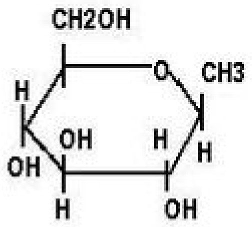
CARBOHYDRATES

Carbohydrates have the general molecular formula $(CH_2O)n$.



Carbohydrates were once thought to represent "hydrated carbon". However, the arrangement of atoms in carbohydrates has little to do with water molecules.

Starch and cellulose are two common carbohydrates. Both are macromolecules with molecular weights in the hundreds of thousands. Both are polymers (hence "**polysaccharides**"); that is, each is built from repeating units, monomers, much as a chain is built from its links.

The monomers of both starch and cellulose are the same: units of the sugar **glucose**.

Sugars

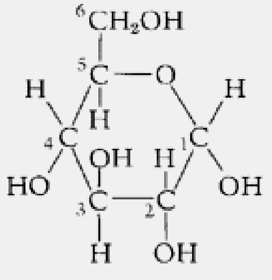
Monosaccharides

These are simple sugars that serve as fuel molecules as well as fundamental constituents of living organisms, are the simplest carbohydrates, and are required as energy sources. The most commonly known ones are perhaps glucose and fructose.

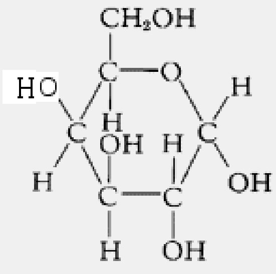
Three common sugars share the same molecular formula: $C_6H_{12}O_6$. Because of their six carbon atoms, each is a **hexose**.

They are:

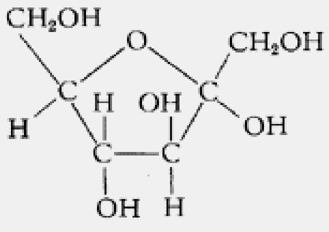
- **glucose**, "blood sugar", the immediate source of energy for cellular respiration
- **galactose**, a sugar in milk (and yogurt), and
- **fructose**, a sugar found in honey.



GLUCOSE



GALACTOSE



FRUCTOSE

Although all three share the same molecular formula ($C_6H_{12}O_6$), the arrangement of atoms differs in each case. Substances such as these three, which have identical molecular formulas but different structural formulas, are known as **structural isomers**.

Glucose, galactose, and fructose are "single" sugars or **monosaccharides**. Two monosaccharides can be linked together to form a "double" sugar or **disaccharide**.

Disaccharides

Three common disaccharides:

- **sucrose** — common table sugar = glucose + fructose
- **lactose** — major sugar in milk = glucose + galactose
- **maltose** — product of starch digestion = glucose + glucose

Although the process of linking the two monomers is rather complex, the end result in each case is the loss of a hydrogen atom (H) from one of the monosaccharides and a hydroxyl group (OH) from the other. The resulting linkage between the sugars is called a **glycosidic bond**. The molecular formula of each of these disaccharides is

$$C_{12}H_{22}O_{11} = 2\ C_6H_{12}O_6 - H_2O$$

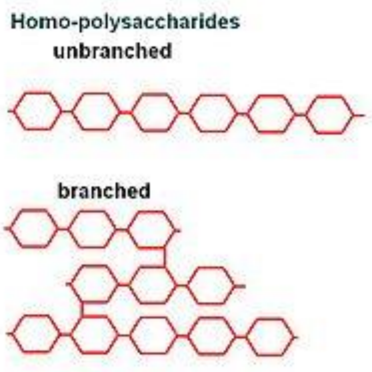
All sugars are very soluble in water because of their many hydroxyl groups. Although not as concentrated a fuel as fats, sugars are the most important source of energy for many cells.

Carbohydrates provide the bulk of the calories (4 kcal/gram) in most diets, and starches provide the bulk of that. Starches are polysaccharides.

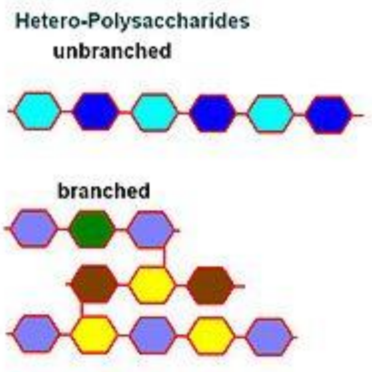
Polysaccharides

Polysaccharides are complex carbohydrate polymers consisting of more than two monosaccharides linked together covalently by glycosidic linkages in a **condensation reaction**. Being comparatively large macromolecules, polysaccharides are most often insoluble in water. Polysaccharides are extremely important in organisms for the purposes of energy storage and structural integrity.

There are two types of polysaccharides: homo-polysaccharides and hetero-polysaccharides. A homo-polysaccharide is defined to have only one type of monosaccharide repeating in the chain; whereas, a hetero-polysaccharide is composed of two or more types of monosaccharides. In both types of polysaccharide, the monosaccharide can link in a linear fashion or they can branch out into complex formations. It should also be noted that for a polysaccharide to be considered acidic it must contain one or more of the following groups: phosphate, sulfuric, or carboxyl.



Homo-polysaccharides can be branched or unbranched as long as they all have the same monosaccharide unit

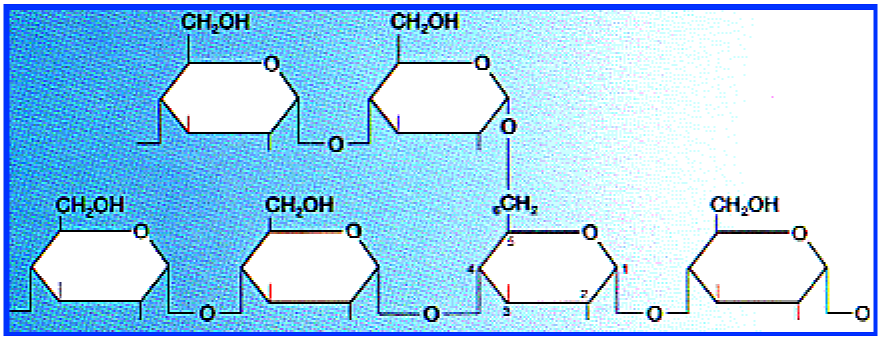


The different colors represent different monosaccharides

What is the basic structure of a polysaccharide?
Plants synthesize two types of polysaccharides, **starch** and **cellulose**. The glycosidic bonds between **glucose** units in plant **starch** are similar to those in animal **glycogen**.
Accordingly, **starch** molecules are structurally similar, forming compact coils, and play a similar role in energy storage for plants. Examples include storage polysaccharides such as **starch** and **glycogen**, and structural polysaccharides such as **cellulose** and **chitin**.

Starches

Starches are polymers of glucose.

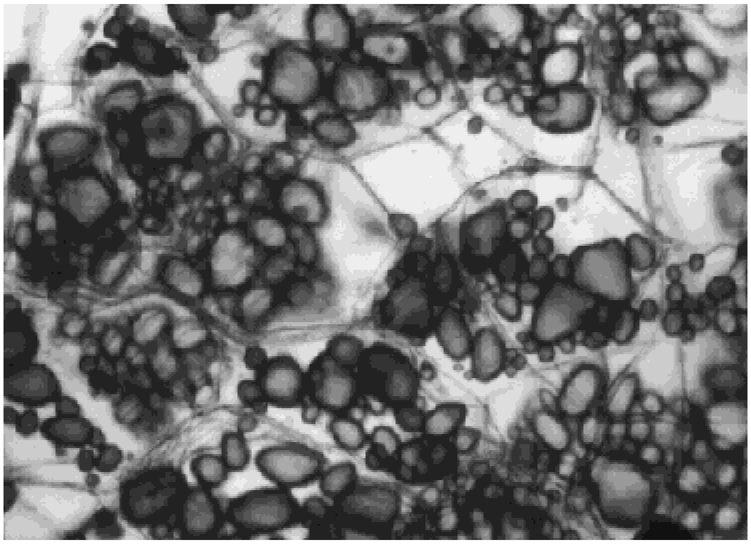


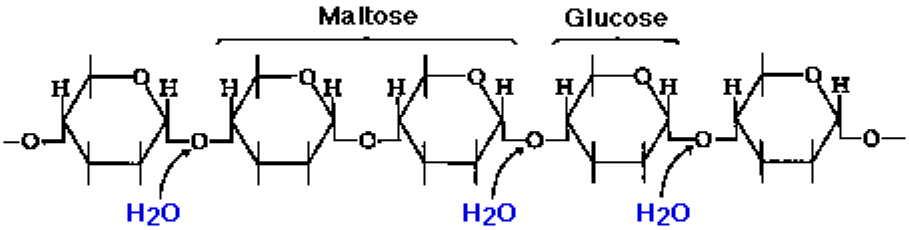
Two types of starches are found:

- **amylose** consists of linear, unbranched chains of several hundred glucose residues (units). The glucose residues are linked by a glycosidic bond between their #1 and #4 carbon atoms.

- **amylopectin** differs from amylose in being highly branched. At approximately every thirtieth residue along the chain, a short side chain is attached by a glycosidic bond to the #6 carbon atom (the carbon above the ring). The total number of glucose residues in a molecule of amylopectin is several thousand.

Starches are insoluble in water and thus can serve as storage depots of glucose. Plants convert excess glucose into starch for storage. The image shows starch grains (lightly stained with iodine) in the cells of the white potato. Rice, wheat, and corn (maize) are also major sources of starch in the human diet.





Before starches can enter (or leave) cells, they must be digested. The hydrolysis of starch is done by amylases. With the aid of an **amylase** (such as pancreatic amylase), water molecules enter at the 1 -> 4 linkages, breaking the chain and eventually producing a mixture of **glucose** and **maltose**. A different amylase is needed to break the 1 -> 6 bonds of amylopectin.

Glycogen

Animals store excess glucose by polymerizing it to form **glycogen**. The structure of glycogen is similar to that of amylopectin, although the branches in glycogen tend to be shorter and more frequent.

Glycogen is broken back down into glucose when energy is needed (a process called glycogenolysis).

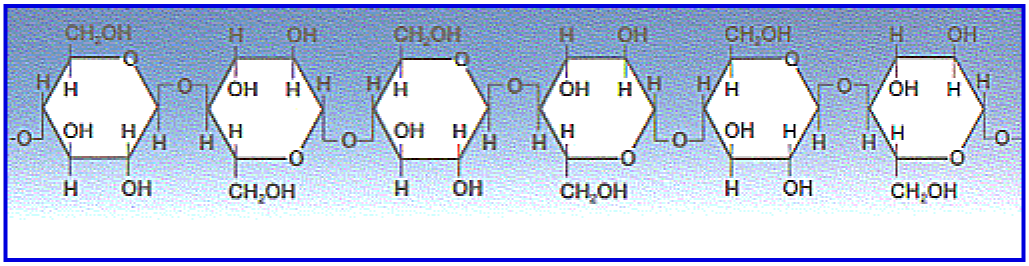
In **glycogenolysis**,

- Phosphate groups — not water — break the 1 -> 4 linkages
- The phosphate group must then be removed so that glucose can leave the cell.

The liver and skeletal muscle are major storage depots of glycogen.

There is some evidence that intense exercise and a high-carbohydrate diet ("carbo-loading") can increase the reserves of glycogen in the muscles and thus may help marathoners work their muscles somewhat longer and harder than otherwise. But for most of us, carbo loading leads to increased deposits of fat.

Cellulose

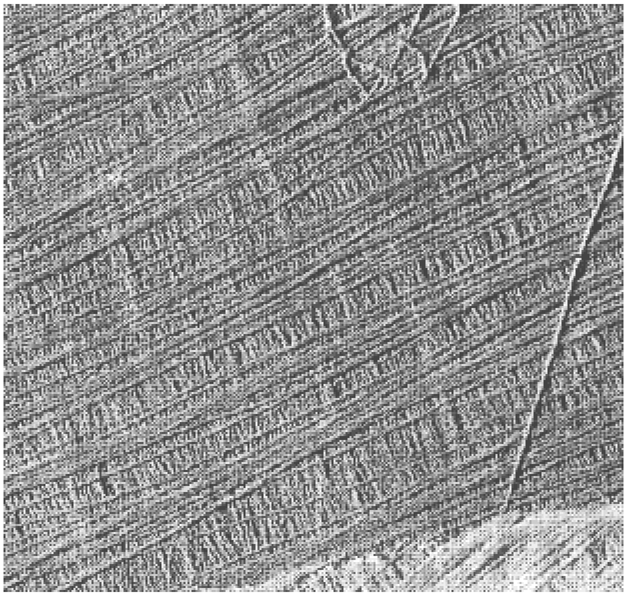


Cellulose is probably the single most abundant organic molecule in the biosphere. It is the major structural material of which plants are made. Wood is largely cellulose while cotton and paper are almost pure cellulose.

Like starch, cellulose is a polysaccharide with glucose as its monomer. However, cellulose differs profoundly from starch in its properties.

- Because of the orientation of the glycosidic bonds linking the glucose residues, the rings of glucose are arranged in a flip-flop manner. This produces a long, straight, rigid molecule.
- There are no side chains in cellulose as there are in starch. The absence of side chains allows these linear molecules to lie close together.
- Because of the many -OH groups, as well as the oxygen atom in the ring, there are many opportunities for hydrogen bonds to form between adjacent chains.

The result is a series of stiff, elongated fibrils — the perfect material for building the cell walls of plants.



This electron micrograph (SOURCE: http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/C/Carbohydrates.html) shows the cellulose fibrils in the cell wall of a green alga. These long, rigid fibrils are a clear reflection of the nature of the cellulose molecules of which they are composed.

STORAGE AND STRUCTURAL ROLES OF POLYSACCHARIDES

Polysaccharides have several roles. Polysaccharides such as starch, glycogen, and dextrans are all stored in the liver and muscles to be converted to energy for later use. Amylose and Amylopectin are polysaccharides of starch. Amylose has a linear chain structure made up of hundreds of glucose molecules that is linked by a alpha 1,4 glycosidic linkage. Due to the nature of these alpha 1,4 bonds, the macromolecule often assumes a bent shape. The starch molecules form a hollow helix that is suitable for easy energy access and storage. This gives starch a less fibrous quality and a more granule-like shape which is better suited for storage. Unlike the linear structure of Amylose, the Amylopectin starches are branched containing an alpha 1,6 glycosidic linkage about every 30 glucose units. Like amylose it is a homopolymer composed of many glucose units. Glycogen is found in animals, and it is branched like amylopectin. It is formed by mostly alpha 1,4 glycosidic linkages but branching occurs more frequently than in amylopectin as alpha 1,6 glycosidic linkages occur about every ten units. Other polysaccharides have structural functions. For example, cellulose is a major component in the structure of plants. Cellulose is made of repeating beta 1,4-glycosidic bonds. These beta 1,4-glycosidic bonds, unlike the alpha 1,4 glycosidic bonds, force celullose to form long and sturdy straight chains that can interact with one another through hydrogen bonds to form fibers.

Many organisms store energy in the form of polysaccharides, commonly homopolymers of glucose. Glycogen, the sugar used by animals to store energy, is composed of alpha-1,4-glycosidic bonds with branched alpha-1,6 bonds present at about every tenth monomer. Starch, used by plant cells, is similar in structure but exists in two forms: amylose is the helical form of starch comprised only of alpha-1,4 linkages, and amylopectin has a structure like glycogen except that the branched alpha-1,6 linkages are present on only about one in 30 monomers. These polysaccharides often contain tens of thousands of monomers, and each type is synthesized in the cell and broken down when energy is needed.

Glycogen metabolism is an intricate process involving many enzymes and cofactors resulting in the regular release and storage of glucose. This metabolic process is in turn broken down to glycogen degradation and synthesis. Glycogen synthesis is carried out by the enzyme glycogen synthase in which the activated form of glucose, UDP-glucose (uridine diphosphate), is formed by way of the reaction between UTP and glucose-1 phosphate. From this synthesis two outer phosphoryl groups are released from UTP producing the pyrophosphate compound. Pyrophosphate becomes an important aspect in this portion of the synthesis as the reaction to produce UDP-glucose is readily reversible. What allows the reaction to be driven forward is the hydrolysis of the pyrophosphate to orthophosphate in an irreversible reaction thus allowing the production of UDP-glucose to continue unhindered. The UDP-glucose is then attached to the non-reducing ends of glycogen. How this is accomplished is through an alpha-1,4-glycosidic linkage at the C-4 terminal with the terminal hydroxyl group ready to bind on glycogen. At this point the enzyme glycogen synthase plays the important role of catalyzing the attachment of UDP. Since an oligomer of at least four monomers is required for glycogen synthase to extend a chain, the process uses a primer that is itself provided by another enzyme, glycogenin. After several units of UDP have been attached to the glycogen by way of alpha-1,4 linkages, branching begins to take place by breaking an alpha-1,4 link and forming a alpha-1,6-link.A number of other enzymes, including insulin, play important roles in glycogen's synthesis. The breakdown of glycogen is completed through an entirely different biochemical pathway. Epinephrine and glucagon are signaling molecules whose binding to certain 7TM receptors activate the degradation, which is carried out in the cells by glycogen phosphorylase. This enzyme breaks up the polysaccharide chain by replacing the glycosidic bond with a phosphate group. As with its synthesis, glycogen's degradation requires numerous enzymes besides those mentioned here.

Starch is a good storage of carbohydrates because it is an intermediate compared to ATP and lipids in terms of energy. In plants, starch storage folds to allow more space inside cells. It is also insoluble in water, making it so that it can stay inside the plant without dissolving into the system. Starch can also be used as a back up source of energy when plants cannot obtain carbon dioxide, light, or nutrients from the surrounding soil.

Discussion on plants' metabolism of starch....

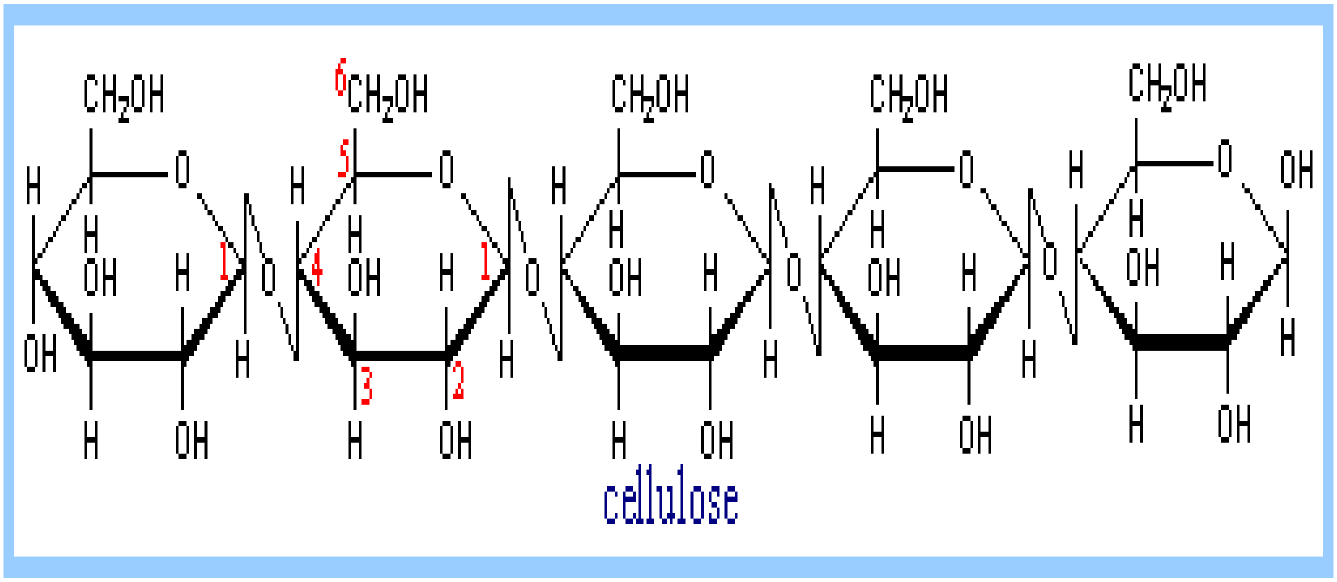
Cellulose is the major polysaccharide found in plants responsible for structural role. It is one of the most naturally abundant organic compounds found on the planet. Cellulose is an unbranched polymer of glucose residues put together via beta-1,4 linkages, which allow the molecule to form long and straight chains. This straight chain conformation is ideal for the formation of strong fibers.

Although mammals cannot digest cellulose, it and other plant forms are necessary soluble fibers that mammals can digest. Pectin, for example, slows down the movement of food molecules in the digestive tract, which thereby allows for more necessary nutrients to be absorbed by the body instead of being quickly passed through as waste. Likewise, insoluble fibers like cellulose expedite the digestive movement of food molecules, which is imperative in the quick removal of harmful toxins.

Although human can't digest cellulose because we lack cellulases that allow us to cleave the beta 1,4 linkages. Some animals do eat and obtain energy from cellulose. One example of that is termites. These animals digest cellulose in a stepwise manner, using a combination of their own cellulases (produced in the foregut) and those of a microbial community resident in the distal parts of their digestive tract. This is a great example of symbiosis relationship.

Cellulose is insoluble in water and aqueous solutions. It forms crystals and hydrogen bonds with amino acids. This quality of using intra and intermolecular hydrogen bonds to make crystals renders cellulose excessively insoluble in water and aqueous solutions. However, individual strands of cellulose aren't very hydrophobic as compared to other polysaccharides. It is the property of forming crystals that makes cellulose so insoluble.

Structure of Cellulose



Use of Cellulose

Cellulose has many uses, for example, as a gelling agent because of cellulose's properties of holding on to water. It is also used as an anticake agent, stabilizer, thickener and dispersing agent. Water cannot enter crystalline cellulose but dry cellulose absorbs water and it becomes flexible. Cellulose can give improved volume and texture particularly as a fat replacer in sauces and dressings but its insolubility means that all products will be cloudy.

Most papers are made of cellulose. The most important role of cellulose is that it is the major constituent of paper and cardboard and of textiles made from cotton, linen, and other plant fibers.

Cellulose can also be converted into cellophane, a thin transparent film, and into rayon, an important fiber that has been used for textiles since the beginning of the 20th century. Both cellophane and rayon are identical to cellulose in chemical structure. They are known as "regenerated cellulose fibers" and are usually made from viscose, a viscous solution made from celluloseare . A more recent and environmentally friendly method to produce rayon is the Lyocell process.

In the laboratory, cellulose is used as the stationary phase for TLC (thin layer chromatography). It is the raw material in the manufacture of nitrocellulose (cellulose nitrate) which was historically used in smokeless gunpowder and as the base material for celluloid used for photographic and movie films until the mid-1930s.

About a third of the world's production of purified cellulose is used as the base material for a number of water-soluble derivatives with pre-designed and wide-ranging properties dependent on groups involved and the degree of derivatization. Cellulose is also used to make hydrophilic and highly absorbent sponges. Derivatizing cellulose interferes with the orderly crystal-forming hydrogen bonding, described above, so that even hydrophobic derivatives may increase the apparent solubility in water. Methyl is thermogelling, which is made by methylating about 30% of the hydroxyl groups, forming gels above a critical temperature due to hydrophobic interactions between high-substituted regions and consequentially stabilized intermolecular hydrogen bonding. Such gels break down when cooling, in a manner similar to that causing the solubility minimum for non-polar gases; hydrophobic saccharides becoming less soluble as the temperature increases. This property is useful in forming films as barriers to water loss and for holding on to small gas bubbles. Cellulose fibers are also used to make filter bed of inert material in liquid filtration.

Cellulase, an enzyme found in organisms that can digest cellulose, has recently garnered the attention of the scientific community and especially of alternative energy researchers who hope to produce biofuel (such as ethanol) by enzymatically breaking down the cellulose found in plants. How cellulase operates is not yet fully understood, but as more knowledge about the mechanism is uncovered researchers will be able to improve its efficiency (known cellulases are currently too slow to be used in industry) and apply its use to producing "green" energy sources. In this way, the most abundant source of bioenergy on Earth, cellulose, can become a part of the world's accessible energy supply. Some types of cellulase already find uses in industry, for example in food production and the textile industry.

Useful Web Links and sources of content:

1. http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/C/Carbohydrates.html

Likely examination questions

i) Discuss plants' metabolism of starch.
ii) Describe the recycling of glucose in humans.
iii) Discuss the occurrence of cellulases in nature.