Consortium for Educational Communication

Module on

CARBOHYDRATES

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Text

The carbohydrates are a loosely defined group of molecules that contain carbon, hydrogen, and oxygen in the molar ratio 1:2:1. They constitute an important class of compounds like glucose, fructose, starch, cellulose etc., which play a vital role in our everyday life. They are also known as saccharides. Originally, the name carbohydrate was given to the compounds pertaining to general formula C_x $(H_2O)_y$, and were considered to be hydrates of carbon. However, this definition could not hold ground for long due to the following reasons:

(i) Many compounds like formaldehyde (CH_2O), acetic acid ($C_2H_2O_2$) etc., conform to formula $C_x(H_2O)_y$ but they do not exhibit the characteristic properties of carbohydrates.

(ii) Some carbohydrates like rhamnose ($C_6H_{12}O_5$), deoxyribose ($C_5H_{10}O_4$) do not conform to the formula $C_x(H_2O)_y$, and

(iii) Carbon is not known to form hydrates.

The above facts ultimately gave way to the modern definition of carbohydrates. Carbohydrates are now defined as optically active polyhydroxy aldehydes or polyhydoxy ketones or the compounds which can be hydrolysed to them. They have two major biochemical roles:

1. They act as a source of energy that can be released in a form usable by body tissues.
2. They serve as carbon skeletons that can be rearranged to form other molecules that are essential for biological structures and functions.

Classification of carbohydrates

The carbohydrates can be classified in various ways. The classification may be on the basis of their chemical structure, composition, nature of carbonyl function, reaction with oxidizing agents or physiological roles. According to the Food and Agriculture Organization and the World Health Organizaion, the carbohydrates should be classified primarily by molecular size. Accordingly, the carbohydrates are classified in to sugars, oligosaccharides, and polysaccharides.

Sugars

The sugars are also called simple carbohydrates and consist of monosaccharides and disaccharides. The monosaccharides (mono-, "one"; saccharide, "sugar"), are the simplest groups of carbohydrates and are often referred to as simple sugars. They cannot be further hydrolysed. They are the monomers out of which the larger carbohydrates are constructed. The monosaccharides are divided in to different categories, based on the functional group and the number of carbon atoms.

Based on the functional groups, monosaccharides are of two types- aldoses and ketoses. When the functional group in monosaccharide is an aldehyde, they are known as aldoses, e.g. glyceraldehyde, glucose, ribose. When the functional group is a keto group, they are referred to as ketoses, e.g., dihydroxyacetone, fructose, ribulose.

Based on the number of carbon atoms, the monosaccharides are regarded as:

Trioses (3C), e.g. glyceraldehyde, dihydroxyacetone,
Tetroses (4C), e.g. erythrose, threose,
Pentoses (5C), e.g. ribose, ribulose, xylose, arabinose, deoxyribose,
Hexoses (6C), e.g. glucose, fructose, galactose, mannose, and
Heptoses (7C), e.g. sedoheptulose, glucoheptose.

The disaccharides (di-, "two") consist of two similar or dissimilar monosaccharides linked together by glycosidic bonds. The disaccharides on hydrolysis produce two molecules of the same or different monosaccharides, e.g., Maltose=Glucose+Glucose; Sucrose=Glucose+Fructose and Lactose=Glucose+Galactose.

The disaccharides are crystalline, water-soluble and sweet to taste. They are of two types-Reducing disaccharides with free aldehyde or ketone group, e.g., maltose, lactose and Non-reducing disaccharides with no free aldehyde or ketone group, e.g., sucrose, trehlose.

Oligosaccharides

The oligosaccharides (*oligo*-, "several") are made up of several (3 to 9) monosaccharide units or residues, joined by glycosidic bonds. The glycosidic bond is normally formed between carbon atoms 1 and 4 of the neighbouring units (α-1,4 bond). The monosaccharide units when linked up are called residues. Therefore, oligosaccharides belong to the category of compound carbohydrates. Depending upon the number, monosaccharide units condense to form oligosaccharides, the latter are known as disaccharides (sucrose, lactose), trisaccharides (raffinose), tetrasaccharides (stachyose), pentasaccharides, hexasaccharides, heptasaccharides etc.

The oligosaccharides occur wildly in small quantities in plant food products like cereals, such as wheat and rye; vegetables including onions, garlic, asparagus, and chicory and in bananas and honey. Raffinose is a trisaccharide found in free state in the sugar beet. It consists of a molecule each of galactose, glucose and fructose linked in the same sequence. Stachyose, on the other hand, is a tetrasaccharide found in pea and has four monosaccharides.

Polysaccharides

Polysaccharides (poly-, "many"), consist of chains of monosaccharides containing more than 9 units and may extend to hundreds or thousands of units. The number of monosaccharide units in a polysaccharide, termed its degree of polymerization (DP) varies, only a few polysaccharides have a degree of polymerization less than 100; most have DP's in the range of 200-3000. The larger ones like cellulose have a DP of 7,000-15,000. It is estimated that more than 90% of the considerable mass in nature is in the form of polysaccharides. The polysaccharides are usually tasteless (non-sugars) e.g., starch glycogen, inulin, cellulose.

Some polysaccharide molecules such as cellulose are linear chains, whereas others such as glycogen and starch are mixtures of straight and branched chain molecules. Starch is a mixture of two large polymers; amylose, which consists of linear chains of glucose, and amylopectin, which is a highly branched polymer with a higher molecular weight. Glycogen also has a structure similar to that of starch, the only difference being that the chains are shorter and there are more branches. Polydextrose and inulin are the polymers of glucose and fructose, respectively. These are used as bulking agents and as sucrose replacements in food products.

The plant polysaccharides and lignin which are resistant to hydrolysis by the digestive enzyme in human beings are loosely called dietary fibres. The main components of dietary or the crude fibre are cellulose, hemicelluloses, hexosans (galactans and fructosans etc), pectic substances, gums, mucilage and lignin. The dietary fibers are also called the non-starch polysaccharides (NSP).

The polysaccharides are also called glycans. Depending up on the composition, polysaccharides are of two types-homopolysaccharides and heteropolysaccharides. Homopolysaccharides or homoglycans are those complex carbohydrates which are formed by polymerization of only one type of monosaccharide monomers. For example, starch, glycogen and cellulose are composed of a single type of monosaccharide called glucose. Depending up on monosaccharide unit involved, polysaccharide is called glucan (made of glucose), fructan (made of fructose), xylan (made of xylose), araba (made of arabinose), galactan (made of galactose), etc. Heteropolysaccharides or heteroglycan are those complex carbohydrates which are produced by condensation of two or more types of monosaccharide derivatives, e.g., agar, peptidoglycan, arabanogalactans, arabanoxylans, etc.

During the formation of polysaccharides, a molecule of water is released at each condensation. This reduces the bulk, makes the polysaccharide almost insoluble and decreases its effect on water potential or osmotic potential of the cell. They are, therefore, ideal for storage and as structural components. Polysaccharides are of three main types: (i) Storage polysaccharides-reserve foods which can be hydrolysed to produce monosaccharide sugars, e.g. glycogen, starch, inulin, (ii) Structural polysaccharides-fibrous polysaccharides forming exoskeleton in arthropods, cell walls of fungi and plants, e.g. chitin, cellulose and (iii) Mucopolysaccharides-slime or mucilage producing heteropolysaccharides, e.g., pectins, phycocolloids (agar-agar), hyaluronic acid, keratin sulphate.

Properties of Carbohydrates

1. Absorption of Water

All the carbohydrates categorized as simple sugars are good in absorbing moisture and water. Due to this, they are said to be hygroscopic in nature. Because of their great hydrophilicity, they are used as preservatives and humectants in food products.

2. Solubility

All the sugars dissolve in water easily. The solubility of sugars in water affects its use in food preparation and processing. At room temperature the order of solubility is as follows:

Fructose > Sucrose > Glucose > Maltose > Lactose

The presence of sugar in water increases the boiling point of water. This again is important in food processing. The solubility of polysaccharides like starch is quite different. It is completely insoluble in cold water. However, on heating a solution of starch in water, the granules initially swell up, finally turning into a paste. On cooling most of the starches form a gel, the process is called gelatinization.

3. Mutarotation

The optical rotation of the α and β forms of glucose is found to be different. While the α form shows a specific rotation of +112.2°, the value for the β form is +18.7°. Further, when dissolved in water, the specific rotation changes slowly until it reaches equilibrium value of +52.7°. This gradual change in specific rotation from +112.2° or +18.7° to 52.7° is called mutarotation. It is a result of the inter-conversion between the two forms through the open form of glucose to an equilibrium mixture containing 36% α- and 64% β-anomer.

4. Inversion of Sugar

It is an important property of sucrose. Sucrose is dextrorotatory i.e., it rotates the plane of polarized light to right. On hydrolysis with mild acids or an enzyme called invertase, it gives equal amounts of glucose and fructose. Of these two, the glucose is dextrorotatory and fructose is highly laevorotatory. As a result the mixture has a net laevorotation. Since there is an inversion in the direction of rotation, this phenomenon is called inversion of sugar and the sugar is called invert sugar.

Fructose is sweetest of all sugars, the invert sugar is much sweeter than sucrose and finds extensive applications in confectionary industry.

5. Taste Carbohydrates

All the sugars are sweet in taste; their degree of sweetness varies from one another and according to the literature reports the decreasing order of sweetness of these sugars is as follows:

Fructose> Sucrose > Glucose > Maltose > Lactose

Thus fructose being the sweetest and lactose the least sweet; polysaccharides like starch are tasteless.

6. Crystallization

Crystallization is the process of formation of crystals from the solution of a substance and is closely related to the property of solubility. It has an inverse relationship with the solubility i.e., more soluble the substance, lesser is the tendency to form crystals. Crystallization also depends upon factors like, nature of the solution and addition of some other ingredients in the solution. The property of crystallization finds use in preparation of confectioneries. In certain food products the crystallization of sugars is undesirable, for example, the crystallization of lactose in sweetened condensed milk or ice creams. This is due to the low solubility of lactose. When milk is condensed to about one third of its volume, the concentration of lactose is large enough to be easily crystallized on cooling. Therefore, when the sweetened condensed milk is cooled, the lactose crystallizes out and the crystals may grow to a size that may lead to grittiness or sandiness in the mouth. This crystallization of lactose may be prevented by a process called seeding, in which finely ground crystals of lactose are mixed with the concentrated product. These micro crystals provide a large number of nuclei for the lactose to crystallize out and as a consequence the size of lactose crystals does not increase much.

7. Cryostabilization

Polysaccharides are cryostabilizers, because they do not increase the osmolality or depress the freezing point of water significantly. Since they are large, high molecular weight molecules and these are colligative properties. Most polysaccharides provide cryostabilization by producing freeze-concentrated matrix, which severely limits molecular mobility. They also provide cryostabilization by restricting ice-crystal growth of adsorption to nuclei or active crystal growth sites.

Thus both high and low molecular weight carbohydrates are generally effective in protecting food products stored at freezer temperatures (typically -18°C) from destructive changes in texture and structure. Thus there is improvement in product quality and storage stability.

8. Effect of Heat

When sugars are heated, these melt at their melting points. Above the melting points, these dehydrate, decompose and polymerize forming a brown mass called caramel. The process of caramel formation is called caramelization. Toasting of bread and roasting of rice flakes are some of the examples. Starch also becomes brown on heating and its flavour changes. Besides this, heating changes the solubility of starch. It forms dextrins, becomes more soluble which is desirable in some food preparations. Different sugars have different caramelization temperatures, for example, galactose, glucose and sucrose caramelize at 160°C, fructose caramelizes at 110°C and maltose caramelizes at 180°C. Caramels produced after heating sugars are of deep brown amber colour and with new flavours.

9. Gel Formation by Starches

When starch is heated in water, starch granules undergo a process called gelatinization. Gelatinization is the disruption of molecular order within ggranules. Evidence for the loss of order includes irreversible granule swelling, loss of birefringence and loss of crystallinity. Leaching of amylose occurs during gelitinization. Total gelatinization occurs over a temperature range, with larges granules generally gelatinizing first. Continued heating of starch granules in excess water results in further granule swelling, additional leaching of soluble components (primarily amylose) and eventually, especially with the application of sheer forces, total disruption of granules. This phenomenon results in the formation of a starch paste. Due to this phenomenon starches take up water and produce viscuous fluids/paste and gels to give desired textural qualities. The extent of starch gelatinization in baked goods strongly affects product properties, including storage behaviour and rate of digestion.

Importance of Carbohydrates

The carbohydrates perform many important functions in living bodies and in our day to day life. These are:

1. The carbohydrates act as biofuels to provide energy for functioning of living organisms. In human systems, all the carbohydrates except cellulose can serve as source of energy. Starch and various sugars which are taken as food are first hydrolysed to glucose by the enzymes present in the digestive system. Glucose on slow oxidation to carbon dioxide and water in the presence of enzymes liberates large amount of energy which is used by the body for carrying out various functions. In order to fulfil the emergency requirements, our body also stores some of the carbohydrates as glycogen in the liver, which on hydrolysis gives glucose.

It may be noted that cellulose cannot be hydrolysed in our body because enzymes required for its hydrolysis are not present in our body. However, grazing animals are capable of hydrolysing cellulose to glucose. In these animals, cellulolytic bacteria present in the rumen break down cellulose with the help of enzyme cellulase and is subsequently digested and converted in to glucose.

2. The simple as well as complex carbohydrates are one of the most significant nutrients as these meet most of the energy requirements. However, all the carbohydrate constituents in the food do not participate in the energy generation and have many other nutritional roles. A significant component of starches in the diet does not get degraded in the stomach and is called resistant starch. These are also grouped into dietary fibres and serve as substrate for the intestinal microflora which synthesise important vitamins. Hemicelluloses are good sources of dietary fibre and stimulate the immune system. These are also good for promoting weight loss, relieving constipation and controlling carcinogens in the intestinal tract. These are also helpful in reducing postprandial serum glucose level; reduce insulin response and serum cholesterol level. Certain hydrocolloids also have positive health effects. These are good laxatives. Dietary intake of hydrocolloids are associated with the reduction of blood glucose level, insulin response and cholesterol lowering effect.

3. Lactose occurs in milk, mainly free, but to a small extent as a component of higher oligosaccharides. The concentration of lactose in milk varies with the mammalian source from 2.0-8.5%; cow and goat milk contains 4.5-4.8% and human milk about 7.0%.

Milk also contains 0.3-0.6% of lactose containing oligosaccharides, many of which are important as energy source for growth of specific variant of *Lactobacillus bifids* which as a result is the predominant micro-organisms of the intestinal flora of breast-fed infants. Lactose stimulates intestinal absorption and retention of calcium.

Some people are unable to digest lactose due to deficiency of enzyme lactase, these people are lactose intolerant. In such cases, some of the unhydrolyzed lactose passes into the intestine and its presence tends to draw fluid into interstitial rumen by osmosis. Intake of milk by them leads to abdominal distention, cramps and diarrhoea. From a nutritional standpoint, sugars should be consumed in relatively small quantities as they provide no other nutrients than carbohydrates.

4. Carbohydrates are involved in the structural organization of many tissues, both in plants and animals. Cellulose, hemicelluloses (xylans and mannans) and pectic substances are common structural carbohydrates in plants. The primary cell wall in plants contain about 43% of cellulose. Lignin is also present in the cell walls of the older tissues. Chitin, hyaluronic acid and chondroitin sulphates are important structural polysaccharides of animals. They are present in the shells of lobsters, crabs and insects and in the cartilage, adult bones, heart valves and cornea. D-ribose and 2-deoxy-D-ribose are present in nucleic acids. The carbohydrates are found in biosystems in combination with many proteins and lipids.

5. All types of the carbohydrates are widely distributed in nature. The large proportions of carbohydrates are found in certain plant tissues. They play a variety of roles as ingredients in various food products. The most obvious role of sugar in foods is to impart sweetness. The combination of sugars and fats in confections provide a sweet taste and texture that complement each other. In beverages, sucrose provides sweetness without altering the subtle flavours of the beverage. Sugars make an important contribution to the texture of foods, commonly referred to as 'mouthfeel'. Sugars also acts to tenderize bakery products by slowing the rate at which starch molecules become interlinked and proteins break down. Glucose, fructose, sucrose and maltose are used in bread making to increase product and prevent excessive stickiness.

6. In many products, sugars play an important role in preservation. The addition of monosaccharides, such as glucose or fructose, to jams and jellies inhibits microbial growth and subsequent spoilage. Sugars have a great affinity for water, thus slowing moisture loss in foods, like baked foods and extending the shelf-life of these products. Both honey and invert sugar help to retain moisture due to their high fructose content, as do sorbitol (sucrose alcohol) and corn syrup.

7. Maillard browning products, including soluble and insoluble polymers are formed when reducing sugars and amino acids, proteins and other nitrogen containing compounds are heated together such as soy sauce and bread crusts. Maillard containing products are important contributors to the flavour of milk chocolate, also important in production of caramels, toffees and fudges, during which reducing sugars react with milk proteins.

Caramelization products such as Brown Caramel colour made by heating a sucrose solution with ammonium bisulfite is used in Cola soft drinks, acidic beverages, baked goods, syrups, candies, pet foods and dry seasonings. Reddish brown caramel colour made by heating sugar with ammonium salts is used in puddings and baked goods.

Certain Pyrolytic reactions of sugars produce unsaturated ring systems that have unique flavours and fragrances in addition to colouring materials such as Maltol and Isomaltol contribute to the flavour of bread.

8. Low molecular weight carbohydrates such as sucrose, dextrose, corn syrup etc. Function as humectants. These are employed in meat and meat products for lowering the water activity, so as to extend the shelf stability of these products.

9. Utilization of sugars especially some monosaccharides and disaccharides by bacteria, yeasts and molds produces compounds such as lactic acid, acetic acid, diacetyl and acetaldehyde. These compounds impart characteristic chroma/flavour to fermented food products such as cultured butter and butter milks, yeast leavened breads etc.

10. The production of chemicals by fermenting various sugars has been in practice since long. Ethanol has been made since ancient times by the fermentation of sugars. All beverage ethanol and more than half of industrial ethanol is still made by this process. Sugars, which are used to activate yeast for fermentation, are important in the brewing and baking industries.

11. Many carbohydrates are excellent scavengers of metal ions. Glucose, fructose and sugar alcohols (sorbitol and mannitol) have the ability to block the reactive sites of ions, such as copper, iron and to a lesser extent, cobalt. This is characteristic of monosaccharides and aids in food preservation by retarding catalytic oxidation reactions. Furthermore, maillard reaction products are known to have antioxidant properties in food systems.

12. Starches find numerous applications in food because of easy availability and low cost. The starch absorbs water and swells up. If the amylase content of the starch is more, its long water soluble chains increase the viscosity and thicken gravies, sauces and pudding. The water absorbing property of starches is also responsible for the mouthfeel of many food products containing them and may be used as fat substitutes e.g. in salad dressings and dairy products.

13. As starch readily absorbs moisture, it checks its escape from the food product and in some dishes like cakes, it retains the moisture and yet does not allow it to be wet. The high water binding ability of starches leading to their swelling up can provide body and texture to the food stuff. The partial hydrolysis of starch yields dextrins (glucose polysaccharides of intermediate size). These are more easily digested than starch and therefore are extensively used in the preparation of infant foods.

Besides these, starches find applications as adhesives (in stamps), binder (in formed meats and breaded items); and as bulking agent (in baking powder, fat). Modified starches find applications in instant desserts, jellies, salad dressings, canned soups and many more.

14. The most important application of non-starch polysaccharides like cellulose is 'water retention'. The dry amorphous cellulose becomes soft and flexible on absorbing water. Besides this, the cellulose finds applications as emulsifier, anticaking agents, dispersing agent, thickener and gelling agent. Cellulose also is used to improve the volume and texture of food. In addition, an important derivative of cellulose i.e., carboxymethyl cellulose (CMC) also finds many applications as a stabilizer due to its being soluble in cold water.

15. The hemicelluloses find applications as emulsifier, stabilizer and binder in flavour bases, dressings and pudding mixtures. These are also used as bulking agents and as fat replacer.

16. Derivatives of cellulose such as cellulose nitrates are used in explosives, lacquers, celluloid and collodion. Cellulose acetate is used in photographic film and packing materials.

17. Function as physiological anticoagulant (Heparin).

18. Humans utilize carbohydrate not only for their food, but also for their clothing (cotton, linen, rayon), Shelter (wood), fuel, and paper wood.

19. Hyaluronic acid is an important component of the vitreous body of the eye, the umbilical cord and as a lubricant in synovial fluid of the joints.

20. Many glucosides (Carbohydrate derivative from plants) are important drugs, such as glucoside of digitalis which is utilized for the treatment of heart diseases.

21. Carbohydrates are essential components of milk, especially lactose. Sialic acids, which are acetyl derivatives of neuraminic acid (Sugar acid), occur as chief components of tissues, especially in mucins and blood group substances. Sialic acid with glycolyl group substituted in neuraminic acid in the place of acetyl group is found in salivary mucin and erythrocytes. Blood group polysaccharides, made up of D-galactosamine, D-glucosamine, D-galactose, L-fucose,and N-acetyl neuraminic acid (NANA or Sialic acid) is present in saliva, gastric mucin, cystic fluid, and other body secretions. They combine with proteins in erythrocytes to form the A, B, O, Rh and other antigens and hence help in the differentiation between different blood groups.

22. Proteoglycans (Proteins+Oligosaccharides) are important for the absorption by fibroblasts, as receptors and carriers of macromolecules, cell growth regulators and also influence the protein synthesis and intranuclear functions.

23. Chondroitin sulfates A and C form the major structural components of cartilage, tendons and bones. They are often associated with collagen.

24. Agar agar is an important polysaccharide, which is of great value in preparation of foodstuffs, and is utilized in laboratories as culture media.

25. Carageenans extracted from red seaweeds. A useful property of carageenans is their reactivity with proteins, particularly those of milk. They are used as secondary stabilizer in ice cream and related products, preparation of evaporated milk, infant formulas, freeze-than stable whipped cream, dairy desserts and chocolate milk. Carageenans coatings on meats can serve as a mechanical protection and as a carrier for seasonings and flavours. Carageenan improves adhesion, increases water holding capacity of meat emulsion product, and improves texture and quality of low-fat meat products.

26. Alginates extracted from brown algae, forms non-melting gels (dessert gels, fruit analogs), used as meat analogs, alginic acid forms soft, thixotropic non-melting gels (gelly-type bakery fillings, filled fruit containing breakfast cereal products).

27. Guar-gum obtained from guar seeds binds water, prevents ice crystal growth, improves mouth feel, softens texture, and slows melt down in ice cream and ices. It is used in prepared meals, bakery products, dairy products, sauces, pet foods, increases water holding capacity of low fat meat products.

Locust bean gum, obtained from locust bean, provides excellent heat-shock resistance, smooth melt down and desirable texture and chemicals in ice cream and other frozen dessert products.

28. Gum Arabica obtained from Acacia tree prevents sucrose crystallization in confections, emulsifies and distributes fatty components in confections, used as component of coating of pan-coated candies and preparation of flavour powders.

Pectins: Commercial pectins are galacturonoglycans [Poly α-D-galactopyranosyluronic acids] with varying degree of methyl ester groups. Commercial pectin is obtained from citrus peel and apple ------. Pectin from lemon and lime peel is the easiest to isolate and is of the highest quality. Pectins have a unique ability to form spreadable gels in the presence of sugar and acid or in the presence of calcium ions and are used almost exclusively in these types of applications.

Preparations in which more than half of the carbonyl groups are in the methyl ester form (-COOCH3) are classified as high-methoxyl (HM) pectins, the remainder of the carboxyl groups will be present as a mixture of free acids (-COOH) and salt (-COO-Na+) forms. Preparations in which less than half of the carbonyl groups are in methyl ester forms are called low-methyl (LM) pectins.

Uses: Pectins are soluble in water, forms jelly- and jelly-type jells in presence of sugar and acid or with calcium. High methoxy pectins are used in high-sugar jellies, jams, preserves and marmalades. They are also used in acid milk drinks and due to their high water holding capacity they are used as fat substitutes in restructural meat products. Low methoxy pectins are used in dietetic jellies, jams, preserves and marmalades.