formed by β linkages is optimal for the construction of fibers having a high tensile strength.
8. In contrast, the open helix formed by α linkages is well suited to forming an accessible store of sugar.
9. Mammals lack cellulases and therefore cannot digest wood and vegetable fibers.

Cellulose (a linear polyglucose jained by β-1,4 bonds)



---------- intra and intermolecular hydrogen bonds

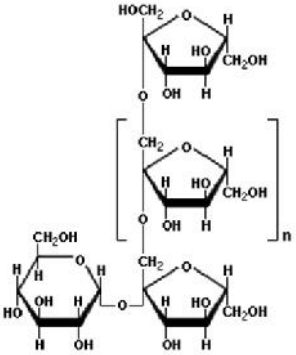
OTHER POLYSACCHARIDES

- **Inulin and Oligofructose**
  1. Some plants store carbohydrates in the form of **inulin** as an alternative, or in addition, to starch.

Jerusalem artichokes

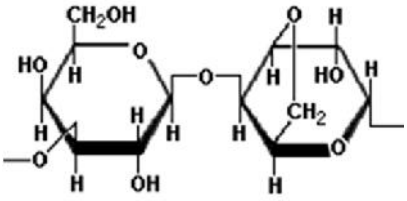
  1. Inulins are present in many vegetables and fruits, including onions, leeks, garlic, bananas, asparagus, chicory, and Jerusalem artichokes.
  1. Inulins, also called fructans, are polymers consisting of fructose units that typically have a terminal glucose.
  2. It is an unbranched polymer of fructosans joined by β-1,4 linkages, and has a lower molecular weight than starch does.

- Inulin reacting with iondine give yellow color, yields fructose on hydrolysis, and is used as **diagnostic agent** for the evaluation of glomerular filtration rate (renal function test)
- **Oligofructose** has the same structure as inulin, but the chains consist of 10 or fewer fructose units.
- Inulin and oligofructose are non-digestible by human intestinal enzymes, and totally fermented by colonic microflora. The short-chain fatty acids and lactate produced by fermentation contribute 1.5 kcal per gram of inulin or oligofructose.



Inulin, n = approx. 35

- **Agar and Carrageenan**
  1. **Agar** (agar-agar) is extracted from seaweed and is used in many foods as a gelling agent. Agar is a polymer of **agarobiose**, a disaccharide composed of D-galactose and 3,6-anhydro-L-galactose.
  2. Highly refined agar is used as a medium for culturing bacteria, cellular tissues, and for DNA fingerprinting.
  3. Agar is used as an ingredient in desserts in Japan and other Asian countries. The gels produced with agar have a crispier texture than the desserts made with animal gelatin.

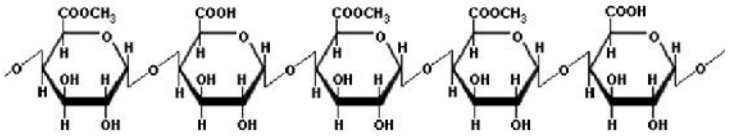


Agarobiose (the repeating disaccharide unit in agar

  4. **Carrageenan** is a generic term for several polysaccharides also extracted from seaweed. Carrageenan compounds, different from agar, have sulfate groups (-OSO3-) in place of some hydroxyl groups. Carrageenan is also used for thickening, suspending, and gelling food products.

- **Pectin**
  1. **Pectins** are heteropolysaccharide that acts as a cementing material in the cell walls of all plant tissues. The white portion of the rind of lemons and oranges contains approximately 30% pectin.
  2. Pectin is the methylated ester of polygalacturonic acid consisting of chains of 300 to 1000 galacturonic acid units joined with α-1,4-linkages.

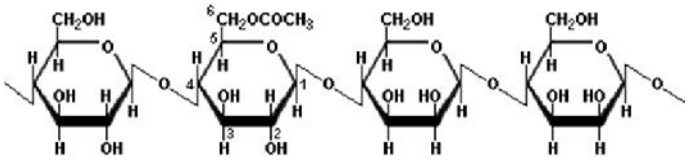
3. Pectins are composed of galactans and arabans and used as gelling agents (to make jellies)
4. The structure shown below has three methyl ester forms (**-$COOCH_3$**) for every two carboxyl groups (**-COOH**), hence it is has a 60% degree of esterification, normally called a DE-60 pectin.
5. On hydrolysis pectins yield galacturonic acid, galactose, arabinose, methanol and acetic acid



Pectin is a polymer of α-Galacturonic acid with a variable number of methyl ester groups

- **Glucomannan**
  1. **Glucomannan** is a dietary fiber obtained from tubers of *Amorphophallus konjac* cultivated in Asia. Flour from the konjac tubers is used to make Japanese shirataki noodles, also called konnyaku noodles, which are very low in calories.
  2. The polysaccharide consists of glucose (G) and mannose (M) in a proportion of 5:8 joined by 1β→4 linkages. The basic polymeric repeating unit has the pattern: GGMMGMMMMMGGM.
  3. Short side chains of 11-16 monosaccharides occur at intervals of 50-60 units of the main chain attached by 1β→3 linkages. Also, acetate groups on carbon 6 occur at every 9-19 units of the main chain.

A portion (GGMM) of the glucomannan repeating unit.
The second glucose has an acetate group



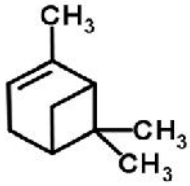
4. Glucomannan is used as a hunger suppressant because it produces a feeling of fullness by creating very viscous solutions that retard absorption of the nutrients in food.
5. One gram of this soluble polysaccharide can absorb up to 200 ml of water, so it is also used for absorbent articles such as disposable diapers and sanitary napkins.
6. Hydrolysis of the acetate groups favors the formation of intermolecular hydrogen bonds that are responsible for the gelling action.

RESIN

1. **Resin** is a "solid or highly viscous substance, usually containing prepolymers with reactive groups, and derived from plants or syntheticcally.
2. Notable examples of plant resins include amber ,and, balsam from trees of *Protium copal,* dammar gum from trees of the family *Dipterocarpaceae*, benzoin resin from various Styrax species, and turpentine from pine trees.
3. **Benzoin resin,** commonly called "benzoin", is a balsamic resin from the trees in the genus *Styrax,* different from chemical compound benzoin*,* and used in perfumes, some kinds of incense, as a flavoring, and medicine.

4. Turpentine is composed of mainly the monoterpenes alpha-pinene and beta-pinene with lesser amounts of carene, camphene, dipentene, and terpinolene.

Resin of a pine



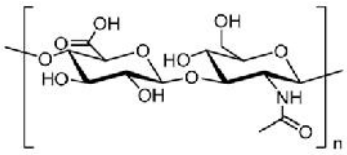
Pinene ($C_{10}H_{16}$) a component of terpene from resin

Benzoin resin (*kemenyan*) as sold in Gombong, Central Java

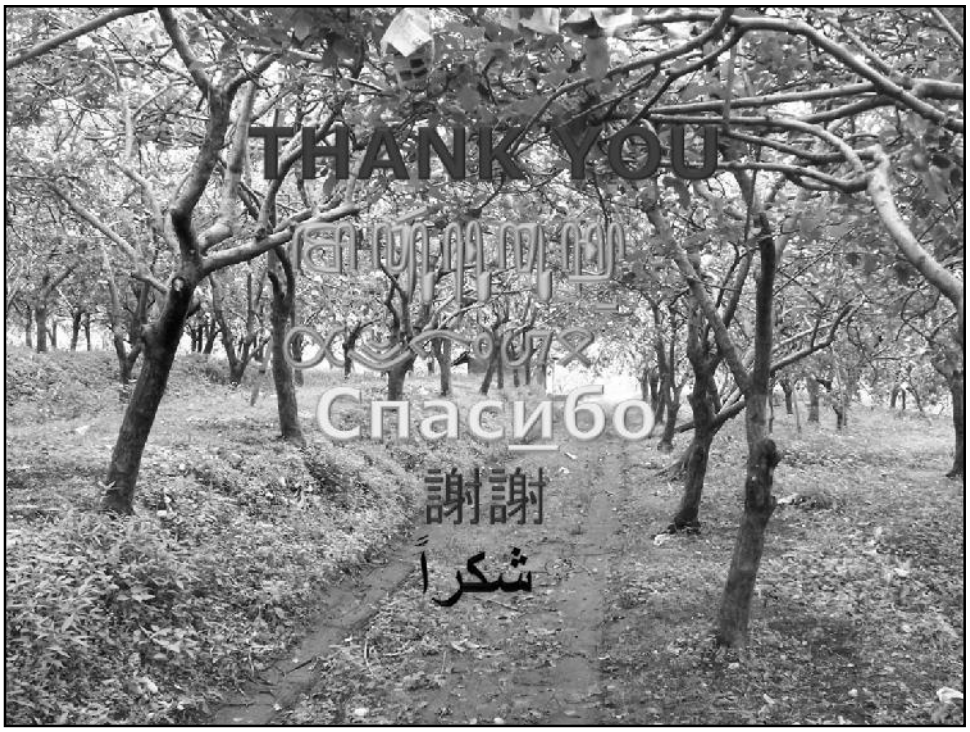
GLYCOSAMINOGLYCANS

- Glycosaminoglycans are found in the lubricating fluid of the joints and as components of cartilage, synovial fluid, vitreous humor, bone, and heart valves.
- Glycosaminoglycans are long unbranched polysaccharides containing repeating disaccharide units that contain either of two amino sugar compounds, and a uronic acid such as glucuronate.
- **Hyaluronic acid** (HA) is one of the physiologically most important glycosaminoglycans

Hyaluronic acid, more specifically a mucopolysaccharide, is a carbohydrate comnposed of up to thousands of sugars



HA was discovered in 1934, by Karl Meyer and his assistant, John Palmer



Dextrans

- products of the reaction of glucose and the enzyme transglucosidase from *Leuconostoc mesenteroides*
- contains a (1,4), a (1,6) and a (1,3) linkages
- MW: 40,000; 70,000; 75,000
- used as plasma extenders (treatment of shock)
- also used as molecular sieves to separate proteins and other large molecules (gel filtration chromatography)
- components of dental plaques

Dextrins

- produced by the partial hydrolysis of starch along with maltose and glucose
- dextrins are often referred to as either amylodextrins, erythrodextrins or achrodextrins
- used as mucilages (glues)
- also used in infant formulas (prevent the curdling of milk in baby's stomach)

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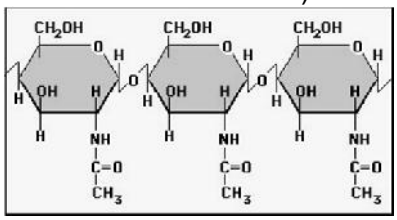
Products obtained from cellulose

- Microcrystalline cellulose : used as binder-disintegrant in tablets
- Methylcellulose: suspending agent and bulk laxative
- Oxidized cellulose: hemostat
- Sodium carboxymethyl cellulose: laxative
- Cellulose acetate: rayon; photographic film; plastics
- Cellulose acetate phthalate: enteric coating
- Nitrocellulose: explosives; collodion (pyroxylin)

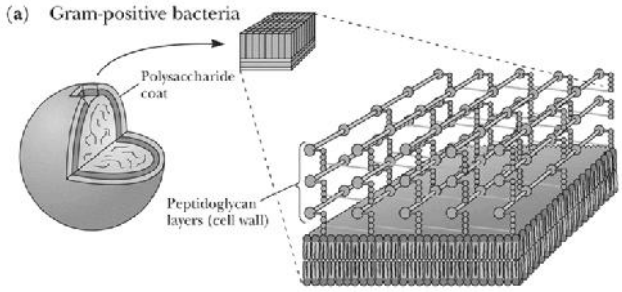
Chitin

- chitin is the second most abundant carbohydrate polymer
- present in the cell wall of fungi and in the exoskeletons of crustaceans, insects and spiders
- chitin is used commercially in **coatings** (extends the shelf life of fruits and meats)



Bacterial cell wall

- provide strength and rigidity for the organism
- consists of a polypeptide-polysaccharide known as petidoglycan or murein
- determines the Gram staining characteristic of the bacteria



Steps in the ring closure (hemiacetal synthesis):

1. The electrons on the alcohol oxygen are used to bond the carbon #1 to make an ether (red oxygen atom).
2. The hydrogen (green) is transferred to the carbonyl oxygen (green) to make a new alcohol group (green).

The chair structures are always written with the orientation depicted on the left to avoid confusion.

Hemiacetal Functional Group:

- Carbon # 1 is now called the **anomeric carbon** and is the center of a hemiacetal functional group.
- A carbon that has both an ether oxygen and an alcohol group is **a hemiacetal**.