COURSE 12 - UNIT 5 - FOOD CHEMISTRY I - CARBOHYDRATES PART I

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Dear Students, I welcome you all for our lecture series on FOOD SCIENCE & TECHNOLOGY. In today's lecture, let's make an attempt to know about '**Carbohydrates'.**

Carbohydrates are the most widely distributed and abundant organic compounds on earth. Carbohydrates comprise more than 90% of the dry matter of plants. Carbohydrates occur as both natural components as well as added ingredients in foods we eat. Carbohydrate biosynthesis in plants starts from carbon dioxide and water with the help of light energy which is known as'photosynthesis'. Carbohydrate is the basis for the existence of all organisms which are depending on the intake of organic substances in food for nutrition.Carbohydrates represent one of the basic nutrients and are quantitatively the most important source of energy.

Carbohydrates are the highest component in terms of consumption and they are present in various foods in numerous forms. They have a central role in the metabolism of animals and plants. They have many different molecular structures, sizes, and shapes, exhibit a variety of chemical and physical properties, and differ in their physiological effects on the human body.The carbohydrates in foods will be dealt in two parts. The following aspects will be covered under part I:-

1. What are Carbohydrates?
2. Classification of carbohydrates
3. Monosccharides
4. Oligosaccharides
5. Polysaccharides
6. Properties and structure of important polysaccharides

1. What are Carbohydrates?

A carbohydrate is a biological molecule consisting of carbon (C), hydrogen (H) and oxygen (O) atoms, usually with a hydrogen–oxygen atom ratio of 2:1. The term carbohydrates goes back to times when it was thought that all the compounds under this class were **hydrates of carbon**, on the basis of their empirical formula e. g. glucose, $C_6H_{12}O_6$(6C+6H2O).Carbohydrates represent one of the basic nutrients and are quantitatively the most important source of energy. Carbohydrates also include other compounds which vary in the general formula but retain the chemical nature of carbohydrates. These include deoxy sugars (e.g. deoxyribose, fucose, rhamnose), amino sugars (e.g. glucosamine, sialic acid) and sugar carboxylic acids (e.g. glucuronic acid, neuraminic acid).

Carbohydrates contain 'chiral' carbon atoms.Achiral carbon atom is one that can exist in two different arrangements/configurations. These have four different groups attached tothem. The two different arrangements of the four groups are mirror images of each other as shown in Figure 1.

Carbohydrates are common components of foods, both as natural components and as added ingredients. They are found in various foods &food products and are one of the major macronutrients consumed as a source of energy. They have many different molecular structures, sizes and shapes. Theyexhibit a variety of chemical and physical properties. They also differ in their physiological effects onthe human body. They are reactive to both chemical and biochemical modifications which are employed commercially in improving their properties and extending their use. The non-digestible carbohydrates which act as bulk material in the gut are an important part of the balanced diet. Several other important functions in food are fulfilled by carbohydrates. They act for instance as sweetening agents, gel or paste-forming agents, thickening agents, stabilizers and are also precursors for aroma and coloring substances.

Carbohydrates perform numerous roles in living organisms. They serve as the storage form of energy (e.g. starch in plants and glycogen in animals) and as structural components (e.g. cellulose in plants and chitin in arthropods). Ribose is an important component of coenzymes (e.g. Adenosine Triphosphate, FlavinAdenine Dinucleotide and NicotinamideAdenine Dinucleotide) and the backbone of the genetic molecule known as Ribonucleic Acid (RNA). The related deoxyribose is a component of Deoxy Ribonucleic Acid (DNA).

2. Classification of carbohydrates

Carbohydrates are classified based on the number of sugar units they contain as Monosaccharides, oligosaccharides and polysaccharides as depicted in figure no 2.The term *'saccharide'* meaning sugar or sweetness is related to the characteristic taste of the many of the simple carbohydrates.

Now let's study each type of carbohydrates one by one

3. *Monosaccharides*

Monosaccharides are carbohydrates containing short chains of carbon atoms with one aldehyde or ketonic group (carbonyl group), each of the remaining carbon atoms bearing a hydroxyl group. Monosaccharides containing aldehyde group are known as 'aldoses' (name ending with 'ose') and those containing ketones are known as 'ketoses' (name ending with 'ulose').They are the monomeric units that are joined together to form larger structures, namely, oligosaccharides and polysaccharideswhich can be converted into their constituent monosaccharides by hydrolysis.Monosaccharides cannot be broken down to simpler carbohydrate molecules by hydrolysis, so they are sometimes referred to as 'simple sugars'. Depending on the total number of carbon atoms present, they are designated as triose (3 C-atoms), tetrose (4 C-atoms), pentose (5 C-atoms) and Hexoses (6-C atoms).

Glucose is one of the simplest and abundant carbohydrates.It is an aldose because it contains an aldehyde group.The chemical structure of glucose in a straight-chain fashion commonly known as acyclic structure or Fisher Projection is shown in Figure no 3, Where the aldehyde group (carbon atom 1) is at the top andthe primary hydroxyl group (carbon atom 6) at the bottom. Thus it has four chiral carbon atoms resulting in 2^n or $2^4 = 16$ isomers. Isomers are compounds having the same chemical formula but a different arrangement if atoms in the molecule.Other isomers of glucose have unique names, e.g., mannose, galactose, etc.Chiral compounds exist in right handed and left handed forms designated by the symbols 'D' and 'L' respectively.They are mirror images of each other.The L form of D mannose is also shown in the figure no 4.

Carbonyl groups (C=O) of aldehydes and ketones are reactive and readily undergo attack by the oxygen atom of a hydroxyl group to produce a cyclic hemiacetal.The representations of the cyclic sugars are called *Haworth projections*. Hemiacetal formation can occur within the same aldose or ketose sugar molecule, that is, the carbonyl group of a sugar molecule can react with one of its own hydroxyl groups, as illustrated in Figure no 3.

The six-membered sugar ring that results from reaction of an aldehyde group with the hydroxyl group at C-5 is called a pyranose ring and from the reaction of an aldehyde group with the hydroxyl group at C-6 is called a furanose ring as shown in fig no 5.The carbon atom C-1 is known as anomeric carbon atom.With D-sugars, the configuration that has the hydroxyl group located below the plane of the ring is the alpha form and above the plane is the beta form. For sugars in the L-series, the opposite is true, where the anomeric hydroxyl group is up in the alpha anomer and down in the beta anomer.An example of alpha and beta forms of D-Glucopyranose is shown in fig no 3.

Some of the important derivatives of monosaccharides occurring as components of polysaccharides are amino sugars (one of the hydroxyl group is replaced by an amino group) e.g. glucosamine and galactosamine; Deoxy sugars (a hydroxyl group replaced with a hydrogen atom) e.g. L-rhamnose and L-fucose and Glycosides (products formed from replacement of a hydroxyl group with a non-sugar compound such as phenol or alcohol) e.g. salicin, amygdalin etc.

4. *Oligosaccharides*

An oligosaccharide contains from 2 to 20 sugar units and is formed by the polymerization of monosaccharides by a glycosidicbond with the elimination of water. Depending on the number of monosaccharides, the oligosaccharides are classified as di-, tri-, tetra- saccharides etc. Reducing oligosaccharides are formed when anomeric hydroxyl group is linked to alcoholic hydroxyl group of other monosaccharide. Non reducing oligosaccharides are formed between anomeric hydroxyl groups of different monosaccharides.The commonly found oligosaccharides in foods are sucrose, maltose, lactose, raffinose andstachyose. Some of these occur as such in food products while others are partial hydrolytic products of naturally occurring polysaccharides. The structure of sucrose and maltose are shown in figure no 6. Some of the common disaccharides are discussed as follows.

3.1 Maltose is a reducing sugar consisting of two molecules of glucose. It does not occur in natural foods. Maltose is produced by hydrolysis of starch using the enzyme amylase on starch.Maltose is used sparingly as a mild sweetener in foods.

3.2 Lactose is a component of mammalian milk and is made up of glucose and galactose. Lactose is the primary carbohydrate source for developing mammals and is hydrolyzed by the enzyme *lactase*in the gut.Other lactose containing oligosaccharides are important as energy sources for growth of *Lactobacillus bifidus* which is the predominant microorganism of the intestinal flora of breast-fed infants.

3.3 Sucroseis made up of glucose and fructose. It is usually called simply sugar or table sugar. The sucraseenzyme in the human intestinal tract catalyzes hydrolysis of sucrose into D-glucose and D-fructose. The two principal source of sucrose are sugarcane sugar beets. Sucrose is used in bakery products and various commercial products.

3.4 Raffinoseis a trisaccharide composed of galactose, glucose, and fructose.Stachyose is a tetrasaccharide consisting of two galactose units, one glucose unit and one fructose unit.They are not digested in humans due to the lack of enzyme alpha galactosidase. These occur naturally in numerous vegetables (e.g. green beans, soybeans and other beans) and whole grains.

4.1Function of sugars in foods

Sugars have numerous other functions apart from their nutritive value. They function as humectants (which absorb moisture form air), texturizing agents, flavor producing agents and sweeteners.The hygroscopic nature of sugars and their mixtures are of use in food processing. Sugars such as maltose and lactose have limited uptake of water and are used in confections and bakery toppings. The non-enzymatic browning reactions are responsible for the colour and flavor of foods such as dates, honey and chocolate. The distinctive flavours developed in coffee beans, groundnuts and cashewnuts develop are due to the browning reaction.

5. Polysaccharides

They are high molecular weight substances composed of a large number of monosaccharide units combined to form a polymer. The number of monosaccharide units in a polysaccharide, which is termed its degree of polymerization (DP), varies. Only a few polysaccharides have DPs less than 100; most have DPs in the range 200–3000. The larger ones such as cellulose have a DP of 7,000–15,000.They consist of a primary chain and sometimes a branched chain. It is estimated that more than 90% of the carbohydrate mass in nature is in the form of polysaccharides.The general scientific term for polysaccharides is ‘glycans’. If they are composed of a single type of monosaccharide unit they are called as homoglycans and if they have more than two types, they are called heteroglycans.

Glycansthat release only glucose on hydrolysis are known as glucans, xylose and xylans. Depending on the sugar released on hydrolysis, other homoglycans are called mannan, galactan, fructan etc. Heteroglycans composed of two sugars are called galactomannan, glucomannan, arabinogalactan etc.

Polysaccharides commonly found in foods are starch, dextrins, glycogen, cellulose, hemicellulose and pectin. Polysaccharides found in plants such as cellulose, hemicellulose and pectin provide structural material (cell walls, fibres, seed coats, peels and husks). Chitin and polysaccharides containing amino sugars serve this purpose in animals.Structural polysaccharides are indigestible substances in humans but are important for human health. They form bulk in the diet and aid in excretion. Starch in plants and glycogen in animals provide food reserveswhich can be used for producing energy.

Polysaccharides can modify and control the mobility of water in food systems and water can influence the physical and functionalproperties of polysaccharides. Together, polysaccharides and water control many functional propertiesof foods including texture. Some polysaccharides disperse rapidly in water, some disperse as swollen particles and some are insoluble in water. Some can form either translucent or opaque gels at low and high concentration and some do not form gels. Such variations among polysaccharides are attributed to the nature of monosaccharide, type of chemical linkages, hydrogen bonding and ionic interaction between polymers.

6. Properties and Structure of important polysaccharides

6.1Starch:is the predominant food reserve substance in plants, seen in cereals, pulses, tubers, bulbs and fruits in varying amounts and provides 70–80% of the calories consumed by humans worldwide.Starch and starch hydrolysis products constitute most of the digestible carbohydrate in the human diet. Starch is mostly consumed in the form as available in foods and refined starch, either natural or modified has an important role in food preparations.Starch contains only glucose residues. Starch granules are composed of a mixture of two polymers: a linear polysaccharide called amylose and a highly branched polysaccharide called amylopectin.Cereal starches contain usually 25% amylose and 75% amylopectin whereas waxy starch as in corn starch has little amylose.

Amylose consists of glucose units linked by α1-4 linkages. The chain length of amylose varies and has a molecular weight of 1.1 -1.9 million. Amylose is not truly water soluble but can form micelles.Amylopectin has a backbone of α 1-4 linkages but in addition, the molecule is branched through α 1-6 linkages to the extent of 4-5 % with a molecular weight of 10 million. The structure of amylose and amylopectin is shown in figure no7.

Starch occurs in granules inside the cells which remain intact during most types of processing such as milling, separation and purification of starch. These granules are a mixture of amylose and amylopectin arranged radially. The appearance,size, shapes, location and appearance under polarized light vary with different sources of granules.

*6.2Glycogen*is the storage polysaccharide in animals which is mainly present in liver. Glycogen is a branched chain polysaccharide resembling amylopectin but with more branching as shown in figure no 8.

*6.3Cellulose*is the main constituent of plant cell walls and makes up to 25% of cell walls in higher plants. Cellulose together with other polysaccharides constitute the indigestible carbohydrate of plant food (vegetables, fruits or cereals), referred to as dietary fiber which is of importance in gut health.Cellulose consists of long chains of glucose residues joined by 1→4 linkages which are in β configuration as shown in figure no 9.The DP can range from 1000 to 14,000 making it a high molecular weight compound and is insoluble in water.Modified celluloses such as microcrystalline cellulose, carboxy methyl cellulose, methyl cellulose are of use in food industries.

6.4*Hemicellulose*s refer to substances which occupy the spaces between the cellulose fibers within the cell walls of plants. They are insoluble in water but soluble in alkali. Some of the hemicelluloses are composed of pentose and other contains hexuronic acids. Besides glucose, sugar monomers in hemicellulose can include xylose, mannose, galactose, rhamnose, and arabinose. It consists of shorter chains – 500–3000 sugar units. The structure of hemicelluloses is shown in figure no 10.

*6.5Pectin*is widely distributed in plants found in cell walls of terrestrial plants. Pectin is a mixture of galactose, arabinose and galacturonic acid (at least 65%) esterified in an α 1-4 chain as shown in figure no 11. In pectins the galacturonic groups are esterified with methanol. Protopectin is the water insoluble parent of pectin occurring in plants. In fruits during ripening the protopectin decreases and soluble pectin increases. Pectin is capable of forming gels with sugar and acids.It is produced commercially mainly by extraction from citrus fruits and is used in food as a gelling agent, particularly in jams and jellies. It is also used in fillings, medicines, sweets, as a stabilizer in fruit juices and milk drinks, and as a source of dietary fiber.

*6.6Gums*are hydrophilic substances that give a viscous solution or dispersion when treated with hot or cold water. Most of the gums are polysaccharides which include starches,pectins and some of their derivatives. Seed gums and seaweed gums are other naturally occurring gums. The commonly used gums are guar obtained from common guar beans and locust bean gum obtained from seeds of carob tree. These are polysaccharides of β D Mannose and α D galactose with branched units. They form highly viscous gels stable over a wide range of pH and temperature. The commonly use plant exudates are gum Arabic (acacia), karaya and tragacanth. These are mixtures of heteroglycans containing D-galactose, L-arabinose, D-galacturonic acid, L-fucose and L-rhamnose. Gum Arabic is more soluble in water leading to formation of low viscosity gels compared to other gums.

Agar is an extract from red and brown algae. It mainly comprises of β D and α L galactan. The gel formed from agar is transparent and reversible upon heating and cooling. Carrageenan is a polysaccharide extracted from sea weeds and can form stable complexes with proteins and other gums. They are especially used in dairy products for improvement of texture.Xanthan is a gum formed from action of *Xanthomonascompestris* on D glucose. Xanthans contain D-glucose, D-mannose and D-galacturonic acid. The structure of guar gum and xanthan are provided in figure no 12.

Conclusion

Carbohydrates in foods have a wide range of properties apart from their nutritive value being one of the three macronutrients in the diet. Carbohydrates are primarily composed of carbon, hydrogen and oxygen in the ratio of 1:2:1.They exist in many forms depending on the number and arrangement of sugar units into monosaccharides, saccharides and polysaccharides. Each of these types of carbohydrates possess different characteristics of importance in food processing some of which are formation of distinctive color and flavor compounds, gel formation and hygroscopic function.