



Chapter 5:

Chemistry of Carbohydrates

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> Textbook of BIOCHEMISTRY for Medical Students

By DM Vasudevan, et al.

TENTH EDITION

Functions of Carbohydrates

- TAYPED
- 1. Carbohydrates are the main sources of **energy** in the body.
- 2. Brain cells and RBCs are almost wholly dependent on carbohydrates as the energy source.
- 3. Energy production from carbohydrates will be 4 kcal / g.
- 4. Storage from of energy (starch and glycogen)

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- 5. Excess carbohydrate is converted as fat.
- Components of nucleic acids and co-enzymes 6.
- Glycoproteins and glycolipids are components of cell 7. membranes and receptors.
- 8. Structural basis of many organisms: Cellulose of plants; exoskeleton of insects, promotic realing for COVID-19 included cell wall of micro-organisms, mucopolysaccharides as ground substance in higher organisms.



- Widely distributed in nature both in plants and animals
- Plants- Photosynthesis Starch storage form of CHO
- Cellulose constitute the structural frame work.
- Animals- present in all tissues & body fluids- blood, milk etc.



Definition



The general molecular formula of carbohydrates is $Cn(H_2O)n$.

For example, glucose has the molecular formula C6H12O6.

Carbohydrates in general are polyhydroxy aldehydes or ketones or compounds which yield these on hydrolysis.

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But this is not true due to

- 1. All sugars cannot be represented by this general formula. Eg. Deoxy Ribose $-C_5H_{10}O_4$.
- 2. All compounds having H and O in ratio of 2:1 are not carbohydrates Eg. Acetic acid $-C_2(H_2O)_2$ Lactic acid $-C_3(H_2O)_3$
- 3. Apart from C, H & O, many sugars contain N, S, P etc. Eg. Aminosugars, Phosphosugars etc







Nomenclature



Molecules having only one actual or potential sugar group are called **monosaccharides** (Greek, mono = one); they cannot be further hydrolysed into smaller units.

When two monosaccharides are combined together with elimination of a water molecule, it is called a **<u>disaccharide</u>**





<u>Trisaccharides</u> = three sugar groups. Tetrasaccharides Pentasaccharides and so on, **Oligosaccharides** (**Greek**, **oligo** = a few).

When more than 10 sugar units are combined, they are generally named as polysaccharides (Greek, poly = many).

Homopolysaccharides Heteropolysaccharides.

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Sugars having aldehyde group are called <u>aldoses</u>

Sugars with keto group are ketoses.

Depending on the number of carbon atoms, the monosaccharides are named as triose (C3), tetrose (C4), pentose (C5), **hexose (C6),** heptose (C7).

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Depending on the number of C atom further classified to

No of C	Aldose	Ketose
3C - Triose	Glyceraldehyde	Dihydroxy acetone
4C- Tetrose	Erythrose	Erythrulose
5C - Pentose	Ribose	Ribulose
6C - Hexose	Glucose	Fructose
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Disaccharides



- Sugars which yield 2 sugar units on hydrolysis. Monosaccharide unit may be the same or different.
- Biologically important disaccharides are
 Sucrose → Glc + Fru
 Maltose → Glc + Glc
 Lactose → Glc + Gal

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Disaccharides



Depending on whether a disaccharide contains a free functional group or not, classified to

- Reducing disaccharides Lactose Maltose
- Nonreducing disaccharides Sucrose Trehalose



Oligosaccharides

Sugars on hydrolysis yield 3-10 sugar units

- Rhamnose, Raffinose
- Carbohydrate moiety of glycoproteins
- Carbohydrate moiety of Proteoglycans

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(Berzelius in 1832) - Isos - Equal Meros - Part

Definition: Compounds having the same molecular formula, but differ in chemical and physical properties.
Phenomenon is called Isomerism.
2 Types of Isomerism

- Structural (Positional) Dependence of the Comp
- Stereo

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Structural Isomers CH₂COOH Citrate HO C COOH $C H_2 COOH$ Isocitrate HO CH COOH **CH COOH** CH₂COOH



• Stereo Isomers : Same molecular formula, but differ in the spatial configuration of substituent groups.

Geometrical

2 Types



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• Geometrical isomerism – Cis trans isomerism Differ in spatial configuration of atoms around a double bonded C atom.

HC COOH HC COOH HC COOH HOOC CH Maleic acid Fumaric acid

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- Optical isomers (Configurational) differ from disposition of various atoms or groups in space around an asymmetric Carbon atom (Chiral center)
- An asymmetric Carbon atom is a Carbon atom the four valences of which is attached to four different atoms or groups of atoms.



Stereoisomers



Compounds having same structural formula, but differ in spatial configuration are known as stereoisomers.

Asymmetric carbon means that four different groups are attached to the same carbon.

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H - C = O H - C - OH C + OH C + 2 - OH



D-glyceraldehyde L-glyceraldehyde

The reference molecule is glyceraldehyde which has a single asymmetric carbon atom.



H-C=O H-C--OH HO-C--H H-C--OH 1 H-C=O HO-C--H $Textbol2_k$ 5.04 4 As per revised MCI curriculum HO-C--H 6 CH₂--OH CH₂--OH **D-glucose** (natural) L-glucose

Penultimate (reference) carbon atom





number of possible stereoisomers

formula 2ⁿ where n is the number of asymmetric carbon atoms.

 $2^4 = 16$

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Glucose, Mannose and Galactose

They are the common aldohexoses.

Glucose

It is the most predominant sugar in human body.

It is the major source of energy.

It is present in blood.

D-glucose (dextrose)

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Galactose is a constituent of lactose (milk sugar) and glycoproteins.

Greek word gala, meaning milk

Mannose is a constituent of many glycoproteins.

Mannose was isolated from plant mannans; hence the name.

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Optical Activity



When a beam of plane-polarised light is passed through a solution of carbohydrates,

it will rotate the light either to right or to left.

dextrorotatory (+) (d)

or levorotatory (-) (l)

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D- and L-notation has no bearing with the optical activity (d or l)

Thus D-glucose is dextrorotatory but D-fructose is levorotatory.

Equimolecular mixture of optical isomers has no net rotation

(racemic mixture).

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Anomerism of Sugars



When a fresh solution of D glucose is prepared, its specific rotation of polarised light is +112°;

but after 12-18 hours it changes to +52.5°.

This change in rotation with time is called <u>mutarotation</u>.



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Explanation:

D-glucose has two anomers, alpha and beta varieties.

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These anomers are produced by the spatial configuration with reference to the first carbon atom in aldoses and second carbon atom in ketoses.

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Hence these carbon atoms are known as anomeric carbon atoms.



Alpha-D-glucose has specific rotation of +112 degree and beta-D-glucose has +19 degree.

Both undergo mutarotation and at equilibrium one-third molecules are alpha type and 2/3rd are beta variety.

to get the specific rotation of +52.5.

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The differences between alpha and beta anomeric forms are dependent on the 1st carbon atom only.

Previously 16 stereoisomers of glucose are described. Each of them will have 2 anomers; and hence there are a total of 32 isomers for glucose.

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H - C = O H - C - OH H - C - H H - C - OH H - C - OH H - C - OHH - C - OH

D-glucose, open chain projection formula




According to Haworth, glucose exists as 6 membered ring Pyranose forms.



Pyran

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Different representations of D-glucose





Glucose and Fructose have the same molecular formula but they iffer in the functional group. Glc has an aldehyde gp and Fru a keto group.

H C=O H C OH HOC H H C OH H C OH H C OH CH₂OH D Glucose

CH2OH C=OHOC H H C OH H C OH Sreekumari CH2OH **D** Fructose









Fructose is a Ketohexose



In fructose, the keto group is on the 2nd carbon atom. Thus second carbon atom is the anomeric carbon atom.

Fructose has D and L forms with regard to 5th carbon atom.

D fructose is levorotatory. Only D variety is seen in biological systems.

Fructose is a major constituent of honey.

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Reactions of Monosaccharides



In sugars, the following 3 properties will be seen together:

- A. Mutarotation
- B. Reducing property
- C. Formation of osazone with phenylhydrazine.



Enediol Formation



In mild alkaline solutions, carbohydrates containing a free sugar group (aldehyde or keto) will tautomerise to form *enediols*.

- In mild alkaline conditions, glucose is converted into fructose and mannose.
- The interconversion of sugars through a common enediol form is called
- Lobry de Bruyn-Van Ekenstein transformation.







Glucose





Benedict's reagent is very commonly employed to detect the presence of glucose in urine (glucosuria) and is a standard aboratory test employed in diabetes mellitus.

Benedict's reagent contains sodium carbonate, copper solution sulphate and sodium citrate.

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Benedict's solution

5 ml solution + 0.5 ml glucose + boil for 2 min

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Osazone Formation



All reducing sugars will form osazones with excess of phenylhydrazine when kept at boiling temperature.

Osazones are insoluble. Each sugar will have characteristic crystal form of osazones.







HC=NNHC₆H₅ C=NNHC₆H₅ OHCH HCOH HCOH HCOH

Glucososazone; Needle shaped crystals arranged like a broom or sheaves of corn

Differences in glucose, fructose and mannose are dependent on the first and second carbon atoms, and when the osazone is formed these differences are masked.

Action of Strong Alkali on Sugars



- When treated with strong alkali, sugars are enolised and the double bond will shift from 1:2 to 2:3, 3:4 or 4:5 to form the corresponding ene diols and gets fragmented.
- The fragmented molecules will polymerise to form a yellow resinous material called Caramel.



Action of Acids on Sugars

- Dilute acids Aldoses in general are relatively stable. Ketoses degraded.
- Concentrated acids Dehydrated to cyclical derivatives
 Pentoses: Furfural
 Hexoses : Hydroxy methyl furfural
- Ketoses are more susceptible to the action of acids





Action of Acids on Sugars









Gluconic acid



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Glucose is reduced to sorbitol Mannose to mannitol Fructose to sorbitol and mannitol. Galactose is reduced to dulcitol

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Sorbitol, mannitol and dulcitol are used to identify bacterial colonies. Mannitol is also used to reduce intracranial tension by forced diuresis.

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The osmotic effect of sorbitol and dulcitol produces changes in tissues when they accumulate in abnormal amounts, e.g. cataract of lens.

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Glycosides





Methyl-alpha-D-glucopyranoside

Hemi-acetal group is condensed with an alcohol or phenol group, it is called a glycoside

The non-carbohydrate group is called aglycone.

Glycosides do not reduce
Benedict's reagent,
because the sugar group is masked.

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Glycosides



Sugar + Aglycon	= Glycoside	Source	Importance
Glucose + phloretin	Phlorhizin	Rose bark	Renal damage
Galactose+ digitogenin + xylose	Digitonin	Leaves of foxglove	Cardiac stimulant
Glucose + indoxyl	Plant indican	Leaves of indigofera	Stain

Formation of Esters





Glycosides





Amino Sugars







<u>Glucosamine</u> is seen in hyaluronic acid, heparin and blood group substances. <u>Galactosamine</u> is present in chondroitin of cartilage, bone and tendons.

<u>N-acetyl-glucosamine</u> (GluNac)is seen in glycoproteins, mucopolysaccharides and cell membrane antigens.

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Amino sugars will not show reducing property. Will not produce osazones.

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L Fucose – 6 Deoxy L Galactose

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• Occurs in glycoproteins and in blood group substances



Pentoses Sugars of Nucleic Acids



Disaccharides



When two monosaccharides are combined together by glycosidic_linkage, a disaccharide is formed.

Important disaccharides

- 1. Sucrose
- 2. Maltose
- 3. Lactose

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Sucrose is the sweetening agent known as cane sugar.It is present in sugarcane and various fruits.Sucrose is not a reducing sugar; and it will not form osazone.This is because the linkage involves first carbon of glucose and second carbon of fructose, and free sugar groups are not available.





When sucrose is hydrolysed, the products have reducing action.

A sugar solution which is originally nonreducing, but becomes reducing after hydrolysis, is inferred as sucrose (specific sucrose test).



Lactose







Lactose is the sugar present in milk. It is a reducing disaccharide.



Lactose forms osazone which resembles "pincushion with pins" or "hedgehog" or flower of "touch-me-not" plant.

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Lactose and Lactate are different

Lactose is the milk sugar; a disaccharide made of galactose and glucose.

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Lactate or Lactic acid is a product of anaerobic metabolism of

glucose.

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Maltose







Maltose is a reducing disaccharide.



Sunflower shaped or petal shaped crystals of Maltosazone

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Glucososazone Needle shaped Crystals, arranged like a broom or sheaves of corn

The differences in glucose, fructose and mannose are dependent on the first and second carbon atoms, and when the osazone is formed these differences are masked.

Isomaltose



Partial hydrolysis of glycogen and starch produces isomaltose.



Salient Features of Important Sugars



Monosaccharides

Glucose Galactose Mannose Fructose

Disaccharides

Glucose Glucose Glucose aldohexose 4th epimer of glucose 2nd epimer of glucose Ketohexose

+ Galactose = Lactose (reducing)

- + Glucose = Maltose (reducing)
 - + Fructose = Sucrose (nonreducing)

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Polysaccharides



Polymerised products of many monosaccharide units.

- **1.** <u>**Homoglycans**</u> composed of single kind of monosaccharides, e.g. starch, glycogen and cellulose.
- 2. <u>Heteroglycans</u> are composed of two or more different monosaccharides, eg., hyaluronic acid, chondroitin sulphate.





It is the reserve carbohydrate of plant kingdom. **Sources:** Potatoes, tapioca, cereals (rice, wheat) and other food grains.

Glucose units with alpha-1,4 glycosidic linkages to form a long chain.

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Highly branched. The branching points are made by alpha-1,6 linkage.

Starch forms a blue coloured complex with iodine; this colour disappears on heating; reappears when cooled. Sensitive test for starch.



Starch is non reducing because the free sugar groups are negligible in number.

When starch is hydrolysed by mild acid, smaller and smaller fragments are produced.

Hydrolysis for a short time dextrin which gives violet colour with iodine and is nonreducing.

Hydrolysis for a long time Maltose and glucose Reducing

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Action of Amylases on Starch



- i) Salivary and pancreatic amylases are alpha-amylases, which act at random on alpha-1,4 glycosidic bonds to split starch into smaller units (dextrins), and finally to alphamaltose.
- ii) Beta-amylases are of plant origin. It acts to release, maltose units from the ends of the branches of amylopectin. The action stops at branching points, leaving a large molecule, called limit dextrin or residual dextrin.



Glycogen



It is the reserve carbohydrate in animals. It is stored in liver and muscle. About 5% of weight of liver is made up by glycogen.

Glycogen is composed of glucose units joined by alpha-1,4 inks in the straight chains. It also have alpha-1,6 glycosidic linkages at the branching points







Exterior branches are composed of 6-7 glucose units and there are about 3-4 units between branches.

Cellulose



Supporting tissues of plants. Cellulose constitutes 99% of cotton, 50% of wood Most abundant organic material in nature.

Made up of glucose units combined with beta-1,4 linkages.

Synthetic fibres, celluloids, nitrocellulose and plastics are made from cellulose.

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Beta-1,4 bridges are hydrolysed by the enzyme cellobiase. This enzyme is absent in animal and human digestive system, and hence cellulose cannot be digested

Herbivorous animals have large caecum, which harbor bacteria. These bacteria can hydrolyse cellulose, and the glucose produced is utilised by the animal.



Inulin



Homoglycan Composed of D-fructose units with repeating beta-1, 2 linkages.

It is the reserve carbohydrate present in various bulbs and tubers such as chicory, dahlia, dandelion, onion, garlic.

It is clinically used to find renal clearance value and glomerular filtration rate.

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Inulin is a polysaccharide (carbohydrate) made up of fructose units. It was used for renal function studies.

Insulin is a polypeptide (protein) hormone, with wide ranging actions on carbohydrate and lipid metabolism.



Chitin



It is present in exoskeletons of crustacea and insects.

It is composed of units of N-acetyl-glucosamine combined by beta-1,4 glycosidic linkages.

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Heteroglycans



These are polysaccharides containing more than one type of sugar residues.

Agar and Agarose Hyaluronic acid Textbook of BIOCHEMISTRY for Medical Students

Heparin and Heparan Sulphate same for compared by Chondroitin Sulphate

Keratan Sulphate Dermatan Sulphate

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Prepared from sea weeds. Contains galactose, glucose and other sugars.

It is dissolved in water at 100°C, which upon cooling sets into a gel.

Agar cannot be digested by bacteria and hence used widely as a supporting agent to culture bacterial colonies.





Agar

supporting medium for immuno-diffusion and immunoelectrophoresis.

Agarose galactose units; used as matrix for electrophoresis.

MUCOPOLYSACCHARIDES or **glycosamino** glycans (GAG) are heteropolysaccharides, containing uronic acid and amino sugars.



N-Acetyl groups, sulfate and carboxyl groups are also present.

These charged groups attract water molecules; viscous solutions

Mucopolysaccharides in combination with proteins form mucoproteins.



Hyaluronic Acid



It is present in connective tissues, tendons, synovial fluid and vitreous humor.

Glucuronic acid \rightarrow

It is composed of repeating units of N-Acetyl-glucosamine

Heparin



Anticoagulant for taking blood. used *in vivo to* prevent intravascular coagulation.

It activates antithrombin III, which in turn inactivates thrombin, so blood is not clotted.

Heparin is present in liver, lungs, spleen and monocytes.







Heparin contains repeating units of sulphated glucosamine \rightarrow alpha-1, 4-L-iduronic acid \rightarrow and so on.

Sulphated heparin or heparan sulfate is also present in tissues.

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Chondroitin Sulphate



Connective tissues -- in cartilage, bone, tendons, cornea and skin.



Repeating units of glucuronic acid \rightarrow N-acetyl galactosamin sulphate \rightarrow and so on.

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It is the only GAG which does not contain any uronic acid.

The repeating units are galactose and N-acetyl glucosamine

It is found in cornea and tendons.

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Dermatan Sulphate



L-iduronic acid and N-acetyl galactosamine in beta -1, 3 linkage.

It is found in skin, blood vessels and heart valves.

Mucopolysaccharides Hyaluronic acid Heparin Chondroitin Sulphate Keratan Sulphate Dermatan Sulphate

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Repeating Units in



Polysaccharide	Repeating units
Homoglycans	
Inulin	D-fructose, beta-1,2 linkages
Dextran	Glucose, 1-6, 1-4, 1-3 linkages
Chitin	N-acetyl glucosamine; beta 1-4 links
Heteroglycans	
Agar	Galactose, glucose
Agarose	Galactose, anhydrogalactose
Hyaluronic acid	N-acetyl glucosamine, glucuronic acid
Heparin	Sulfated glucosamine, L-iduronic acid
Chondroitin S	Glucuronic acid, Nacetyl galactosamine
Keratan S	Galactose, N-acetyl glucosamine
Dermatan S	L-iduronic acid, N-acetyl galactosamine

Glycoproteins and Mucoproteins



When the carbohydrate chains are attached to a polypeptide it is called a proteoglycan.

If the carbohydrate content is less than 10%, it is generally named as a glycoprotein.

If the carbohydrate content is more than 10% it is a mucoprotein.

Functions: enzymes, hormones, transport proteins, structural proteins and receptors.

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The oligosaccharide chains:

Glucose (Glu); mannose (Man); galactose (Gal); N-acetyl glucosamine (GluNAc); N-acetyl galactosamine (GalNAc); L-fucose (Fuc) and N-acetyl neuraminic acid (NANA).

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Derivatives of Monosaccharide

Aminosugar acids: Sialic acids

- Naturally occurring N acetyl derivatives
- Example-N acetyl Neuraminic acid NANA
- 9 C, 3 deoxy amino sugar acid
- Present in Glycoproteins and Gangliosides









Acesulfame-Potassium (Ace K) is made from acetoacetic acid. It is 200 times sweeter than sugar; but calorie content is negligible.

Aspartame is made from aspartic acid and phenyl alanine, both are amino acids. It is 200 times sweeter than sugar. Aspartame is not suitable for people with phenyl ketonuria.

Saccharin is made from anthranilic acid. It is 300 times sweeter than sugar. The calorie content is nil.

Sucralose is made from sucrose. Sucralose is approximately 600 times as sweet as sugar.

Cyclamate (Sodium cyclohexyl sulfamate) is 30–50 times sweeter than sugar.

Saccharin (Benzoic sulfimide) is an artificial sweetener. Although saccharin has no food energy, it can trigger the release of insulin in humans and rats, apparently as a result of its taste.

Dietary Fiber



Dietary fiber is contributed by the unavailable carbohydrates in the diet. They contribute the bulk and assist in normal bowel movements. Cellulose, emicellulose, pectin, alginates, and gums are the usual glycans which form dietary fiber. Cellulose is found in bran, flour, and tubers. Pectins are mixtures of homoglycans found in fruits. Gums and alginates are found in legumes and oatmeal.



Aquasomes



They are peptide/protein carriers with three layered selfassembled structures. They comprise the central solid nanocrystalline core coated with polyhydroxy oligomers onto which biochemically active molecules are adsorbed. The solid core provides structural stability. The carbohydrate coating acts as a protectant and stabilizes the biochemically active molecules. As the conformational integrity of bioactive molecule is maintained, aquasomes are being proposed as a carrier system for the delivery of peptide based pharmaceuticals. The system has been successfully utilized for the delivery of insulin, hemoglobin and various antigens. Oral delivery of enzymes like serratiopeptidase has also been achieved.