

NATIONAL OPEN UNIVERSITY OF NIGERIA

COURSE CODE: CHM 315

COURSE TITLE: CARBOHYDRATE CHEMISTRY

Course Code	CHM 315
Course Title	Carbohydrate Chemistry
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Introduction

Carbohydrate chemistry is a semester course which is part of the courses designated as part of the requirements for the award of B.Sc Chemistry

What you will learn in this Course

The course consists of units and a course guide. The course guide is primarily a simple description of what the course is made up of, the materials to be used and how you can work with these materials. In addition, it advocates some general guidelines for the time you are likely to spend on each unit of the course in order to complete it successfully.

Also, you find in it your Tutor Marked Assignment which will be made available in the assignment file. Moreover, there are regular tutorial questions and classes that will assist in the better understanding of the course. You are advised to make yourselves available during the tutorial classes.

Course Aims

The aim of the course is to provide a basic understanding of the basic nature of chemical materials and the emerging trend. In addition, it seeks to address the massive drive to understand these materials and improve their properties in order to meet material requirements.

Course Objectives

To achieve the set aims, the course has a set of objectives. Each of the unit contained in a specific module has stated objectives which are included at the beginning of the particular unit. A clearer understanding of each of the objectives is a prerequisite for the better comprehension of the contents of the unit. It is highly essential to reflect, as you work through each unit, on the objectives.

The main objectives of the course are listed below. By meeting these objectives, you should have achieved the aims for which the course has been studied. At the end of this course, you should be able to:

- i. Know what carbohydrates are
- ii. Understand the different classifications of carbohydrates
- iii. Give various examples of monosacchades, disaccharides and polysaccharides
- iv. Describe chemical properties of carbohydrates
- v. State the forms in which these carbohydrates occur naturally

Working through this Course

In order to be able to successfully complete this course, you are required to carefully study each unit along with recommended textbooks and other materials that may be provided by the National Open University. You may also need to exploit other e-reading such internet for further useful information on the course.

Each unit contains self assessment exercise and at certain points in the course you would be required to submit assignment for grading and recording purposes. You are also to participate in the final examination at the end of the course. It is recommended that you devote an abundant time for reading and comprehension. It is highly necessary that you avail yourselves the opportunity of attending the tutorial sessions where you will be able to compare your understanding of the course contents with your colleagues.

The Course Materials

The main components of this course are:

1. The Course Guide
2. Study Units
3. Self Assessment Exercise
4. Tutor Marked Assignments
5. Further Readings

Study Unit

The study units in this course are as follows:

Module 1 Carbohydrates

- | | |
|--------|--------------------------------------|
| Unit 1 | Forms of Carbohydrates |
| Unit 2 | Chemical properties of Carbohydrates |

Module 2 Monosaccharides

- | | |
|--------|--------------------------------|
| Unit 1 | Structures of Monosaccharides |
| Unit 2 | Derivatives of Monosaccharides |

Module 3 Disaccharides

- | | |
|--------|----------------------------|
| Unit 1 | Diversity of Disaccharides |
|--------|----------------------------|

Module 4 Polysaccharides

- | | |
|--------|-----------------------|
| Unit 1 | Homopolysaccharides |
| Unit 2 | Heteropolysaccharides |

The first unit addresses the forms of carbohydrates. It focuses on classification, importance and forms of carbohydrates. The second unit described in details the different chemical properties of carbohydrates. The third unit is primarily concerned with the structures of monosaccharides. The fourth unit addresses the derivatives of monosaccharides and their characteristics. The fifth unit deals with the diversity of disaccharides. The sixth unit explains the structures and functions of homopolysaccharides. The seventh unit enumerated the various examples of heteropolysaccharides and their structures and significance.

Each of the unit is made up of one or two weeks' work consisting of introduction, objectives, reading materials, self assessment exercise, conclusion, summary and Tutor marked Assignment (TMA), suggestion for further reading and source materials. The unit directs you to work on exercises related to the required reading. Together with the TMAs, they are meant to test your basic understanding and comprehension of the course materials, which is a prerequisite for the achieving the stated aims and objectives of the course.

Presentation Schedule

The course materials have important dates for the timely completion and submission of your TMAs and tutorial lessons. You are vividly reminded of the need to promptly submit answers to tutorials and assignments as at when due.

Assessment

The course assessment consists of three aspects namely the self assessment exercise, the tutor marked assignment and the written examination/end of course examination.

It is essential that you attempt all exercises and assignments and submit appropriately to the course facilitator for grading. Let your answers be concise and as accurate as possible. You are expected to consult other material course in addition to your course materials in order to be able to present accurate answers to the questions. Kindly note that the tutor marked assignment covers only 30% of the total marked for the course.

Tutor Marked Assignment (TMA)

The TMA is a continuous assessment component of your course. It accounts for 30% of the total score. You will be given five (5) TMAs to answer. Three of these must be answered before you are allowed to sit for the end of the course examination. The TMAs will be given to you by your facilitator and returned after you have done the assignment. Note that these assignments are already contained in the assignment file to be given to you. You may do yourself good by reading and researching well before you attempt to answer the questions.

You are warned to submit these assignments to the facilitator at the stipulated time as could be seen in the assignment file. However, if for any reason you are unable to meet the deadline, you are highly required to intimate the facilitator of your problem before the due date and seek for an extension which may be granted or not.

Final Examination and Grading

The end of the course examination for Colour Chemistry and Technology will be for about 3 hours with maximum score value of 70% of the total course work. The examination will be made up of questions which normally reflect on what you have learnt in the course materials/further reading. In addition, they may be prototype of the self assessment exercises and the TMAs. The end of the course examination is intended to cover information from all parts of the course.

Avail yourself the opportunity of the time-lag between the completion of the course content and the beginning of the examination to revise as much as possible the whole course materials, the exercise and assignments.

Course Marking Scheme

Assignment	Marks
Assignments 1-5	Five assignments, best three marks of the five count at 10% each i.e. 30% of the course marks
End of course Examination	70% of overall course marks
Total	100% of the course materials

Facilitators/Tutors and Tutorials

There are 17 hours of tutorials provided in support of this course. You will be informed appropriately of the name, telephone number and e-mail address of your facilitator. In addition, the time, dates and location of the tutorial lessons will be communicated beforehand. You are required to mail or submit your Tutor Marked Assignment to your facilitator, at least two working days, before the schedule date. Note that all the submitted assignments will be duly marked by the facilitator with further comments that can improve on your performances. The facilitator will from time to time takes track record of your comprehension, progress and difficulty in the course.

Be kind enough to attend tutorial lessons at the fixed appointment. It is probably the only avenue to meet face to face and discuss with you facilitator. There, you will be able to ask question or seek clarification on seemingly grey area in the course material. You may as well have prepared questions and comments for your facilitator before the due date. An active participation during the tutorial lessons will be an added advantage to boost confidence level.

In case any of the situations listed below arises, do not hesitate to intimate your facilitator using his or her telephone number or via e-mail address;

- . You do not understand any part of the study or the assigned readings
- . You are not skill enough to attempt the self assessment exercise

- . The questions in the TMAs are not clearly understood

Summary

Carbohydrate chemistry is a course which is intended to provide students with the nature and classes of carbohydrates. Upon completion of this course, you will be highly equipped to answer questions below and related ones:

- . What do carbohydrates represent?
- . What are the different type, chemical nature and features of carbohydrates?
- . Know different classification of carbohydrates
- . Identify the examples of monosaccharide, disaccharides and polysaccharides.
- . Discuss the structures of named examples of carbohydrates

Accept my best wishes in the course and I do hope that you benefit considerably from its application.

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Module 1: Carbohydrates

Unit 1: Forms of Carbohydrates

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1.0 Introduction

Carbohydrates consist of the elements carbon (**C**), hydrogen (**H**) and oxygen (**O**) with a ratio of hydrogen twice that of carbon and oxygen. Carbohydrates include sugars, starches, cellulose and many other compounds found in living organisms. Carbohydrates are called *saccharides* or, if they are relatively small, sugars.

2.0 Objectives

At the end of this unit, students should be able to

- Define carbohydrates
- State the importance of carbohydrates
- Classify carbohydrates using different bases
- Identify the various forms and structures of carbohydrates

3.0 Definition of Carbohydrates

Carbohydrates are the main energy source for the human body. Chemically, carbohydrates are organic molecules in which carbon, hydrogen, and oxygen bond together in the ratio: $C_x(H_2O)_y$, where x and y are whole numbers that differ depending on the specific carbohydrate.

3.1 Importance of Carbohydrates

The carbohydrates are a major source of metabolic energy, both for plants and for animals that depend on plants for food. Aside from the sugars and starches that meet this vital nutritional role, carbohydrates also serve as a structural material (cellulose), a component of the energy transport compound ATP, recognition sites on cell surfaces, and one of three essential components of DNA and RNA.

3.2 Classification of Carbohydrates

Several classifications of carbohydrates have proven useful, and are outlined in the following table.

Complexity	Simple Carbohydrates monosaccharides		Complex Carbohydrates disaccharides, oligosaccharides and polysaccharides		
Size	Tetrose C ₄ sugars	Pentose C ₅ sugars	Hexose C ₆ sugars	Heptose C ₇ sugars	etc.
C=O Function	Aldose sugars having an aldehyde function or an acetal equivalent. Ketose sugars having a ketone function or an acetal equivalent.				
Reactivity	Reducing sugars oxidized by Tollen's reagent (or Benedict's or Fehling's reagents). Non-reducing				

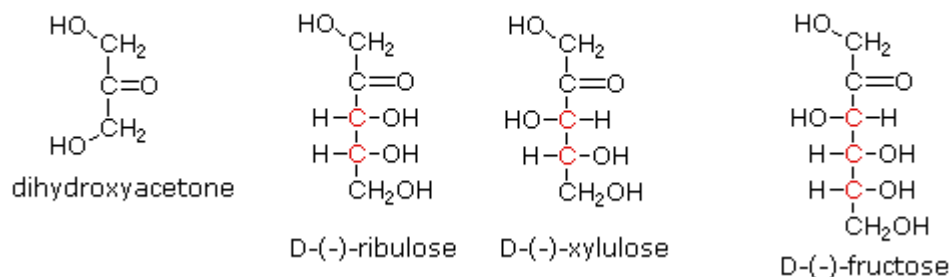
sugars not oxidized by Tollens' or other reagents.

3.3 Ketoses

If a monosaccharide has a carbonyl function on one of the inner atoms of the carbon chain it is classified as a *ketose*. Dihydroxyacetone may not be a sugar, but it is included as the ketose analog of glyceraldehyde. The carbonyl group is commonly found at C-2, as illustrated by the following examples (chiral centers are colored red). As expected, the carbonyl function of a ketose may be reduced by sodium borohydride, usually to a mixture of epimeric products.

D-Fructose, the sweetest of the common natural sugars, is for example reduced to a mixture of D-glucitol (sorbitol) and D-mannitol, named after the aldohexoses from which they may also be obtained by analogous reduction. Mannitol is itself a common natural carbohydrate. Although the ketoses are distinct isomers of the aldose monosaccharides, the chemistry of both classes is linked due to their facile interconversion in the presence of acid or base catalysts. This interconversion, and the corresponding epimerization at sites alpha to the carbonyl functions, occurs by way of an *enediol* tautomeric intermediate.

Ketose Examples



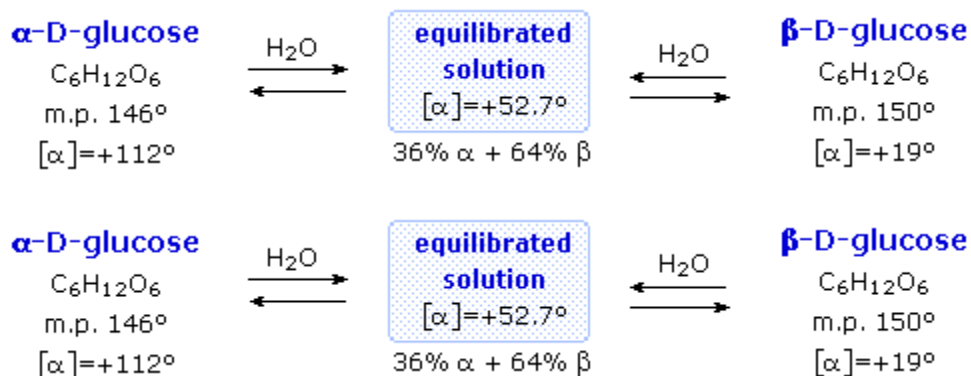
Because of base-catalyzed isomerizations of this kind, the [Tollens' reagent](#) is not useful for distinguishing aldoses from ketoses or for specific oxidation of aldoses to the corresponding aldonic acids. Oxidation by HOBr is preferred for the latter conversion.

Self Assessment Exercise I

- Distinguish between the following pairs;
 - Reducing and non-reducing sugars
 - Simple and complex carbohydrates
 - Aldoses and Ketoses

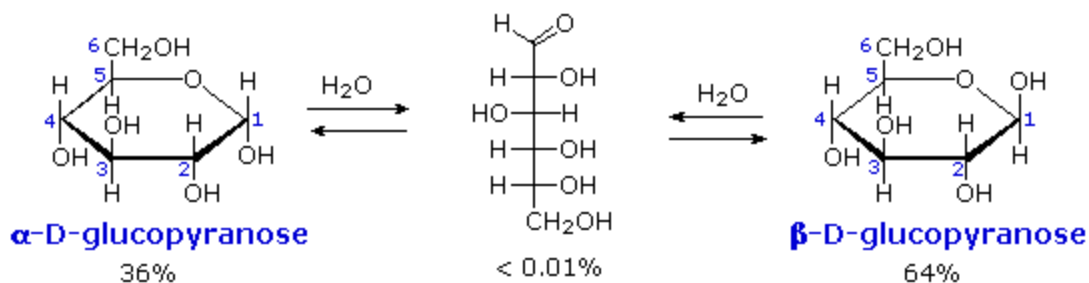
3.4 Anomeric Forms of Glucose

Fischer's brilliant elucidation of the configuration of glucose did not remove all uncertainty concerning its structure. Two different crystalline forms of glucose were reported in 1895. Each of these gave all the characteristic reactions of glucose, and when dissolved in water equilibrated to the same mixture. This equilibration takes place over a period of many minutes, and the change in optical activity that occurs is called *mutarotation*. These facts are summarized in the diagram below.

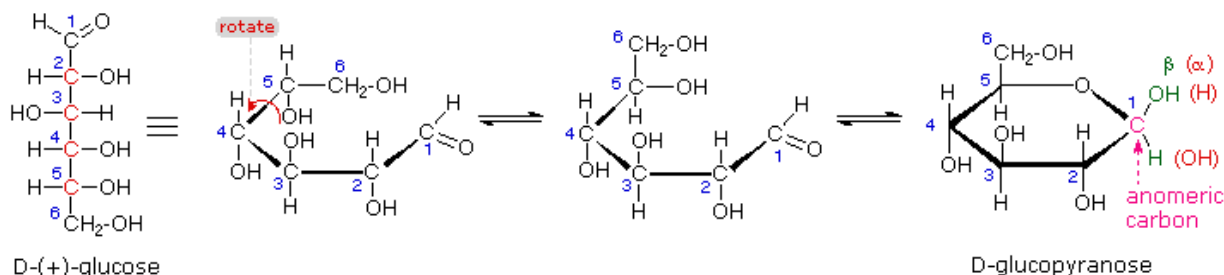
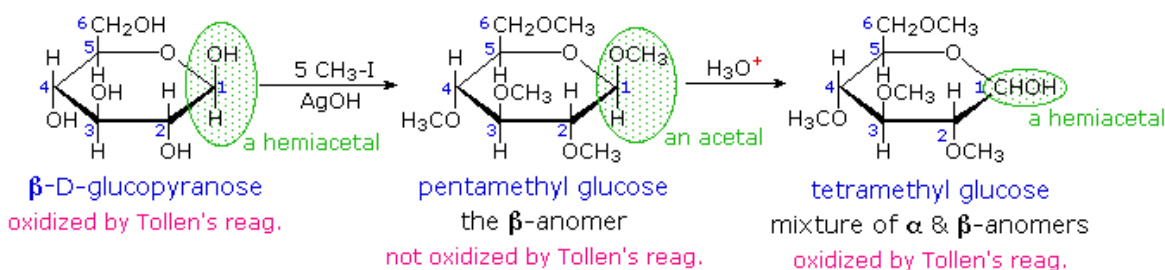


When glucose was converted to its pentamethyl ether (reaction with excess CH_3I and $AgOH$), two different isomers were isolated, and neither exhibited the expected aldehyde reactions. Acid-catalyzed hydrolysis of the pentamethyl ether derivatives, however, gave a tetramethyl derivative that was oxidized by Tollen's reagent and reduced by sodium borohydride, as expected for an aldehyde.

The search for scientific truth often proceeds in stages, and the structural elucidation of glucose serves as a good example. It should be clear from the new evidence presented above, that the open chain pentahydroxyhexanal structure drawn above must be modified. Somehow a new stereogenic center must be created, and the aldehyde must be deactivated in the pentamethyl derivative. A simple solution to this dilemma is achieved by converting the open aldehyde structure for glucose into a cyclic hemiacetal, called a *glucopyranose*, as shown in the following diagram. The linear aldehyde is tipped on its side, and rotation about the C4-C5 bond brings the C5-hydroxyl function close to the aldehyde carbon. For ease of viewing, the six-membered hemiacetal structure is drawn as a flat hexagon, but it actually assumes a chair conformation. The hemiacetal carbon atom (C-1) becomes a new stereogenic center, commonly referred to as the *anomeric carbon*, and the α and β -isomers are called *anomers*.



Mutarotation Equilibrium

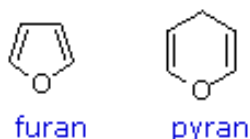


We can now consider how this modification of the glucose structure accounts for the puzzling facts noted above. First, it is known that hemiacetals are in equilibrium with their carbonyl and alcohol components when in solution. Consequently, fresh solutions of either alpha or beta-glucose crystals in water should establish an equilibrium mixture of both anomers, plus the open chain form.

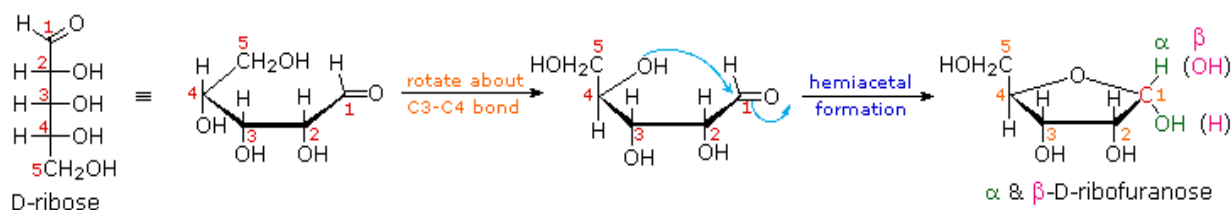
Second, a pentamethyl ether derivative of the pyranose structure converts the hemiacetal function to an acetal. Acetals are stable to base, so this product should not react with Tollen's reagent or be reduced by sodium borohydride. Acid hydrolysis of acetals regenerates the carbonyl and alcohol components, and in the case of the glucose derivative this will be a tetramethyl ether of the pyranose hemiacetal. This compound will, of course, undergo typical aldehyde reactions.

3.5 Cyclic Forms of Sugars

The preferred structural form of many monosaccharides may be that of a cyclic hemiacetal. Five and six-membered rings are favored over other ring sizes because of their low angle and eclipsing strain. Cyclic structures of this kind are termed *furanose* (five-membered) or *pyranose* (six-membered), reflecting the ring size relationship to the common heterocyclic compounds furan and pyran shown on the right.

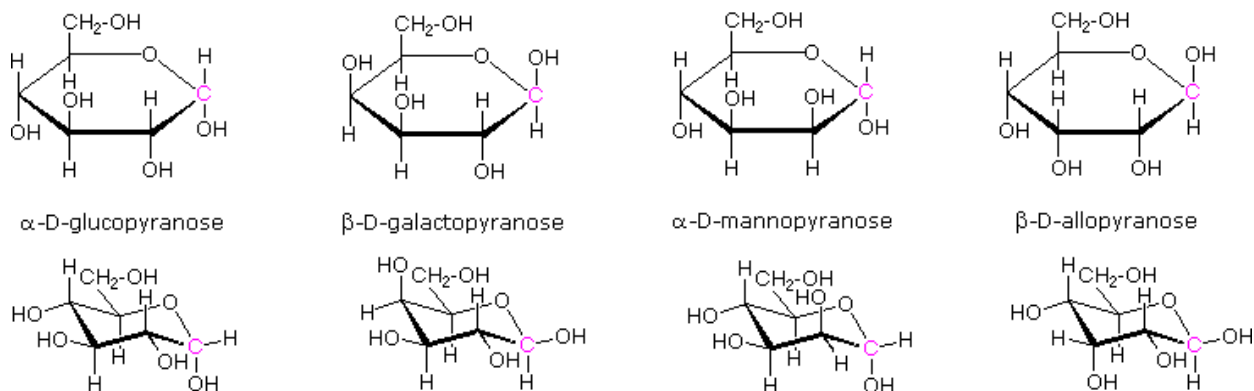


Ribose, an important aldopentose, commonly adopts a furanose structure, as shown in the following illustration. By convention for the D-family, the five-membered furanose ring is drawn in an edgewise projection with the ring oxygen positioned away from the viewer. The anomeric carbon atom (colored red here) is placed on the right. The upper bond to this carbon is defined as *beta*, the lower bond then is *alpha*.



The cyclic pyranose forms of various monosaccharides are often drawn in a flat projection known as a *Haworth formula*, after the British chemist, [Norman Haworth](#). As with the furanose ring, the anomeric carbon is placed on the right with the ring oxygen to the back of the edgewise view. In the D-family, the alpha and beta bonds have the same orientation defined for the furanose ring (beta is up and alpha is down). These Haworth formulas are convenient for displaying stereochemical relationships, but do not represent the true shape of the molecules. These molecules are actually puckered in a fashion we call a [chair conformation](#). Examples of four typical pyranose structures are shown below, both as Haworth projections and as the more representative chair conformers. The anomeric carbons are colored red.

Examples of Some Pyranose Forms of Hexoses



The size of the cyclic hemiacetal ring adopted by a given sugar is not constant, but may vary with substituents and other structural features. Aldohexoses usually form pyranose rings and their pentose homologs tend to prefer the furanose form, but there are many counter examples. The formation of acetal derivatives illustrates how subtle changes may alter this selectivity. Acetal derivatives have been prepared by acid-catalyzed reactions with benzaldehyde and acetone. As a rule, benzaldehyde forms six-membered cyclic acetals, whereas acetone prefers to form five-membered acetals. The top equation shows the formation and some reactions of the 4,6-O-benzylidene acetal, a commonly employed protective group. A methyl glycoside derivative of this compound leaves the C-2 and C-3 hydroxyl groups exposed to reactions such as the periodic acid cleavage, shown as the last step. The formation of an isopropylidene acetal at C-1 and C-2, center structure, leaves the C-3 hydroxyl as the only unprotected function.

Selective oxidation to a ketone is then possible. Finally, direct di-O-isopropylidene derivatization of glucose by reaction with excess acetone results in a change to a furanose structure in which the C-3 hydroxyl is again unprotected.

4.0 Conclusion

Carbohydrate is a one of the major classes of biomolecules. The simplest and commonest form of carbohydrate is glucose. Sugars that possess keto group (C=O) as their functional group are referred to as Ketoses while those that have aldehyde are called Aldoses. By convention for the D-family, the five-membered furanose ring is drawn in an edgewise projection with the ring oxygen positioned away from the viewer. The anomeric carbon atom (colored red here) is placed on the right. The upper bond to this carbon is defined as *beta*, the lower bond then is *alpha*.

5.0 Summary

In this unit, we have learnt that

- i. Carbohydrates consist of the elements carbon (C), hydrogen (H) and oxygen (O).
- ii. Carbohydrates can be classified based on complexity, size, function and reactivity.
- iii. Cyclic structures of sugars can either occur as a five-membered ring (furanose) or a six-membered ring (pyranose).
- iv. The structures of sugars can be represented in a closed form as a Fisher or Haworth projection

6.0 Tutor Marked Assignment

- i. Using all criteria, outline the classes of carbohydrates
- ii. With the of illustration, describe anomerism
- iii. Distinguish between furanose and pyranose and give examples

7.0 Further reading

Nelson, D. L. and Cox, M. M. (2004): Lehninger Principles of Biochemistry, 4th edition. Freeman Publisher, USA.



Module 1: Carbohydrates

Unit 2: Chemical Properties of Carbohydrates

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1.0 Introduction

Since carbohydrates is made up of elements which makes them a chemical compound, carbohydrates exhibited varying chemical properties. These chemical properties exhibited by different carbohydrates could serve as basis for the different classification such reducing and non-reducing sugars as well as aldoses and ketoses.

2.0 Objectives

At the end of this unit, students should be able to

- Know the reactions carbohydrates take part in.
- Differentiate between reducing and non-reducing sugars
- Know glycosides formed from carbohydrates and their examples
- Distinguish sugars based on their chemical properties

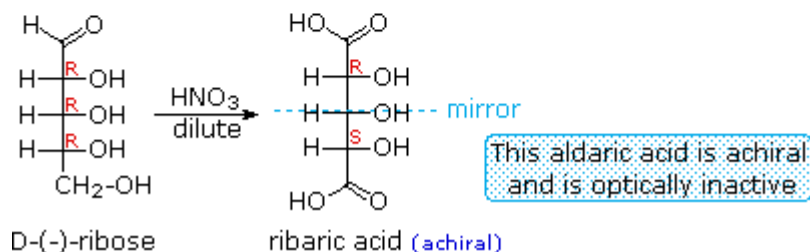
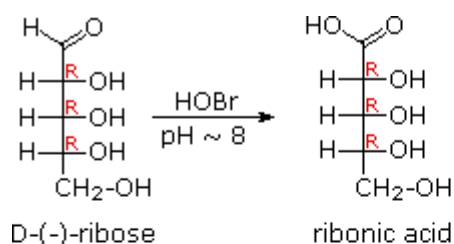
3.0 Reactions involving Carbohydrates

3.1 Oxidation

Sugars may be classified as *reducing* or *non-reducing* based on their reactivity with [Tollens', Benedict's or Fehling's reagents](#). If a sugar is oxidized by these reagents it is called *reducing*, since the oxidant ($\text{Ag}^{(+)}$ or $\text{Cu}^{(+2)}$) is reduced in the reaction, as evidenced by formation of a silver mirror or precipitation of cuprous oxide. The Tollens' test is commonly used to detect aldehyde functions; and because of the facile [interconversion of ketoses and aldoses](#) under the

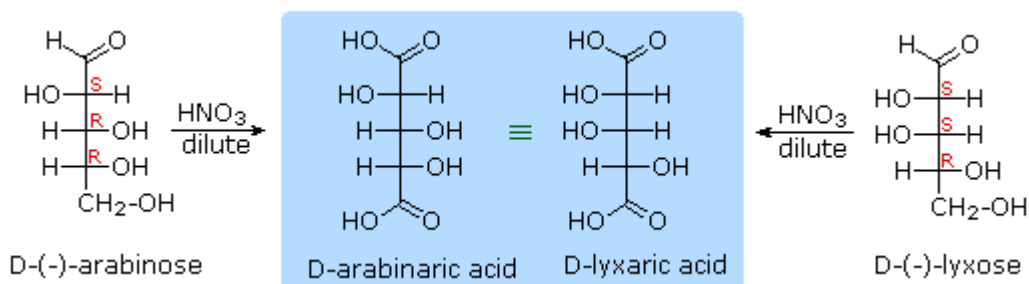
basic conditions of this test, ketoses such as fructose also react and are classified as reducing sugars.

When the aldehyde function of an aldose is oxidized to a carboxylic acid the product is called an *aldonic acid*. Because of the 2° hydroxyl functions that are also present in these compounds, a mild oxidizing agent such as hypobromite must be used for this conversion (equation 1). If both ends of an aldose chain are oxidized to carboxylic acids the product is called an *aldaric acid*. By converting an aldose to its corresponding aldaric acid derivative, the ends of the chain become identical (this could also be accomplished by reducing the aldehyde to CH₂OH, as noted below). Such an operation will disclose any latent symmetry in the remaining molecule. Thus, ribose, xylose, allose and galactose yield achiral aldaric acids which are, of course, not optically active. The ribose oxidation is shown in equation ii below.



ii

Other aldose sugars may give identical chiral aldaric acid products, implying a unique configurational relationship. The examples of arabinose and lyxose shown in equation iii above illustrate this result.

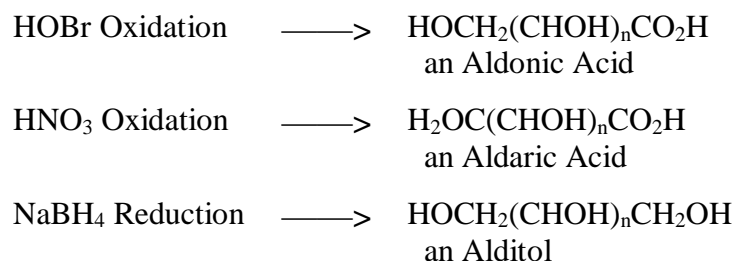


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3.2 Reduction

Sodium borohydride reduction of an aldose makes the ends of the resulting *alditol* chain identical, $\text{HOCH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$, thereby accomplishing the same configurational change produced by oxidation to an aldaric acid. Thus, allitol and galactitol from reduction of allose and galactose are achiral, and altrose and talose are reduced to the same chiral alditol. A summary of these redox reactions, and derivative nomenclature is given in the following table.

Derivatives of $\text{HOCH}_2(\text{CHOH})_n\text{CHO}$

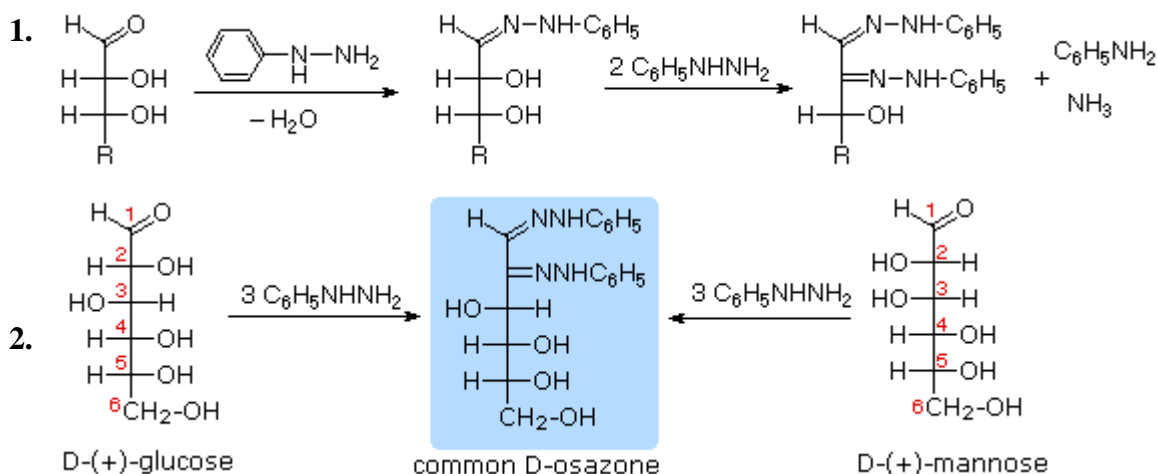


Self Assessment Exercise I

- Distinguish between aldonic and aldaric acid
- Describe the formation of alditol

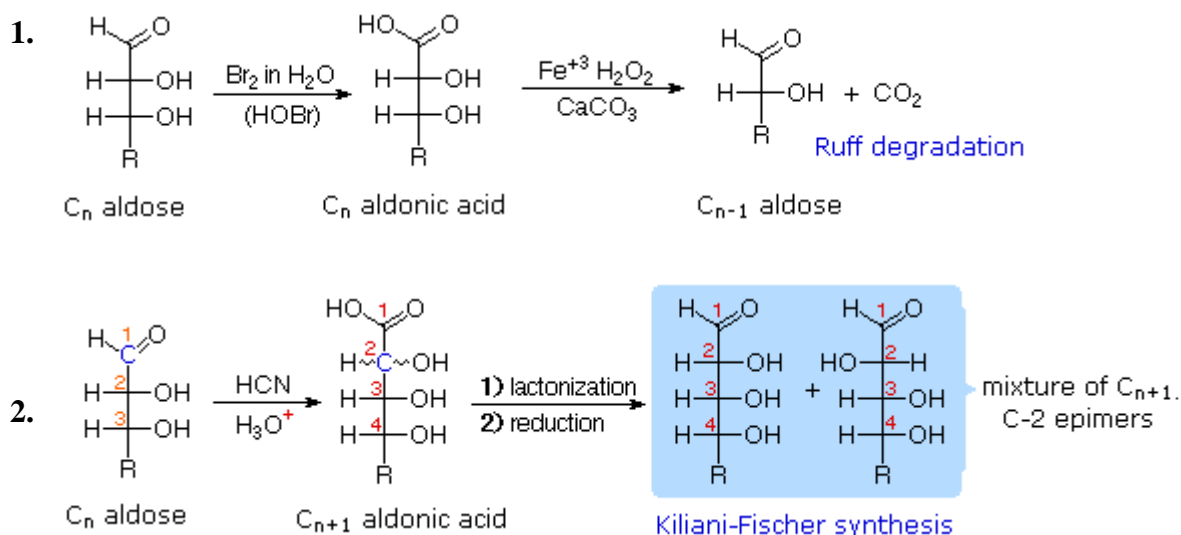
3.3 Osazone Formation

The osazone reaction was developed and used by Emil Fischer to identify aldose sugars differing in configuration only at the alpha-carbon. The upper equation shows the general form of the osazone reaction, which effects an alpha-carbon oxidation with formation of a bis-phenylhydrazone, known as an osazone. Application of the osazone reaction to D-glucose and D-mannose demonstrates that these compounds differ in configuration only at C-2.



3.4 Chain Shortening and Lengthening

These two procedures permit an aldose of a given size to be related to homologous smaller and larger aldoses. Thus Ruff degradation of the pentose arabinose gives the tetrose erythrose. Working in the opposite direction, a Kiliani-Fischer synthesis applied to arabinose gives a mixture of glucose and mannose. An alternative chain shortening procedure known as the Wohl degradation is essentially the reverse of the Kiliani-Fischer synthesis.

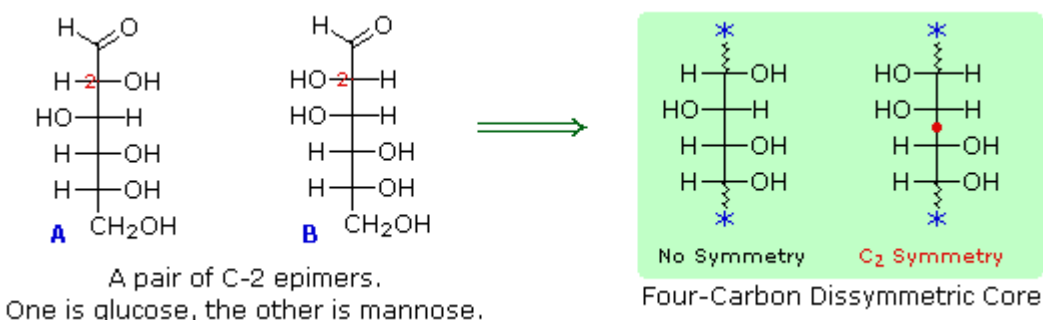


3.4.1 Summary of these reactions

1. Ribose and arabinose (two well known pentoses) both gave erythrose on Ruff degradation. As expected, Kiliani-Fischer synthesis applied to erythrose gave a mixture of ribose and arabinose.
2. Oxidation of erythrose gave an achiral (optically inactive) aldaric acid. This defines the configuration of erythrose.

3. Oxidation of ribose gave an achiral (optically inactive) aldaric acid. This defines the configuration of both ribose and arabinose.
4. Ruff shortening of glucose gave arabinose, and Kiliani-Fischer synthesis applied to arabinose gave a mixture of glucose and mannose.
5. Glucose and mannose are therefore epimers at C-2, a fact confirmed by the common product from their osazone reactions.
6. A pair of structures for these epimers can be written, but which is glucose and which is mannose?

In order to determine which of these epimers was glucose, Fischer made use of the inherent C_2 symmetry in the four-carbon dissymmetric core of one epimer (**B**). This is shown in the following diagram by a red dot where the symmetry axis passes through the projection formula. Because of this symmetry, if the aldehyde and 1° -alcohol functions at the ends of the chain are exchanged, epimer **B** would be unchanged; whereas **A** would be converted to a different compound.



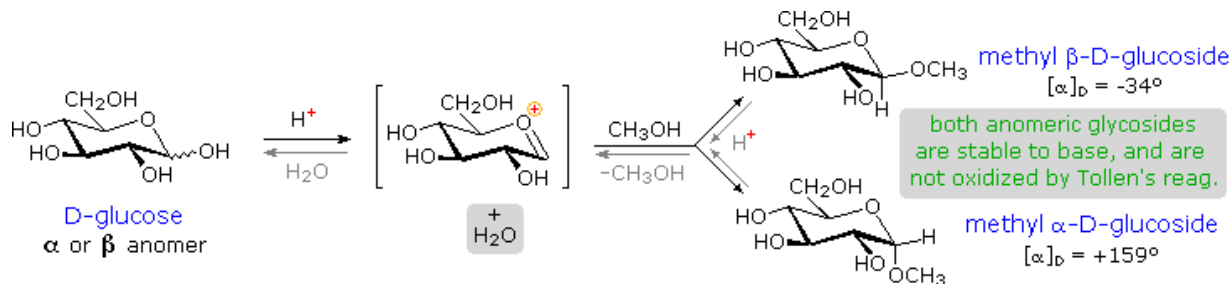
Fischer looked for and discovered a second aldohexose that represented the end group exchange for the epimer lacking the latent C_2 symmetry (**A**). This compound was L-(+)-gulose, and its exchange relationship to D-(+)-glucose was demonstrated by oxidation to a common aldaric acid product. The remaining epimer is therefore mannose.

3.5 Formation of Glycosides

Acetal derivatives formed when a monosaccharide reacts with an alcohol in the presence of an acid catalyst are called *glycosides*. This reaction is illustrated for glucose and methanol in the diagram below. In naming of glycosides, the "ose" suffix of the sugar name is replaced by "oside", and the alcohol group name is placed first. As is generally true for most acetals, glycoside formation involves the loss of an equivalent of water. The diether product is stable to base and alkaline oxidants such as Tollen's reagent. Since acid-catalyzed aldolization is reversible, glycosides may be hydrolyzed back to their alcohol and sugar components by aqueous acid.

The anomeric methyl glucosides are formed in an equilibrium ratio of 66% alpha to 34% beta. From the structures in the previous diagram, we see that pyranose rings prefer chair conformations in which the largest number of substituents are equatorial. In the case of glucose, the substituents on the beta-anomer are all equatorial, whereas the C-1 substituent in the alpha-anomer changes to axial. Since substituents on cyclohexane rings prefer an equatorial location

over axial (methoxycyclohexane is 75% equatorial), the preference for alpha-glycopyranoside formation is unexpected, and is referred to as the *anomeric effect*.



Glycosides abound in biological systems. By attaching a sugar moiety to a lipid or benzenoid structure, the solubility and other properties of the compound may be changed substantially. Because of the important modifying influence of such derivatization, numerous enzyme systems, known as glycosidases, have evolved for the attachment and removal of sugars from alcohols, phenols and amines. Chemists refer to the sugar component of natural glycosides as the *glycon* and the alcohol component as the *aglycon*.

Two examples of naturally occurring glycosides and one example of an amino derivative is presented. Salicin, one of the oldest herbal remedies known, was the model for the synthetic analgesic aspirin. A large class of hydroxylated, aromatic oxonium cations called *anthocyanins* provide the red, purple and blue colors of many flowers, fruits and some vegetables. Peonin is one example of this class of natural pigments, which exhibit pronounced pH color dependence. The oxonium moiety is only stable in acidic environments and the color changes or disappears when base is added. The complex changes that occur when wine is fermented and stored are in part associated with glycosides of anthocyanins. Finally, amino derivatives of ribose, such as cytidine play important roles in biological phosphorylating agents, coenzymes and information transport and storage materials.

4.0 Conclusion

Carbohydrates take part in a variety of chemical reactions as a function of their chemical properties. These reactions include oxidation, reduction, oxazone formation and glycoside formation. Examples of glycosides are salicin, anthocyanin and peonin.

5.0 Summary

In this unit, we have learnt that

- When the aldehyde function of an aldose is oxidized to a carboxylic acid the product is called an *aldonic acid*.
- If both ends of an aldose chain are oxidized to carboxylic acids the product is called an *aldaric acid*.
- Acetal derivatives formed when a monosaccharide reacts with an alcohol in the presence of an acid catalyst are called *glycosides*.

iv. The osazone reaction was developed and used by Emil Fischer to identify aldose sugars differing in configuration only at the alpha-carbon.

6.0 Tutor Marked Assignment

- Describe the formation of glycosides.
- Differentiate chemically between a reducing and non-reducing sugar.
- Write a general structure of the following; aldonic acid, aldaric acid and alditol.

7.0 Further reading

Nelson, D. L. and Cox, M. M. (2004): Lehninger Principles of Biochemistry, 4th edition. Freeman Publisher, USA.

Module 2: Monosaccharides

Unit 1: Structures of Monosaccharides

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1.0 Introduction

Monosaccharides are the simplest carbohydrates in that they cannot be [hydrolyzed](#) to smaller carbohydrates. They are aldehydes or ketones with two or more hydroxyl groups. The general [chemical formula](#) of an unmodified monosaccharide is $(C \cdot H_2O)_n$, literally a "carbon hydrate." Monosaccharides are important fuel molecules as well as building blocks for nucleic acids. The smallest monosaccharides, for which $n = 3$, are dihydroxyacetone and D- and L-glyceraldehyde.

2.0 Objective

At the end of this study, should be able to

- Know the classes of monosaccharide
- Understand the importance of monosaccharides
- Identify isomers and enantiomers of monosaccharides

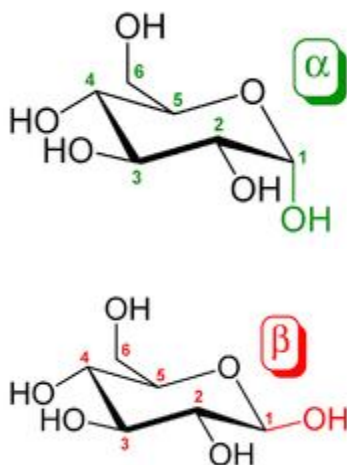
3.0 Classification of monosaccharides

Monosaccharides are classified according to three different characteristics:

- the placement of its [carbonyl](#) group
- the number of [carbon](#) atoms it contains
- its [chiral](#) handedness.

If the carbonyl group is an [aldehyde](#), the monosaccharide is an [aldose](#); if the carbonyl group is a [ketone](#), the monosaccharide is a [ketose](#). Monosaccharides with three carbon atoms are called [trioses](#), those with four are called [tetroses](#), five are called [pentoses](#), six are [hexoses](#), and so on. These two systems of classification are often combined. For example, [glucose](#) is an [aldohexose](#) (a six-carbon aldehyde), [ribose](#) is an [aldopentose](#) (a five-carbon aldehyde), and [fructose](#) is a [ketohexose](#) (a six-carbon ketone).

Each carbon atom bearing a [hydroxyl group](#) (-OH), with the exception of the first and last carbons, are [asymmetric](#), making them [stereocenters](#) with two possible configurations each (R or S). Because of this asymmetry, a number of [isomers](#) may exist for any given monosaccharide formula. The aldohexose D-glucose, for example, has the formula (C·H₂O)₆, of which all but two of its six carbons atoms are stereogenic, making D-glucose one of $2^4 = 16$ possible [stereoisomers](#). In the case of [glyceraldehyde](#), an aldotriose, there is one pair of possible stereoisomers, which are [enantiomers](#) and [epimers](#). [1,3-dihydroxyacetone](#), the ketose corresponding to the aldose glyceraldehyde, is a symmetric molecule with no stereocenters). The assignment of D or L is made according to the orientation of the asymmetric carbon furthest from the carbonyl group: in a standard Fischer projection if the hydroxyl group is on the right the molecule is a D sugar, otherwise it is an L sugar. The "D-" and "L-" prefixes should not be confused with "d-" or "l-", which indicate the direction that the sugar [rotates](#) plane [polarized light](#). This usage of "d-" and "l-" is no longer followed in carbohydrate chemistry.



The [α](#) and [β anomers](#) of glucose.

Note the position of the hydroxyl group (red or green) on the anomeric carbon relative to the CH₂OH group bound to carbon 5: they are either on the opposite sides (α), or the same side (β).

3.1 Ring-straight chain isomerism

The aldehyde or ketone group of a straight-chain monosaccharide will react reversibly with a hydroxyl group on a different carbon atom to form a [hemiacetal](#) or [hemiketal](#), forming a [heterocyclic](#) ring with an oxygen bridge between two carbon atoms. Rings with five and six atoms are called [furanose](#) and [pyranose](#) forms, respectively, and exist in equilibrium with the straight-chain form.

During the conversion from straight-chain form to the cyclic form, the carbon atom containing the carbonyl oxygen, called the [anomeric carbon](#), becomes a stereogenic center with two possible configurations: The oxygen atom may take a position either above or below the plane of the ring. The resulting possible pairs of stereoisomers are called [anomers](#). In the *α anomer*, the -OH

substituent on the anomeric carbon rests on the opposite side ([trans](#)) of the ring from the CH₂OH side branch. The alternative form, in which the CH₂OH substituent and the anomeric hydroxyl are on the same side (*cis*) of the plane of the ring, is called the β *anomer*. Because the ring and straight-chain forms readily interconvert, both anomers exist in [equilibrium](#). In a [Fischer Projection](#), the α anomer is represented with the anomeric hydroxyl group *trans* to the CH₂OH and *cis* in the β anomer.

Self Assessment Exercise I

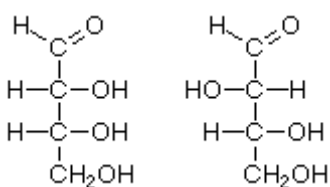
- i. With the aid of appropriate examples, define the following
 - (a) Aldopentose (b) Ketohexose (c) Aldotetrose
- ii. Distinguish between alpha and beta anomer

3.2 Monosaccharide classifications based on the number of carbons

Number of Carbons	Category Name	Examples
4	Tetrose	Erythrose, Threose
5	Pentose	Arabinose, Ribose, Ribulose, Xylose, Xylulose, Lyxose
6	Hexose	Allose, Altrose, Fructose, Galactose, Glucose, Gulose, Idose, Mannose, Sorbose, Talose, Tagatose
7	Heptose	Sedoheptulose, Mannoheptulose

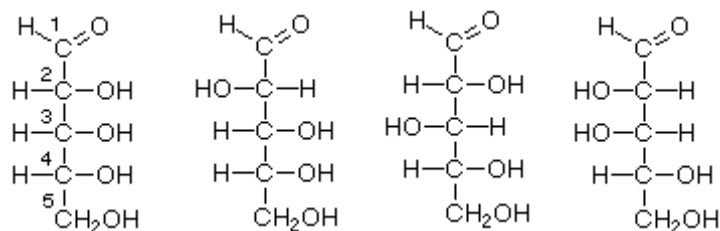
Many saccharide structures differ only in the orientation of the hydroxyl groups (**-OH**). This slight structural difference makes a big difference in the biochemical properties, organoleptic properties (e.g., taste), and in the physical properties such as melting point and Specific Rotation (how polarized light is distorted). A chain-form monosaccharide that has a carbonyl group (**C=O**) on an end carbon forming an aldehyde group (**-CHO**) is classified as an *aldose*. When the carbonyl group is on an inner atom forming a ketone, it is classified as a *ketose*.

Tetroses



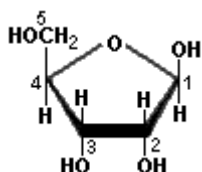
D-Erythrose D-Threose

Pentoses

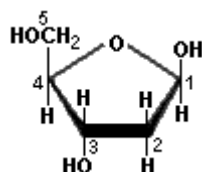


D-Ribose D-Arabinose D-Xylose D-Lyxose

The ring form of ribose is a component of ribonucleic acid (RNA). Deoxyribose, which is missing oxygen at position 2, is a component of deoxyribonucleic acid (DNA). In nucleic acids, the hydroxyl group attached to carbon number 1 is replaced with nucleotide bases.



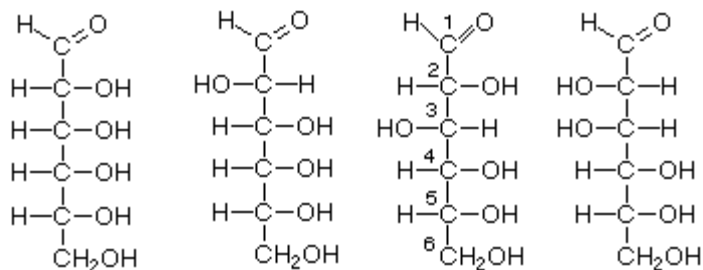
Ribose



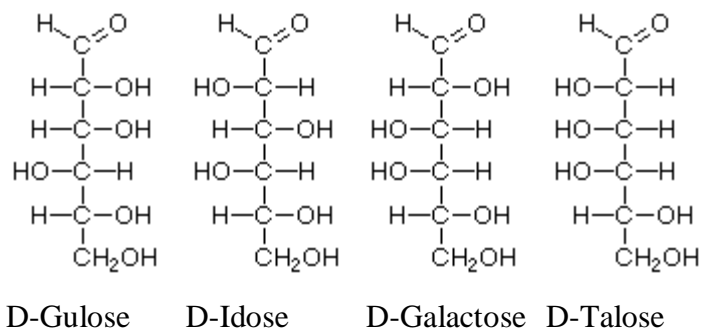
Deoxyribose

Hexoses

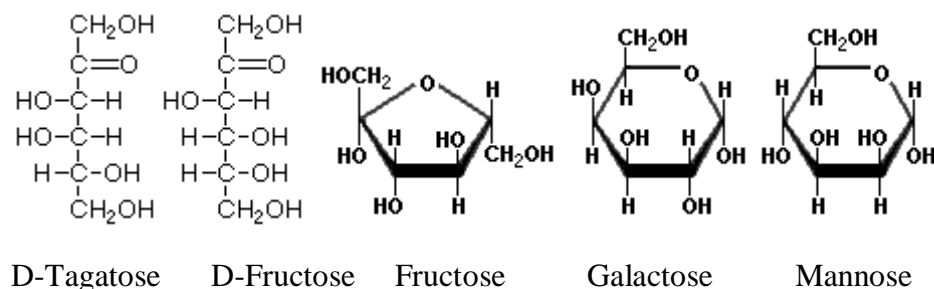
Hexoses, such as the ones illustrated here, have the molecular formula $\text{C}_6\text{H}_{12}\text{O}_6$. [German chemist Emil Fischer](#) (1852-1919) identified the stereoisomers for these aldohexoses in 1894. He received the 1902 Nobel Prize for chemistry for his work.



D-Allose D-Altrose D-Glucose D-Mannose

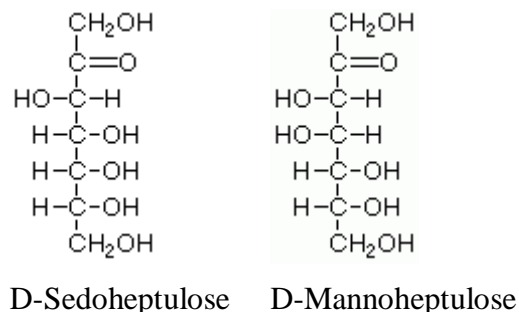


that have opposite configurations of a hydroxyl group at only one position, such as glucose and mannose, are called *epimers*. *Glucose*, also called *dextrose*, is the most widely distributed sugar in the plant and animal kingdoms and it is the sugar present in blood as "blood sugar". The chain form of glucose is a polyhydric aldehyde, meaning that it has multiple hydroxyl groups and an aldehyde group. Fructose, also called levulose or "fruit sugar", is shown here in the chain and ring forms. Fructose and glucose are the main carbohydrate constituents of honey.



Heptoses

Sedoheptulose has the same structure as fructose, but it has one extra carbon. Sedoheptulose is found in carrots. Mannoheptulose is a monosaccharide found in avocados.



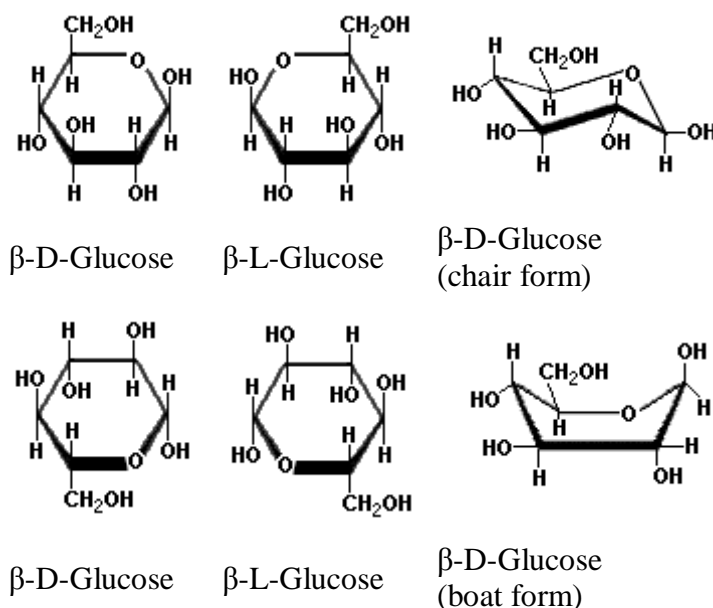
3.3 Chain and Ring Structure

Many simple sugars can exist in a chain form or a ring form, as illustrated by the hexoses above. The ring form is favored in aqueous solutions, and the mechanism of ring formation is similar for most sugars. The *glucose* ring form is created when the oxygen on carbon number 5 links with the carbon comprising the carbonyl group (carbon number 1) and transfers its hydrogen to the carbonyl oxygen to create a hydroxyl group. The rearrangement produces *alpha* glucose when the hydroxyl group is on the opposite side of the **-CH₂OH** group, or *beta* glucose when the

hydroxyl group is on the same side as the **-CH₂OH** group. Isomers, such as these, which differ only in their configuration about their carbonyl carbon atom are called *anomers*. The little D in the name derives from the fact that natural glucose is *dextrorotary*, i.e., it rotates polarized light to the right, but it now denotes a specific configuration. Monosaccharides forming a five-sided ring, like ribose, are called *furanoses*. Those forming six-sided rings, like glucose, are called *pyranoses*.

3.4 Stereochemistry

Saccharides with identical functional groups but with different spatial configurations have different chemical and biological properties. Stereochemistry is the study of the arrangement of atoms in three-dimensional space. Stereoisomers are compounds in which the atoms are linked in the same order but differ in their spatial arrangement. Compounds that are mirror images of each other but are not identical, comparable to left and right shoes, are called *enantiomers*. The following structures illustrate the difference between β -D-Glucose and β -L-Glucose. Identical molecules can be made to correspond to each other by flipping and rotating. However, enantiomers cannot be made to correspond to their mirror images by flipping and rotating. Glucose is sometimes illustrated as a "chair form" because it is a more accurate representation of the bond angles of the molecule. The "boat" form of glucose is unstable.



3.5 Monosaccharides in living organisms

Monosaccharides are the major source of fuel for [metabolism](#), being used both as an energy source (glucose being the most important in nature) and in [biosynthesis](#). When monosaccharides are not immediately needed by many cells they are often converted to more space-efficient forms, often [polysaccharides](#). In many animals, including humans, this storage form is [glycogen](#), especially in liver and muscle cells. In plants, [starch](#) is used for the same purpose.

4.0 Conclusion

Monosaccharides are classified according to three different characteristics; the placement of its [carbonyl](#) group, the number of [carbon](#) atoms it contains and its [chiral](#) handedness. Stereochemistry is the study of the arrangement of atoms in three-dimensional space. Stereoisomers are compounds in which the atoms are linked in the same order but differ in their spatial arrangement

5.0 Summary

In this chapter, we have learnt that

- i. Monosaccharides are majorly classified into tetroses, pentoses, hexoses and heptoses
- ii. A chain-form monosaccharide that has a carbonyl group ($\text{C}=\text{O}$) on an end carbon forming an aldehyde group ($-\text{CHO}$) is classified as an *aldose*. When the carbonyl group is on an inner atom forming a ketone, it is classified as a *ketose*.

6.0 Tutor marked Assignment

- i. Outline the classification of monosaccharides based on the number of carbon atoms.
- ii. Write the structures of ten named examples of hexoses
- iii. Describe stereochemistry

7.0 Further reading

Nelson, D. L. and Cox, M. M. (2004): Lehninger Principles of Biochemistry, 4th edition., Freeman Publisher, USA.

Module 2: Monosaccharides

Unit 2: Derivatives of Monosaccharides

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1.0 Introduction

The reactions of monosaccharides yield many important derivatives which ranges from sugar alcohols, amino sugars and uronic acids. These derivatives serve as important components of many organisms and biologically important substances.

2.0 Objective

At the end of this study, students should be able to

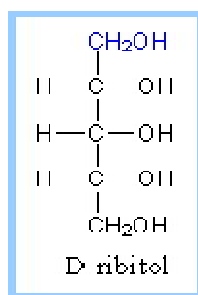
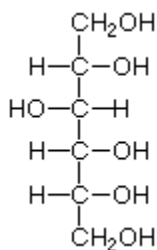
- Know the derivatives of monosaccharides
- Give examples of all the derivatives of monosaccharides
- Understand the reactions involving monosaccharides

3.0 Types of Sugar derivatives

Sugars may be modified by natural or laboratory processes into compounds that retain the basic configuration of saccharides, but have different functional groups.

3.1 Sugar alcohols

Sugar alcohols, also known as polyols, polyhydric alcohols, or polyalcohols, are the hydrogenated forms of the aldoses or ketoses. For example, glucitol, also known as sorbitol, has the same linear structure as the chain form of glucose, but the aldehyde (-CHO) group is replaced with a -CH₂OH group. Other common sugar alcohols include the monosaccharides erythritol and xylitol and the disaccharides lactitol and maltitol. Sugar alcohols have about half the calories of sugars and are frequently used in low-calorie or "sugar-free" products.



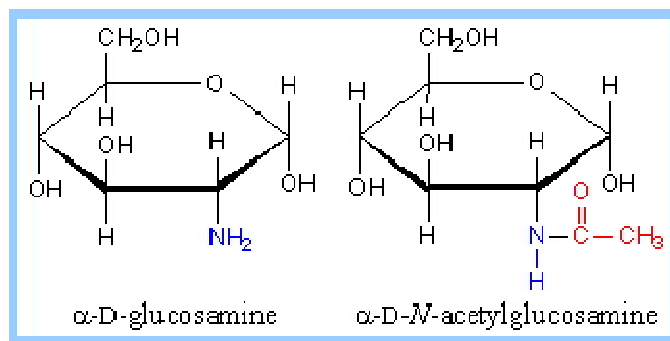
Glucitol or sorbitol

Xylitol, which has the hydroxyl groups oriented like xylose, is a very common ingredient in "sugar-free" candies and gums because it is approximately as sweet as sucrose, but contains 40%

less food energy. Although this sugar alcohol appears to be safe for humans, xylitol in relatively small doses can cause seizures, liver failure, and death in dogs.

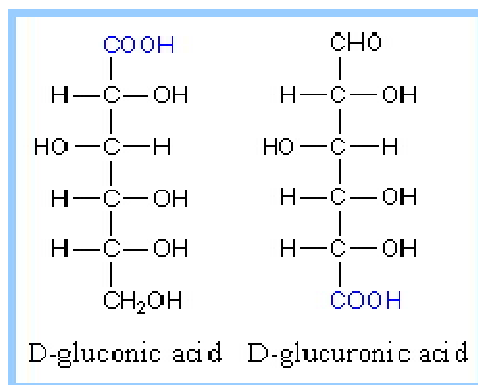
3.2 Amino sugars

Amino sugars or aminosaccharides replace a hydroxyl group with an amino ($-\text{NH}_2$) group. Glucosamine is an amino sugar used to treat cartilage damage and reduce the pain and progression of arthritis.



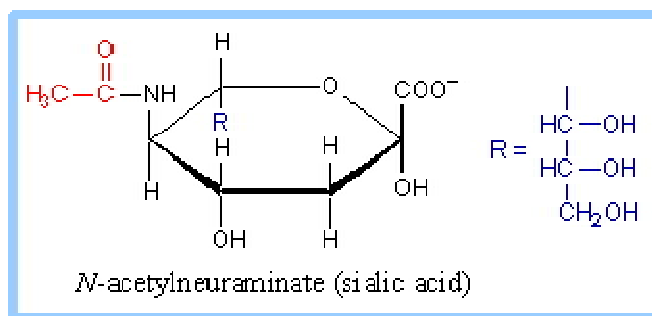
3.3 Uronic acids

Uronic acids have a carboxyl group ($-\text{COOH}$) on the carbon that is important part of the ring. The aldehyde at C1, or the hydroxyl on the terminal carbon, is oxidized to a carboxylic acid. Their names retain the root of the monosaccharides, but the *-ose* sugar suffix is changed to *-uronic acid*. For example, galacturonic acid has the same configuration as galactose, and the structure of glucuronic acid corresponds to glucose.



3.4 N-acetylneuraminic acid

N-acetylneuramate, (N-acetylneuraminic acid, also called sialic acid) is often found as a terminal residue of oligosaccharide chains of glycoproteins. Sialic acid imparts negative charge to glycoproteins, because its carboxyl group tends to dissociate a proton at physiological pH, as shown here.

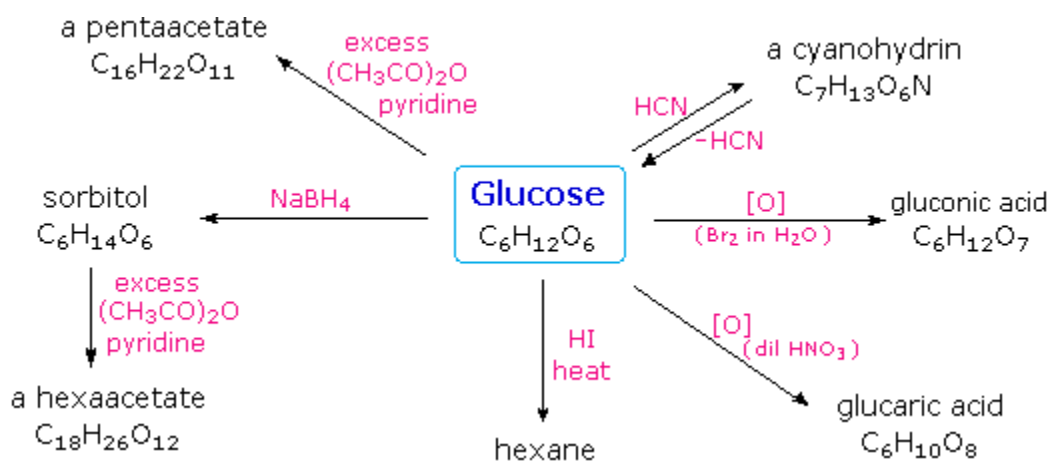


Self Assessment Exercise I

- How are sugar alcohols and amino sugars formed?
- Distinguish between gluconic and glucuronic acids.

3.5 Reactions of Monosaccharides

Carbohydrates have been given non-systematic names, although the suffix **ose** is generally used. The most common carbohydrate is *glucose* ($C_6H_{12}O_6$). Applying the terms defined above, glucose is a monosaccharide, an aldohexose (note that the function and size classifications are combined in one word) and a reducing sugar. The general structure of glucose and many other aldohexoses was established by simple chemical reactions. The following diagram illustrates the kind of evidence considered, although some of the reagents shown here are different from those used by the original scientists.



Hot hydriodic acid (HI) was often used to reductively remove oxygen functional groups from a molecule, and in the case of glucose this treatment gave hexane (in low yield). From this it was concluded that the six carbons are in an unbranched chain. The presence of an aldehyde carbonyl group was deduced from cyanohydrin formation, its reduction to the hexa-alcohol sorbitol, also called glucitol, and mild oxidation to the mono-carboxylic acid, glucuronic acid. Somewhat

stronger oxidation by dilute nitric acid gave the diacid, glucaric acid, supporting the proposal of a six-carbon chain. The five oxygens remaining in glucose after the aldehyde was accounted for were thought to be in hydroxyl groups, since a penta-acetate derivative could be made. These hydroxyl groups were assigned, one each, to the last five carbon atoms, because [geminal hydroxyl groups](#) are normally unstable relative to the carbonyl compound formed by loss of water. By clicking on the above diagram, it will change to display the suggested products and the gross structure of glucose. The four middle carbon atoms in the glucose chain are centers of chirality and are colored red. Glucose and other saccharides are extensively cleaved by periodic acid, thanks to the abundance of [vicinal diol moieties](#) in their structure. This oxidative cleavage, known as the *Malaprade reaction* is particularly useful for the analysis of selective O-substituted derivatives of saccharides, since ether functions do not react. The stoichiometry of aldohexose cleavage is shown in the following equation.

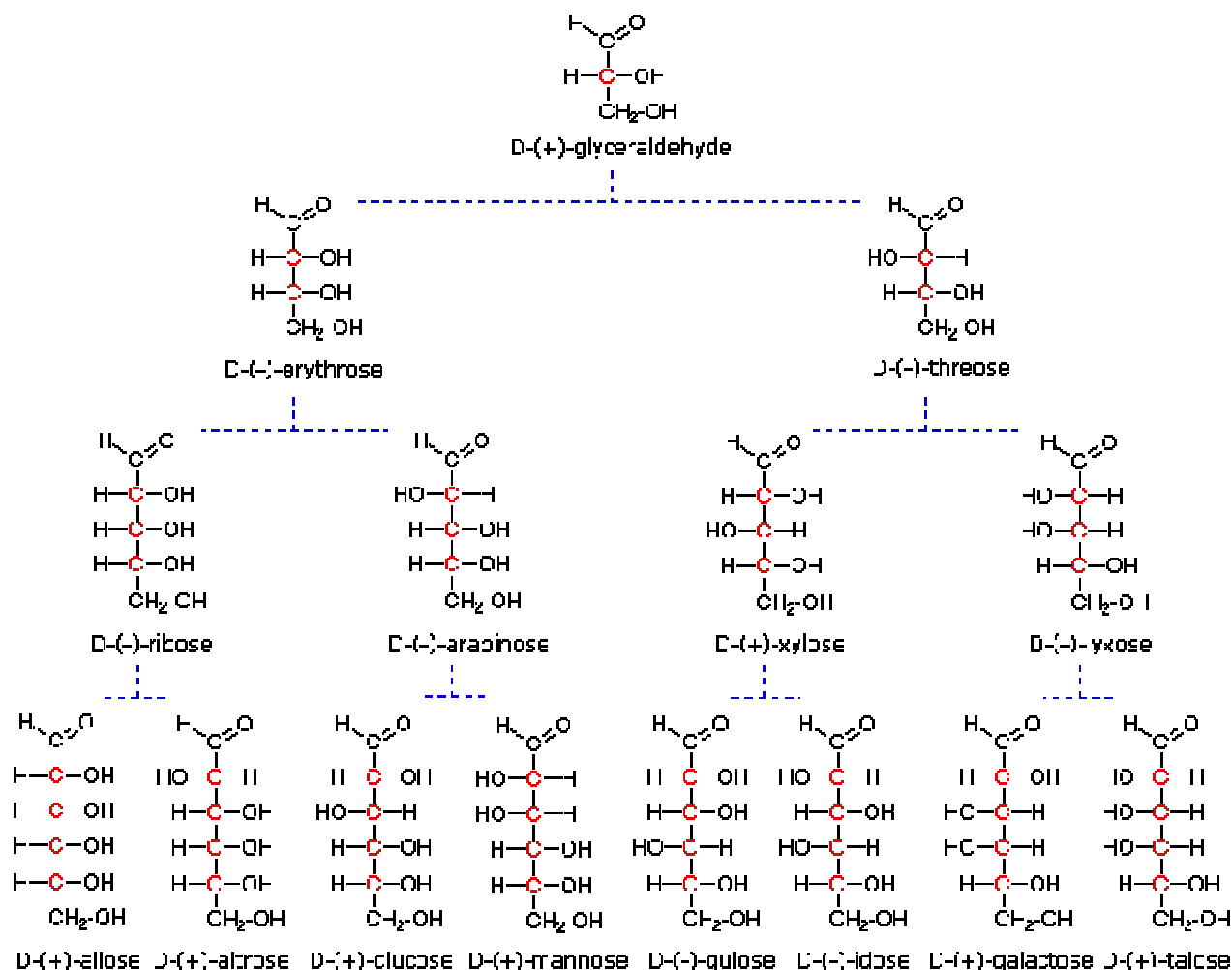


3.6 The Configuration of Glucose

The four chiral centers in glucose indicate there may be as many as sixteen (2^4) stereoisomers having this constitution. These would exist as eight [diastereomeric](#) pairs of enantiomers, and the initial challenge was to determine which of the eight corresponded to glucose. This challenge was accepted and met in 1891 by the German chemist [Emil Fischer](#). His successful negotiation of the stereochemical maze presented by the aldohexoses was a logical tour de force, and it is fitting that he received the 1902 Nobel Prize for chemistry for this accomplishment. One of the first tasks faced by Fischer was to devise a method of representing the configuration of each chiral center in an unambiguous manner. To this end, he invented a simple technique for drawing chains of chiral centers, that we now call the [Fischer projection formula](#). At the time Fischer undertook the glucose project it was not possible to establish the absolute configuration of an enantiomer. Consequently, Fischer made an arbitrary choice for (+)-glucose and established a network of related aldose configurations that he called the **D-family**. The mirror images of these configurations were then designated the **L-family** of aldoses. To illustrate using present day knowledge, Fischer projection formulas and names for the D-aldose family (three to six-carbon atoms) are shown below, with the asymmetric carbon atoms (chiral centers) colored red. The last chiral center in an aldose chain (farthest from the aldehyde group) was chosen by Fischer as the D / L designator site. If the hydroxyl group in the projection formula pointed to the right, it was defined as a member of the D-family. A left directed hydroxyl group (the mirror image) then represented the L-family.

Fischer's initial assignment of the D-configuration had a 50:50 chance of being right, but all his subsequent conclusions concerning the relative configurations of various aldoses were soundly based. In 1951 x-ray fluorescence studies of [\(+\)-tartaric acid](#), carried out in the Netherlands by Johannes Martin Bijvoet (pronounced "buy foot"), proved that Fischer's choice was correct. It is important to recognize that the sign of a compound's [specific rotation](#) (an experimental number) does not correlate with its configuration (D or L). It is a simple matter to measure an optical

rotation with a polarimeter. Determining an absolute configuration usually requires chemical interconversion with known compounds by stereo specific reaction paths.



4.0 Conclusion

Sugars may be modified by natural or laboratory processes into compounds that retain the basic configuration of saccharides, but have different functional groups. Numerous examples of derivatives of monosaccharides include xylitol, sorbitol, gluconic acid, acetylglucosamine and N-acetylneuraminic acid.

5.0 Summary

In this chapter, we have learnt that

- i. Monosaccharides has many important derivatives.
- ii. Sugar acids, amino sugars and uronic acids are some classes of sugar derivatives.
- iii. Glucose, the simplest and commonest example of monosaccharides, take part in many chemical reactions to produce derivatives.

6.0 Tutor marked Assignment

- i. Using appropriate examples, account for the derivatives of monosaccharides.
- ii. Write the scheme of reactions of glucose to produce various derivatives.
- iii. What is the biological importance of acetylglucosamine and N-acetylneuraminic acid.

7.0 Further reading

Nelson, D. L. and Cox, M. M. (2004): Lehninger Principles of Biochemistry, 4th edition., Freeman Publisher, USA.

Module 3: Disaccharides

Unit 1: Diversity of Disaccharides

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1.0 Introduction

Two joined monosaccharides are called a [disaccharide](#) and these are the simplest polysaccharides. Examples include [sucrose](#) and [lactose](#). They are composed of two monosaccharide units bound together by a [covalent](#) bond known as a [glycosidic linkage](#) formed via a [dehydration reaction](#), resulting in the loss of a [hydrogen](#) atom from one monosaccharide and a [hydroxyl group](#) from the other. The [formula](#) of unmodified disaccharides is $C_{12}H_{22}O_{11}$. Although there are numerous kinds of disaccharides, a handful of disaccharides are particularly notable.

2.0 Objectives

At the end of this exercise, students should be able to

- Know the constituents of all disaccharides
- Write the structures of most disaccharides
- Compare and contrast among disaccharides

3.0 Composition of Disaccharides

Disaccharides are made up of two monosaccharides. An illustration of this is shown in the table below.

Disaccharide	Description	Component monosaccharides
sucrose	common table sugar	glucose 1 α →2 fructose
maltose	product of starch hydrolysis	glucose 1 α →4 glucose
trehalose	found in fungi	glucose 1 α →1 glucose
lactose	main sugar in milk	galactose 1 β →4 glucose
melibiose	found in legumes	galactose 1 α →6 glucose

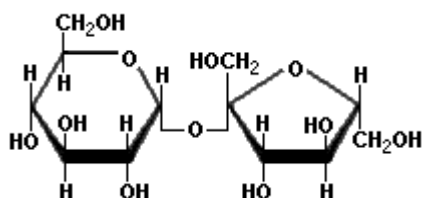
3.1 Sucrose

Sucrose, also called saccharose, is common table sugar refined from sugar cane or sugar beets. It is the main ingredient in turbinado sugar, evaporated or dried cane juice, brown sugar, and confectioner's sugar. [Sucrose](#) is the most abundant disaccharide, and the main form in which carbohydrates are transported in [plants](#). It is composed of one [D-glucose](#) molecule and one [D-fructose](#) molecule. The [systematic name](#) for sucrose, *O*- α -D-glucopyranosyl-(1→2)-D-fructofuranoside, indicates four things:

- Its monosaccharides: glucose and fructose
- Their ring types: glucose is a [pyranose](#), and fructose is a [furanose](#)

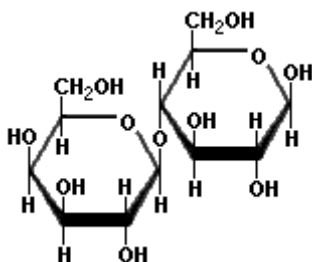
- How they are linked together: the oxygen on carbon number 1 (C1) of α -D-glucose is linked to the C2 of D-fructose.
- The *-oside* suffix indicates that the [anomeric carbon](#) of both monosaccharides participates in the glycosidic bond.

It has a glycosidic bond linking the anomeric hydroxyls of glucose and fructose. Because the configuration at the anomeric carbon of glucose is α (O points down from the ring), the linkage is designated α (1 \rightarrow 2).



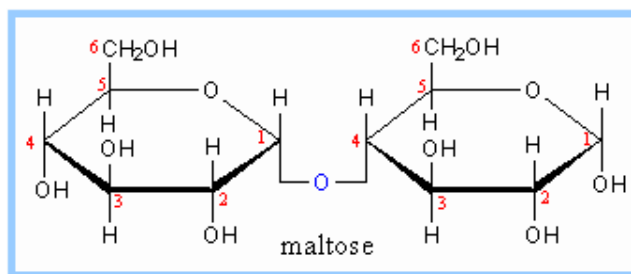
3.2 Lactose

Lactose has a molecular structure consisting of galactose and glucose with β (1 \rightarrow 4) linkage from the anomeric hydroxyl of galactose. Its full name is β -D-galactopyranosyl-(1 \rightarrow 4)- β -D-glucopyranose. It occurs naturally in mammalian milk. It is of interest because it is associated with *lactose intolerance* which is the intestinal distress caused by a deficiency of lactase, an intestinal enzyme needed to absorb and digest lactose in milk. Undigested lactose ferments in the colon and causes abdominal pain, bloating, gas, and diarrhea. Yogurt does not cause these problems because lactose is consumed by the bacteria that transform milk into yogurt.



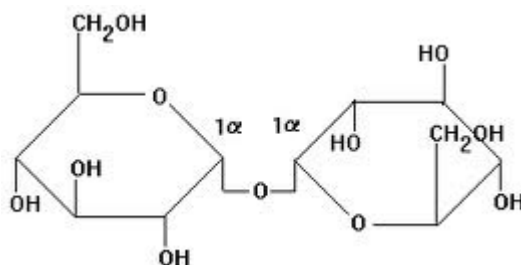
3.3 Maltose

Maltose consists of two α -D-glucose molecules with the alpha bond at carbon 1 of one molecule attached to the oxygen at carbon 4 of the second molecule. This is called a $1\alpha\rightarrow 4$ glycosidic linkage. It is a disaccharide with an α (1 \rightarrow 4) glycosidic linkage between the C1 hydroxyl of one glucose and the C4 hydroxyl of a second glucose. Maltose is the β -anomer, because the O at C1 points down from the ring.



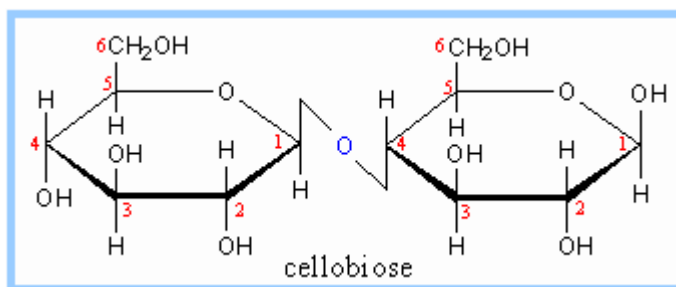
3.4 Trehalose

Trehalose has two α -D-glucose molecules connected through carbon number one in a $1\alpha \rightarrow 1$ linkage. It is also known as mycose or tremalose, is a natural alpha-linked [disaccharide](#) formed by an α, α -1,1-glucoside bond between two α -glucose units. Trehalose is a [nonreducing sugar](#) formed from two glucose units joined by a 1-1 alpha bond, giving it the name of α -D-glucopyranosyl-(1 \rightarrow 1)- α -D-glucopyranoside. The bonding makes trehalose very resistant to acid [hydrolysis](#), and therefore is stable in solution at high temperatures, even under acidic conditions.



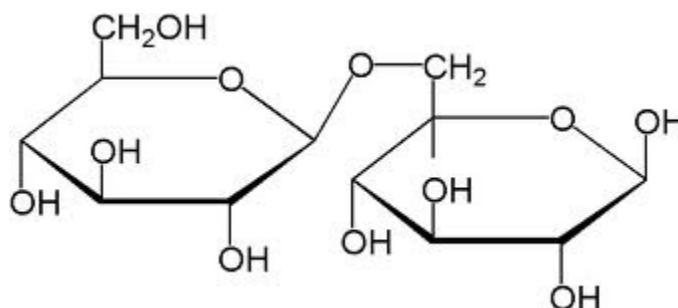
3.5 Cellobiose

Cellobiose is a disaccharide consisting of two β -D-glucose molecules that have a $1\beta \rightarrow 4$ linkage as in cellulose. It is a product of cellulose breakdown. The configuration at the anomeric C1 is β (O points up from the ring). The β (1 \rightarrow 4) glycosidic linkage is represented as a "zig-zag" line, but one glucose residue is actually flipped over relative to the other. Cellobiose has no taste, whereas maltose and trehalose are about one-third as sweet as sucrose.



3.6 Gentiobiose

Gentiobiose is a [disaccharide](#) composed of two units of [D-glucose](#) joined with a $\beta(1\rightarrow6)$ linkage. It is a white crystalline solid that is soluble in water or hot [methanol](#). Gentiobiose is incorporated into the chemical structure of [crocin](#), the chemical compound that gives [saffron](#) its color. It is a product of the [caramelization](#) of [glucose](#) and its systematic name is 6-O- β -D-Glucopyranosyl-D-glucose



Self Assessment Exercise

- Draw the structure of maltose
- Give the structural difference between maltose, cellobiose, trehalos and gentiobiose
- Describe the structure of sucrose

4.0 Reducing and Non-reducing Disaccharides

When the alcohol component of a glycoside is provided by a hydroxyl function on another monosaccharide, the compound is called a *disaccharide*. Acid-catalyzed hydrolysis of these disaccharides yields glucose as the only product. Enzyme-catalyzed hydrolysis is selective for a specific glycoside bond, so an alpha-glycosidase cleaves maltose and trehalose to glucose, but

does not cleave cellobiose or gentiobiose. A beta-glycosidase has the opposite activity. In order to draw a representative structure for cellobiose, one of the glucopyranose rings must be rotated by 180°, but this feature is often omitted in favor of retaining the usual perspective for the individual rings. The bonding between the glucopyranose rings in cellobiose and maltose is from the anomeric carbon in ring A to the C-4 hydroxyl group on ring B. This leaves the anomeric carbon in ring B free, so cellobiose and maltose both may assume alpha and beta anomers at that site. Gentiobiose has a beta-glycoside link, originating at C-1 in ring A and terminating at C-6 in ring B. Its alpha-anomer is drawn in the diagram. Because cellobiose, maltose and gentiobiose are hemiacetals they are all reducing sugars (oxidized by Tollen's reagent). Trehalose, a disaccharide found in certain mushrooms, is a bis-acetal, and is therefore a non-reducing sugar. A systematic nomenclature for disaccharides exists, but as the following examples illustrate, these are often lengthy.

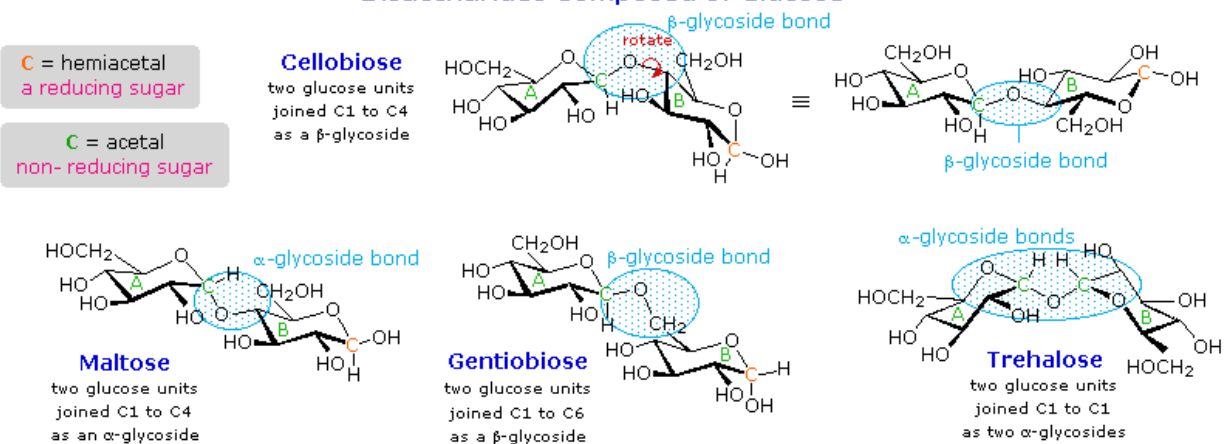
Cellobiose: 4-O- β -D-Glucopyranosyl-D-glucose

Maltose: 4-O- α -D-Glucopyranosyl-D-glucose

Gentiobiose: 6-O- β -D-Glucopyranosyl-D-glucose

Trehalose: α -D-Glucopyranosyl- α -D-glucopyranoside

Disaccharides Composed of Glucose



4.1 Comparison of Disaccharides

Although all the disaccharides are made up of two glucopyranose rings, their properties differ in interesting ways. Maltose, sometimes called malt sugar, comes from the hydrolysis of starch. It is about one third as sweet as cane sugar (sucrose), is easily digested by humans, and is fermented by yeast. Cellobiose is obtained by the hydrolysis of cellulose. It has virtually no taste, is indigestible by humans, and is not fermented by yeast. Some bacteria have beta-glucosidase enzymes that hydrolyze the glycosidic bonds in cellobiose and cellulose. The presence of such bacteria in the digestive tracts of cows and termites permits these animals to use cellulose as a food. Finally, it may be noted that trehalose has a distinctly sweet taste, but gentiobiose is bitter.

Disaccharides made up of other sugars are known, but glucose is often one of the components. Lactose, also known as milk sugar, is a galactose-glucose compound joined as a beta-glycoside. It is a reducing sugar because of the hemiacetal function remaining in the glucose moiety. Many adults, particularly those from regions where milk is not a dietary staple, have a metabolic intolerance for lactose. Infants have a digestive enzyme which cleaves the beta-glycoside bond in lactose, but production of this enzyme stops with weaning. Cheese is less subject to the lactose intolerance problem, since most of the lactose is removed with the whey. Sucrose, or cane sugar, is our most commonly used sweetening agent. It is a non-reducing disaccharide composed of glucose and fructose joined at the anomeric carbon of each by glycoside bonds (one alpha and one beta).

5.0 Conclusion

Disaccharides are carbohydrates consisting of two monosaccharide units. They include maltose, lactose, sucrose, trehalose and cellobiose. They occur generally in nature such in milk (lactose), table sugar (sucrose) and malt sugar (maltose).

6.0 Summary

In this chapter, we have learnt that

- i. Disaccharides occur naturally and are diverse.
- ii. Examples of disaccharides include maltose, sucrose, lactose and cellobiose.
- iii. Glucose is a component of most disaccharides.

7.0 Tutor-marked Assignment

- i. What are Disaccharides?
- ii. Give five examples of disaccharides and state the composition of each.
- iii. Write the structures of sucrose, trehalose and maltose.

8.0 Further reading

Nelson, D. L. and Cox, M. M. (2004): Lehninger Principles of Biochemistry, 4th edition., Freeman Publisher, USA.

Module 4: Polysaccharides

Unit 1: Homopolysaccharides

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1.0 Introduction

Polysaccharides are large high-molecular weight molecules constructed by joining monosaccharide units together by glycosidic bonds. They are sometimes called *glycans*. The most important compounds in this class, cellulose, starch and glycogen are all polymers of glucose. This is easily demonstrated by acid-catalyzed hydrolysis to the monosaccharide.

2.0 Objectives

At the end of this unit, students should be able to

- i. understand the term homopolysaccharides
- ii. State in specific terms examples of homopolysaccharides
- iii. write structures of some homopolysaccharides

3.0 Homopolysaccharides

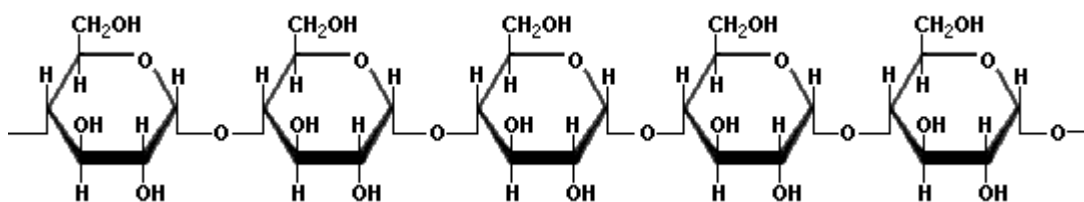
These are polysaccharides that consist of a single type of monosaccharides in their structures. Examples include starch, glycogen and cellulose.

3.1 Starch

Starches are carbohydrates in which 300 to 1000 glucose units join together. It is a polysaccharide which plants use to store energy for later use. Starch forms in grains with an insoluble outer layer which remain in the cell where it is formed until the energy is needed. Then it can be broken down into soluble glucose units. Starches are smaller than cellulose units, and can be more readily used for energy. In animals, the equivalent of starches is glycogen, which can be stored in the muscles or in the liver for later use. Foods such as potatoes, rice, corn and wheat contain starch granules which are important energy sources for humans. The human digestive process breaks down the starches into glucose units with the aid of enzymes, and those glucose molecules can circulate in the blood stream as an energy source.

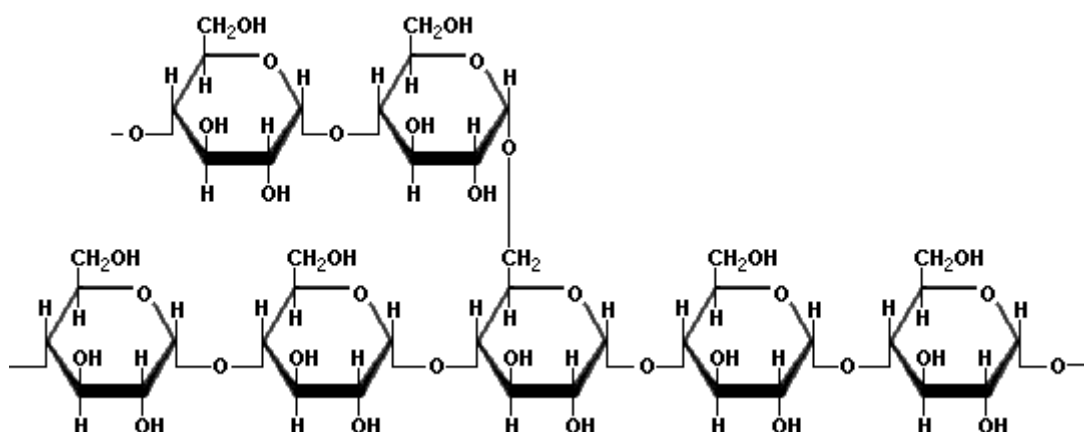
Starch is the major form of stored carbohydrate in plants. Starch is composed of a mixture of two substances: *amylose*, an essentially linear polysaccharide, and *amylopectin*, a highly branched polysaccharide. Both forms of starch are polymers of α -D-Glucose. Natural starches contain 10-20% amylose and 80-90% amylopectin. Amylose forms a colloidal dispersion in hot water (which helps to thicken gravies) whereas amylopectin is completely insoluble. Most animals, including humans, depend on these plant starches for nourishment. The structure of starch is more complex than that of cellulose. The intact granules are insoluble in cold water, but grinding or swelling them in warm water causes them to burst.

Amylose molecules consist typically of 200 to 20,000 glucose units which form a helix as a result of the bond angles between the glucose units. Molecules of amylose are linear chains of several thousand glucose units joined by alpha C-1 to C-4 glycoside bonds. Amylose solutions are actually dispersions of hydrated helical micelles.



Amylose

Amylopectin differs from amylose in being highly branched. Short side chains of about 30 glucose units are attached with $1\alpha \rightarrow 6$ linkages approximately every twenty to thirty glucose units along the chain. Amylopectin molecules may contain up to two million glucose units. Molecules of amylopectin are branched networks built from C-1 to C-4 and C-1 to C-6 glycoside links, and are essentially water insoluble.



Amylopectin

Starches are transformed into many commercial products by hydrolysis using acids or enzymes as catalysts. Hydrolysis is a chemical reaction in which water is used to break long polysaccharide chains into smaller chains or into simple carbohydrates. The resulting products are assigned a Dextrose Equivalent (DE) value which is related to the degree of hydrolysis. A DE value of 100 corresponds to completely hydrolyzed starch, which is pure glucose (dextrose).

Dextrins are a group of low-molecular-weight carbohydrates produced by the hydrolysis of starch. Dextrins are mixtures of polymers of D-glucose units linked by $1\alpha \rightarrow 4$ or $1\alpha \rightarrow 6$ glycosidic bonds.

Maltodextrin is partially hydrolyzed starch that is not sweet and has a DE value less than 20. Syrups, such as corn syrup made from corn starch, have DE values from 20 to 91. Commercial dextrose has DE values from 92 to 99.

Corn syrup solids, which may be labeled as soluble corn fiber or resistant maltodextrin, are mildly sweet semi-crystalline or powdery amorphous products with DEs from 20 to 36 made by drying corn syrup in a vacuum or in spray driers. Resistant maltodextrin or soluble corn fiber are not broken down in the digestive system, but they are partially fermented by colonic bacteria thus providing only 2 Calories per gram instead of the 4 Calories per gram in corn syrup.

High Fructose Corn Syrup (HFCS), commonly used to sweeten soft drinks, is made by treating corn syrup with enzymes to convert a portion of the glucose into fructose. Commercial HFCS contains from 42% to 55% fructose, with the remaining percentage being mainly glucose.

Modified starch is starch that has been changed by mechanical processes or chemical treatments to stabilize starch gels made with hot water. Without modification, gelled starch-water mixtures lose viscosity or become rubbery after a few hours.

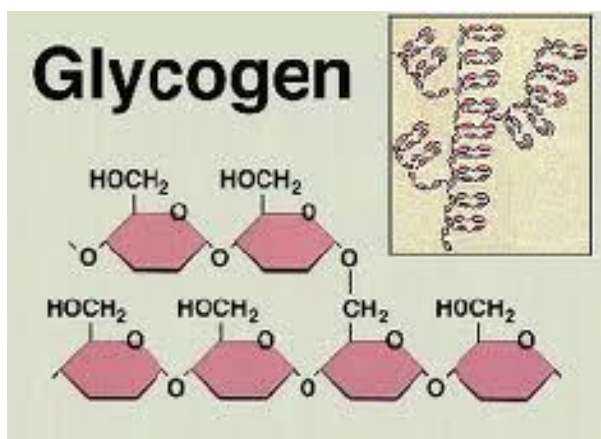
Hydrogenated glucose syrup (HGS) is produced by hydrolyzing starch, and then hydrogenating the resulting syrup to produce sugar alcohols like maltitol and sorbitol, along with hydrogenated oligo- and polysaccharides.

Polydextrose (poly-D-glucose) is a synthetic, highly-branched polymer with many types of glycosidic linkages created by heating dextrose with an acid catalyst and purifying the resulting water-soluble polymer. Polydextrose is used as a bulking agent because it is tasteless and is similar to fiber in terms of its resistance to digestion. The name resistant starch is applied to dietary starch that is not degraded in the stomach and small intestine, but is fermented by microflora in the large intestine.

3.2 Glycogen

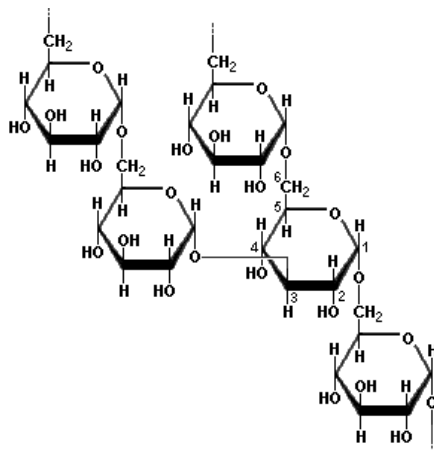
Glucose is stored as glycogen in animal tissues by the process of glycogenesis. When glucose cannot be stored as glycogen or used immediately for energy, it is converted to fat. Glycogen is a polymer of α -D-Glucose identical to amylopectin, but the branches in glycogen tend to be shorter (about 13 glucose units) and more frequent. The glucose chains are organized globularly like branches of a tree originating from a pair of molecules of *glycogenin*, a protein with a molecular weight of 38,000 that acts as a primer at the core of the structure. Glycogen is easily converted back to glucose to provide energy.

Glycogen is the glucose storage polymer used by animals. It has a structure similar to amylopectin, but is even more highly branched (about every tenth glucose unit). The degree of branching in these polysaccharides may be measured by enzymatic or chemical analysis.



3.3 Dextran

Dextran is a polysaccharide similar to amylopectin, but the main chains are formed by 1α→6 glycosidic linkages and the side branches are attached by 1α→3 or 1α→4 linkages. Dextran is an oral bacterial product that adheres to the teeth, creating a film called plaque. It is also used commercially in confections, in lacquers, as food additives, and as plasma volume expanders.



Dextran

Self Assessment Exercise

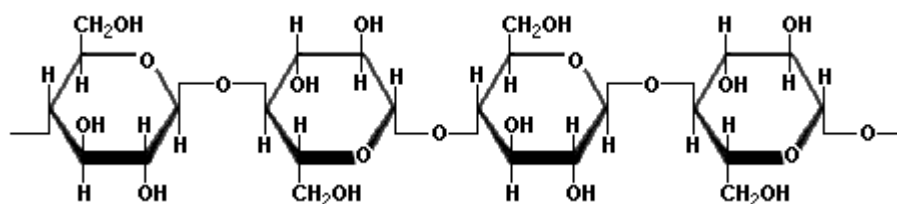
- Describe the composition of starch
- Distinguish between glycogen and dextran

3.4 Cellulose

Cellulose is a polymer of β-D-Glucose, which in contrast to starch, is oriented with -CH₂OH groups alternating above and below the plane of the cellulose molecule thus producing long, unbranched chains. The absence of side chains allows cellulose molecules to lie close together and form rigid structures. Cellulose is the major structural material of plants. Wood is largely cellulose, and cotton is almost pure cellulose. Cellulose can be hydrolyzed to its constituent

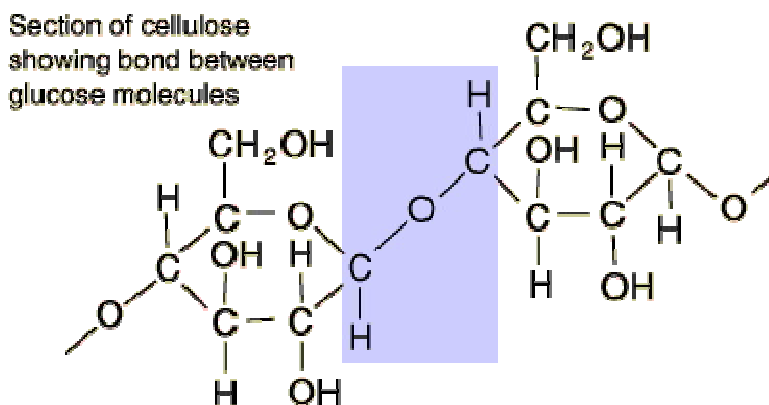
glucose units by microorganisms that inhabit the digestive tract of termites and ruminants. Cellulose may be modified in the laboratory by treating it with nitric acid (HNO_3) to replace all the hydroxyl groups with nitrate groups ($-\text{ONO}_2$) to produce cellulose nitrate (nitrocellulose or guncotton) which is an explosive component of smokeless powder. Partially nitrated cellulose, known as pyroxylin, is used in the manufacture of collodion, plastics, lacquers, and nail polish.

Over half of the total organic carbon in the earth's biosphere is in cellulose. Cotton fibers are essentially pure cellulose, and the wood of bushes and trees is about 50% cellulose. As a polymer of glucose, cellulose has the formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ where n ranges from 500 to 5,000, depending on the source of the polymer. Cellulose molecules tend to be straight chains, and the fibers which result from collections of cellulose molecules have the strength to form the supporting structures of plants. Even though human digestion cannot break down cellulose for use as a food, animals such as cattle and termites rely on the energy content of cellulose. They have protozoa and bacteria with the necessary enzymes in their digestive systems. Cellulose in the human diet is needed for fiber.

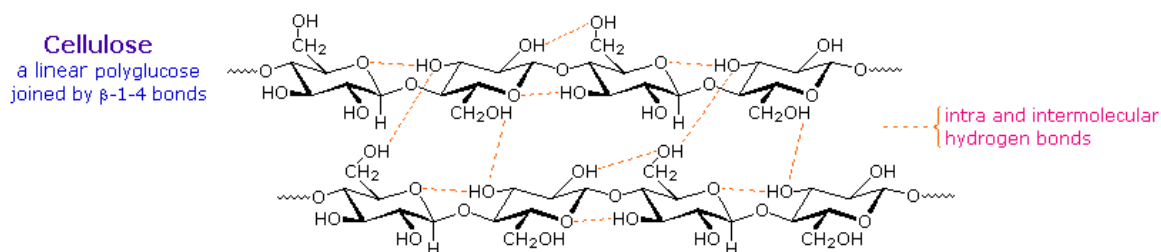


Cellulose

Cellulose Gum or **Carboxymethyl Cellulose (CMC)** is a chemical derivative of cellulose where some of the hydroxyl groups ($-\text{OH}$) are substituted with carboxymethyl groups ($-\text{CH}_2\text{COOH}$). The properties of cellulose gum depend on the degree of substitution and the length of the cellulose chains. The degree of substitution (DS) is the number of carboxymethyl groups per glucose unit and may vary in commercial products from 0.4 to 1.5. Cellulose gum is non-toxic and becomes very viscous when combined with water. It is used as a thickener for foods and as an emulsion stabilizer in products like ice cream. Cellulose gum is also used in personal lubricants, diet pills, water-based paints, detergents and paper coatings.



Most animals cannot digest cellulose as a food, and in the diets of humans this part of our vegetable intake functions as roughage and is eliminated largely unchanged. Some animals (the cow and termites, for example) harbor intestinal microorganisms that breakdown cellulose into monosaccharide nutrients by the use of beta-glycosidase enzymes. Cellulose is commonly accompanied by a lower molecular weight, branched, amorphous polymer called hemicellulose. In contrast to cellulose, hemicellulose is structurally weak and is easily hydrolyzed by dilute acid or base. Also, many enzymes catalyze its hydrolysis. Hemicelluloses are composed of many D-pentose sugars, with xylose being the major component. Mannose and mannuronic acid are often present, as well as galactose and galacturonic acid.



3.5 Synthetic Modification of Cellulose

Cotton, probably the most useful natural fiber, is nearly pure cellulose. The manufacture of textiles from cotton involves physical manipulation of the raw material by carding, combing and spinning selected fibers. For fabrics the best cotton has long fibers, and short fibers or cotton dust are removed. Crude cellulose is also available from wood pulp by dissolving the lignan matrix surrounding it. These less desirable cellulose sources are widely used for making paper.

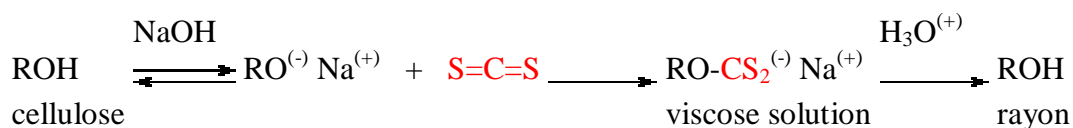
In order to expand the ways in which cellulose can be put to practical use, chemists have devised techniques for preparing solutions of cellulose derivatives that can be spun into fibers, spread into a film or cast in various solid forms. A key factor in these transformations are the three free hydroxyl groups on each glucose unit in the cellulose chain, $--[C_6H_7O(OH)_3]_n--$. Esterification of these functions leads to polymeric products having very different properties compared with cellulose itself.

Cellulose Nitrate, first prepared over 150 years ago by treating cellulose with nitric acid, is the earliest synthetic polymer to see general use. The fully nitrated compound, $--[C_6H_7O(ONO_2)_3]_n--$, called guncotton, is explosively flammable and is a component of smokeless powder. Partially nitrated cellulose is called *pyroxylin*. Pyroxylin is soluble in ether and at one time was used for photographic film and lacquers. The high flammability of pyroxylin caused many tragic cinema fires during its period of use. Furthermore, slow hydrolysis of pyroxylin yields nitric acid, a process that contributes to the deterioration of early motion picture films in storage.

Cellulose Acetate, $--[C_6H_7O(OAc)_3]_n--$, is less flammable than pyroxylin, and has replaced it in most applications. It is prepared by reaction of cellulose with acetic anhydride and an acid catalyst. The properties of the product vary with the degree of acetylation. Some chain

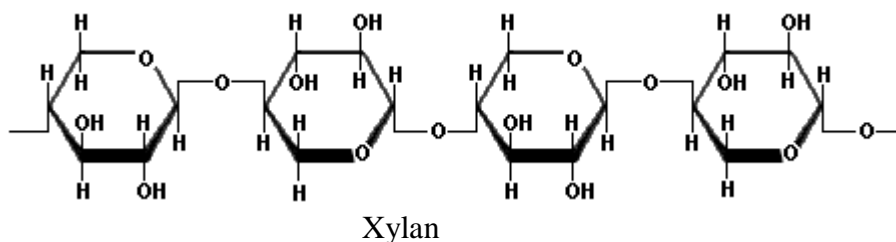
shortening occurs unavoidably in the preparations. An acetone solution of cellulose acetate may be forced through a spinneret to generate filaments, called *acetate rayon* that can be woven into fabrics.

Viscose Rayon is prepared by formation of an alkali soluble xanthate derivative that can be spun into a fiber that reforms the cellulose polymer by acid quenching. The following general equation illustrates these transformations. The product fiber is called *viscose rayon*.



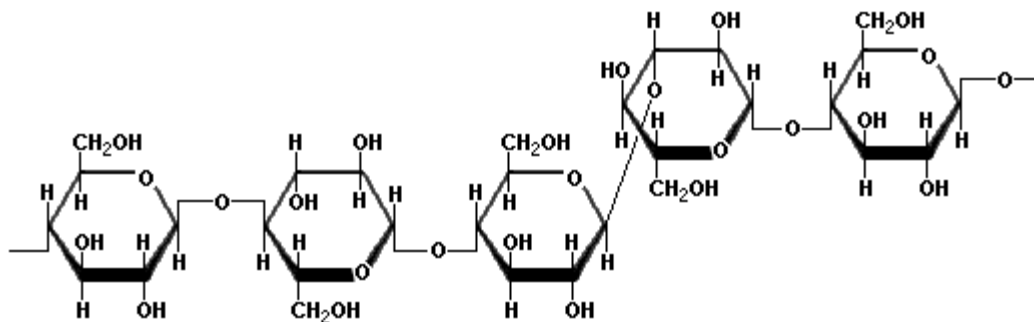
Hemicellulose

The term "hemicellulose" is applied to the polysaccharide components of plant cell walls other than cellulose, or to polysaccharides in plant cell walls which are extractable by dilute alkaline solutions. Hemicelluloses comprise almost one-third of the carbohydrates in woody plant tissue. The chemical structure of hemicelluloses consists of long chains of a variety of pentoses, hexoses, and their corresponding uronic acids. Hemicelluloses may be found in fruit, plant stems, and grain hulls. Although hemicelluloses are not digestible, they can be fermented by yeasts and bacteria. The polysaccharides yielding pentoses on hydrolysis are called *pentosans*. Xylan is an example of a pentosan consisting of D-xylose units with 1 β →4 linkages.



3.6 Beta-Glucan

Beta-glucans consist of linear unbranched polysaccharides of β -D-Glucose like cellulose, but with one 1 β →3 linkage for every three or four 1 β →4 linkages. Beta-glucans form long cylindrical molecules containing up to about 250,000 glucose units. Beta-glucans occur in the bran of grains such as barley and oats, and they are recognized as being beneficial for reducing heart disease by lowering cholesterol and reducing the glycemic response. They are used commercially to modify food texture and as fat substitutes.



Beta-Glucan

4.0 Conclusion

Homopolysaccharides have only one type of monosaccharides within them. They are present within plants and animals. They include starch, glycogen and cellulose.

5.0 Summary

In this chapter, we have learnt that

- i. Polysaccharides can be classified into homopolysaccharides and heteropolysaccharides.
- ii. Homopolysaccharides consist of only one type of monosaccharide.
- iii. Examples of homopolysaccharides include starch, glycogen and cellulose.

6.0 Tutor-marked Assignment

- i. What are Homopolysaccharides?
- ii. Give three examples of homopolysaccharides and state the composition of each.
- iii. Write the structures of starch.

7.0 Further reading

Nelson, D. L. and Cox, M. M. (2004): Lehninger Principles of Biochemistry, 4th edition., Freeman Publisher, USA.



Module 4: Polysaccharides

Unit 2: Heteropolysaccharides

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1.0 Introduction

Heteropolysaccharides are polysaccharides which consist of two or more different types of monosaccharides. They include chitin, agar and alginic acid.

2.0 Objectives

At the end of this unit, students should be able to

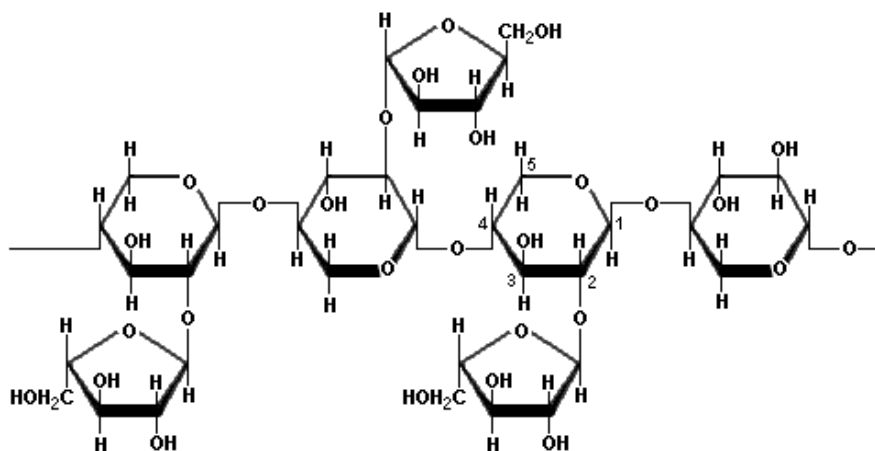
- i. Define heteropolysaccharides.

- ii. Highlight specific examples of heteropolysaccharides.
- iii. Describe chitin, caragenaan and agar.

3.0 Types of heteropolysaccharides

3.1 Arabinoxylan

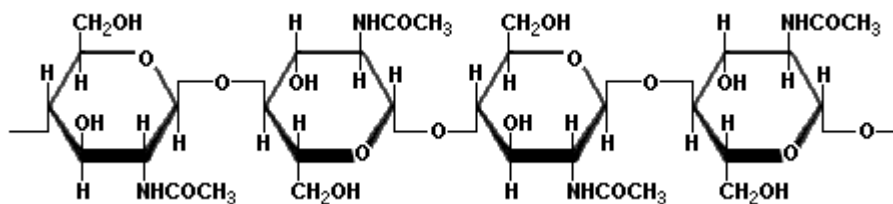
Arabinoxylans are polysaccharides found in the bran of grasses and grains such as wheat, rye, and barley. Arabinoxylans consist of a xylan backbone with L-arabinofuranose (L-arabinose in its 5-atom ring form) attached randomly by $1\alpha\rightarrow2$ and/or $1\alpha\rightarrow3$ linkages to the xylose units throughout the chain. Since xylose and arabinose are both pentoses, arabinoxylans are usually classified as pentosans. Arabinoxylans are important in the baking industry. The arabinose units bind water and produce viscous compounds that affect the consistency of dough, the retention of gas bubbles from fermentation in gluten-starch films, and the final texture of baked products.



Arabinoxylan

3.2 Chitin

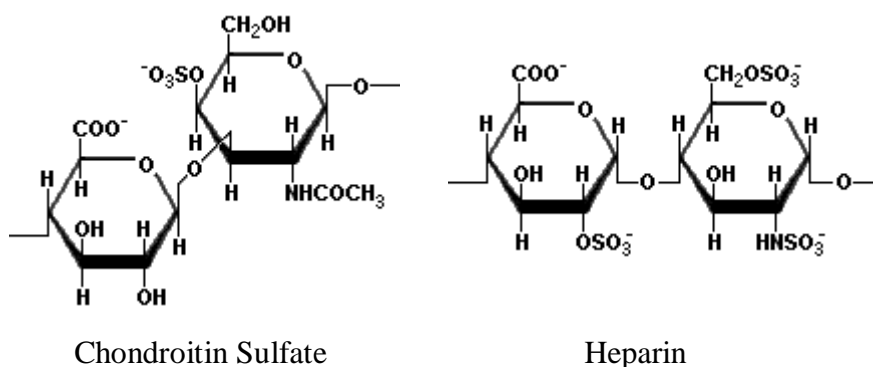
Chitin is an unbranched polymer of N-Acetyl-D-glucosamine. It is found in fungi and is the principal component of arthropod and lower animal exoskeletons, e.g., insect, crab, and shrimp shells. It may be regarded as a derivative of cellulose, in which the hydroxyl groups of the second carbon of each glucose unit have been replaced with acetamido ($-\text{NH}(\text{C}=\text{O})\text{CH}_3$) groups.



Chitin

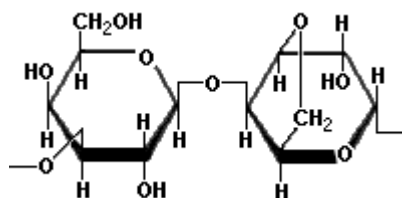
3.3 Glycosaminoglycans

Glycosaminoglycans are found in the lubricating fluid of the joints and as components of cartilage, synovial fluid, vitreous humor, bone, and heart valves. Glycosaminoglycans are long unbranched polysaccharides containing repeating disaccharide units that contain either of two amino sugar compounds -- N-acetylgalactosamine or N-acetylglucosamine, and a uronic acid such as glucuronate (glucose where carbon six forms a carboxyl group). Glycosaminoglycans are negatively charged, highly viscous molecules sometimes called *mucopolysaccharides*. The physiologically most important glycosaminoglycans are hyaluronic acid, dermatan sulfate, chondroitin sulfate, heparin, heparan sulfate, and keratan sulfate. Chondroitin sulfate is composed of β -D-glucuronate linked to the third carbon of N-acetylgalactosamine-4-sulfate as illustrated here. Heparin is a complex mixture of linear polysaccharides that have anticoagulant properties and vary in the degree of sulfation of the saccharide units.



3.4 Agar and Carrageenan

Agar (agar agar) is extracted from seaweed and is used in many foods as a gelling agent. Agar is a polymer of agarobiose, a disaccharide composed of D-galactose and 3,6-anhydro-L-galactose. Highly refined agar is used as a medium for culturing bacteria, cellular tissues, and for DNA fingerprinting. Agar is used as an ingredient in desserts in Japan and other Asian countries. The gels produced with agar have a crispier texture than the desserts made with animal gelatin.



Agarobiose

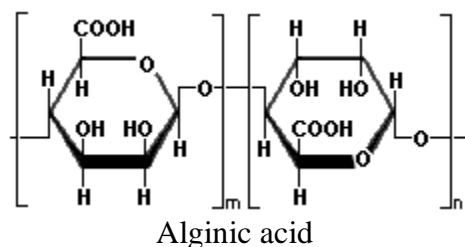
Carrageenan is a generic term for several polysaccharides also extracted from seaweed. Carrageenan compounds differ from agar in that they have sulfate groups ($-\text{OSO}_3^-$) in place of some hydroxyl groups. Carrageenan is also used for thickening, suspending, and gelling food products.

Self Assessment Exercise

- Describe the structure and function of chitin.
- Distinguish between agar and carageenan

3.5 Alginic acid (Alginates)

Alginate is extracted from seaweeds, such as giant kelp (*Macrocystis pyrifera*). The chemical constituents of alginate are random sequences of chains of β -D-mannuronic and α -L-guluronic acids attached with 1 \rightarrow 4 linkages. Alginates are insoluble in water, but absorb water readily. They are useful as gelling and thickening agents. Alginates are used in the manufacture of textiles, paper, and cosmetics. The sodium salt of alginic acid, sodium alginate, is used in the food industry to increase viscosity and as an emulsifier. Alginates are found in food products such as ice cream and in slimming aids where they serve as appetite suppressants. In dentistry, alginates are used to make dental impressions.

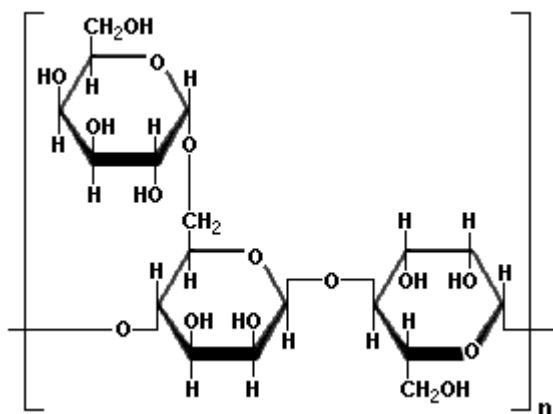


3.6 Galactomannan

Galactomannans are polysaccharides consisting of a mannose backbone with galactose side groups. The mannopyranose units are linked with 1 β \rightarrow 4 linkages to which galactopyranose units are attached with 1 α \rightarrow 6 linkages. Galactomannans are present in several vegetable gums that are used to increase the viscosity of food products. These are the approximate ratios of mannose to galactose for the following gums:

- **Fenugreek gum**, mannose:galactose 1:1
- **Guar gum**, mannose:galactose 2:1
- **Tara gum**, mannose:galactose 3:1
- **Locust bean gum** or **Carob gum**, mannose:galactose 4:1

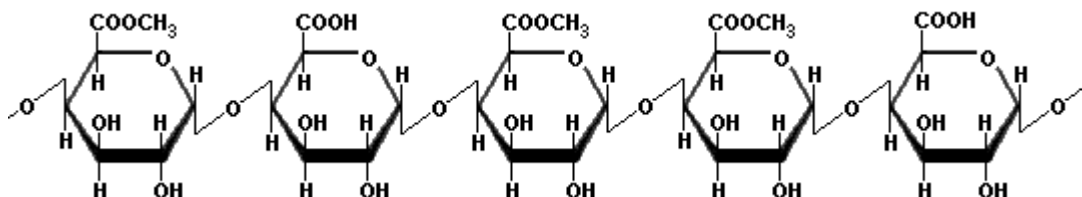
Guar is a legume that has been traditionally cultivated as livestock feed. Guar gum is also known by the name *cyamopsis tetragonoloba* which is the Latin taxonomy for the guar bean or cluster bean. *Guar gum* is the ground endosperm of the seeds. Approximately 85% of guar gum is *guaran*, a water soluble polysaccharide consisting of linear chains of mannose with 1 β \rightarrow 4 linkages to which galactose units are attached with 1 α \rightarrow 6 linkages. The ratio of mannose to galactose is 2:1. Guar gum has five to eight times the thickening power of starch and has many uses in the pharmaceutical industry, as a food stabilizer, and as a source of dietary fiber.



Guaran is the principal polysaccharide in guar gum.

3.7 Pectin

Pectin is a polysaccharide that acts as a cementing material in the cell walls of all plant tissues. The white portion of the rind of lemons and oranges contains approximately 30% pectin. Pectin is the methylated ester of polygalacturonic acid, which consists of chains of 300 to 1000 galacturonic acid units joined with $1\alpha \rightarrow 4$ linkages. The Degree of Esterification (DE) affects the gelling properties of pectin. The structure shown here has three methyl ester forms ($-\text{COOCH}_3$) for every two carboxyl groups ($-\text{COOH}$), hence it has a 60% degree of esterification, normally called a DE-60 pectin. Pectin is an important ingredient of fruit preserves, jellies, and jams.

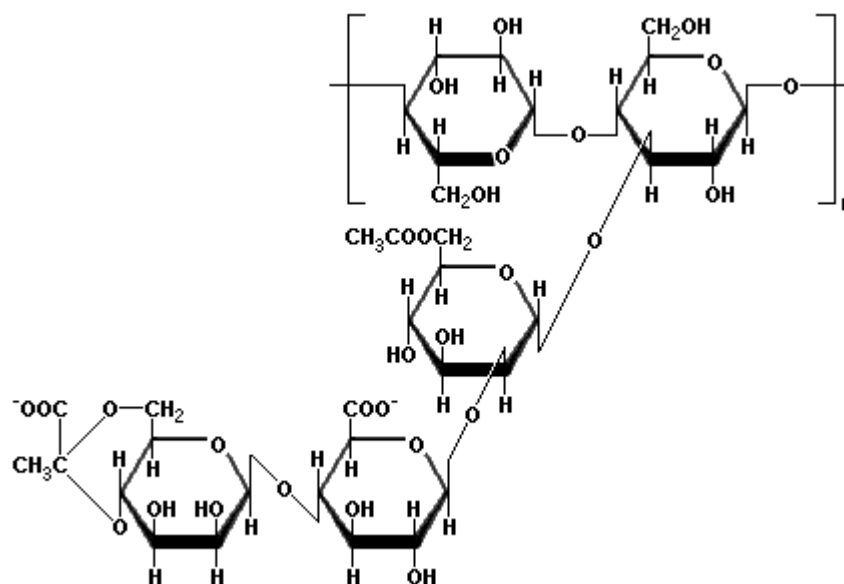


Pectin is a polymer of α -Galacturonic acid with a variable number of methyl ester groups.

3.8 Xanthan Gum

Xanthan gum is a polysaccharide with a β -D-glucose backbone like cellulose, but every second glucose unit is attached to a trisaccharide consisting of mannose, glucuronic acid, and mannose. The mannose closest to the backbone has an acetic acid ester on carbon 6, and the mannose at the end of the trisaccharide is linked through carbons 6 and 4 to the second carbon of pyruvic acid. Xanthan Gum is produced by the bacterium *Xanthomonas campestris*, which is found on cruciferous vegetables such as cabbage and cauliflower. The negatively charged carboxyl groups on the side chains cause the molecules to form very viscous fluids when mixed with water. Xanthan gum is used as a thickener for sauces, to prevent ice crystal formation in ice cream, and

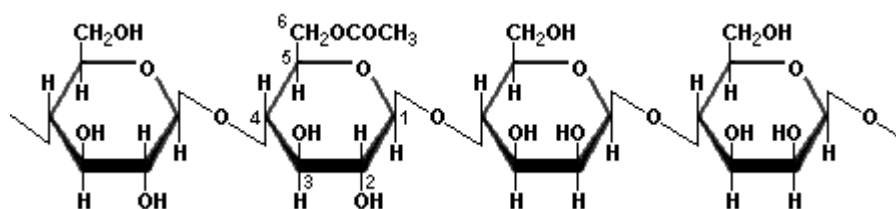
as a low-calorie substitute for fat. Xanthan gum is frequently mixed with guar gum because the viscosity of the combination is greater than when either one is used alone.



The repeating unit of Xanthan Gum

3.9 Glucomannan

Glucomannan is a dietary fiber obtained from tubers of *Amorphophallus konjac* cultivated in Asia. Flour from the konjac tubers is used to make Japanese shirataki noodles, also called konnyaku noodles, which are very low in calories. Glucomannan is used as a hunger suppressant because it produces a feeling of fullness by creating very viscous solutions that retard absorption of the nutrients in food. One gram of this soluble polysaccharide can absorb up to 200 ml of water, so it is also used for absorbent articles such as disposable diapers and sanitary napkins. The polysaccharide consists of glucose (G) and mannose (M) in a proportion of 5:8 joined by $1\beta\rightarrow4$ linkages. The basic polymeric repeating unit has the pattern: GGMMGMMMMMMGGM. Short side chains of 11-16 monosaccharides occur at intervals of 50-60 units of the main chain attached by $1\beta\rightarrow3$ linkages. Also, acetate groups on carbon 6 occur at every 9-19 units of the main chain. Hydrolysis of the acetate groups favors the formation of intermolecular hydrogen bonds that are responsible for the gelling action.

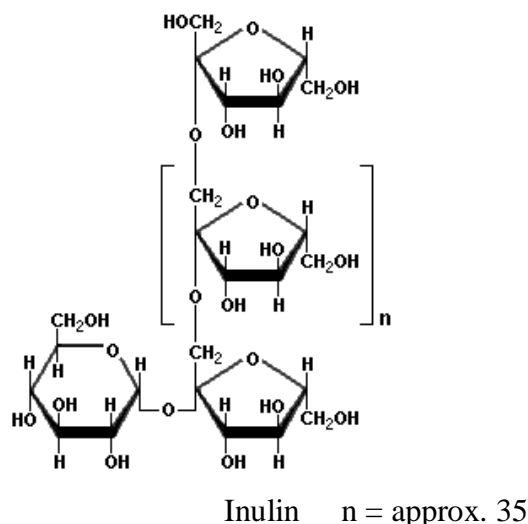


A portion (GGMM) of the glucomannan repeating unit.

The second glucose has an acetate group.

3.10 Inulin

Some plants store carbohydrates in the form of inulin as an alternative, or in addition, to starch. Inulins are present in many vegetables and fruits, including onions, leeks, garlic, bananas, asparagus, chicory, and Jerusalem artichokes. Inulins, also called fructans, are polymers consisting of fructose units that typically have a terminal glucose. *Oligofructose* has the same structure as inulin, but the chains consist of 10 or fewer fructose units. Oligofructose has approximately 30 to 50 percent of the sweetness of table sugar. Inulin is less soluble than oligofructose and has a smooth creamy texture that provides a fat-like mouthfeel. Inulin and oligofructose are nondigestible by human intestinal enzymes, but they are totally fermented by colonic microflora. The short-chain fatty acids and lactate produced by fermentation contribute 1.5 kcal per gram of inulin or oligofructose. Inulin and oligofructose are used to replace fat or sugar and reduce the calories of foods like ice cream, dairy products, confections and baked goods.



4.0 Conclusion

Heteropolysaccharides are polysaccharides which are characterised by more than one unit of monosaccharides. Examples of heteropolysaccharides include chitin, agar, caragenaan, pectin and inulin.

5.0 Summary

In this chapter, we have learnt that

- Heteropolysaccharides are made up of more than one type of monosaccharides.
- Heteropolysaccharides are present naturally in plants, animals and micro-organisms
- Examples of heteropolsaccharides include chitin, pectin and inulin.

6.0 Tutor-marked Assignment

- What are Heteropolysaccharides?
- Give three examples of heterolysaccharides and state the composition of each.

iii. Describe the structures of chitin and inulin.

7.0 Further reading

Nelson, D. L. and Cox, M. M. (2004): Lehninger Principles of Biochemistry, 4th edition.
Freeman Publisher, USA.