Course 12 - Unit 5 - FOOD CHEMISTRY I - Carbohydrates part II

By

Chandan Vinay. S

Research Scholar

DOS in Food Science & Nutrition, University of Mysore, Mysore

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

This is the second part of the lectureseries on 'Carbohydrates'. We have learnt that carbohydrates are an important source of energy for animals and are found as natural food components and as added ingredients in the food. The reactive nature of carbohydrates to both chemical and biochemical modification makes them as one of the widely used product in commercial food processing. Carbohydrates can lead to improvement in the properties of the food on modification and owing to their reactivity to various chemicals thus extending their use in many products. The mono saccharides have the ability to react with acids, alkali, amino acids and also on heating to form various derivatives that can improve flavor and color of a food substance.Maillard reaction and Caramelization are important reactions of carbohydrates especially monosaccharides which are practically used in the preparation of a wide variety of processed foods. Starch is an important polysaccharide of interest in terms of applications in food processing. The intermediate and end products of starch have wide applications.

The following aspects will be covered under part II:-

- 1. Chemical reactions of carbohydrates
- 2. Hydrolysis of starch
- 3. Modified starches and their applications
- 4. Modified Cellulose and its applications

1. Chemical reactions of carbohydrates

All carbohydrate molecules have hydroxyl groups available for chemical reaction. Simple monosaccharides and most other low-molecular-weight carbohydrate molecules also have carbonyl groups available for reaction. The individual type of reactions is dealt one by one as follows:

1.1 Oxidation – aldonic, uronic and dicarboxylic acids

Aldoses are oxidized to aldonic acidsunder mild conditions for instance with bromine water in buffered neutral or alkaline media. β -Pyranose is oxidized more rapidly than the α -form. Fehling's solution is an alkaline solution of copper(II) that oxidizes an aldose to an aldonate and in the process gets reduced to copper(I) which precipitatesinto a brick-redcolored cupric oxide. The acid name is obtained by adding the suffix– 'onic acid' (e. g. aldose \rightarrow aldonic acid). A simple and specific method for quantitative oxidation of d-glucose to d-gluconic acid uses the enzyme glucose oxidase, the initial product being the 1,5-lactone (an intramolecular ester) of the acid. The conversion of D-glucose to D-gluconic acid is shown in figure no 1.

Oxidation of thehydroxymethyl group(CH2OH) by retaining the carbonyl function at C-1 leads to the formation of uronic acids.Depending on their configuration, the uronicacids can form lactone rings in pyranose or furanose forms.The structure of D-galacturonic acid is shown in figure no2.Some of them areconstituents of polysaccharides which are of importance in food processing such as gel-forming and thickening agents e. g. pectin.

Treatment of aldose with more vigorous oxidizing agents such as nitric acid brings about oxidation of the C-1 aldehyde group and the hydroxymethyl (CH2OH) group resulting in formation of a dicarboxylicacid.An example is D-glucaric acid as shown in the figure no 3.

1.2 Reduction – sugar alcohols

Hydrogenation is the addition of hydrogen to a double bond. When applied to carbohydrates, it entails addition of hydrogen to the double bond between the oxygen atom and the carbon atom of the carbonyl group of an aldose or ketose. The alcohol name is derived from the sugar namein each case by replacing the suffix -ose or –ulosewith the suffix –itol. The hydrogenation of D-glucose leads to the formation of D-glucitol, commonly known as sorbitol as shown in figure no 4. Sorbitol is widely distributed in plants and is and is used as a general humectant.

D-Mannitol can be obtained by hydrogenation of D-mannose. It has been used as a nonsticky coating on candies. It is 65% as sweet as sucrose and is used in sugar-free chocolates. Xylitol is produced from hydrogenation of d-xylose obtained from hemicelluloses from trees. They are used as sugar substitutes in dietetic food formulations and as softeners in dehydrated foods.

1.3 Esters

The hydroxyl groups of carbohydratesform esters with organic and some inorganic acids. Reaction of hydroxyl groups with an activated form of a carboxylic acid in the presence of a suitable base produces an ester (esters are chemical compounds derived from an acid in which at least one –OH hydroxyl group is replaced by an –O–alkyl group). Carbohydrates occur in nature as esters of acetates, succinates and carboxylic acid. They are especially found as components of polysaccharides such as potato and corn starch. The formation of glucose 1 phosphate from glucose is shown in figure no 5.

1.4 Ethers

The hydroxyl groups of carbohydrates have the ability to form ethers as well. (Ethers are classes of organic compounds that contain an ether group that is an oxygen atom connected to two alkyl groups)Ethers of carbohydrates are less prevalent in the nature. Commerciallypolysaccharides are etherified with an intention to modify their properties and to make them more useful.Examples are the production of methyl (-O-CH3), sodium carboxymethyl (-O-CH2-CO-2 Na+) and hydroxypropyl (-O-CH2-CHOH-CH3) ethers of cellulose and hydroxypropyl ethers of starch. These derivatives are used in food industry.

1.5 Caramelization

Heating of carbohydrates (especiallythe disaccharide sucrose and other reducing sugars) without nitrogencontaining compounds result in a series of reactions known as Caramelization. This reaction is facilitated by small amounts of acids and certain salts. This process is similar to non-enzymatic browning but does not involve amino acids. The final product is termed as 'caramel'contains a complex mixture of polymeric compounds which are made up of unsaturated cyclic (five- and six-membered ring) compounds. The caramelization of sucrose shown in figure no 6. Compounds with flavor and aroma are also obtained. Heating causes dehydration of the sugar molecule followed by introduction of double bonds or formation of *anhydro* rings. These unsaturated rings further condense to form conjugated double-bond containing polymers with brown colour.

Caramel is also produced commercially by heating a carbohydrate alone in the presence of an acid, alkali or salt.D-Glucose, invert sugar, glucose syrups andmalt syrups are also used apart from sucrose to produce caramels. Food grade acids are used namely food grade sulphuric, phosphoric, aceticand citric acids. Baseswhich can be used are ammonium, sodium, potassium, and calcium hydroxides. Salts that may be used are ammonium, sodium, and potassium carbonates, bicarbonates, phosphatesetc.

1.6Reaction with amino compounds – Maillard reaction

The browning of foods commonly seen on heating or on storage of foods is due to a chemical reaction between reducing sugars, mainly d-glucose and a primary amino group (a free amino acid or amino group on a side chain of a protein molecule.) This reaction is called the *Maillard reaction* and the overall process and termed as *Maillard browning*. This reaction does not involve the role of enzymes thus is also known as non-enzymatic browning. Enzymatic browning can be seen in freshly cut fruits and vegetables. The end products include soluble and insoluble polymers. The main sugars which react are mainly glucose, fructose, maltose, lactose and to a smaller extent ribose. The volatile compounds produced by the Maillard reaction during baking, frying, or roasting often produce desirable aromas. The end products are also important contributors to the flavor of milk chocolate, caramels and toffee's during which reducing sugars react with milk proteins. The Maillard reaction also produces flavors with bitter substances that may be desired in foods like coffee. The Maillard reaction can also result in off-flavors and off-aromas which are most likely to be produced during pasteurization, storage of dehydratedfoods, and grilling of meat or fish.

The three stages occurring in the maillard reaction are condensation of a reducing sugar and an amino group leading to the formation of N-glycosylamine, in case of aldoses which rearrange to form 'amadori product'. The second step is the fragmentation of the complex amadori product. The last step involves dehydration, fragmentation and polymerization leading to the formation of end products with flavor.

1.7 Acrylamide formation

The Maillard reaction is also responsible for the formation of acrylamide in many foods that have been heated to a high temperature during processing or preparation. Acrylamide is derived primarily from the reaction between reducing sugars and the α -amino group of free L-asparagine. Foods with free L aspargine and reducing sugars are susceptible to the formation of acrylamides on heating to a high temperature such asfried potato products which includes chips andFrench fries.

2. Hydrolysis of starch

Starch molecules undergo depolymerization by hot acids similar to other polysaccharide molecules. Hydrolysis of the glycosidiclinkage occurs initially to produce very large fragments. Acid modified starches form gels with improved clarity and increased strength and they provide less viscosity when solutions are formed. More extensive depolymerization of granular starch with acid produces dextrins. Dextrins produce lower viscosities in solutions and can be used at high concentrations in food processing.

Incomplete hydrolysis of cookedstarch dispersions with either an acid or an enzyme produces mixtures of malto-oligosaccharides which are industrially referred to as maltodextrins.Maltodextrins are usually described by their dextrose equivalency (DE).Dextrose equivalent (DE) is a measure of the amount of reducing sugars present in a sugar productrelative to dextrose. DE is expressed as a percentage on a dry basis. For example, a maltodextrin with a DE of 10 would have 10% of the reducing power of dextrose (which has a DE of 100).DE is inversely related to average molecular weight.Maltodextrins of lowest DE, that is, highest average molecular weight, are nonhygroscopic, while those of highest DE tend to absorb moisture.If hydrolysis is continued, starch produces a mixture of d-glucose, maltose, and other malto-oligosaccharides.They are used in concentrations of high osmolality (about 70% solids) which is high enough to avoid growth of microbes.

Various enzymes are also used in the hydrolysis of starch into D-glucose. α -Amylaseis an enzymethat cleaves both amylose and amylopectin molecules producing oligosaccharides.Glucoamylase (amyloglucosidase) is another enzyme used commercially in combination with α -amylase for the production of d-glucose (dextrose) syrups and crystalline d-glucose. There are several otherdebranching enzymes that specifically catalyze the hydrolysis of $(1\rightarrow 6)$ linkages in amylopectinnamelyisoamylase and pullulanase. For the production of d-fructose, a d-glucose solution is passed through a column containing glucose isomeraseenzyme leading to formation ofend product with higher fructose content. The overall scheme of starch hydrolysis is presented in figure no 7.

3. Modified starches and their applications

Starch properties can be modified by physical and chemical methods. Such modifications are done by the food processors they require starches with better physicochemical properties than that of native starch (starch in their natural form). When cooked, the native starches are known to producerubbery pastes which form gels with undesirable consistencywhen the pastes are cooled. Thus modification is donewith an aim to improve the characteristics of the pastes and gels. The specific targets of these modifications will be to improve the ability to withstand the conditions of heat, shear, and acid associated with particular processing conditions and some specific functional properties. Modified food starches are functional, useful, and are abundantly used asfood ingredients and additives.

Chemical modifications lead to the formation of crosslinked, stabilized, oxidized, and depolymerized (acid-modified, thin-boilingetc) products. Physical modifications lead to the formation of pre-gelatinized and cold-water-swelling products. The overview of starch modification is shown in figure no 8.

3.1 Stabilized starches

Starch products that are esterified or etherified with mono-functional reagents resist interchainassociations. This phenomenon reduces the tendency of the starch paste to form a gel and also the tendency for precipitation to occur. Hence, this modification is often called stabilization and the products are called stabilized starches. Stabilized products have lower gelatinization and pasting temperatures and they are easier to re-disperse when pregelatinized. They also produce pastes and gels with a reduced tendency for retrogradation(realignment of amylose and amylopectin chains after gelatinization). In other terms the end products have a greater stability, improved freeze-thaw stability and greater clarity as compared to the untreated starch.

Hydroxypropylation is the most often used reaction to prepare a stabilized starch product. Hydroxypropylstarchis prepared by reacting starch with propylene oxide to produce a low level of etherification. They are used as thickeners and extenders.

3.2 Cross linked starches

Crosslinking in the starch granules occur when the granules are made to react with bifunctional reagents that react with hydroxyl groups on two different molecules within the same granule.Cross-linked starches are obtained by the reaction of starch with bi-or polyfunctional reagents such as sodium trimetaphosphate, phosphorus oxychloride, epichlorohydrin or mixed anhydrides of acetic and dicarboxylic acids. The starch granule thus treated will have increase in the gelatinization temperature and lowered swelling power.

Starch stability remains high at extreme pH values. Cross-linked starch derivatives are generally used when high starch stability is demanded.Cross-linked have increased resistance to shear and increased stability to low pH conditions and they can produce pastes with greater viscosities and stability as compared to the native form of starch.

3.3Oxidized starches

Starch hydrolysis and oxidation occur when aqueous starch suspensions are treated with sodium hypochlorite at a temperature below the starch gelatinization temperature range. The productsobtained have an average of one carboxyl groupper 25–50 glucose residues.Oxidized starch is used as lowviscosity filler for salad dressings and mayonnaise. Oxidized starch does not retrograde nor form an opaque gel.

3.4Thin boiling starches

Partial acidic hydrolysis of starch yields a product which is readily soluble in boiling water but not in cold water. The solution has a lower viscosity than the untreated starch and remains as a fluid after cooling. These starches are utilized as thickeners and as protective films.

3.5Cold-Water-Swelling Starch

Granular starch that swells extensively in cold water is made by heating corn starch in 75–90% ethanol or by spray-drying process. The granules will remain intact, thus when added to water they can swell as if they were being cooked. The dispersion made by incorporating cold-water-swelling starch into sugar solutions or glucose syrups by rapid stirring can be poured into molds which further sets to form a rigid gel. This gel can be sliced and is used in making desserts and muffins.

3.6Pre gelatinized starch

Heating of starch suspensions followed by drying results in the formation ofend products that have the ability to swell in cold water and can form gels on heating. The granules in the end product will be destroyed because of the heating. The advantage of pre-gelatinized starches is that they can be used without cooking. They are used in dry mixessuch as instant pudding mixes.

4. Modified Cellulose and its applications

Cellulose can be modified into a number of derivatives with good swelling properties and improved solubility. Such derivatives have a wide field of application in food industry.

4.1 Carboxymethylcellulose

Carboxymethylcellulose is widely used as a food gum. Treatment of purified wood pulp with 18% sodium hydroxide solution produces alkaline cellulose.Carboxymethylcellulose is obtained by treating thus alkaline cellulose with chloroacetic acid.Carboxymethylcellulose is an inert binding and thickening agent used to adjust or improve the texture of many food products such as jellies, paste fillings, cheeses, salad dressings, cake fillings and icings.

4.2Methylcelluloses and Hydroxypropylmethylcelluloses

The reaction of cellulose with methylchloride or propylene oxide in the presence of a strong alkali introduces methyl or hydroxypropyl groups into cellulose molecules.Depending on the nature of the substituent (methyl, ethyl,hydroxymethyl, hydroxyethyl or hydroxypropyl) and the degree of substitution, products are obtained with variable swelling capacity and solubility. The presence of methyl and methylhydroxypropylcelluloses in baked products obtained from rice, wheat or corn decreases the crumbliness of the product and enables a larger volume of water to beadded into the dough. This improves the extent of

starch swelling during oven baking. They are also used to reduce the amount of fat in food products because they can provide fat-like properties to the food product leading to the reduction in fat addition and they reduce adsorption of fat in subjected to frying.

Conclusion

The structure of many carbohydrates appears to be complex but the chemistry of these substances involves only two functional groups- ketone or aldehyde carbonyls and alcohol hydroxyl groups. The intermediates and derivatives they form are dependent on the many aspects such as the substituent used, chemical used, temperature applied and enzymes used. Many of these derivatives have important food applications which lead to improvement in functional andsensory properties of foods.