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SEM-2

PAPER-IV: Fundamentals of Biochemistry

**Lesson: Disaccharides, Oligosaccharides and
Polysaccharides**

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Introduction

Monosaccharides are the functional units of disaccharides, oligosaccharides and polysaccharides. Monosaccharides even though being present independently in nature, also exist in polymeric forms. These molecules are linked with each other through a covalent linkage called glycosidic bond typically seen in carbohydrates. These polymeric forms of carbohydrates perform a wide variety of function in living systems. The prominent functions associated with these molecules are either structural or storage in nature. The present chapter tries to understand the structure, the physicochemical properties and the functions associated with several such molecules. The chapter also tries to understand the isomerism as is seen in the most common hexose-Glucose. It also tries to understand the functional and structural features of the various derivatives of glucose.

Disaccharides

An attachment of two monosaccharides using a glycosidic bond constitutes a disaccharide. There are several disaccharides available naturally in nature the notable ones being Lactose, Maltose and Sucrose. While maltose contains two glucose units, lactose is the combination of galactose and glucose. Again sucrose is the amalgamation of fructose and glucose linked with each other.

The glycosidic linkage

Disaccharides, Oligosaccharides and Polysaccharides

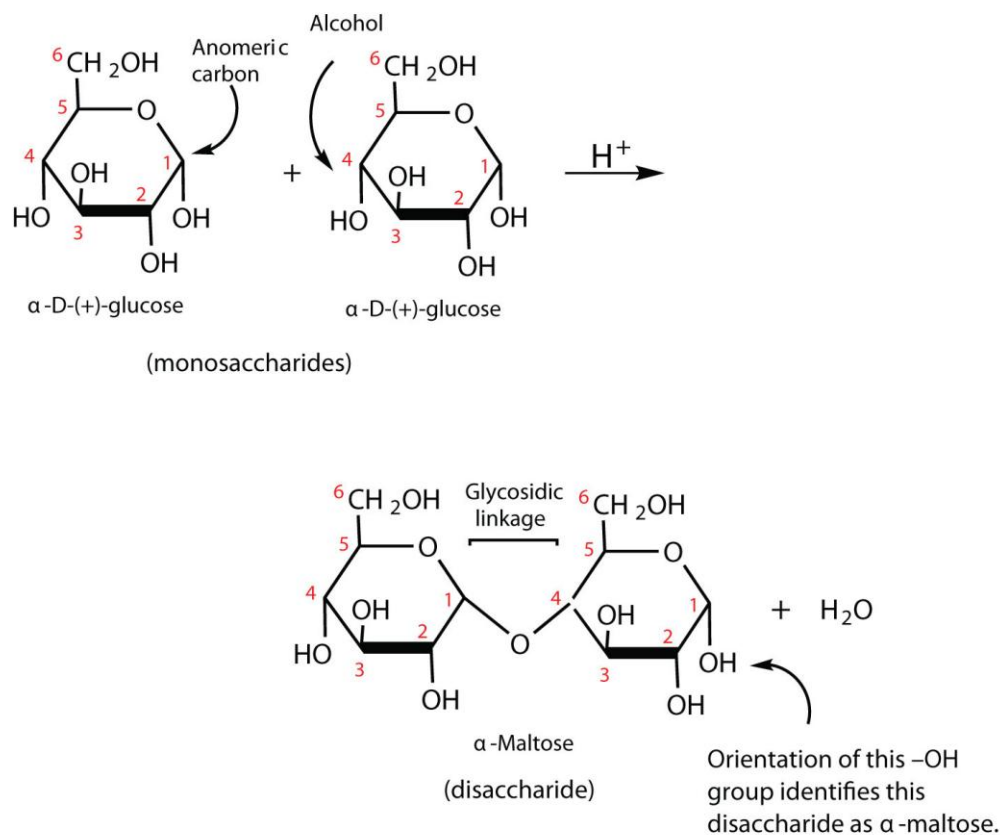


Figure: The glycosidic linkage: is formed by the reaction of anomeric carbon of one cyclic monosaccharide with the OH group of the second monosaccharide.

Source: <http://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological/s19-carbohydrates.html>

A typical disaccharide synthesis entails condensation of sugar moieties which behave as hemiacetals and alcohols (from another monosaccharide) to form acetals or glycosides. The reaction can be catalyzed by either acids on heating chemically or enzymes in the living systems.

The glycosidic bond formed between the two carbon atoms of both the monosaccharides could either be an alpha or a beta glycosidic bond. The alpha form represents the linkage which indicates below the left acetal carbon while in the beta form the hydroxyl moiety on the number one carbon is directed upward. Glycosides can be easily hydrolyzed and maltose and lactose are reducing in nature (hemiacetals containing a reactive carbonyl group which can be easily oxidized) except for sucrose which is non-reducing in nature as both the anomeric carbons are utilized in glycosidic linkage. Similarly owing to the union of two aldoses in the case of maltose and lactose, the two molecules can easily open up and swap

their forms thus causing mutarotation. However in the case of sucrose the glycosidic link between the two anomeric carbons i.e. C-1 of glucose and the C-2 of fructose does not permit the ring structures to unravel and thus no mutarotation is observed.

Amongst the three important disaccharides, maltose and sucrose possess the alpha type, lactose contains the beta variety. The two sugar ring structure linkage is represented not only in terms of the alpha and the beta form but also the positions of the two carbons which are involved in the linkage. The linkage amongst the disaccharide not only represents the alpha and the beta form but also the location numbers of the carbons which are involved in the linkage.

The common disaccharides

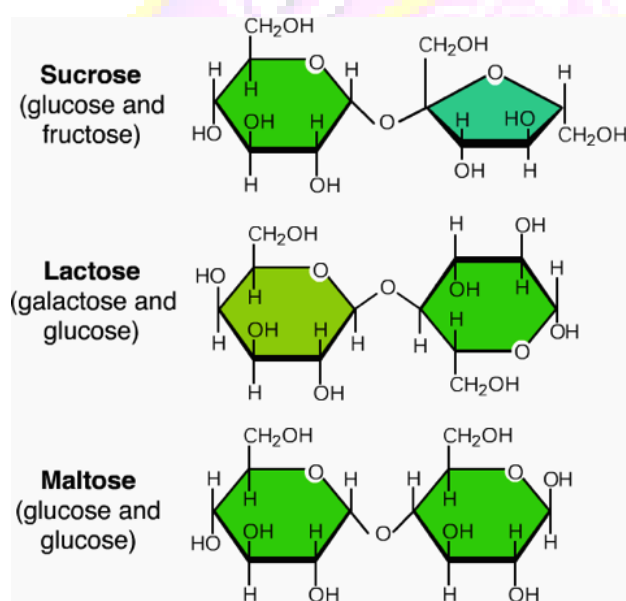


Figure: The three common disaccharides

Source: <http://bio1151.nicerweb.com/Locked/media/ch05/disaccharides.html>

Maltose

- Also called Malt sugar and is present in beverages, cereal, pasta, potatoes and sweetened processed food.
- Contains 2 glucose molecules in a $\alpha(1\rightarrow4)$ linkage and branching in position $\alpha(1\rightarrow6)$.
- Reducing in nature due to the free aldehydic group which can easily be oxidized also due to O-glycosidic link maltose can reduce Fehling's reagent

Disaccharides, Oligosaccharides and Polysaccharides

- Can mutarotate
- Produced during the germination of seeds like barley, caramelization of glucose and fermentation by yeast mostly due to the hydrolysis of starch into maltose and glucose by amylase. Maltose does not occur freely.
- 1/3 as sugary as sucrose
- Easily assimilated by humans due to the presence of alpha glycosidic bond
- Degradation with the help of maltase enzyme into glucose residues which further help in providing energy to the body
- Isomaltose is an isomeric form of maltose which has glucose moieties linked through α (1 \rightarrow 6) bonds as is seen in the branching of glycogen.
- Perceived to be the primary carbon source for chloroplasts at night
- Maltose intolerance or Congenital Sucrase-Isomaltase Deficiency is caused due to the absence of Sucrase-Isomaltase enzyme. The disease occurs due to a recessive autosomal mutation predominantly in infants. Symptoms occur when starch is present in the food and symptoms are analogous to lactose intolerance which is discussed subsequently thereby leading to lesser body weight and growth. Treatment involves restricted intake of starch and subsequent improvements with maturity.

Sucrose

- Also called cane sugar or common table sugar
- Sweetening agent
- Contains glucose and fructose in a α (1-2) linkage i.e. O- α -D-glucopyranosyl-(1 \rightarrow 2)- β -D-fructofuranoside
- Rotation of fructose residue by 180° of its normal view for the glycosidic linkage
- Extracted from sugarcane (15-20%), maple syrup and sugar beets (10-17%) etc and is readily available. Occurs in low percentages in honey and maple sap
- Is not a reducing sugar and does not exhibit mutarotation
- Readily digested by humans with the help of sucrose enzyme. However sucrose has a low glycemic index value of 65 due to negligible effect of fructose residue on blood glucose levels. While the glucose released due to its degradation is added to the blood or stored as glycogen, the fructose moves out along with cellulose or gets converted into citrates, aldehydes or lipids.
- Also known as invert sugar due to its ability to change the direction of specific rotation of plain polarized light from a positive to a negative value.

Lactose

- Also known as milk sugar (0-8% content in milk).
- Can be isolated from milk and milk products especially whey
- Contains galactose-glucose joined as a beta-glycoside β (1-4)
- Reducing sugar owing to the availability of hemiacetal in the glucose moiety.
- Can mutarotate
- Applications include its utilization as an additive, filler and carrier of pharmaceuticals, infant foods and aromas.
- Degradation of lactose is performed in intestine using the enzyme lactase which is capable of breaking the beta bond leading to the release of glucose and galactose as products. However reduced utilization in adults' leads to decreased production of the enzyme resulting in intolerance towards lactose.
- Symptoms of lactose intolerance include gastric discomfort which includes intestinal gas, bloating, cramping, diarrhea, vomiting etc. This is due to the metabolic breakdown of non-degraded lactose by bacteria in the large intestine into acids and gases. More prevalent in Southeast Asians and native North Americans than in north Europeans
- Several forms of intolerance are there while primary lactose maldigestion is highly prevalent (75% of the world population) and is due to insufficient lactase content, Secondary lactose maldigestion is a transitory state due to other diseases like intestinal diarrhea
- Treatment includes gradual increase in milk products consumption, spreading and mixing milk products with other meals though the day, use of cheese (maltose goes along with the whey), acidophilus milk, lactase pills and yoghurt (contains degraded maltose)

Oligosaccharides and Polysaccharides

An attachment of two to ten monosaccharides through glycosidic bonds constitutes an oligosaccharide while more than ten and up to 1000 or even more monosaccharides linked with each other in long chains both branched and linear typically are considered as polysaccharides. Oligosaccharides are many times linked with lipids and proteins as side chains. Based on the linkage two types have been identified. They are O-linked (o-glycosidic bonds with hydroxyl functional moiety of serine and threonine side chains) and N-linked (N-glycosidic bond with amino residue of asparagine side chain) Most of these oligo and

polysaccharides are a combination of only one or two monosaccharides being linked with each other. Hence they are also classified as homo and hetero polysaccharides. Most of the polysaccharides with dietary significance like cellulose, starch and glycogen are polymers of glucose and hence are also called glycans. The polysaccharides are mainly involved with providing structural characteristics as well as storage form of energy in all living systems. Examples include:

Structural polysaccharides-cellulose, hemicelluloses, pectin, chitin, mucilage

Storage – starch, inulin

Plant starch comprised of amylose and amylopectin is an important energy constituent of plant and animal diet. Plant constituent of our food also includes fibers which we humans are unable to digest. These various components of fibers are cellulose, hemicelluloses, lignins, pectins, gums, and mucilages. They can further be classified into insoluble or poorly fermented fibers (cellulose, hemicelluloses, and lignins) and soluble or viscous fibers (pectins, gums, and mucilages). While insoluble fibers are excreted undigested from our body as they are human enzyme resistant, soluble fibers are metabolized by intestinal bacteria.

Structural Polysaccharides

Cellulose

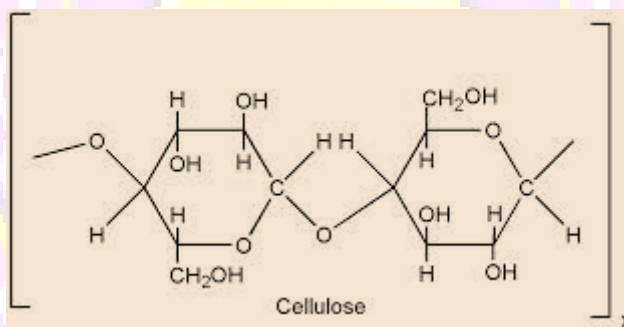


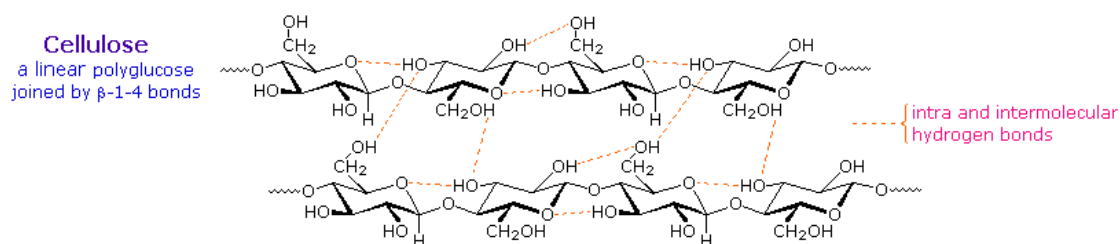
Figure: The structure of cellulose

Source: ILLL Inhouse

- Approximately half of the organic carbon in biosphere is constituted in cellulose content is highest in cotton fiber (90%). It is present in high amounts in wood (40-50%) and hemp (45%)
- The structural formula of cellulose is $(C_6H_{10}O_5)_n$ where n ranges from 500 to 5,000
- Polymer of glucose which is linearly linked with each other using the beta-glycoside bonds (β (1-4)), permits the stretching of cellulose chains as well as stabilizes the chair conformation and limits the flexibility. These chains are further stabilized with

Disaccharides, Oligosaccharides and Polysaccharides

the help of intramolecular hydrogen bonds. A parallel conformation of cellulose fibers is further supported by intermolecular hydrogen bonds. Thus cellulose is a linear polymer with no folds or branches and hence acquires a stiff rod like conformation with high tensile strength.



Source: http://chemwiki.ucdavis.edu/Biological_Chemistry/Carbohydrates/Carbohydrates

- There is a varied degree of polymerization seen in the case of various cellulose sources wherein wood pulp has around 300-1700 glucose moieties while plant and bacterial cellulose has 800 to 10,000 glucose molecules.
- Insoluble, non-reducing, chiral and biodegradable can be degenerated chemically in presence of concentrated acids at high temperature into glucose moieties. One of the breakdown small chain length product called cellodextrin is however soluble in water and organic solvents.
- Cellulose has large pores as straw like cavities in its conformation thereby leading to its ability to hold onto water.
- These insoluble fibers cannot be digested by most animals including humans as we lack beta glycosidase- an enzyme required for the breakdown of cellulose chain into individual glucose moiety and therefore excrete it out undigested. However ruminants possess intestinal microorganisms that can breakdown cellulose using beta-glycosidase similarly certain protozoa can breakdown cellulose by producing cellulase enzyme.
- Provides structural conformation to the plants and certain algae by intermeshing cellulosic microfibrils and polysaccharide matrix into a strong cell wall which can withstand high pressures and works as roughage to clean the colon in human beings.
- Synthesis of cellulose occurs in a hexameric protein complex called rosette terminal complex (RTCs) comprising of three varied cellulose synthase which play a critical role in the process.

- Cellulolysis or breakdown of cellulose is a difficult hydrolytic process leading to the synthesis of cellodextrins or glucose units. Only a few microorganisms like symbiotic anaerobic bacteria like *Cellulomonas* and certain flagellate protozoa produce cellulase- an endoenzyme which assists in the breakdown of cellulose. Cellulase along with glucosidases an exoenzyme can cleave cellulose.
- Besides the use of cotton fiber in textile industry, other uses include paper and related products and derivatives generation, formation of drug tablets, as thickeners, anti cake agent, emulsifier, dispersing agent, fat replacer and stabilizers in processed foods, as a stationary phase and inert matrix in chromatography, as a moldable substitute to plastics and resins in building construction and its insulation, as an adhesive and paste followed by its potential use in the production of biofuels. Several derivatives of cellulose like cellulose acetate, methylcellulose and nitrocellulose are available commercially for a wide variety of purpose like celluloid film formation, gluten substitutes and as an explosive.

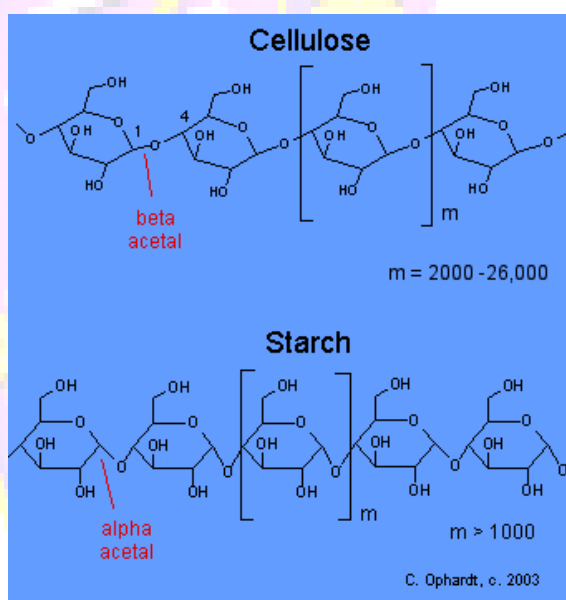


Figure: Difference between starch and cellulose

Source: http://chemwiki.ucdavis.edu/Biological_Chemistry/Carbohydrates/Polysaccharides/Cellulose

Hemicellulose

Disaccharides, Oligosaccharides and Polysaccharides

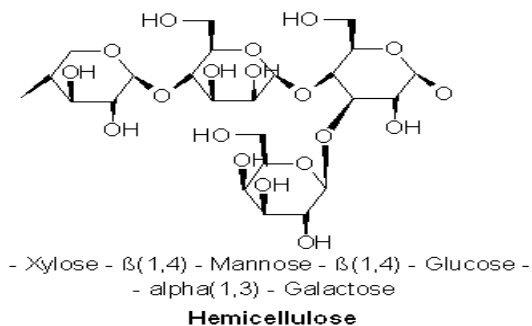


Figure: The structure of hemicellulose

Source: <http://upload.wikimedia.org/wikipedia/commons/6/69/Hemicellulose.png>

- Also called polyose
- A low molecular weight heteropolysaccharide comprised of several other monosaccharides like xylose (predominant one), mannose, galactose, rhamnose and arabinose besides glucose. Even acidified sugars can be seen in the molecule
- Contains mostly D-pentose form of sugars with occasional L-forms.
- Common associate of cellulose, 20% of the total biomass in plants.
- Contains smaller chains ($\sim 500-3000$ units) and branched thus it is weak in structure and can be easily degraded by enzymes, dilute acid or base unlike cellulose.
- Assists in the cross linking of microfibrils along with pectin of the cell wall further strengthening provided by lignin

Pectin

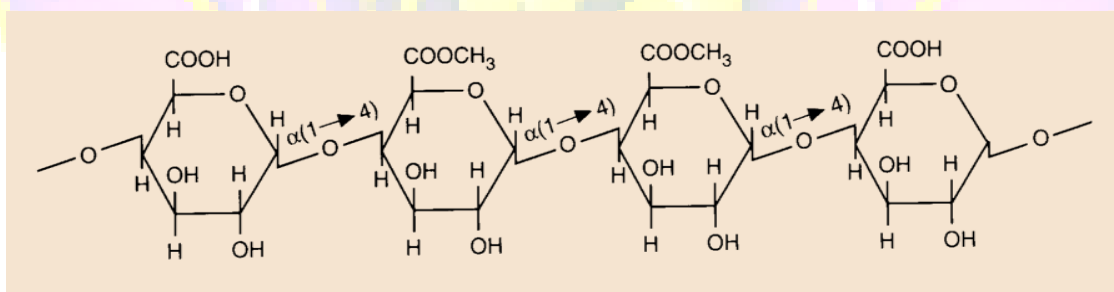


Figure: The structure of pectin

Source: ILL Inhouse

Structural homo and heteropolysaccharide, present in middle lamella and primary cell walls of non-woody parts of the terrestrial plants

Disaccharides, Oligosaccharides and Polysaccharides

- Several types identified amongst them while the homo polysaccharide is rich in D-galacturonic acid linked with α -(1-4) glycosidic bonds in linear chains in others the galacturonans are interspersed/branched with residues like D-xylose or D-apiose, in certain pectins alternating galacturonic acid and rhamnose with branching of neutral sugars like D-galactose, L-arabinose and D-xylose are observed. The level of branching is also different in varieties of pectin.
- The pectins can also be classified on the basis of the degree of esterification of galactouronans as high and low ester pectins. The non esterified acid groups in pectins however form salts and are known as pectinates while low esterified pectins are also called pectates. Even amidated forms of pectins have been observed which are able to degrade galactouronans into ammonia and acid.
- The high ester pectins at a high solid content ($> 60\%$) form a 3-D molecule net due to hydrogen bond and hydrophobic bonds leading to the formation of gel. The low ester pectins however need the support of calcium ions to form ionic bridges and cast itself into a gel. The temperature requirement for gel casting is also higher for high ester pectins than low ester pectins.
- Important role in plant growth by extending the primary cell wall
- Breaks down during fruit ripening and at leaf fall by the enzymes pectinase and pectin esterase thereby causing fruit and leaf fall
- Can be isolated from citrus fruits especially citrus peels or apple pomace while acetylated non gelling pectins can also be isolated from sugar beet, potatoes and pears
- Important role in human nutrition consumed through fruits and vegetables. Uses include it being used as gelling and thickening agent, fillings, medicines, sweets, and stabilizer and as a source of soluble dietary fiber. Can bind cholesterol as well as entrap sugar molecules thereby reducing their levels in the body. They also have a prebiotic effect as the microbes of the large intestine and colon degrade pectin and releases short chain fatty acids.

Chitin

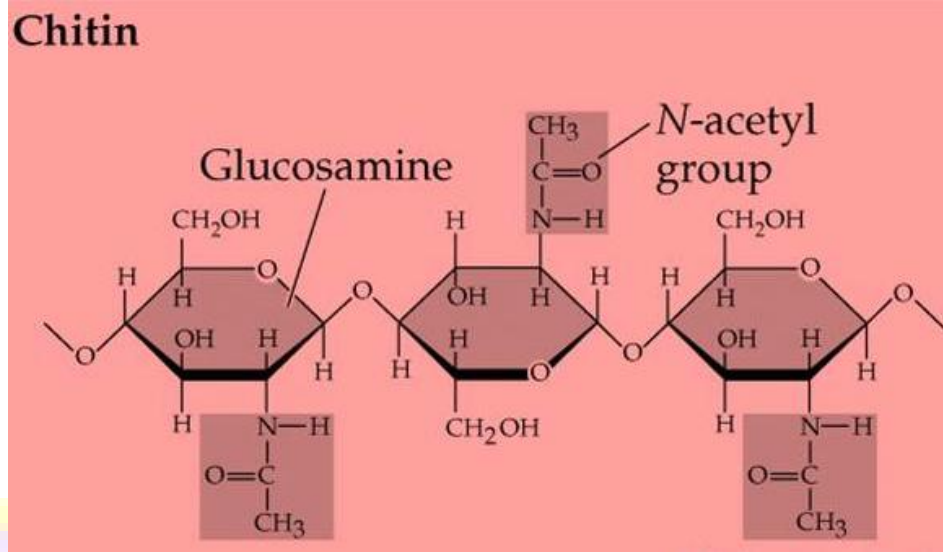


Figure: The structure of chitin

Source: ILL Inhouse

- Composed of long chain nitrogen containing polysaccharide of N-acetylglucosamine in a β-1-4 linkage forming nanofibrils or whiskers. Analogous to keratin in terms of functions.
- Commonly present in fungus (Cell wall), insects and crustaceans (exoskeleton), mollusks (radulus), cephalopods (beaks and internal shells) as a modified composite material and is many a times entrenched in proteinaceous matrix like sclerotin in the case of arthropods.
- Chitin is lucent, flexible, pliant, and quite strong.
- Uses include it to be a fertilizer and as a good inducer of protective procedures in plants, in food processing as a thickener and stabilizer even for drugs, as a binder for dyeing and in chromatographic resins. It is also used as a surgical thread it is also being used in the affinity separation of the recombinant expressed protein products by ligating a chitin binding domain to the designed protein.

Mucilage

- An exopolysaccharide, typically thick and sticky material produced mainly by all the plants (even in carnivorous plants as an ensnare for insects) and microbes (mainly in soil algae like unicellular and filamentous green algae as well as cyanobacteria) as a polar glycoprotein in alliance with tannins and alkaloids.

Disaccharides, Oligosaccharides and Polysaccharides

- Predominantly present in cacti and aloe vera like succulents as well as in flax, fenugreek and kelp seeds.
- Plays an important function of microaggregation in soil, storage of water and food and germination of seeds
- Uses of mucilage include its role in medication as a demulcent, as a cough suppressant and as a topical anti-inflammatory agent; for adhesive purpose; in food industry due to it helping in developing unique smell and flavor.

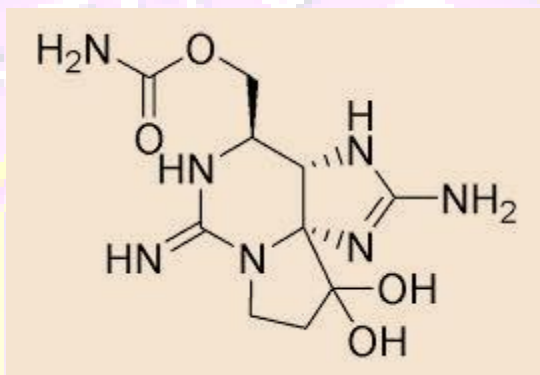


Figure: The structure of mucilage

Source: ILL Inhouse

Storage Polysaccharides

Starch

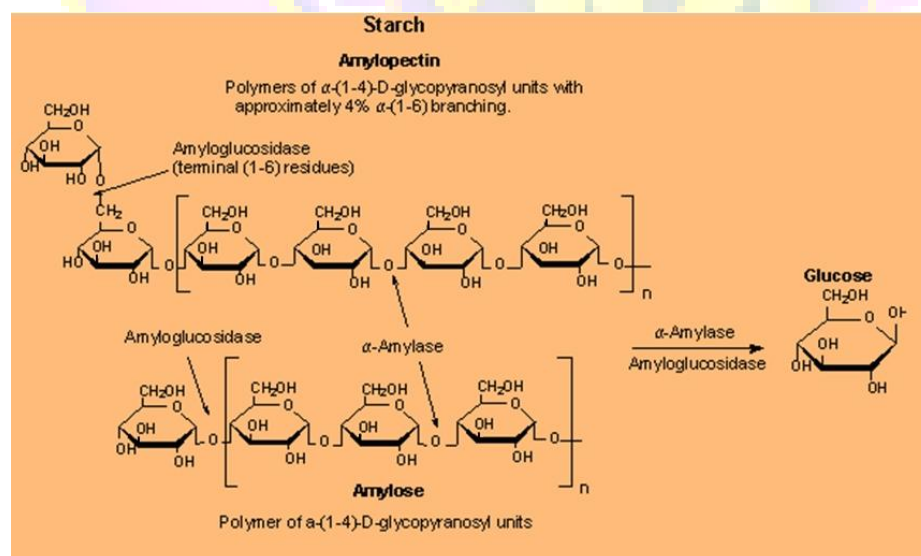


Figure: The structure of Starch

Source: ILL Inhouse

- Homopolysaccharide containing a large number of glucose moieties as linear chain as well as branches with α (1-4) and α (1-6) glycosidic linkage respectively.
- The starch granules contains two types of structures- the amylose (~20-25%, linear, extended and left handed helical) and amylopectin (~75-80%, branched, huge but compact). Amylose is a shorter (500-20,000 glucose residues) but far greater in number than amylopectin (more than a million glucose moieties). Amylomaize has around 50% amylose residues compared to waxy maize which has mainly amylopectin and less than 3% amylose content. Also the percentage of branching varies with plants however starch is less branched (1 in 10 glucose residues compared to 1 in 30 glucose residues) than glycogen-the animal storage polysaccharide.

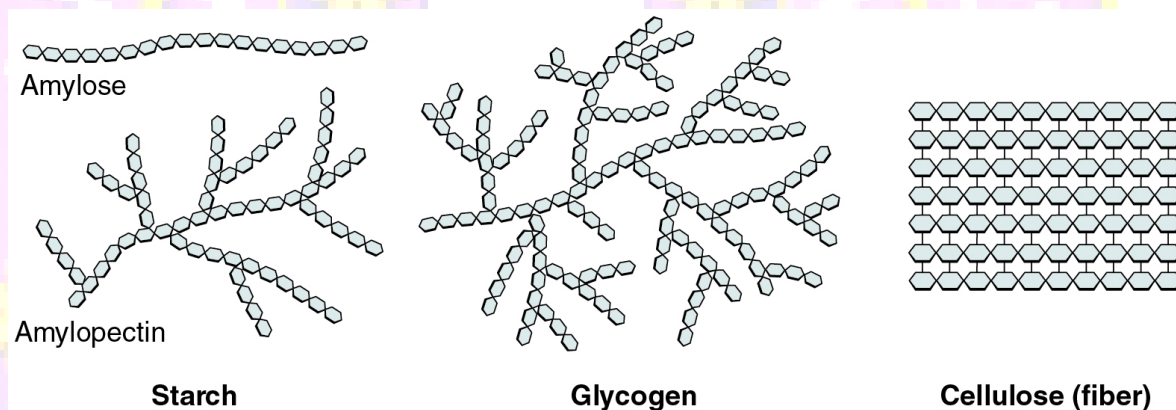


Figure: Structural difference in amylose, amylopectin and glycogen

Source: <http://cnx.org/content/m46008/latest/?collection=col11540/latest> (CC)

- The widespread inter and intra chain hydrogen bondings as seen in amylose are known to be responsible for providing hydrophobic characteristics and lower solubility attributes to starch. Around 5% of the total glucose molecules are involved with branching in the case of amylopectin. The amylopectin is comprised of unbranched outer chains called A chains and the branched inner chains called B chains besides a single C chain which is reducing in nature. In certain amylopectin structures presence of phosphate functional groups have been observed which confers more solubility to the molecule.

Disaccharides, Oligosaccharides and Polysaccharides

- Produced in most green plants especially cereals, seed endosperm fruits and root and tubers vegetables as an energy storage form of polysaccharides especially in potato, wheat, maize (largest source), rice, tapioca, banana etc.
- Starch is physically a white bland and fragrance-free powder which is insoluble in cold water and even alcohol. Gets solubilized in warm solutions by forming a network and increasing the viscosity of the solution using a process called gelatinization.
- In terms of digestion, starch can be categorized as rapidly digestible (amorphous), slowly digestible and resistant (crystalline) starch. The slowly digestible form is better suited for a diabetic diet as it does not shoot up the post prandial glucose levels.
- Starch is synthesized by the plant using the process of photosynthesis wherein the manufactured glucose is accumulated as starch particles in plastids. Subsequently it is transferred to fruit, seeds, rhizomes and tubers for the subsequent seasons and unfavorable circumstances.
- Degraded and hydrolyzed easily using acids and enzymes like α amylase, an enzyme present in plants and animals or both to yield dextrans. This is unlike cellulose and chitin, beta glycosidic molecules which are difficult to break. Even β amylase, as seen in brewing can help in the breakdown of starch however the end product is maltose rather than glucose residues. The starch can even be degraded by dry heat and the process is known as dextrinization as the end products are dextrans.
- Enzymes like Glucose-1-phosphate adenytransferase, starch synthase and starch branching enzyme play critical role in the conversion of osmotically active glucose molecules of plants into starch, an osmotically inactive and a condensed storage molecule.
- A unique chemical test performed to detect the presence of starch is performed using iodine wherein a dark blue color is observed in the presence of starch. Amylose is known to play a critical role in this test as the iodide ions get entrapped inside the coils and gives a blue color spectrum. Absence of amylose leads to the development of red color. The starch indicator procedure is also used in redox titrations.
- Uses include its role as an additive, sweetener and thickener in food processing industry; as a stiffener, thickener and to size yarns in laundry and textile industry; as an excipient, as tablet disintegrant or as binder in pharmaceuticals; to provide sizing (wet and dry strength) at the wet end as well as surface sizing (strength and water hold out properties especially for printing) at the dry end of paper making so as to impart enhanced smoothness, stiffness, paleness and shiny finish and thus

enhances printing attributes to the paper besides working as an adhesive and glue in book and paper industry; in the gypsum wall board construction process as a glue as well as to provide rigidity; in regulating drilling in petroleum extraction process as well as in producing bioethanol from corn as well as in hydrogen production.

Inulin

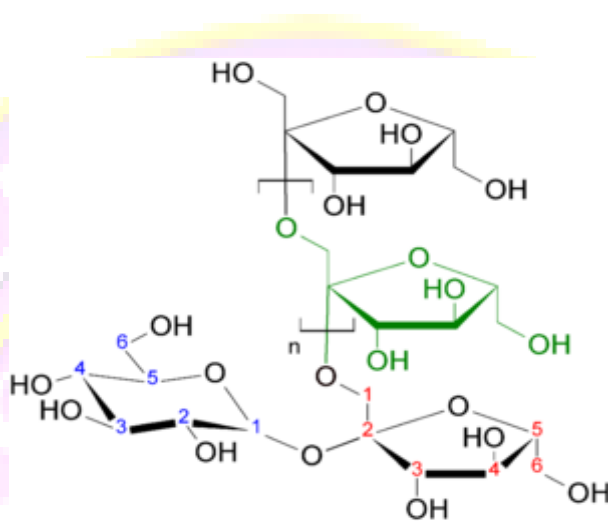


Figure: The structure of Inulin

Source:http://upload.wikimedia.org/wikipedia/commons/thumb/2/29/Inulin_strukturformel.png/300px-Inulin_strukturformel.png

- Categorized as soluble dietary fibers which are called fructans with or without a typical terminal glucose
- A heteropolysaccharide comprised of glucose and fructose with a β (2-1) glycosidic linkage. Any fructan with a degree of polymerization more than 10 to 60 is considered to be a classic high quality inulin molecule. When the degree of polymerization is less than 10, the molecule is called an oligofructose.
- Present in some plants (the ones which do not store starch) especially in roots and rhizomes, most notably in chicory. Other plants containing inulin are wheat, onion, bananas, garlic and asparagus
- Major functions include storage of energy as well as adaptability to cold and draught conditions. The osmolarity of the plant under these circumstances are regulated by altering the level of polymerization in inulin molecule by altering its hydrolysis.
- Important dietary functions like low caloric value, increased calcium and magnesium absorption, a soluble dietary fiber as well as prebiotic effect are known to be

associated with inulin due to the inability of our enzymes in breaking down the β (2-1) bonds. Thus inulin remains undigested in our digestive route and its breakdown ultimately occurs by colon microbes thereby emanating lots of gaseous end products like carbon dioxide, hydrogen and methane.

- While oligofructose being 35% as sugary as sucrose can work as sweetener, inulin is little or no sweet, colorless, odorless, can easily be solubilized as a gel network withholding huge volumes of water and can resemble a creamy paste mimicking fat. It is also known to strengthen foams and emulsions.
- The uses of inulin include its extensive utility in food processing industry as it is virtually able to replace carbohydrates, lipids and cereals flour due to its multifaceted properties. Besides being a dietician delight and extensively being used in processed food it is considered to be an important component of diabetics diet chart as it helps in regulating the blood glucose levels. The side effect of introducing inulin in the diet involves unwanted additional propagation of methanogenic bacteria leading to gas production, gastric discomfort, bloating and cramping followed by diarrhea and growth of pathogenic bacteria.
- Medically inulin is being used as a gold marker for determining kidney function by measuring glomerular filtration rate as the molecule can neither be secreted nor reabsorbed and hence is completely filtered. Inulin is also being recognized to support and endorse our immune system and its development besides it being used as a vaccine adjuvant. The prebiotic effect wherein inulin not only helps in the propagation of beneficial bacteria but also assists in the killing and suppression of pathogenic bacteria has been well recognized. Inulin is also considered to reduce the cholesterol and triglyceraldehyde content in the blood thereby reducing the risk of cardiovascular diseases. Inulin is also being used for compensation of water loss as well as minerals subsequent to diarrhea.
- Inulin can even be potentially converted into bioethanol through the synchronized fermentation and saccharification.

Isomers and Derivatives of Glucose

Isomers

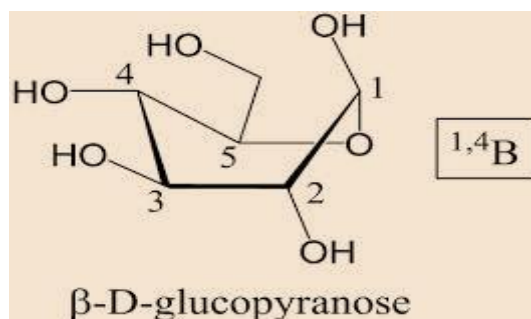


Figure: The most common form of glucose

Source: ILLL Inhouse

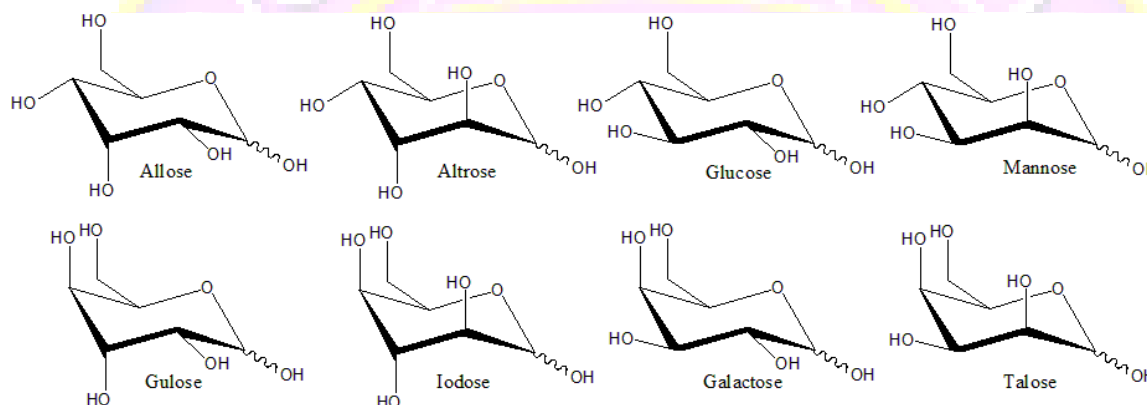


Figure: The various isomers of glucose

Source: [http://upload.wikimedia.org/wikipedia/commons/7/79/Structure of D-hexoses.png](http://upload.wikimedia.org/wikipedia/commons/7/79/Structure_of_D-hexoses.png)

Glucose is an aldohexose consisting of hexose with an aldehydes functional group. The molecule is capable of both stereoisomerism as well as optical isomerism owing to the presence of its chiral carbons. The most prevalent isoform of glucose in nature is α -D glucopyranose.

According to the Fischer projections, in the open chain aldohexose form of glucose all the second to the fifth carbon residues are capable of forming 16 unique stereoisomers and thus can acquire an explicit three-dimensional display with distinct biochemical features. The D and L prefix forms are usually implicated in the so called enantiomers on the basis of the display conformation of the monosaccharide with the core triose molecule-glyceraldehyde and an analogy of the structure to the second carbon of D-glyceraldehyde (right side) indicates them to be the D form which in the test monosaccharide is the second last carbon.

The reverse is true for the L form. These mirror image stereoisomers include D and L forms of glucose, mannose, galactose, talose, allose, altrose, idose and gulose.

These open chain forms of aldohexoses being thermodynamically unstable tend to condense either as 5 and/or 6 cyclic carbon rings which are closed by a single oxygen atom in aqueous solutions. While the 5 carbon ring structure is called a furanose, the 6 carbon rings are called pyranoses. When dissolved in water around 99% of the glucose is present in the form of pyranose ring structure while furanose and open ring forms are there in insignificant amounts.

Amongst the cyclic forms of glucose, the first or the anomeric carbon organizes itself in two different forms i.e. the α and the β forms. While the α form has the hydroxyl moieties of the first and fifth carbon in a trans display, the β isomer has the same hydroxyl moieties in a cis alignment. In aqueous conditions however the two cyclic forms α and β tend to interconvert over a time period at room temperature and acquire an established proportion of 36:64 through a procedure called mutarotation. The process reportedly involves the opening and reclosure of the cyclic ring using dissimilar hydroxyl groups to achieve the equilibrium between α and β anomers. In 3-dimensions both the forms however acquire non-planar configurations of either chair or boat.

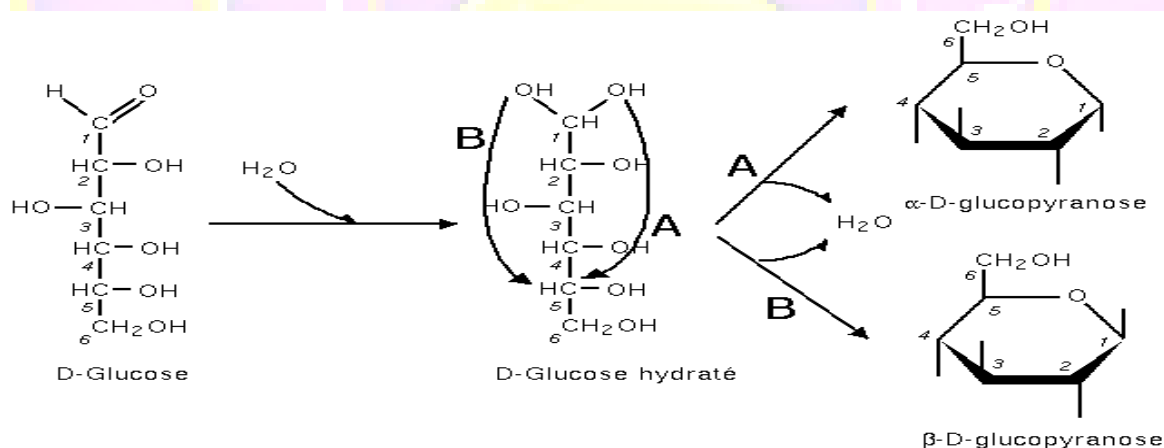


Figure: Interconversion of the α and the β forms of glucose

Source: http://upload.wikimedia.org/wikipedia/commons/4/4c/Glucose_cyclisation.png

The cyclic glucose isomers are also capable of rotational isomerism owing to the torsional angular rotation also notated as ω angle between C-5 and C-6 as well as their constituent

oxygen atoms. These rotamers incorporate gauche-gauche, gauche-trans and trans-gauche conformations.

The glucose molecule being comprised of chiral carbons also exhibits optical rotation. The common occurring form of glucose, α-D glucopyranose is dextrorotatory in nature i.e. it is capable of rotating the unidirectional polarized light towards right. The L-glucose however depicts laevorotation (rotates polarized light to the left). The optical rotatory property of the glucose is attributed to the collective consequence of its four chiral carbons.

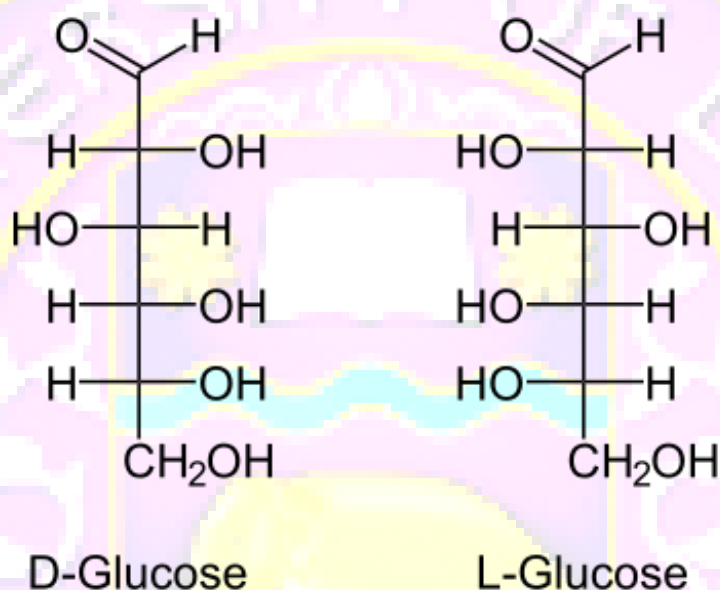


Figure: D and L forms of Glucose

Source: <http://upload.wikimedia.org/wikipedia/commons/thumb/0/06/DL-Glucose.svg/361px-DL-Glucose.svg.png>

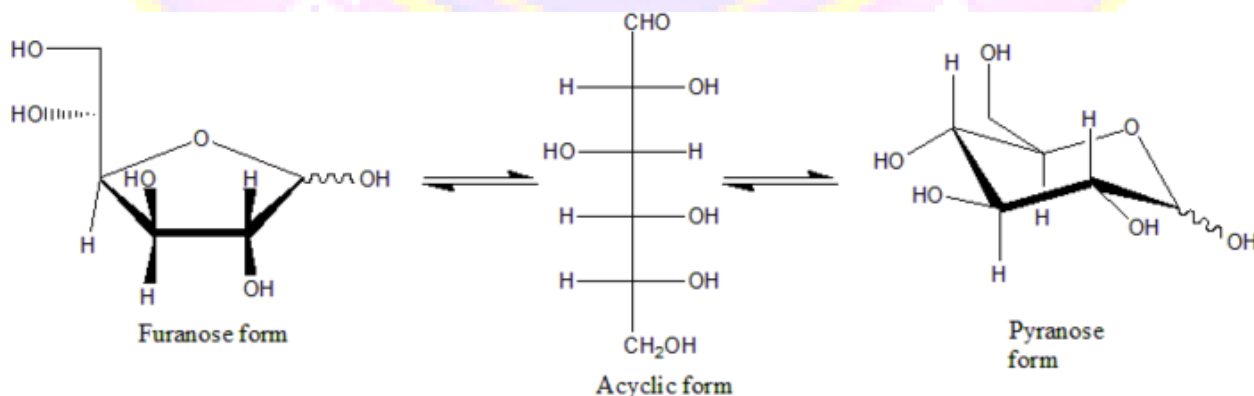


Figure: Conversion between the furanose, acyclic, and pyranose forms of D-glucose.

Source: http://upload.wikimedia.org/wikipedia/commons/thumb/0/09/Existence_in_solution.png/700px-Existence_in_solution.png

Derivatives of Glucose

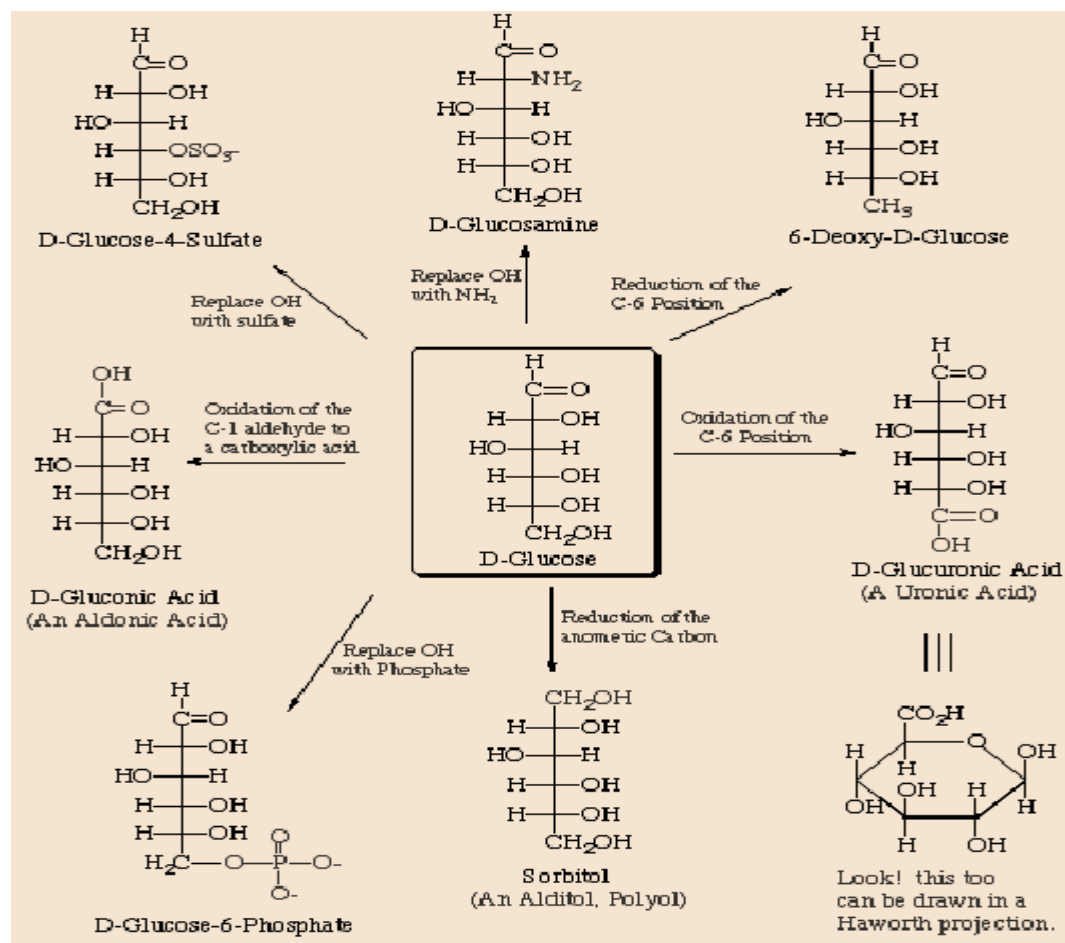


Figure: The various derivatives of Glucose

Source: ILL Inhouse

Glucose is produced in plants through photosynthesis, in other organisms it is the energy provider present in the diet and plays a critical role in carbohydrate metabolism and even acts as a precursor in starch biosynthesis. Glucose is capable of making its biologically significant derivatives wherein the second and the sixth carbon can associate varied functional moieties instead of their respective hydroxyl residues. They include:

Phosphorylated glucose i.e. Glucose 6 Phosphate

- a byproduct of carbohydrate metabolism; an energy intermediate; byproduct of glycolysis; easy permeability through membranes owing to its negative charge; precursor for storage polysaccharides like starch and glycogen

Glucosamine

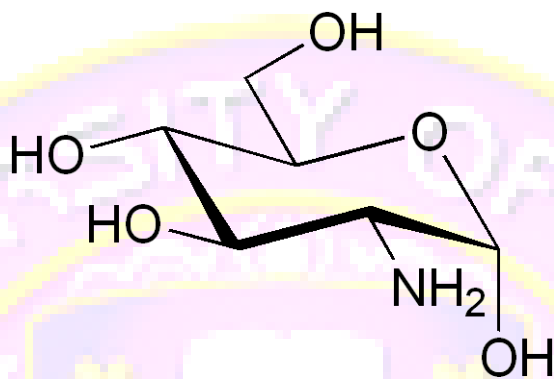


Figure: The structure of Glucosamine

Source: <http://upload.wikimedia.org/wikipedia/commons/5/59/Alpha-D-glucosamine.png>

- A copious amino sugar, an imperative component and precursor of polysaccharides like chitin and chitosan and even many glycoproteins, proteoglycans and glycolipids.
- Usually present in the shells and the bones as well as in bone marrow and even in cell walls of plants and fungi. It is also present in the cartilage associated with joints in humans. Usually isolated from the degradation of exoskeleton of crustaceans.
- Glucosamine 6-phosphate deaminase helps in its synthesis from a sugar i.e. fructose 6-phosphate and an amino acid glutamine. Glucosamine 6-phosphate is the predecessor to glucosamine.
- Use include the diverse forms of glucosamine like glucosamine sulfate, glucosamine hydrochloride, and *N*-acetylglucosamine in association with chondritin sulfate being used as an important adult nutritional add-on and a medicine especially for the protection of joints in osteoarthritis patients and assists in restoring the cartilage.
- One of its derivative *N*-acetylglucosamine is also involved in cell signaling especially for cell mediated immunity and neurons, also associated with insulin release as well absorption of cholesterol.

- Another derivative N-acetyl muramic acid synthesized by the condensation of lactic acid with N-acetyl Glucosamine is an essential feature of peptidoglycan network of bacterial cell walls and is the site of action of penicillin antibiotic.

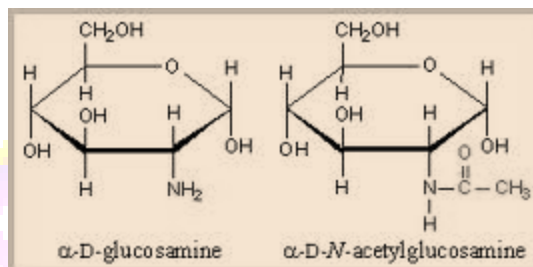


Figure: The two forms of glucosamine

Source: Author

Gluconic acid

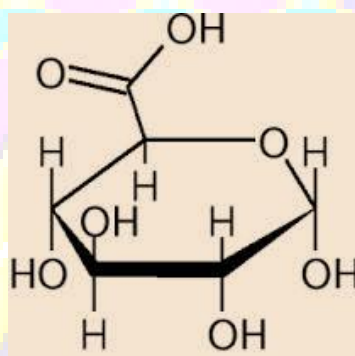


Figure: The structure of Gluconic acid

Source: Author

- Hexameric organic acid comprising of five hydroxyl groups as well as an ultimate carboxylic acid functional moiety. A mild nontoxic compound.
- Gluconic acid, gluconate salts, and gluconate esters are the naturally occurring forms arising from the oxidation of glucose using enzymes like glucose oxidase and glucose dehydrogenase predominantly in microbes and that is the reason why large scale production is done using the fermentation of fungus like aspergillus niger.

Disaccharides, Oligosaccharides and Polysaccharides

- Usually found in plants, fruits, honey, vinegar and wine as well as in various species of bacteria and fungi
- It is generally used in food industry as a foodstuff flavoring, acidulant and leavening agent; as acidity monitor and alkalizing mediator; cleanser and derusting agent, chelating and sequestering molecule and in pharmaceutical industry to treat burn injuries and deep seated necrosis as calcium gluconate, malaria as quinine gluconate, anemia as iron gluconate besides its role in the sterilization of dogs as zinc gluconate.
- Glucuronic acid is another acidic and polar form of glucose which is normally incorporated in proteoglycan network. Functions as a solubilizing agent for bilirubin and pharmaceutical drugs with subsequently assisting in the clearance of drugs.

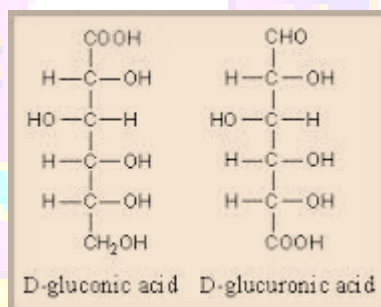


Figure: The two forms of Gluconic acid

Source: Author

Summary

- Monosaccharides are the precursor molecules of disaccharides, oligosaccharides and polysaccharides.
- When two monosaccharides are linked with each other through a glycosidic bond, a disaccharide is formed. Lactose, Maltose and sucrose are few of the disaccharides occurring commonly in nature.
- Maltose commonly called Malt sugar is present in beverages, cereal, pasta, potatoes and sweetened processed food. It contains 2 glucose molecules in α (1-4) linkage and branching in position α (1 \rightarrow 6).

Disaccharides, Oligosaccharides and Polysaccharides

- Sucrose or common table sugar possesses glucose and fructose in a α (1-2) linkage. It is also known as invert sugar due to its ability to change the direction of specific rotation of plain polarized light.
- Lactose or milk sugar can be isolated from milk and milk products and contains galactose-glucose joined as a beta-glycoside β (1-4). Lactose intolerance is a genetic disease associated with lactose owing to decreased production of lactase.
- When more than two to several thousand monosaccharides are linked either linear or branched through glycosidic bonds it constitutes an oligosaccharide or a polysaccharide.
- The polysaccharides are mainly involved with providing structural characteristics as well as storage form of energy in all living systems. Cellulose, hemicelluloses, pectin, chitin, mucilage are structural polysaccharides while starch, inulin are storage polysaccharides.
- Cellulose is one of the most prevalent polysaccharide present in plants. It is a polymer of glucose linearly linked with each other using the beta-glycoside bonds (β (1-4)). Cellulose cannot be digested by animals as they do not possess cellulase enzyme required to digest cellulose.
- Hemicellulose is a low molecular weight heteropolysaccharide comprised of several other monosaccharides like xylose and helps in the cross linking of microfibrils along with pectin of the cell wall.
- Pectin is a structural homo and heteropolysaccharide, present in middle lamella and primary cell walls of non-woody parts of the terrestrial plants and plays an important role in plant growth by extending the primary cell wall
- Chitin is comprised of long chain nitrogen containing polysaccharide of N-acetylglucosamine in a β -1-4 linkage and is commonly present in fungus, insects and crustaceans.
- Mucilage is an exopolysaccharide, typically thick and sticky material produced mainly by all the plants and plays an important function of microaggregation in soil, storage of water and food and germination of seeds
- Starch is a homopolysaccharide containing a large number of glucose moieties as linear chain as well as branches with α (1-4) and α (1-6) glycosidic linkage respectively. The starch granules contains two types of structures- the amylose and amylopectin.
- Inulin, present in some plants which do not contain starch, is a soluble dietary fibers which are comprised of glucose and fructose with a β (2-1) glycosidic linkage.

Major functions include storage of energy as well as adaptability to cold and draught conditions.

- Glucose is capable of both stereoisomerism as well as optical isomerism owing to the presence of its chiral carbons. The most prevalent isoform of glucose in nature is α -D glucopyranose.
- Glucose is capable of making its biologically significant derivatives wherein the second and the sixth carbon can associate varied functional moieties instead of their respective hydroxyl residues.
- Glycosamine is an amino sugar and is an important precursor of polysaccharides like chitin and chitosan and even many glycoproteins, proteoglycans and glycolipids.
- Gluconic acid, gluconate salts, and gluconate esters are the naturally occurring forms arising from the oxidation of glucose.

Exercise/ Practice

Fill in the blanks

1. Chitin is composed of ----- . N-acetyl Glucosamine
2. Amylopectin has ----- linkage. α 1-4 and α 1-6
3. In maltose the two sugars are ----- and ----- and linkage is----- . Glucose, Glucose, α 1-4
4. --- is a nutritional polysaccharide. Starch
5. ---- is not a glucosan. Inulin
6. α -D Glucose and β - D glucose are----- . Anomers
7. Glucose can have ----- isomers due to the presence of chiral carbon.
16
8. Galactose and Glucose are----- . Epimers
9. The polysaccharide found in the exoskeleton of insects is---- . Chitin
10. ---- is used to treat burn injuries. Gluconic acid

State True or false

1. The compounds having same structural formula but differing in configuration around one carbon atom are called anomers. False
2. A Polysaccharide formed by β 1 \rightarrow 4 Glycosidic linkages is Cellulose. True
3. Sucrose is an Invert sugar. True
4. The typical cyclical structure of Glucose is α and β D-Glucofuranose. False
5. Glucosamine 6-phosphate is the predecessor to Glucosamine. True
6. The stereoisomers incorporate gauche-gauche, gauche-trans and trans-gauche conformations. False
7. Corn is the largest source of starch. True
8. Cellulose is also called polyose. False

Short answer questions

1. Why is inulin considered to be a gold marker for determining kidney function?
2. Why is it that inulin is extensively utilized in food processing industry?
3. What is dextrinization?
4. Which molecule is used as the surgical thread?
5. What are the various ways by which pectin can be classified?>
6. Which is being used in the affinity separation of the recombinant expressed protein and how?
7. Which microorganisms can produce cellulase?
8. Differentiate between maltose, lactose and sucrose.

Glossary

The glycosidic bond – a covalent bond formed between the two carbon atoms of both the monosaccharides could either be an alpha or a beta glycosidic bond.

Homopolysaccharide- same precursor sugars

Heteropolysaccharide- Different precursor sugars

Glycemic index- Blood sugar levels

Intolerance- unable to degrade

Stereoisomer-common chemical structure but an explicit three-dimensional display with distinct biochemical features

Enantiomers- possible configurations of two non superimposable mirror image stereoisomers

Optical rotation- an ability to rotate the plane polarized light either to the left or to the right

Chiral carbon- asymmetric carbon, a tetrahedral carbon containing four different functional moieties

References/ Bibliography/ Further Reading

- Lehninger Principles of Biochemistry (Hardcover) by David L. Nelson , Michael M. Cox
- Lippincott's Illustrated Reviews: Biochemistry by Pamela C. Champe, Richard A. Harvey, Denise R. Ferrier
- Harper's Illustrated Biochemistry by Robert K. Murray, Darryl K. Granner, Peter A. Mayes
- Biochemistry by Donald Voet, Judith G. Voet
- Biochemistry by Jeremy M. Berg, John L. Tymoczko, Lubert Stryer
- Biochemistry by Mary K. Campbell, Shawn O. Farrell

Web Links

1. http://chemwiki.ucdavis.edu/Biological_Chemistry/Carbohydrates/Carbohydrates
2. <http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/intro1.htm>