Consortium for
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Module on

Heteroglycans

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TEXT:

Introduction:

After the proteins and lipids, the carbohydrates represent the third most abundant group of organic compounds in the animal body. In contrast, carbohydrates constitute the major class of organic nutrients within the plant tissues. Carbohydrates can be divided into two major groups according to their chemical structure i.e., the sugars and non-sugars. The simplest sugars are called monosaccharides, and these inturn can be divided into five sub-groups depending on the number of carbon atoms present in the molecule, for example, Trioses ($C_3H_6O_3$), Tetroses ($C_4H_8O_4$), Pentoses ($C_5H_{10}O_5$) and Hexoses ($C_6H_{12}O_6$). These monosaccharides may also inturn be linked together (with the elimination of water) to form di-, tri- or poly-saccharides containing two, three or more monosaccharide units or residues, respectively. Here the term ‘sugar’ is restricted to those carbohydrates containing less than ten monosaccharide units. Non-sugars are therefore carbohydrates which contain more than ten monosaccharide units and which do not possess a sweet taste. The non-sugars can be divided into two sub-groups which include homoglycans and heteroglycans. The former consists of identical monosaccharide units while the latter is a mixture of different monosaccharide units. **Figure-1**, given below is the representation of homo- and hetero-glycan:

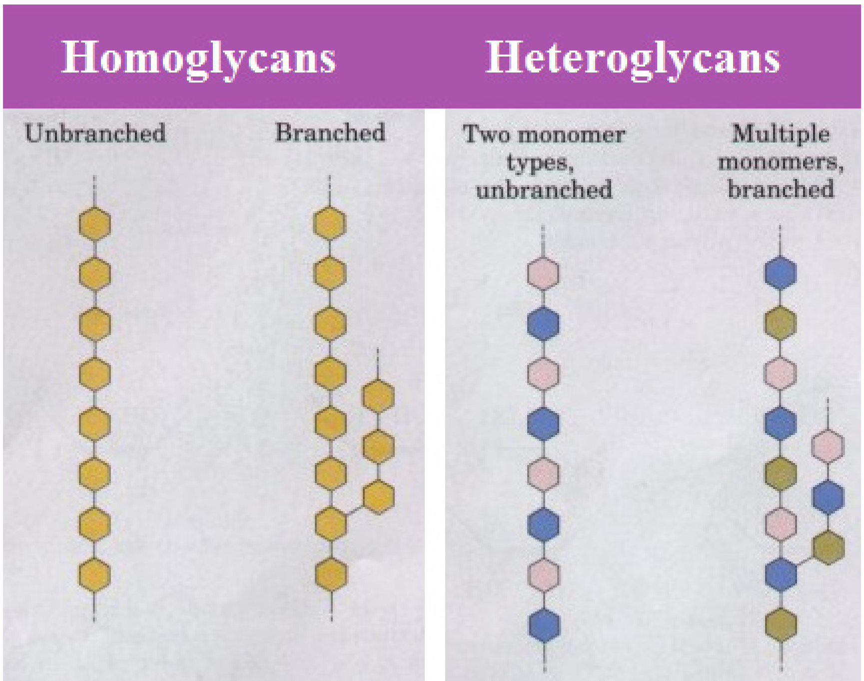

Figure-1: Homo- and Hetero-glycans.

Classification:

A general system of classification of homo- and heteroglycan is shown in **figure-2** given below:

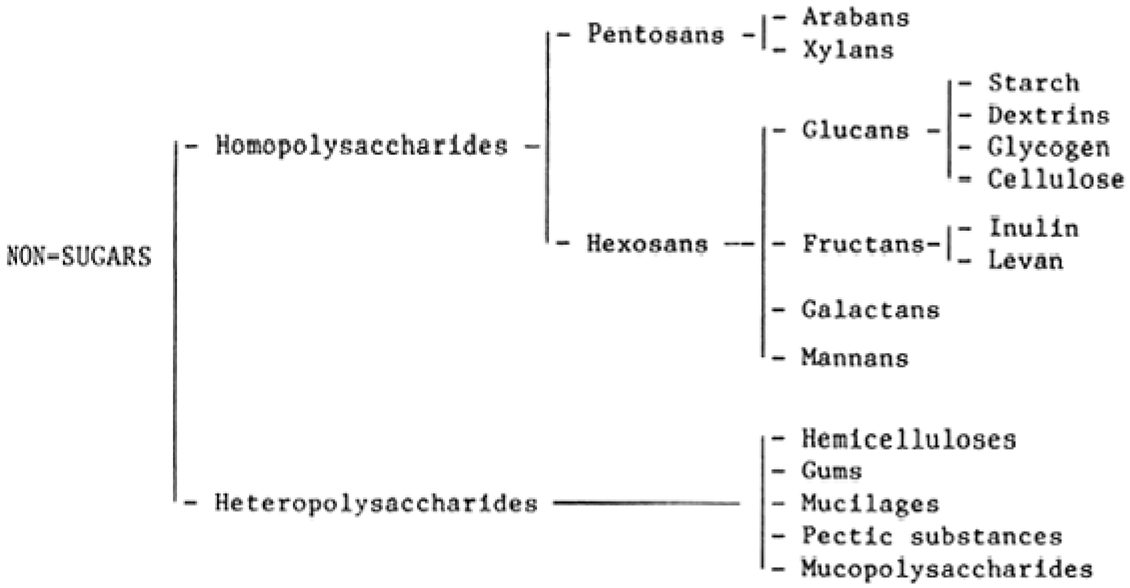

Figure-2: Classification of homo- and hetero-glycans.

Homoglycans are generally classified as pentosans and hexosans. The chief examples of homoglycans are starch, dextrin, glycogen and cellulose. The hetero-glycans are, however, classified into following major classes (**Figure-2**):

- Hemicelluloses.
- Gums and mucilages.
- Pectic substances
- Mucopolysaccharides.

These classes are discussed briefly as below:

I. Hemicelluloses:

Hemicelluloses are heterogeneous polysaccharides which are formed through biosynthetic routes different from that of the cellulose. 'Hemicellulose' is a collective term used to represent a family of polysaccharides such as arabino-xylans, gluco-mannans, galactans, and others that are found in the plant cell wall. These have different composition and structure depending on their source and the extraction method. It can be said that hemicellulose is a copolymer of different C5 and C6 sugars that exist in the plant cell wall. Mannose is the most important monomer of hemicelluloses, present in the form of low molecular weight *O*-acetyl-galactoglucomannan, followed by xylose, glucose, galactose and arabinose. Like cellulose, hemicelluloses commonly function as supporting material in the cell wall. Most hemicelluloses have a degree of polymerization ranging from 150 to not more than 200 units. The amount of hemicellulose of the dry weight of wood is usually between 20 and 30%. The composition and structure of hemicelluloses in the softwood differ in a characteristic way from those in the hardwood with considerable differences in content and composition between the stem, branches, roots, and bark. **Table-1** given below gives the general account of percent hemicelluloses from different plant sources as per the observations of Sun and Cheng, 2002:

Table 1: Composition of hemicellulose in several sources on dry weight basis:

Material	Hemicellulose (%)
Hardwood stems	24–40
Softwood stems	25–35
Nut shells	25–30
Corn cobs	35
Grasses	35–50
Wheat straw	50
Leaves	80–85
Cotton seed hairs	5–20
Waste papers from pulps	10–20
Solid cattle manure	1.4–3.3
Coastal Bermuda grass	35.7

Properties of hemicelluloses:

- It is insoluble in water at low temperature but soluble at elevated temperatures.
- Its hydrolysis temperature is lower than that of cellulose.
- The presence of acid highly improves the solubility of hemicellulose in water.

Principal structural difference between cellulose and hemicelluloses:

- Hemicelluloses are mixed polymers, whereas cellulose is a pure polymer of glucose.
- Apart from arabinogalactan, which is heavily branched, the hemicelluloses have short side-chains. Cellulose is a long unbranched polymer.
- Hemicelluloses are low molecular weight polymers, however, cellulose has a very high degree of polymerization. Hemicelluloses may have large side groups substituting hydroxyl groups on the C2, C3 and C6 positions.
- The solubility and susceptibility to hydrolysis of hemicelluloses are

greater than cellulose (low molecular weight and amorphous structures).

Below given table (**Table-2**) describes the chief differences between cellulose and hemicellulose polymers:

Table-2: Cellulose *vs.* Hemicellulose

Property	Cellulose	Hemicellulose
Monomer	Pure glucose	Mixed sugars
Polymer chain length	Long (5μm)	Short
Polymer morphology	Crystalline + amorphous	Amorphous
Polymer topology	Linear	Branched
Molecular weight	High (10000 units)	Low (100 units)
Substitution	No substitution	On C2, C3, and C6
Reactivity	Less reactive	More reactive
Solubility	Low	High
Hydrolysis	Partial	Readily (susceptible)

II. Gums and mucilages:

Gums are considered to be pathological products formed following injury to the plant or owing to unfavourable conditions, such as drought, injury or breakdown of cell walls (extra cellular formation). Mucilages, on the other hand, are generally normal products of metabolism, formed within the cell (intracellular formation) and may be produced without an injury to the plant. Gums and mucilages have similar hydrophilic constituents and on hydrolysis yield a mixture of sugars and uronic acids. These combine with water to form viscous solutions or gels. The nature of the compounds involved, however, influences the properties of different gums. Linear polysaccharides occupy more space and are more viscous than highly branched compounds of the same molecular weight. The branched compounds form gels more easily and are more stable because of the lack of extensive interaction within the chains. Gums and mucilages have certain similarities, which include:

- Both are hydrocolloids.
- Both are translucent amorphous substances and polymers of

mixed monosaccharides.

- Both have uronic acids in their molecular structure.

Classification of gums and mucilages:

Gums and mucilages are obtained in high quantities, from varieties of plants, animals, seaweeds, fungi and other microbial sources. In general, plants are known to be their largest sources. The different available gums and mucilages can be classified as follows.

- According to the charge

a) Non-ionic seed gums: These include guar, locust bean, tamarind, xanthan and galactomannans.

b) Anionic gums: These include gum arabic, karaya, tragacanth, gellan, agar, algin and carrageenans.

- According to the source

a) Marine origin/algal (seaweed) gums: These include agar, carrageenans, alginic acid and laminarin.

b) Plant origin: These include those obtained from shrubs or tree exudates in the form of exudate gums like arabica, gum ghatti, gum karaya and gum tragacanth. The second important category is of seed gums like guar gum and locust bean gum. The pectin and larch gums are also extracted from plant sources.

c) Animal origin: Chitin, chitosan, chondroitin sulphate and hyaluronic acid are common gums and mucilages obtained from animal sources.

d) Microbial origin (bacterial and fungal): Common gums and mucilages obtained from microbial sources are xanthan, dextran, curdlan, pullulan, zanflo, emulsan, Baker's yeast glycan, schizophyllan, lentinan, krestin and scleroglucan.

- According to manomeric units in chemical structure

a) Di-heteroglycan: The examples of diheteroglycan are algins, carragennans and galactomannans.

b) Tri-heteroglycan: The examples of triheteroglycan are arabinoxylans, gellan and xanthan.

c) Tetra-heteroglycan: The examples of tetra-heteroglycan are gum Arabic and psyllium seed gum.

d) Penta-heteroglycan: The examples of penta-heteroglycan are ghatti gum and tragacanth.

Applications of gums and mucilages:

- Applications in the food industry:

Gums and mucilages have a variety of applications in the food industry. Different gums have different uses like water retention and stabilization (guar and locust bean gum), stabilization for ice-cream, meat products and instant puddings (carrageenanas), dairy, confectionary beverages, baked product, and sauces (gum arabic, tragacanth, pectins, alginates and xanthan gum).

- Pharmaceutical applications

Gums and mucilages have a variety of applications in pharmacy. They are used in medicine for their demulcent properties for cough suppression. They are ingredients of dental and other adhesives and can be used as bulk laxatives. These are useful as tablet binders, disintegrants, emulsifiers, suspending agents, stabilizing agents, thickening agents, film forming agents and sustaining agents in matrix tablets.

- Industrial application

Gums are used in cosmetics (acacia, tragacanth and karayagum), textiles (starch, dextrin, cellulose, pectins, and tamarind gum), adhesives (acacia gum, and tragacanth), lithography (gum arabic, tragacanth and locust bean gum), paints (pectins, hemicellulose and resins) and paper manufacturer (tamarind, and cellulose).

Advantages of natural gums and mucilages:

The following are the important advantages of natural plant gums and mucilages:

- Biodegradable—These represent truly biodegradable and renewable sources for a variety of applications having no adverse impact on humans or environmental health (*e.g.*, skin and eye irritation).
- Biocompatible and non-toxic—Chemically, these are the carbohydrate materials composed of repeating sugar (monosaccharides) units. Hence, they are nontoxic.
- Low cost—The production cost is much lower compared to that of synthetic materials.
- Environment-friendly processing—Gums and mucilages from different sources are easily collected in different seasons in large quantities due to the simple production processes involved.
- Local availability (especially in developing countries)—In developing countries, governments promote the production of plant like guar gum and tragacanth because of the wide applications in a variety of industries.

Disadvantages of Natural Gums and Mucilages

- Microbial contamination—The equilibrium moisture content present in the gums and mucilages is normally 10% or more and, structurally, they are carbohydrates. During production, they are exposed to the external environment where there is an increased chance of microbial contamination. However, this can be prevented by proper handling and the use of preservatives.
- Batch to batch variation—Synthetic manufacturing is a controlled procedure with fixed quantities of ingredients, while the production of gums and mucilages is dependent on environmental and seasonal factors.
- Uncontrolled rate of hydration—Due to differences in the collection of natural materials at different times, as well as differences in region, species

and climate conditions, the percentage of chemical constituents present in a given material may vary.

- Reduced viscosity on storage—When gums and mucilages come into the contact with water, there is an increase in the viscosity of the formulations. However, due to the complex nature of gums and mucilages, it has been found that after storage, the viscosity of solutions reduces.

III. Pectic substances:

Pectins are polysaccharides occurring in all plants primarily in their cell walls. They act as intracellular cementing material that gives body to fruits and helps them keep their shape. When fruit becomes over ripe, the pectin is broken down into its monosaccharide constituents. As a result, the fruit becomes soft and loses its firmness. One of the most prominent characteristics of pectins is their ability to form gels. All pectins are composed of D–galactopyranosyl uronic acid units linked through α-(1, 4)-linkages. They contain methyl esters and acetyl groups to various degrees and show a typical average molecular size of 100,000 Da. The highest concentration of pectins in the cell wall is seen in the middle lamella, with a gradual decrease from the primary cell wall toward the plasma membrane.

Sources and Extraction

Pectin is found in all plants, but is most concentrated in citrus fruits (oranges, lemons, grapefruits) and apples. Pectin obtained from citrus peels is referred to as citrus pectin. The extraction of pectins can lead to large variations in the chemical structure of the final material. Pectins are industrially extracted from citrus peels and apple pomace by hot acidified water. Extraction conditions of pH 1.5 to 3.0 and temperatures of 60 to 100 □C for 0.5 to 6 hours are varied to give the pectin of desired gelling capacity and degree of methylation. The separation of the viscous material from the swollen and partially disintegrated plant material, however, remains a problem. Grinding and washing with ethanol are used but this can lead to co-precipitation with intracellular proteins, starches and nucleic acids. A method by which this contamination may be avoided is by wet ball milling at low temperature. Enzymatic degradation of the pectin is avoided by addition of a surfactant like sodium dodecyl sulphate (SDS). Sodium deoxycholate (SDC) is used to remove pigments and lipids and a treatment with 90% dimethyl sulphoxide (DMSO) is used to remove the bulk of starch. Different plants are known to have different proportion of pectic substances. **Table-3** gives a brief description of differences in the pectin concentration of fruits:

Table 3: Pectin Content of Some Fruits %

Fruit	% pectic substances (ww basis)
Apple (*Malus* spp.)	0.5-1.6
Apple pomace	1.5-2.5
Banana (*Musa acuminata* L.)	0.7-1.2
Beet pulp *(Beta vulgaris)*	1.0
Carambola *(Averrhoa carambola)*	0.66
Carrot *(Daucus carota)*	0.2-0.5
Guava (*Psidium guajava* L.)	0.77-0.99
Lemon pulp *(Citrus limon)*	2.5-4.0
Lychee (*Litchi chinesis* S.)	0.42
Mango (*Mangifera indica* L.)	0.26-0.42
Orange peel *(C. sinesis)*	3.5-5.5
Papaya *(Carcia papaya)*	0.66-1.0
Passion fruit (*Passiflora edulis* S.)	0.5
Peaches *(Prunus persica)*	0.1-0.9
Pineapple (Ananas *comosus* L.)	0.04-0.13
Strawberries *(Fragaria ananassa)*	0.6-0.7

Classification of pectins:

Methyl esterification is commonly seen in native pectins. Overall the degree of substitution is known as the degree of esterification (DE). On this basis, pectins are broadly classified into two categories, that is, high methoxyl pectins and low methoxyl pectins. If degree of esterification in pectin chains is greater than 50%, it is called a high methoxyl pectin (HM pectin) while if the degree of esterification in pectin chains is less than 50%, it is a low methoxyl pectin (LM pectin). Low methoxyl pectins undergo gelation due to the ionic linkages via calcium bridges. These calcium bridges are formed between two carboxyl groups belonging to two different chains in close contact. The mechanism involves the formation of junction zones. In case of high methoxyl pectins, the cross-linking of polymer chains involves extensive segments from two or more pectin molecules that leads to the formation of different junction zones. High methoxyl pectins are only useful in standard jams, above about 60% soluble solids.

Applications of pectin:

Pectins have always been a natural constituent of human foods. The joint FAO/WHO committee on food additives recommended pectin as a safe additive with no limit on acceptable daily intake except as dictated by good manufacturing practice. The common applications of pectins include:

- Jams, Jellies and Preserves:

Jams and jellies are the major food types using large amounts of pectins. Jam making consists of brief cooking of the fruit to liberate juice and pectin through conversion of protopectin to soluble pectin. Depending upon the requirements, additional pectins may be added at any point during this process. These may be added as a dry powder mixed with sugar as dispersing medium or as a solution. It is, however, desirable to use concentrated pectin solutions due to their convenience and complete dissolution.

- Conserves:

Conserves are products that do not contain a sweetener other than the fruit juice or fruit concentrate. As a result, their soluble solid content is slightly lower than the products containing sweetener. They are rated high in quality by consumers, as they do not contain any added sweetener. The soluble solid content of conserves is 55 to 62%. At the upper soluble level, the rapid-set HM pectin is used, while at the lower limit, the LM pectin is added to give the desired mouthfeel and body to the products.

- Bakers' Jellies

Pectin is used to make instant jellies that are applied to many bakery products. HM pectin, being thermally stable, is used to make jellies that are placed in the batter or dough and baked without fluidizing. LM pectin can be used to produce bakery jams or jellies with a wider applicable soluble solids range and acidity. The use of LM pectin, however, requires a higher amount of pectin in the formula, compared with HM pectin, to approximate the same firmness.

- Frozen Barriers

Pectin is used in frozen foods to retard crystal growth, loss of syrup during thawing, and to improve their shape. The greatest firming effect on frozen-then-thawed fruits is due to calcium ions and pectins. Sliced fruits are firmed more than whole fruit by calcium ions and pectin treatment.

- Beverages

Dietetic soft drinks enjoy a significant share of the beverage market. Reduction in the amount of sweetener (sucrose, high fructose corn syrup, or a combination of both) deprives the beverage of a certain mouthfeel or body present in conventional soft drinks. This loss of mouthfeel can be restored by the addition of 0.05-0.10% HM pectin to it.

- Barbecue Sauce

In some retail brands of barbecue sauce, LM pectin is added due to its flavour release attributes and the texture it provides. The LM pectin and calcium content in the formula determines the product's final consistency and texture.

- Pharmaceutical Uses

Pectin has applications in the pharmaceutical industry. It favourably influences the cholesterol levels in blood and acts as a natural prophylactic substance against poisoning with toxic cations. It has been shown to be effective in removing lead and mercury from the gastrointestinal tract and respiratory organs. When injected intravenously, pectin shortens the coagulation time of drawn blood, thus being useful in controlling haemorrhage or local bleeding.

- Other Uses

Pectin has been found useful in other industrial applications. They function as an emulsion stabilizer for water and oil emulsions. Films made from natural products are of increasing interest because they are biodegradable and potentially recyclable and may even be used in some *in vivo* pharmaceutical applications. Thus, a number of studies have been done on pectin films. Because of its film-forming properties, pectin is useful as a sizing agent for paper and textiles.

IV. Mucopolysaccharides:

Mucopolysaccharides are the heteroglycan molecules also called as glycosaminoglycans. These are complex carbohydrates which contain amino sugars and uronic acids, and constitute the mucous secretions of animals. They are acidic in nature and may be rich in sulphate ester groups. The important mucopolysaccharides include chondroitin sulphate (present in cartilage, bone, heart valves, tendons and the cornea of the eye), heparin (anti-coagulant present in blood vessels, liver, lung and spleen), and hyaluronic acid (viscous lubricating fluids present in the skin, vitreous humour of the eye, the synovial fluid of joints, and the umbilical cord of mammals). Mucopolysaccharides also constitute the principal component of the cell wall of many bacteria; consisting of alternating units of N-acetyl-muramic acid and N-acetyl-glucosamine linked to short peptide chains. Some specific functions of mucopolysaccharides are listed below:

- Hyaluronic Acid (Hyaluronate): **It is a lubricant in the synovial fluid of joints,** gives consistency to vitreous humor and contributes to tensile strength and elasticity of cartilages and tendons.

- Chondroitin Sulfates: It contributes to tensile strength and elasticity of cartilages, tendons, ligaments and walls of aorta.

- Dermatan sulphate: It is found mainly in skin, vessels, heart and lungs. The functions are mainly related to coagulation and vascular diseases.

- Keratan sulfate: It generally has a role to play in cornea, cartilage bone and a variety of other structures like nails and hair.

- Heparin: It is a potent natural anticoagulant produced in the

Mast Cells that causes antithrombin bind to thrombin and produce inhibition of blood coagulation.

Glycosaminoglycans are synthesized in the endoplasmic reticulum and golgi. They are degraded by lysosomal hydrolases. A deficiency of one of the hydrolases results in a mucopolysaccharidosis. These are hereditary disorders in which glycosaminoglycans accumulate in tissues, causing symptoms such as skeletal and extracellular matrix deformities, and mental retardation. Examples of these genetic diseases are Hunter and Hurler syndromes. These diseases, caused by different enzyme deficits, are characterized by physical deformities, mental retardation and disturbances in the degradation of heparan sulfate and dermatan sulfate.