COURSE
GUIDE

CHM 315
CARBOHYDRATE CHEMISTRY

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COURSE GUIDE

Introduction

Carbohydrate chemistry is a semester course, which is part of the core courses required for the award of the degree, B.Sc Chemistry.

Course competencies

The course consists of units and a course guide. The course guide is primarily a simple description of what the course entails, the materials needed, and how to work with these materials. Also, it advocates some general guidelines for the time you are likely to spend on each unit of the course to complete it successfully.

Also, you will 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 a better understanding of the course. You are henceforth, advised to make yourselves available during the tutorial classes.

Course Objectives

The course has a set of objectives. Each of the unit contained in a specific module has stated intended learning outcomes which are included at the beginning of the particular unit. A clearer understanding of each 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;

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

To be able to 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 explore other e-reading materials from the 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 your time for reading and doing assignments. You must 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.

Study Unit

The study units in this course are as follows;

Module 1 Carbohydrates

Unit 1 Classification and 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: Starch and Glygogen
Unit 2	Homopolysaccharides: Cellulose and Derivatives
Unit 3	Heteropolysaccharides

Module 1: Carbohydrates. The first unit gives general information about carbohydrates, occurrences, classification and the general physical and chemical properties of carbohydrates.

Module 2: Monosaccharide. The first unit is primarily concerned with the structures of monosaccharides. The second unit addresses the derivatives of monosaccharides and their characteristics.

Module 3: Disaccharides. This unit deals with the diversity of disaccharides.

Module 4: Polysaccharide. The first unit explain homopolysaccharide such as starch and glycogen. The second Unit explain the homopolysaccharide cellulose and the derivatives of cellulose. The third unit enumerated the various examples of heteropolysaccharides and their structures and importance.

Each of the unit is made up of one or two weeks' work consisting of introduction, intending learning outcomes, reading materials, self-assessment exercise, conclusion, summary and suggestion for further reading. 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.

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

How to get the most from the course

To get the most out of this course will require your active participations to every aspect such as; participation in all lectures, engaging in active interaction during lectures. Reviewing your understanding of each module/unit by attempting all self-assessment exercises and cross checking your answers with answers in your lecture materials. Participation in all organized tutorials and doing assignment and submitting at the right time. 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. The examination will be made up of questions that normally reflect on what you have learned in the course materials/further reading.

Facilitation

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 self-Assignment exercises to your facilitator, at least two working days, before the scheduled 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 questions or seek clarification on a seemingly grey area in the course material. You may as well have prepared questions and comments for your facilitator before the due date. 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.

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

- What are carbohydrates and what do they represent?
- What are the different types, 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.

Module 1 Carbohydrates

Module 1, deals with the general introduction to the chemistry of carbohydrates and consist of only one unit.

Unit 1: Classification of carbohydrates

Unit 1: Classification of Carbohydrates

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1.0 Introduction

Carbohydrates are naturally occurring compounds found in both plants and animals and are essential to life. Plants through a process known as photosynthesis, convert carbon dioxide to carbohydrates, mainly starch, cellulose and sugars. Cellulose is the main building block of rigid cell walls and woody tissue in plants. While starch, is the chief storage form of carbohydrates for later use as a food or energy source. Some plants like cane sugar and sugar beets produces sucrose, ordinary table sugar. Another sugar, glucose is an essential component of blood. Two other sugars, ribose and 2-deoxyribose, are components of the genetic materials RNA and DNA. Other carbohydrates are important components of coenzymes, antibiotics, cartilage, the shells of crustaceans, bacterial cell walls and mammalian cell membranes.

The word carbohydrates arose because the molecular formulas of these compounds can be expressed as hydrates of carbon. For example, Glucose has the molecular formula $C_6H_{12}O_6$ (where carbon (C) hydrogen (H) and oxygen (O) are in the ration 1:2:1) which may be written as $C_6(H_{12}O)_6$, which implies, carbon with six water molecules (carbo from carbon and hydrate from water, together they form the word carbohydrate). The study of the chemistry of carbohydrates has over the years gone beyond this formula, but the old name "carbohydrate" still persists.

2.0 Intended learning outcomes (ILOs)

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

- Define carbohydrates
- State the importance of carbohydrates
- Identify the different classes of carbohydrates.
- State the physical and chemical properties of carbohydrates.

3.0 Main content

3.1 Definition of Carbohydrates

Carbohydrates are a large class of naturally occurring polyhydroxy aldehyde or ketones. Chemically, carbohydrates are organic molecules in which carbon, hydrogen, and oxygen bond together in the ratio **1:2:1** ($C_x(H_2O)_y$, where x and y are whole numbers that differ depending on the specific carbohydrate).

3.2 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.

3.3 Classification of Carbohydrates

Carbohydrates can be classified into four different groups; monosaccharides, disaccharides, oligosaccharides and polysaccharides.

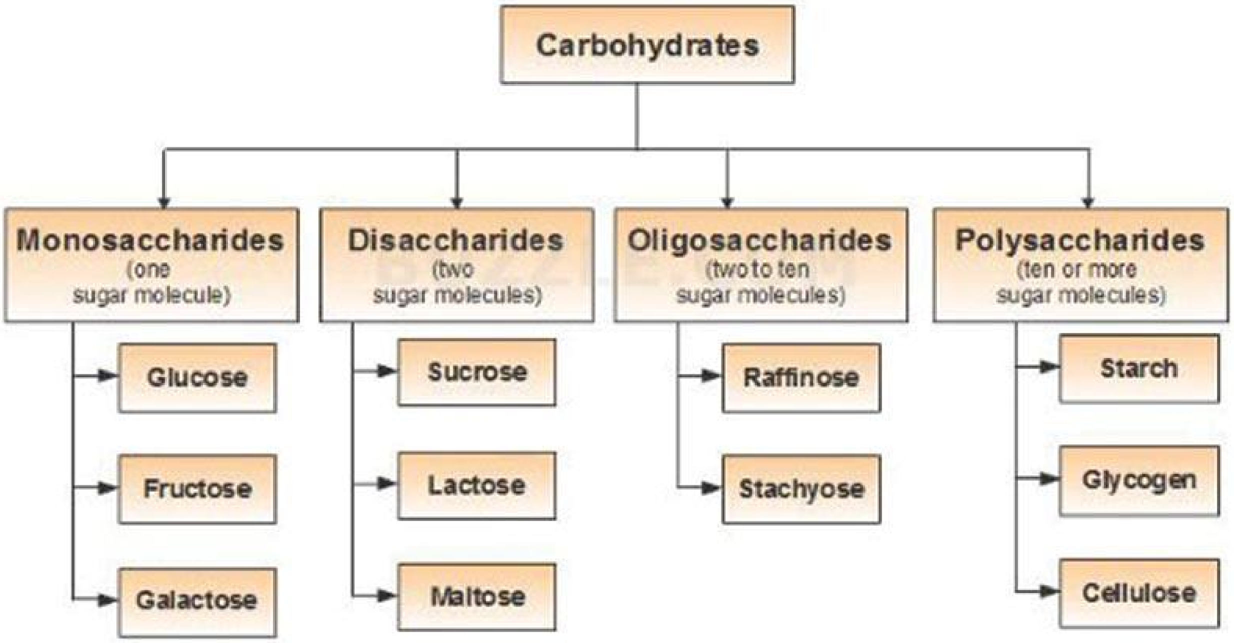

Figure 1: Classification of Carbohydrates

How are the three classes of carbohydrates related to each other through hydrolysis?

Solution: $$\text{Polysaccharide} \xrightarrow[H^+]{H_2O} \text{oligosaccharides} \xrightarrow[H^+]{H_2O} \text{monosaccharides}$$

3.4 Physical Properties of Carbohydrates

Carbohydrates exhibit the following physical properties:

$$\underset{\text{starch (polysaccharide)}}{[C_{12}H_{20}O_{10}]n} \xrightarrow[H^+]{nH_2O} \underset{\text{maltose (a disaccharide)}}{nC_{12}H_{22}O_{11}} \xrightarrow[H^+]{nH_2O} \underset{\text{glucose (a monosaccharide)}}{2n\ C_6H_{12}O_6}$$

3.4.1. Stereoisomerism – Compound shaving the same structural formula but they differ in spatial configuration. Example: Glucose has two isomers with respect to the penultimate carbon atom. They are D-glucose and L-glucose.

3.4.2. Optical Activity – It is the rotation of plane-polarized light forming (+) glucose and (-) glucose.

3.4.3. Diastereo isomers – It the configurational changes with regard to C2, C3, or C4 in glucose. Example: Mannose, galactose.

3.4.4. Annomerism – It is the spatial configuration with respect to the first carbon atom in aldoses and second carbon atom in ketoses.

3.5. Chemical Properties of Carbohydrates

3.5.1. Osazone formation: Osazone are carbohydrate derivatives when sugars are reacted with an excess of phenylhydrazine. eg. Glucosazone

3.5.2. Benedict’s test: Reducing sugars when heated in the presence of an alkali gets converted to powerful reducing species known as enediols. When Benedict’s reagent solution and reducing sugars are heated together, the solution changes its color to orange-red/ brick red.

3.5.3. Oxidation: Monosaccharides are reducing sugars if their carbonyl groups oxidize to give carboxylic acids. In Benedict’s test, D-glucose is oxidized to D-gluconic acid thus, glucose is considered a reducing sugar.

3.5.4. Reduction to alcohols: The C=O groups in open-chain forms of carbohydrates can be reduced to alcohols by sodium borohydride, $NaBH_4$, or catalytic hydrogenation (H2, Ni, EtOH/H2O). The products are known as “alditols”.

4.0 Self-assessment Exercise 1

i. What are carbohydrates?
ii What are the importance of Carbohydrates?
iii what are the physical and chemical properties of carbohydrates?
iv. Give four (4) different classes of carbohydrates with at least two examples each.
v. Differentiate between disaccharides and oligosaccharides.
vi. What are the two important functional groups present in a carbohydrate?

Answers to self-assessment exercise 1

Answers to question i-ii are provided, kindly attempt questions iii-vi

i. Carbohydrates are a large class of naturally occurring polyhydroxy aldehyde or ketones.
ii. The carbohydrates are a major source of metabolic energy, both for plants and for animals that depend on plants for food.

5.0 Conclusion

Carbohydrate is a one of the major classes of biomolecules. They are a major source of metabolic energy, both for plants and for animals that depend on plants for food. Carbohydrates are classified as monosaccharides, disaccharides, oligosaccharides and polysaccharides. They have a general physical and chemical properties.

6.0 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. The general physical properties of carbohydrates such as; stereoisomerism, optical activity, diastereoisomers and annomerism

iv. Chemical properties of carbohydrates include; osazone formation, oxidation, reduction etc

7.0 Further reading

Rawn, J. D and Ouellette, R (2018). Organic Chemistry: Structure, Mechanism, Synthesis, Second Edition, Academic Press, USA.

Module 2 Monosaccharides

Module 2: Chemistry of monosaccharides consist of two units;

Unit 1: Structures of monosaccharides

Unit 2: Derivatives of monosaccharides

Unit 1: Structures of Monosaccharides

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1.0 Introduction

The simplest form of carbohydrates is the monosaccharide. 'Mono' means 'one' and 'saccharide' means 'sugar'. Monosaccharides are polyhydroxy aldehyde or ketone that cannot be hydrolyzed further to give simpler sugar. Monosaccharides are important fuel molecules as well as building blocks for nucleic acids.

2.0 Intended learning outcomes (ILOs)

At the end of this unit, you should be able

to;

i. Know the classes of monosaccharide

ii. Understand the importance of monosaccharides

iii. Identify isomers and enantiomers of monosaccharides

3.0 Main content

3.1 Classification of monosaccharides

Monosaccharides are classified according to three different categories;

i. the placement of its carbonyl group,

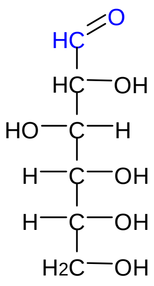
ii. the number of carbon atoms it contains,

iii. its chiral handedness.

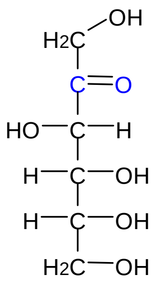
If the carbonyl group is an aldehyde, the monosaccharide is an *aldose*; if the carbonyl group is a ketone, the monosaccharide is a *ketose*. Monosaccharides with three carbon atoms are called *trioses*, those with four are called *tetroses*, five are called *pentoses*, six are *hexoses*, and so on. 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).

In naming the monosaccharide name ends with "**ose**", example;



Glucose: (aldose)



Fructose: (ketose)

Table 1: Naming aldoses and ketoses

Number of carbons	General terms	Aldehyde	ketone
3	triose	aldotriose	ketotriose

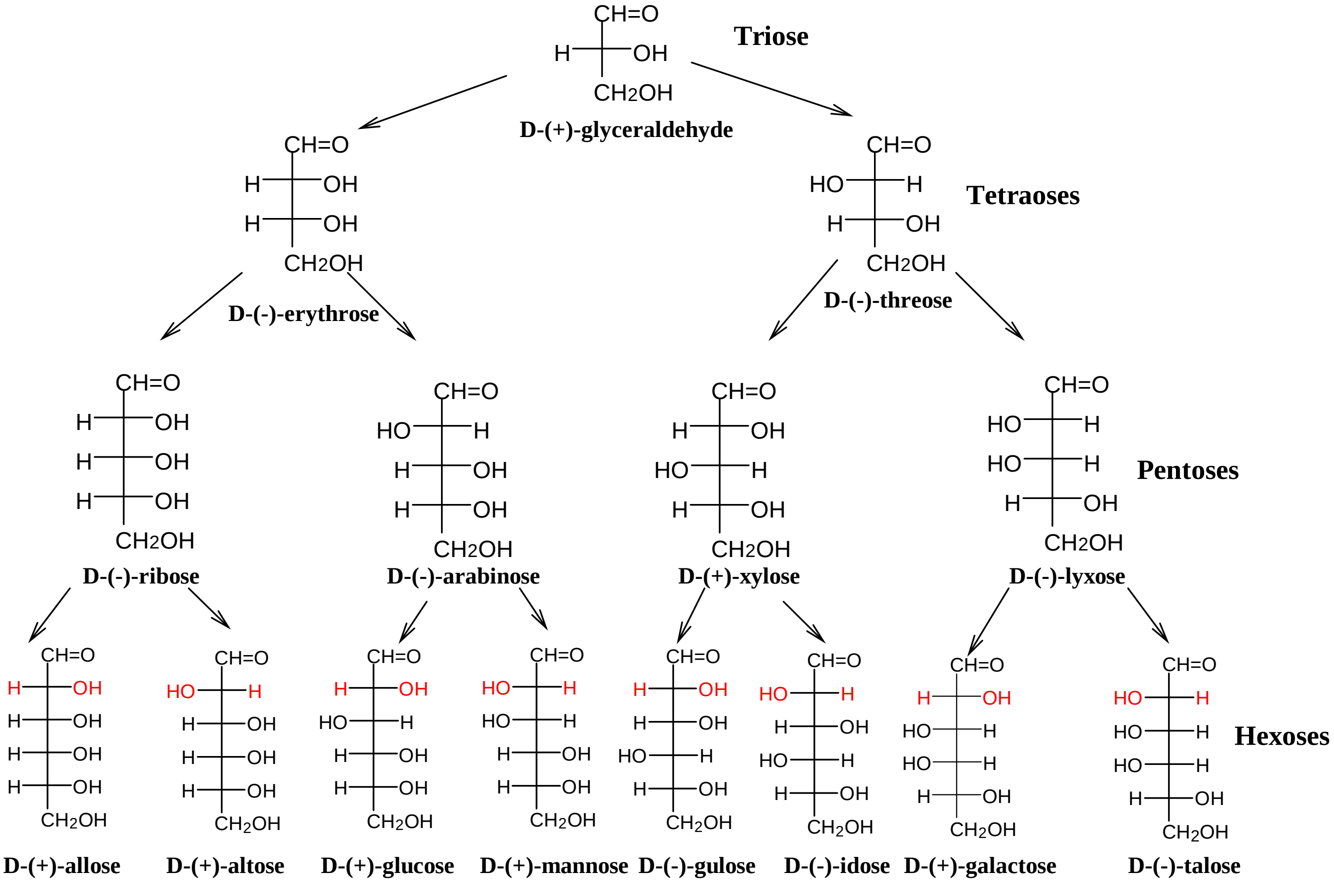
4	tetrose	aldotetrose	ketotetrose
5	pentose	aldopentose	ketopentose
6	hexose	aldohexose	ketohexose
7	heptose	aldoheptose	ketoheptose

Two monosaccharide containing eight and nine carbon atom with a ketone carbonyl will be call what?

Solution:

Eight carbon atom monosaccharide will have a general name octose with ketone carbonyl it will become ketooctose

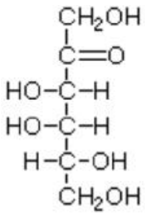
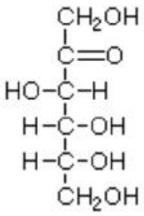
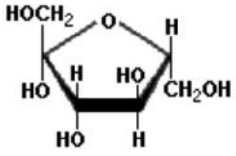
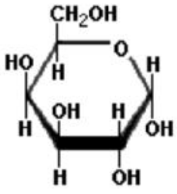
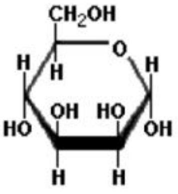
Nine carbon monosaccharide will have a general name of ninose with ketone carbonyl it will become ketoninose.



3.1.1 Hexoses

Hexoses, such as the ones illustrated here, have the molecular formula **$C_6H_{12}O_6$**. 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.

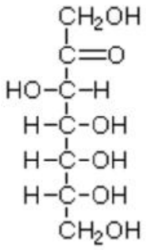
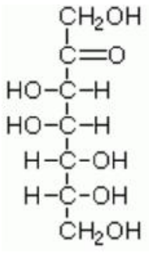
Monosaccharides that have opposite configurations of a hydroxyl group at only one position, such as glucose and mannose, are called ***epimers.*** *Glucose*, also called *dextrose*, is the most widely distributed sugar in the plant and animal kingdoms and it is the sugar present in blood as "blood sugar". 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.

D-Tagatose D-Fructose Fructose Galactose Mannose

3.1.2 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.

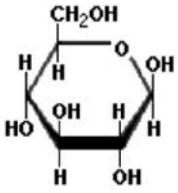
D-Sedoheptulose D-Mannoheptulose

3.2 Chain and Ring Structure of Monosaccharides

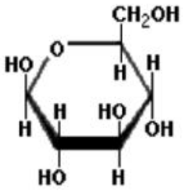
Many simple sugars can exist in a chain form or a ring form, as illustrated by the hexoses above. The ring form is favored in aqueous solutions, and the mechanism of ring formation is similar for most sugars. The *glucose* ring form is created when the oxygen on carbon number 5 links with the carbon 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 **-CH_2OH** group, or *beta* glucose when the hydroxyl group is on the same side as the **-CH_2OH** 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*.

3.3 Stereochemistry

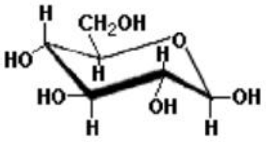
Stereochemisty is the study of the arrangement of atoms in three-dimensional space. Stereoisomers are compounds in which the atoms are linked in the same order but differ in their spatial arrangement. Compounds that are mirror images of each other but are not identical, comparable to left and right shoes, are called enantiomers. Saccharides with identical functional groups but with different spatial configurations have different chemical and biological properties. 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.



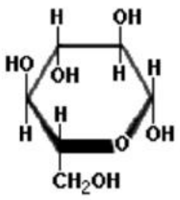
β-D-Glucose



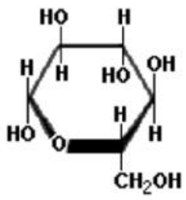
β-L-Glucose



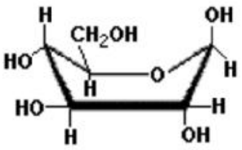
β-D-Glucose (chair form)



β-D-Glucose



β-L-Glucose



β-D-Glucose (boat form)

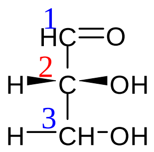
Each carbon atom of a monsaccharide bearing a hydroxyl group (-OH), with the exception of the first and last carbons, are asymmetric, making them stereocenters (chiral centres) with two possible configurations (R or S). Because of this stereocenters, a number of isomers may exist for any given monosaccharide formula. The aldohexose D-glucose, for example, has the formula $(C\cdot H_2O)_6$, 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.

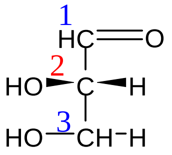
Note the position of the hydroxyl group (red or green) on the anomeric carbon relative to the CH_2OH group bound to carbon 5: they are either on the opposite sides (α), or the same side (β).

3.4 Chirality in monosaccharides, Fisher projection Formulas and D,L-Sugars

Glyceraldehyde the simplest aldose has one stereogenic carbon atom (C-2) and hence can exist in two enantiomeric forms. The R-glyceraldehyde and the S-glyceraldehyde, the dextrorotatory form has the R configuration while the levorotatory form has the S configuration.

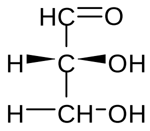


R-(+)-glyceraldyde

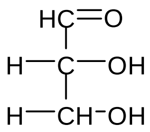


S-(-)-glyceraldyde

It was in connection with this study on carbohydrate stereochemistry that Emil Fisher invented his system of projection formulas. In a Fisher projection formula, horizontal lines show groups that are project above the plane of the paper towards the viewer, vertical lines show groups that project below the plane of the paper away from the viewer.



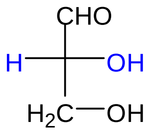
R-(+)-glyceraldyde



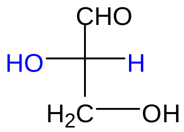
Fisher projection formula for R-(+)-glyceraldyde

Thus, R-(+)-glyceraldehyde can be represented as shown below with the stereogenic center represented by the intersection of two crossed lines.

Fisher also introduced a stereochemical nomenclature that preceded the R,S system and is still in common use for sugars and amino acids. He used a small capital D to represent the configuration of (+)-glyceraldehyde, with the hydroxyl group on the right; its enantiomer, with the hydroxyl group on the left, was designated L-(-)-glyceraldehyde. The most oxidized carbon (CHO) was placed at the top.

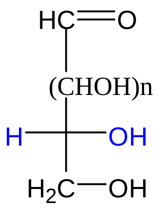


D-(+)-glyceraldyde

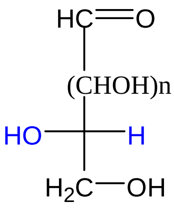


L-(+)-glyceraldyde

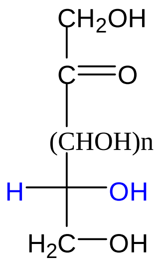
Fisher extended his system to other monosaccharides in the following way. If the stereogenic carbon farthest from the aldehyde or ketone group had the same configuration as D-glyceraldehye (hydroxyl on the right), the compound was called a D-sugar. If the configuration at the remote carbon had the same configuration as L-glyceraldehyde (hydroxyl on the left), the compound was an L-sugar.



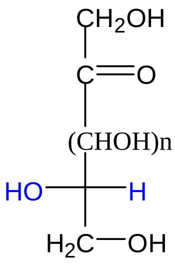
D-aldose



L-aldose



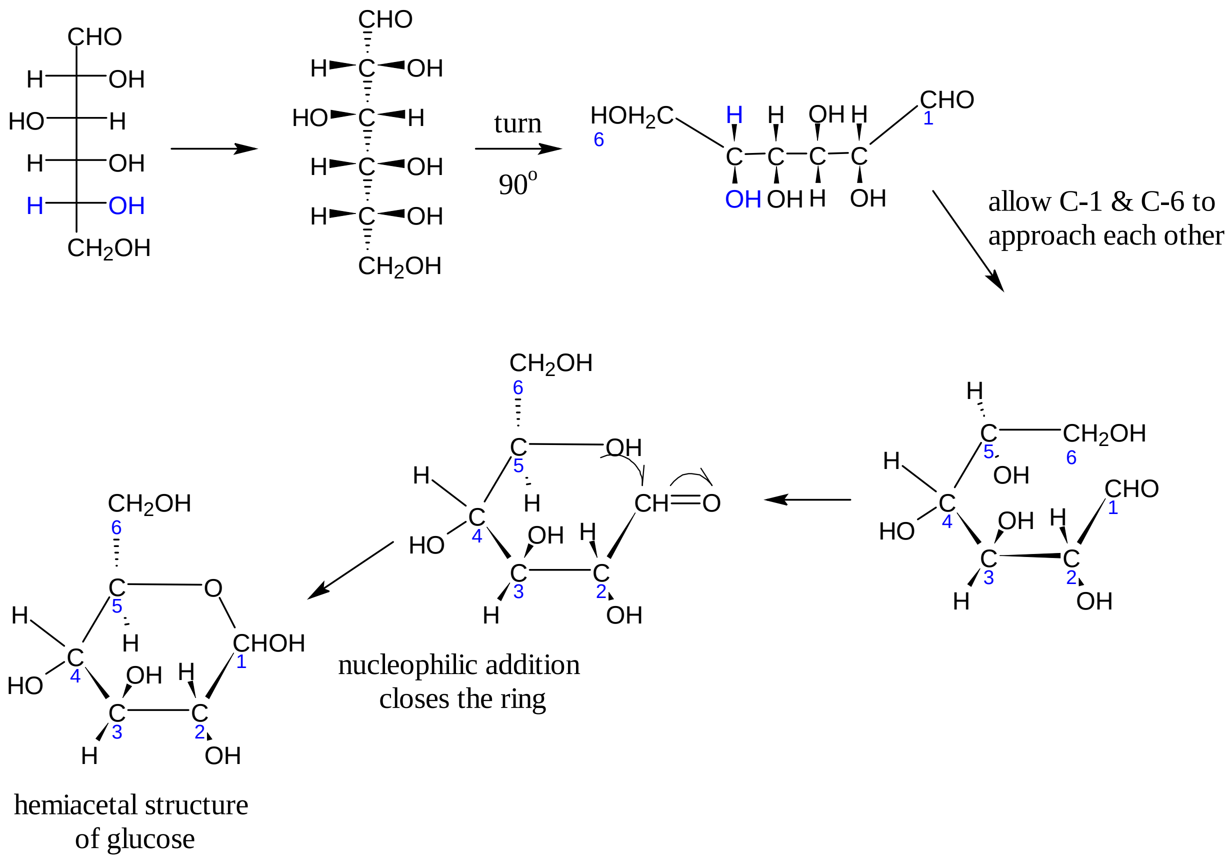
D-ketose



D-ketose

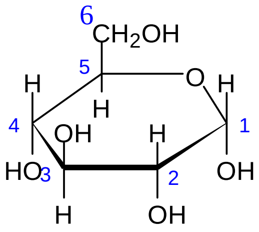
3.5 The Cyclic Hemiacetal Structures of Monosaccharides

Alcohols undergo rapid and reversible addition to the carbonyl group of aldehydes and ketones, to form hemiacetals. This can happen intramolecularly when the hydroxyl and carbonyl groups are properly located in the same molecule, which is the situation in many monosaccharides. Monosaccharides exist mainly in cyclic hemiacetal forms and not in the acyclic aldo- or keto- form depicted so far.



Manipulation of the Fisher projection formula of D-glucose to bring the C-5 hydroxyl group in position for cyclization to the hemiacetal form.

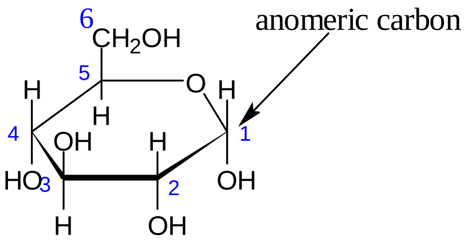
The British carbohydrate chemist W. N. Harworth (Nobel Prize, 1937) introduced a useful way of representing the cyclic forms of sugars. In a **Harworth Projection**, the ring is represented as if it were planar and viewed edge on, with the oxygen at the upper right. The carbon are arranged clockwise numerically with C-1 at the right. Substituents attached to the ring lie above or below the plane. For example, Harworth formula for D-glucose is shown below;



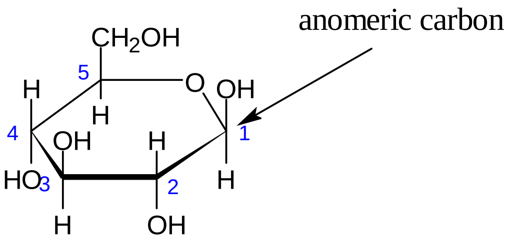
Harworth projection formula for D-glucose

3.6 Anomeric Forms of Glucose

In the acyclic, aldehyde form of glucose, C-1 is achiral (i.e it does not exhibit optical rotation) but in the cyclic structures, this carbon becomes chiral (has four different groups attached to it, hence exhibit optical rotation). Consequently, two hemiacetal structures are possible, depending on the configuration at the new chiral center. The hemiacetal carbon, the carbon that forms the new stereogenic center, is called the **anomeric carbon.** Two monosaccharides that differ only in configuration at the anomeric center are **anomers** (a special kind of epimers). Anomers are called alpha (α) or beta (β) depending on the position of the hydroxyl group. For monosaccharides in the D-series, the hydroxyl group is "down" in the alpha (α) anomer and "up" in the Beta (β) anomer, when structure is written in the usual way. Example;



α -D-glucose

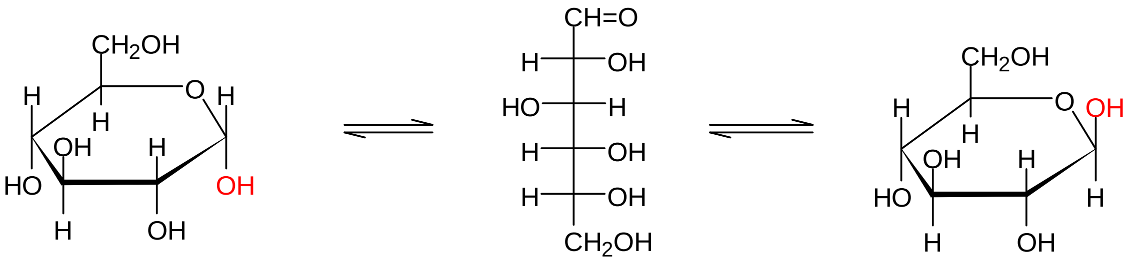


β-D-glucose

The α and β forms of D-glucose have identical configurations at every stereogenic center except at C-1, the anomeric carbon.

How do we know that monosaccharides exit mainly as cyclic hemiacetals? There is direct physical evidence. For example, if D-glucose is crystallized from methanol, the pure alpha form is obtained. On the other hand, crystallization of glucose from acetic acid gives the beta form. The alpha and beta forms of D-glucose are diastereomers, they have different physical properties; melting point; α-D-glucose (mp 146 °C) while β-D-glucose (mp 150 °C), specific optical rotation; α-D-glucose (+112°) while β-D-glucose (+19°).

The alpha and beta forms of D-glucose interconvert in aqueous solution. For example, if crystalline α-D-glucose is dissolved in water, the specific rotation drops gradually from an initial value of +112° to an equilibrium value of +52°. These changes in optical rotation are called **Mutarotation.** At equilibrium, an aqueous solution of D-glucose contains 36% of the alpha form and 64% of the beta form. There is only about 0.01% of the open-chain aldehyde form present.



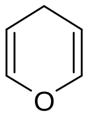
α-D-glucose (36%)
mp 146 °C; [α] +112°

D-glucose (aldehyde form)
< 0.01%

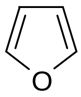
β-D-glucose (64%)
mp 150 °C; [α] +19°

3.7 Cyclic forms of monosaccharides

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;

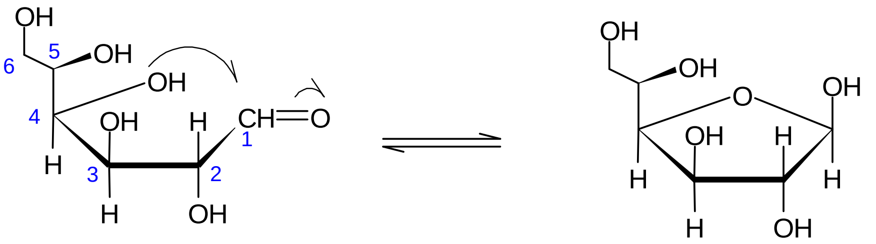


Pyran



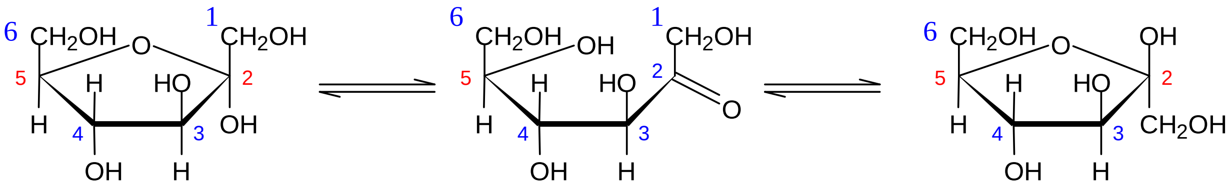
Furan

Pyranoses are formed by the reaction hydroxyl group at C-5 with the carbonyl group (as earlier mentioned). With some sugars, however, the hydroxyl group at C-4 reacts instead. In these cases, the cyclic hemiacetal that is formed has a five-membered ring. This type of cyclic monosaccharide is called a furanose. For example, D-glucose could, in principle, exist in two furanose forms (α and β at C-1) through attach of the C-4 hydroxyl on the aldehyde carbon.



D-glucose **α- and β-D-glucose**

In practice, these forms are present to less than 1% in glucose solutions, but they are important with other monosaccharides. The Ketose D-fructose, for example, exits in solution mainly in two furanose forms. The carbonyl carbon at C-2 and hydroxyl group at C-5 cyclize to give furanose ring.



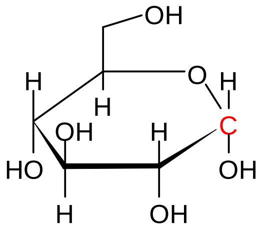
α-D-fructofuranose
(-OH at C-2 is “down”)

D-fructose
(acyclic keto form)

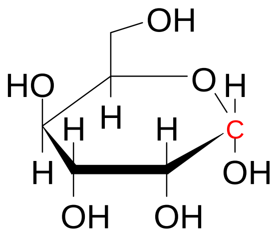
β-D-fructofuranose
(-OH at C-2 is “up”)

Haworth projections depict pyranose rings as planar. However, as with cyclohexane, the rings generally prefer a chair conformation.

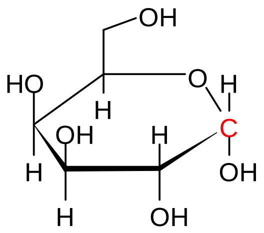
Examples of three typical pyranose structures are shown below, both as Haworth projections and as the more representative chair conformers. The anomeric carbons are colored red.



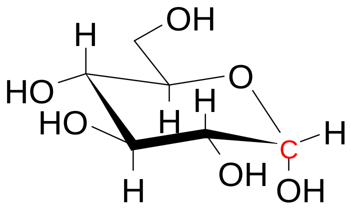
α-D-Glucopyranose



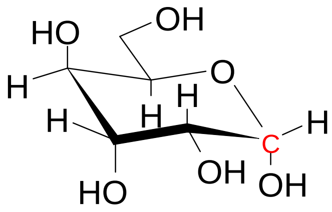
α-D-Gulopyranose



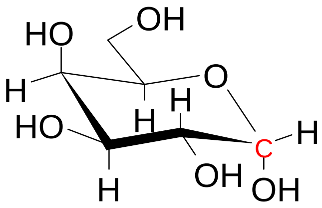
α-D-Galactopyranose



α-D-Glucopyranose



α-D-Gulopyranose



α-D-Galactopyranose

The size of the cyclic hemiacetal ring adopted by a given sugar is not constant, but may vary with substituents and other structural features. Aldolhexoses 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.

3.8 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 Self-Assessment Exercise 2

i. Draw the structure of the following and state clearly the nature of carbonyl carbon present;

(a) aldohexose

(b) ketopentose

(c) aldotriose

(d) ketotetrose

ii. Using the Fisher projection formula, write the structural formula for L-aldotetrose

iii. Convert the fisher projection formula for D-erythrose to a 3-D structural formula.

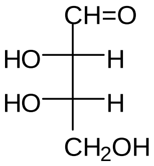
iv. What is the special name given to diastereomers that differ in configuration at the one stereogenic center? Use D-(-)-erythrose and D-(-)-threose as examples.

v. Draw the Haworth projection of the α and β forms of D-glucofuranose.

Answer to self-assessment exercise 2

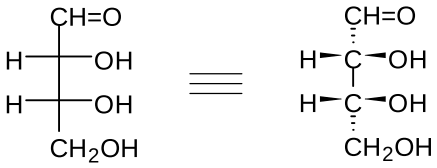
Attempt question i & ii

iii. L- aldotetrose is the enantiomer of D-aldotetrose. Since both hydroxyl (-OH) group are on the right in D-aldotetrose, they will both be on the left in its mirror image (L-aldotetrose) i.e



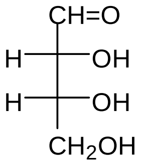
L-aldotetrose

iv. Fisher projection formula for D-erythrose to a 3-D structural formula.

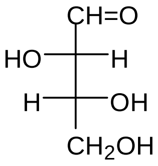


D-erythrose 3D form

v. They are called epimers e.g

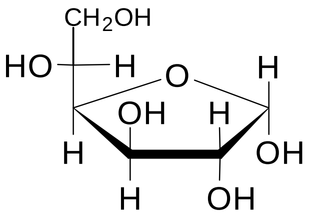


D-(-)-erythrose

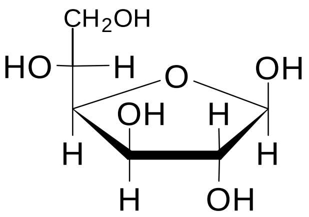


D-(-)-threose

vi. Haworth projection of the α and β forms of D-glucofuranose.



α-D-glucofuranose



β-D-glucofuranose

5.0 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. Stereochemisty 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. Haworth projections depict pyranose rings as planar. The preferred structural form of many monosaccharides may be that of a cyclic hemiacetal.

6.0 Summary

In this module, we have learnt that;

i. Monosaccharides are majorly classified base on the nature of carbonyl (aldehyde or ketone), the chain length and optical activity of the monosaccharide.

ii. 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*.

7.0 Further reading

Rawn, J. D and Ouellette, R (2018). Organic Chemistry: Structure, Mechanism, Synthesis, Second Edition, Academic Press, USA.

Module 2 Monosaccharides

Unit 2: Derivatives of Monosaccharides, this unit deals with the chemical reactions of monosaccharides to form various derivatives.

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, uronic acids etc. These derivatives serve as important components of many organisms and biologically important substances.

2.0 Intended Learning outcomes

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

i. Know the various derivatives of monosaccharides

ii. Give examples of such derivatives of monosaccharides

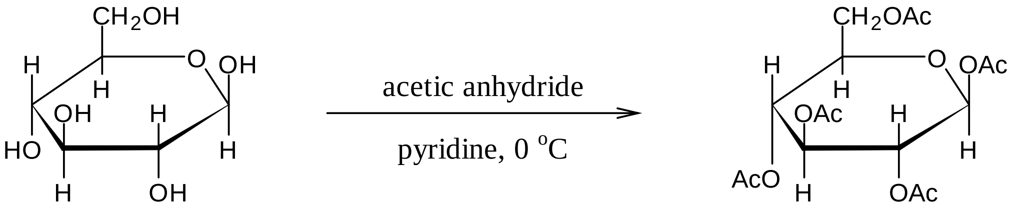
iii. Understand the reactions involving monosaccharides

3.0 Main content

3.1 Chemical reactions of monosaccharides

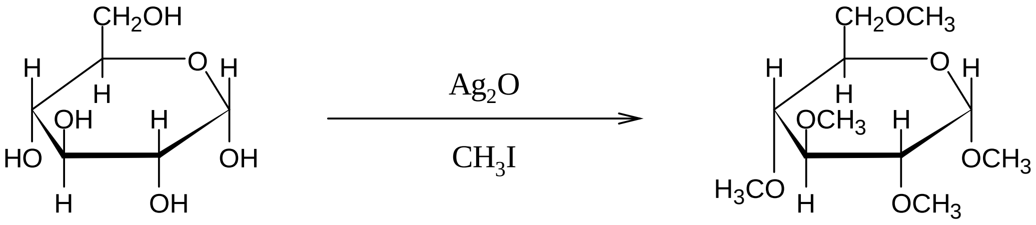
3.1.1 Formation of esters and ether

Monosaccharides contain hydroxyl groups, therefore undergo reactions typical of alcohols. For example, they can be converted to esters by reaction with acid halides or anhydrides. The conversion of β-D-glucose to its pentaacetate by reaction with excess anhydride is typical; all the five hydroxyl groups, including the hydroxyl at the anomeric (C-1) carbon are esterified;



β-glucopyranose **β-glucopyranose pentaacetate**

The hydroxyl can also be converted to ethers by treatment with an alkyl halide and a base (**Williamson synthesis**). Because sugars are sensitive to strong bases, the mild base silver oxide is preferred.

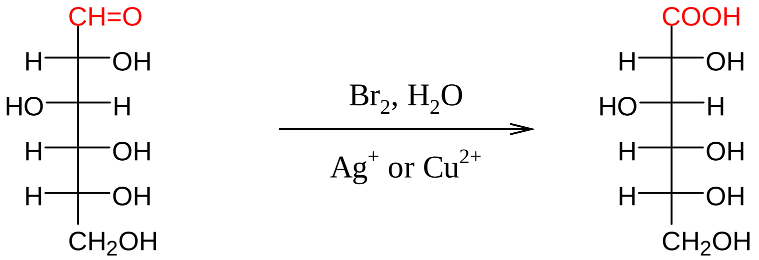


α-glucopyranose **α-glucopyranose pentamethyl ether**

Sugars tend to be soluble in water and insoluble in organic solvents, the reverse is true for their esters and ethers.

3.1.2 Oxidation of Monosaccharides

Most aldoes exist primarily in the cyclic hemiacetal forms but these structures are in equilibrium with a small but finite amount of the open-chain aldehyde. These aldehyde groups can be easily oxidized to acids. The products are called **aldonic acids**. For example, D-glucose is easily oxidized to D-gluconic acid.

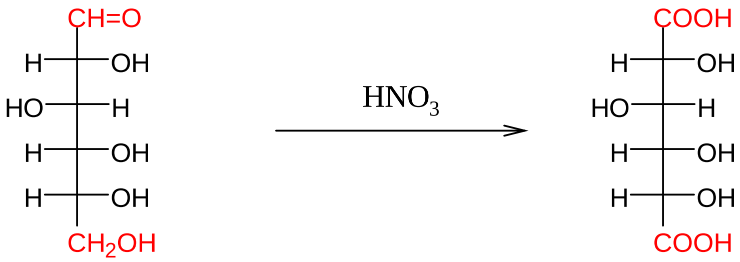


D-glucose D-gluconic acid

The oxidation of aldoses is so easy that they react with such mild oxidizing agents like Tollen's reagent (Ag^+ in aqueous ammonia), Fehling's reagent (Cu^{2+} complexed with tartrate ion) or Benedict's reagents (Cu^{2+} complexed with citrate ion). With Tollen's reagent, they give a silver mirror test and with the copper reagents, the blue solution gives a red precipitate of cuprous oxide, Cu_2O. A carbohydrate that reacts with Ag^+ or Cu^{2+} is called a reducing sugar because reduction of the metal accompanies oxidation of the aldehyde group.

$$RCH{=}O \; + \; \underset{\substack{\text{blue}\\ \text{solution}}}{2Cu^{2+}} \; + 5OH^- \longrightarrow RCOO^- \; + \; \underset{\substack{\text{red}\\ \text{precipitate}}}{Cu_2O} \; + \; 3H_2O$$

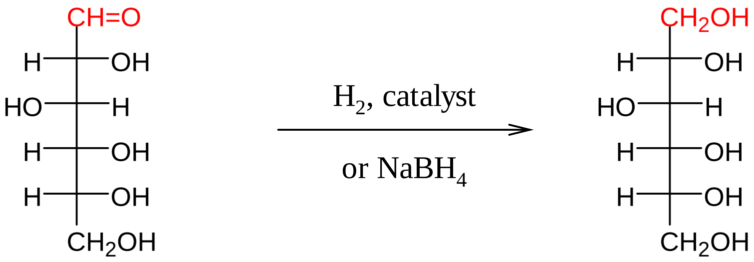
Strong oxidizing agents, such as aqueous nitric acid, attack the aldehyde group and the primary alcohol group to produce dicarboxylic acids called **aldaric acids.** For example, D-glucose gives D-glucaric acid;



D-glucose **D-glucaric acid**

3.1.3 Reduction

The carbonyl group of aldoses and ketoses can be reduced by various reagents, the products are **polyols** called **alditols.** For example, catalytic hydrogenation or reduction with sodium borohydride ($NaBH_4$) converts D-glucose to D-glucitol (also called sorbitol)



D-glucose **D-glucitol (sorbitol)**

The reaction occurs by reduction of the small amount of aldehyde in equilibrium with the cuclic hemiacetal. As that aldehyde is reduced, the equilibrium shifts to the right, so that eventually all of the sugar is converted. Sorbitol is used commercially as a sweetener and sugar substitute.

Sodium borohydride reduction of an aldose makes the ends of the resulting *alditol* chain identical, $HOCH_2(CHOH)_nCH_2OH$, 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.

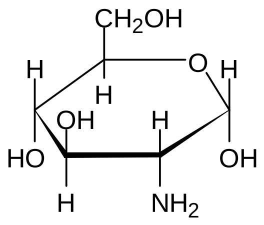
What is the difference in functional group(s) between D-glucose and D-glucitol (sorbitol)?

Solution: D-glucose has an aldehyde functional group which is missing in sorbitol due to its conversion to hydroxyl functional group.

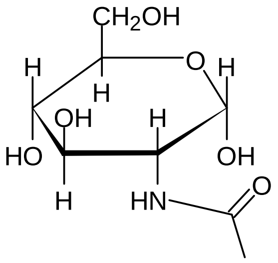
3.1.4 Formation of Amino sugars

Amino sugars or aminosaccharides are formed by the replacement of a hydroxyl group with an amino (-NH_2) group.

Glucosamine is an amino sugar used to treat cartilage damage and reduce the pain and progression of arthritis.



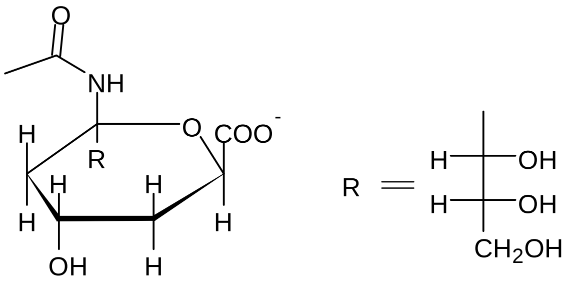
α-D-glucosamine



α-D-*N*-acetylglucosamine

3.1.5 N-acetylneuraminic acid

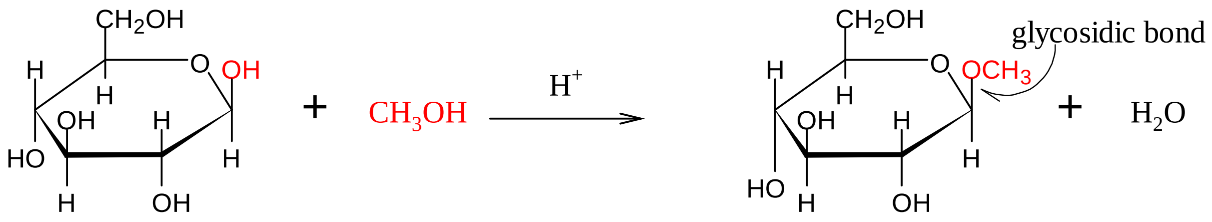
N-acetylneuraminate, (*N*-acetylneuraminic acid, also called sialic acid) is often found as a terminal residue of oligosaccharide chains of glycoproteins. Sialic acid imparts negative charge glycoproteins, because its carboxyl group tends to dissociate a proton at physiological pH, as shown here.



N-acetylneuraminate (sialic acid)

3.1.6 Formation of Glycoside

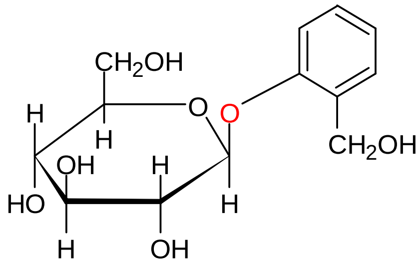
Because monosaccharides exit as cyclic hemiacetals, they can react with one equivalent of an alcohol to form acetals. An example is the reaction of β-D-glucose with methanol.



β-D-glucopyranose **Methyl β-D-glucopyranoside**

Note: Only the hydroxyl (-OH) group on the anomeric carbon is replaced by a methoxy ($-OCH_3$) group. Such acetals are called **glycosides** and the bond from the anomeric carbon to the methoxy ($-OCH_3$) group is called the **glycosidic bond**. Glycosides are named from the corresponding monosaccharides by changing the **–e** ending to **–ide**. Thus, a glucose gives glucoside, mannose gives mannoside etc.

Naturally occurring alcohols or phenols often occur in cells combined as a glycoside with some sugar, most commonly, glucose. In this way, the many hydroxyl groups of the sugar portion of the glycoside solubilize compounds that would otherwise be incompatible with cellular protoplasm. An example is the bitter-tasting glucoside **salicin**, which occurs in willow bark and whose fever-reducing power was known to the ancients.

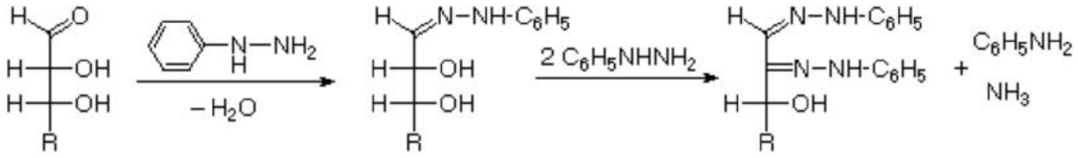


salicin

(β-D-glucoside of salicyl alcohol)

3.1.7 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.



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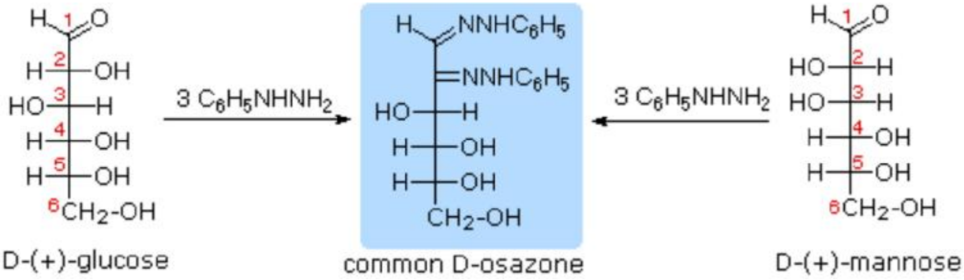
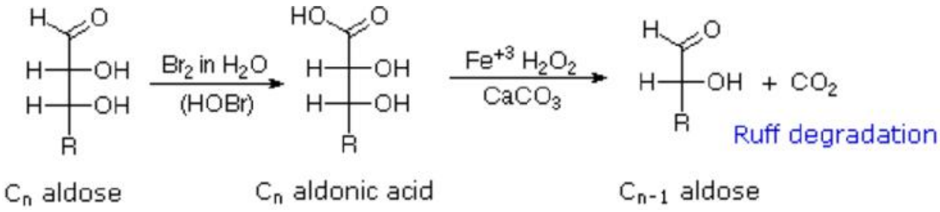


2.

3.1.8 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.



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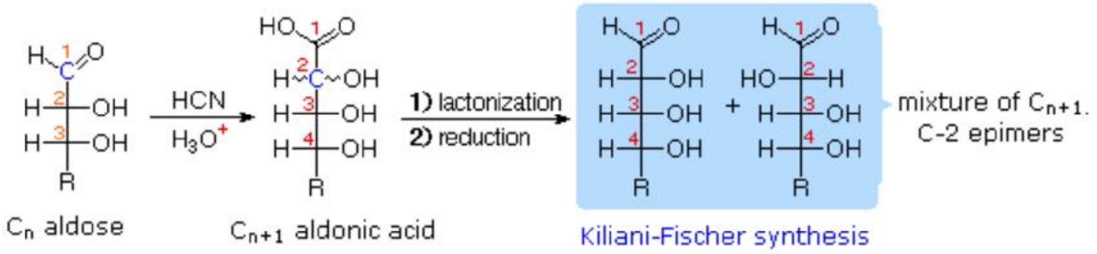
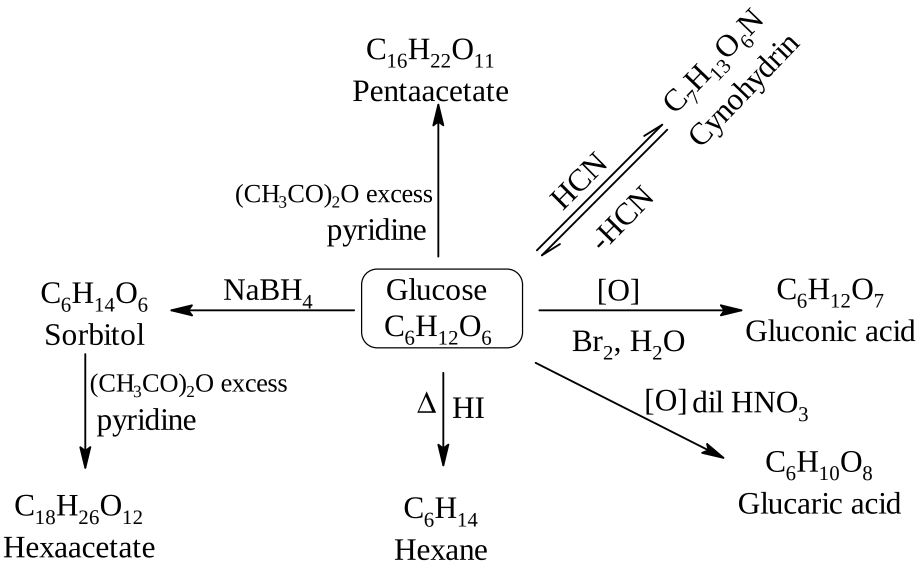


3.1.9 The structure of glucose

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.

3.2 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 1º-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.

4.0 Self-Assessment Exercise 3

i. Show the conversion of D-glucose to D-gluconic acid

ii. Show the formation of sorbitol from D-glucose

iii. What is the difference between gluconic and glucaric acid?

iv. Draw the structure of salicin (β-D-glucoside of salicyl alcohol)

v. When cyclic D-glucose react with methanol, what class of compound is formed? Illustrate with appropriate equation of reaction.

vi. Outline the Williamson synthesis of α-glucopyranose

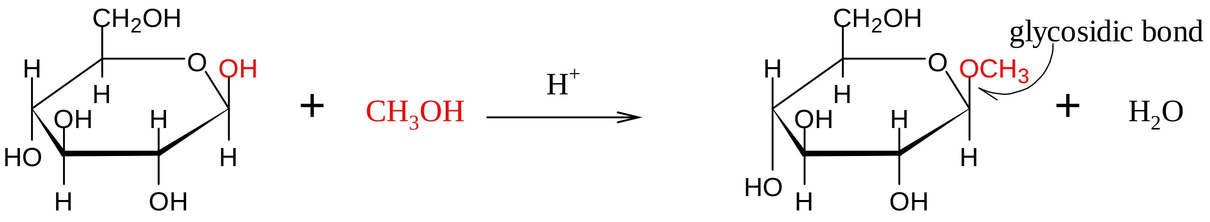
vii. Oxidation of D-glucose with bromine water in the presence of silver ion gives what product? Show the reaction.

viii. Reduction of D-glucose leads to the formation of Sorbitol, outline the reaction.

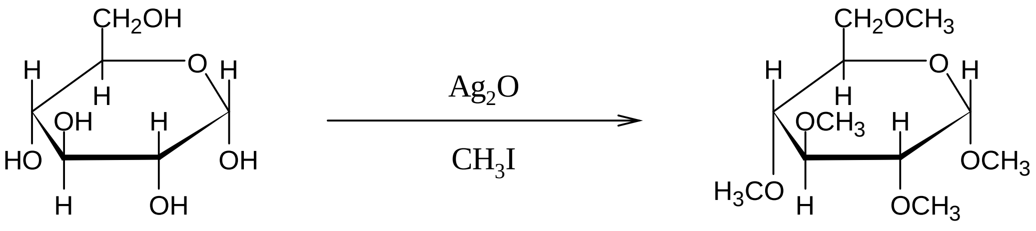
Answers to self-assessment exercise 3

Attempt questions i-iv yourself

v. Glycoside is the class of compound that is formed

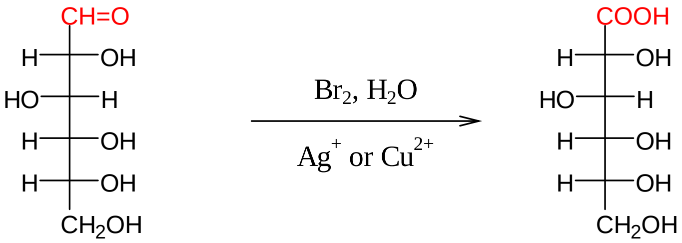


vi. Williamson synthesis of α-glucopyranose

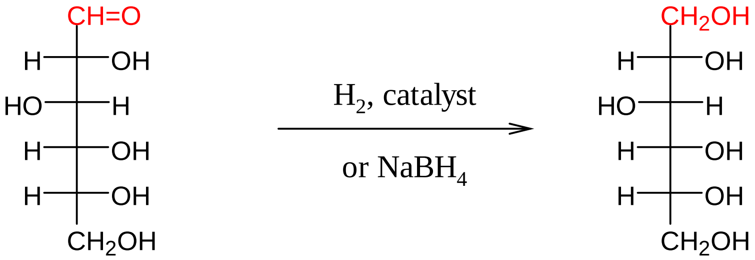


α-glucopyranose **α-glucopyranose pentamethyl ether**

vii. Oxidation of D-glucose with bromine water in the presence of silver ion gives D-gluconic acid.


D-glucose D-gluconic acid

viii. Reduction of D-glucose leads to the formation of Sorbitol as shown;


D-glucose **D-glucitol (sorbitol)**

5.0 Conclusion

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

6.0 Summary

In this unit, we have learnt that;

i. When the aldehyde function of an aldose is oxidized to a carboxylic acid the product is called an *aldonic acid*.

ii. If both ends of an aldose chain are oxidized to carboxylic acids the product is called an *aldaric acid*.

iii. 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.

v. Monosaccharides has many important derivatives.

vi. Sugar acids, amino sugars and uronic acids are some classes of sugar derivatives.

vii. Glucose, the simplest and commonest example of monosaccharides, take part in many chemical reactions to produce derivatives.

7.0 Further reading

Rawn, J. D and Ouellette, R (2018). Organic Chemistry: Structure, Mechanism, Synthesis, Second Edition, Academic Press, USA.

Module 3 Disaccharides

Module 3: Disaccharides consist of only one unit;

Unit 1: Diversity of disaccharides, which deals with the composition and diversity of disaccharide

Unit 1: Diversity of disaccharides

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1.0 Introduction

Disaccharides are the most common oligosaccharides. Disaccharide consist of two monosaccharides linked together by a glycosidic bond between the anomeric carbon of one of the monosaccharide unit and a hydroxyl group on the other monosaccharide unit. Examples are sucrose, maltose and lactose.

The general 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 Intended Learning Outcomes (ILOs)

At the end of this unit, students should be able to;
i. Know the constituents of all disaccharides
ii. Write the structures of most disaccharides iii.
Compare and contrast among disaccharides

3.0 Main content

3.1 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 1α→2 fructose
maltose	product of starch hydrolysis	glucose 1α→4 glucose
trehalose	found in fungi	glucose 1α→1 glucose
lactose	main sugar in milk	galactose 1β→4 glucose
melibiose	found in legumes	galactose 1α→6 glucose

3.1.1 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;

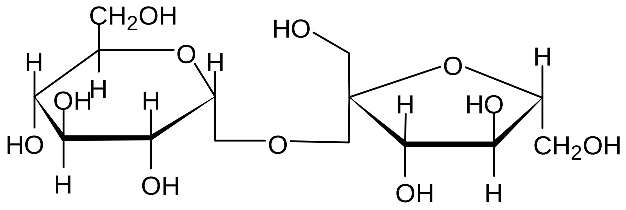
i. **Its monosaccharides:** glucose and fructose

ii. **Their ring types:** glucose is a pyranose, and fructose is a furanose.

iii. **How they are linked together:** the oxygen on carbon number 1 (C1) of α-D-glucose is linked to the C2 of D-fructose.

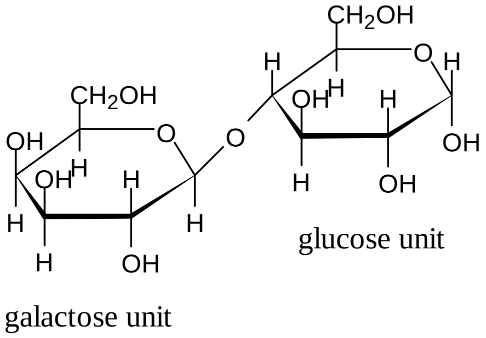
iv. **The *-oside* suffix:** indicates that the anomeric carbon of both monosaccharides participates in the glycosidic bond.

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- - - 2).



3.1.2 Lactose

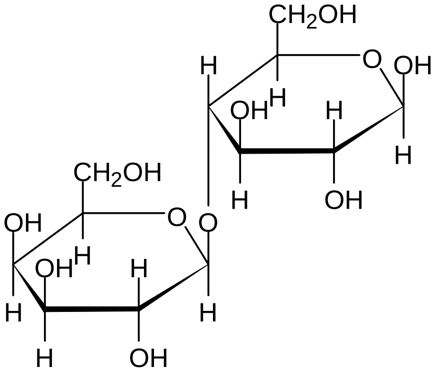
Lacotse is the major sugar in human and cow's milk (4 to 8% lactose). Hydrolysis of lactose gives equimolar amounts of D-galactose and D-glucose. The anomeric carbon of the galactose unit has the β configuration at C-1 and is linked to the hydroxyl group at C-4 of the glucose unit. Its full name is β-D-galactopyranosyl-(1- - - 4)-β-D- glucopyranose. It is of interest because it is associated with *lactose intolerance* (galactosemia) which is the intestinal distress caused by a deficiency of lactase, an intestinal enzyme needed for the isomerization of galactose to glucose hence the baby cannot 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.



Lactose

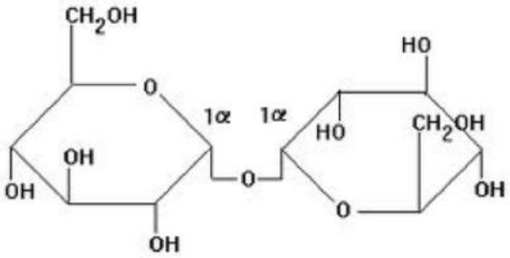
3.1.3 Maltose

Maltose is the disaccharide obtained by the partial hydrolysis of starch. Further hydrolysis of maltose gives only D-glucose, 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 1α→4 glycosidic linkage. It is a disaccharide with an α(1- - - 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.



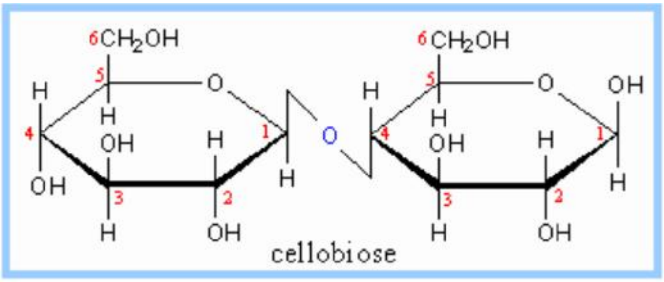
3.1.4 Trehalose

Trehalose has two α-D-glucose molecules connected through carbon number one in a 1α→1 linkage. It isalso 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→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.



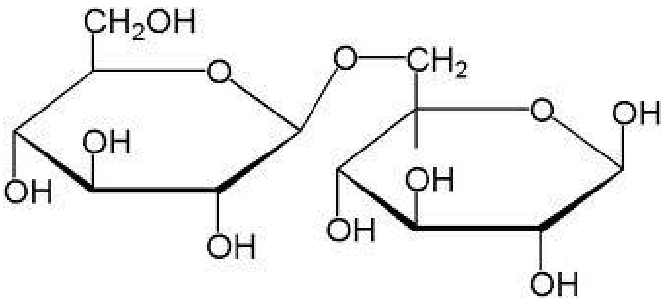
3.1.5 Cellobiose

Cellobiose is the disaccharide obtained by the partial hydrolysis of cellulose. Further hydrolysis of cellobiose give only D-glucose. Cellobiose is an isomer of maltose, it differ from maltose only in having the β configuration at C-1 of the left glucose unit. Otherwise all structural features are identical, including a link from C-1 of the left unit to the hydroxyl group at C-4 in the right unit. Cellobiose has no taste, whereas maltose and trehalose are about one-third as sweet as sucrose.



3.1.6 Gentiobiose

Gentiobiose is a disaccharide composed of two units of D-glucose joined with a β(1->6) 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



3.1.7 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

1. A carbohydrate that reacts with silver ion (Ag^+) or copper (ii) ion (Cu^{2+}) is called what?
2. Tollen's reagent is a mild oxidizing agent, which will react with this reagent, aldoses or ketoses?

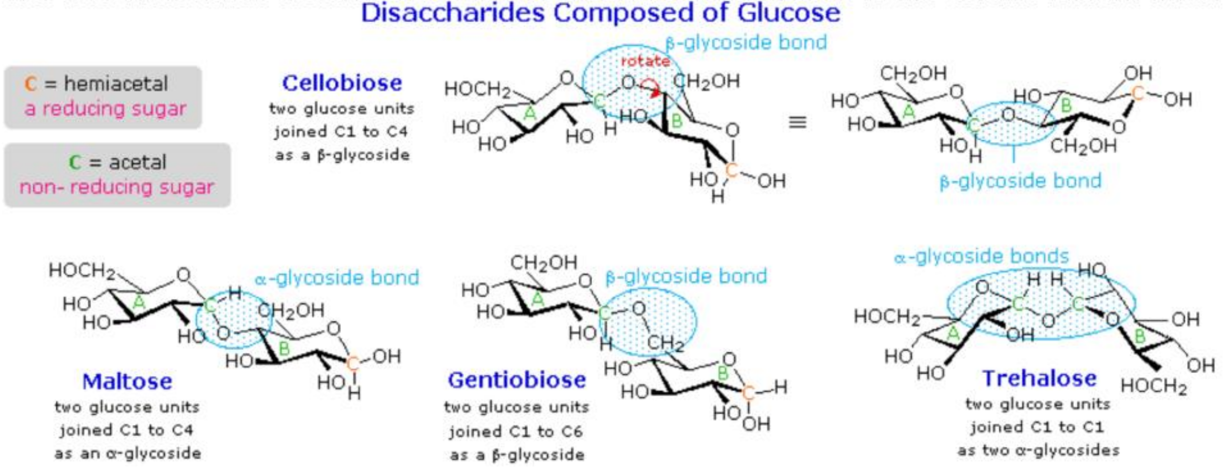
Solutions:

1. Reducing sugars
2. aldoses

3.1.8 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



4.0 Self-Assessment Exercise 4

i. Draw the structure of sucrose

ii. Give the structural difference between maltose, cellobiose, trehalos and gentiobiose

iii. What is the main source of lactose? What type of monosaccharides are present in lactose?

iv. Give five examples of disaccharides and state the composition of each.

v. Write the structures of sucrose, trehalose and maltose.

vi. Kindly explain the infant disease called galactosemia and how it can be avoided.

vii. Draw the structure of lactose indicating the monosaccharides present.

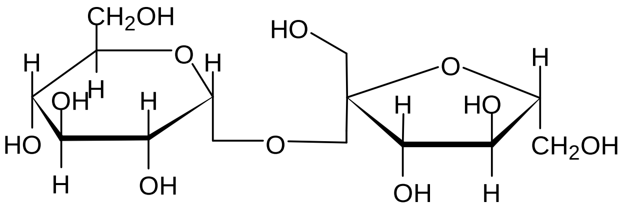
Answers to self-assessment exercise 4

Attempt questions i-iii answers to iv-vii is hereby provided.

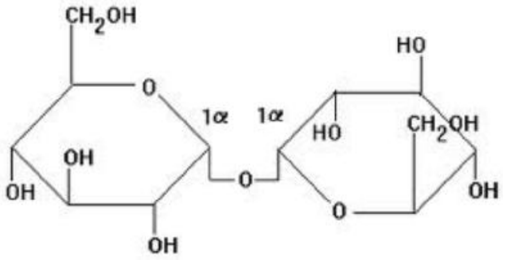
iv. Five examples of Disaccharides and their compositions;

Disaccharide	**Description**	**Component monosaccharides**
sucrose	common table sugar	glucose and fructose
maltose	product of starch hydrolysis	glucose and glucose
trehalose	found in fungi	glucose and glucose
lactose	main sugar in milk	galactose and glucose
melibiose	found in legumes	galactose and glucose

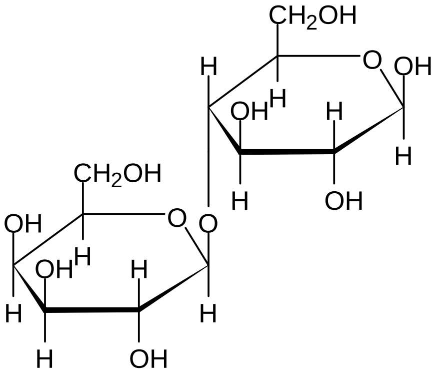
v. the structures of sucrose, trehalose and maltose.



Sucrose



Trehalose

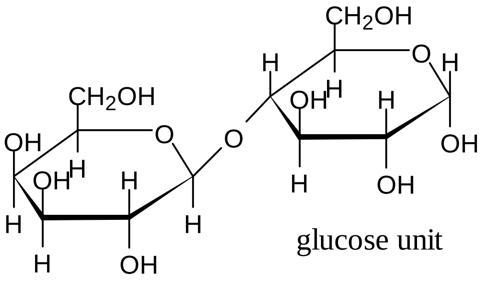


Maltose

vi. galactosemia and how it can be avoided?

Some human infants are born with a disease called galctosemia which arises as a result of lack of the enzyme that isomerizes galactose to glucose, hence the baby cannot digest milk. If therefore milk is excluded from such infant's diet, the disease symptoms caused by accumulation of galactose can be avoided.

vii. the structure of lactose indicating the monosaccharides present



glucose unit

galactose unit

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 as in milk (lactose), table sugar (sucrose) and malt sugar (maltose).

6.0 Summary

In this module, 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 Further reading

Rawn, J. D and Ouellette, R (2018). Organic Chemistry: Structure, Mechanism, Synthesis, Second Edition, Academic Press, USA.

Module 4 Polysaccharides

Module 4: Chemistry of Polysaccharides consist of three units;

Unit 1: Homopolysaccharides; this unit deals with starch and glycogens polysaccharides that gives only one kind of monosaccharides on hydrolysis.

Unit 2: Homopolysacharides; this unit deals with cellulose and derivatives of cellulose.

Unit 3: Heteropolysaccharides, this unit deals with polysaccharides that gives more than one type of monosaccharide on hydrolysis.

Unit 1: Homopolysaccharides; Starch and Glycogen

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1.0 Introduction

Polysaccharides contain many linked monosaccharides and vary in chain length and molecular weight. Monosaccharides in polysaccharides are linked together by glycosidic bonds, these monosaccharides units may be linked linearly or the chains may be branched. Polysaccharides are sometimes called *glycans*. The most important compounds in this class are; cellulose, starch and glycogen all are polymers of glucose. Most polysaccharides give a single monosaccharide (homopolysaccharide) on complete hydrolysis. Those that give different kinds of monosaccharides are referred to as heteropolysaccharides.

2.0 Intended learning Outcomes (ILOs)

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 Main content

3.1 Homopolysaccharides

These are polysaccharides that gives a single type of monosaccharides on complete hydrolysis. Examples include starch, glycogen and cellulose.

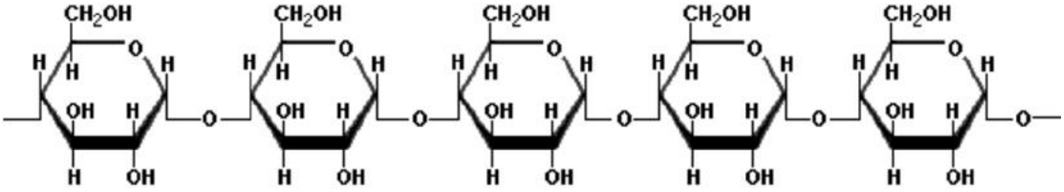
3.1.1 Starch

Starch is the energy-storing carbohydrates of plants. It is the major component of cereals, potatoes, corn and rice. It is the form in which glucose is stored by plants for later use. Starch is made up of 300 to 1000 glucose units join together.

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. 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.

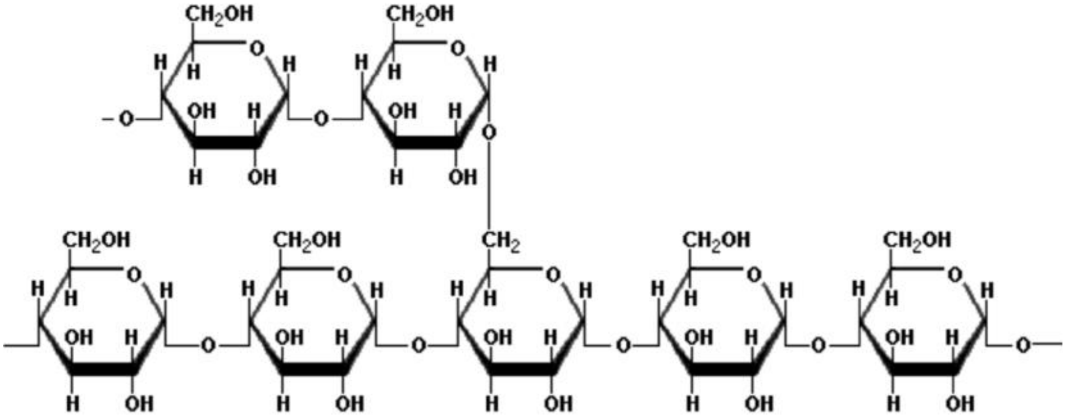
Starch can be separated by various solution and precipitation techniques into two fractions; *amylose,* an essentially linear polysaccharide, and *amylopectin,* a highly branched polysaccharide. Both forms of starch are polymers of α-D-Glucose. Natural starches contain 10-20% amylose and 80-90% amylopectin. 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.

3.1.2 Amylose: *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

3.1.3 Amylopectin differs from amylose in being highly branched. Short side chains of about 30 glucose units are attached with 1α→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).

3.1.4 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.

3.1.5 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.

3.1.6 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.

3.1.7 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.

3.1.8 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.

3.1.9 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.

3.10 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.

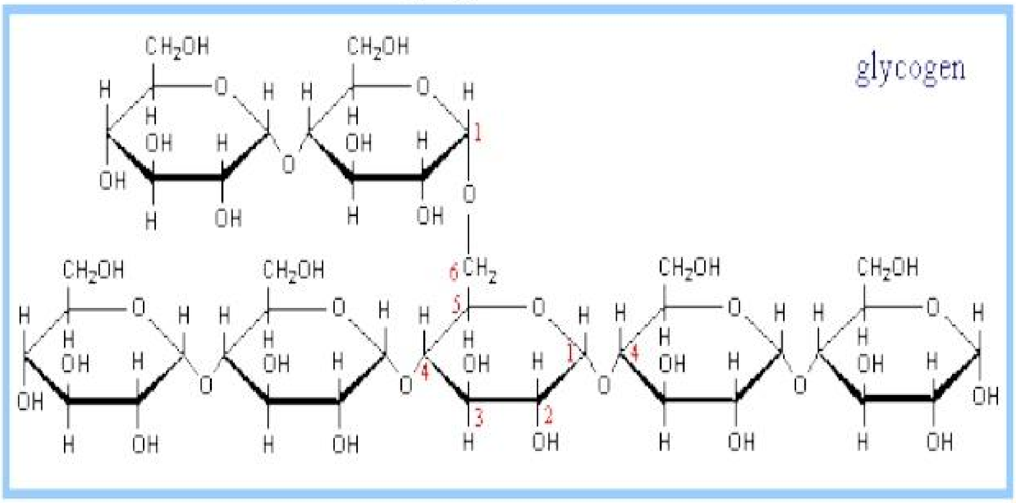
Glycogen is the glucose storage polymer used by animals. It has a structure similar to amylopectin, but is even more highly branched (about every tenth glucose unit). The degree of branching in these polysaccharides may be measured by enzymatic or chemical analysis.

i. Starch can be separated into what?
ii. What is the energy storing carbohydrates of animals with higher molecular weight than starch?

Solution:

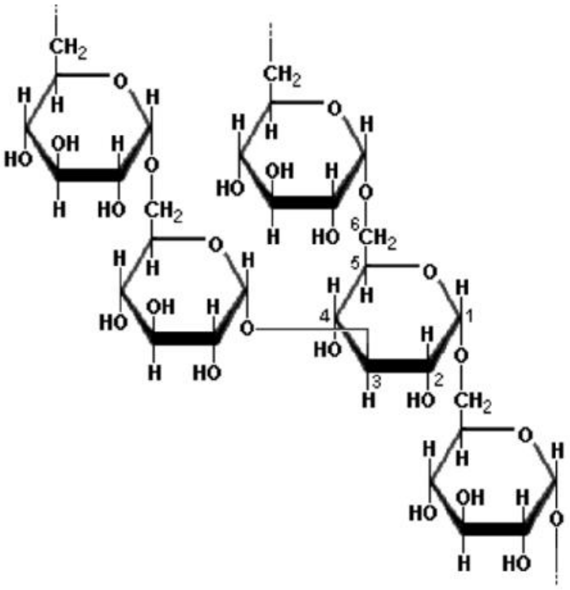
i. Amylose and amylopectin
ii. Glycogen

Structure of Glycogen molecule



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

4.0 Self-Assessment Exercise 5

i. Describe the composition of starch

ii. Distinguish between glycogen and dextran

iii. In what form is carbohydrates stored in the human body?

iv. Draw the structure of dextran

v. What are Homopolysaccharides?

vi. Give three examples of homopolysaccharides and state the composition of each.

vii. Draw the structure of amylose and how does it differ from that of amylopectin

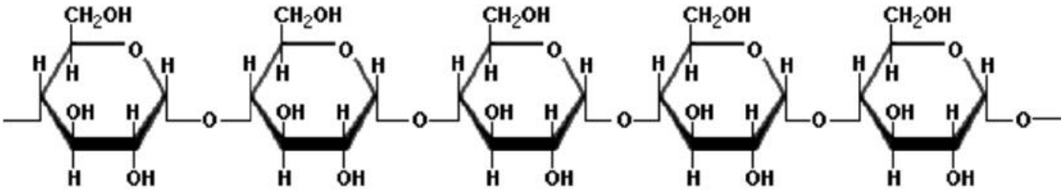
Answers to self-assessment exercise 5

Answers to questions v-vii are provided attempt questions i-iv

v. These are polysaccharides that gives a single type of monosaccharides on complete hydrolysis.

vi. Three examples of homopolysaccharides are starch, glycogen and cellulose, they are all composed of glucose units.

vii. the structure of amylose and how it differ from that of amylopectin



The structure of amylose consist of glucose units arranged in a linear form, whereas that of amylopectin has some branches.

5.0 Conclusion

Homopolysaccharides have only one type of monosaccharides within them. They are present within plants and animals. They include starch, glycogen and cellulose. Starch is the energy-storing carbohydrates of plants, it is made up of glucose units joined by glycosidic bonds.

Starch can be separated into amylose and amylopectin. Glycogen is the energy-storing carbohydrates of animals, with higher molecular weight than starch.

6.0 Summary

In this unit, we have learnt that

i. Polysaccharides can be classified into homopolysaccharides and heteropolysaccharides.

ii. Homopolysaccharides consist of only one type of monosaccharide.

iii. Starch, dextrans and glycogens are examples of homopoysaccharides.

7.0 Further reading

Rawn, J. D and Ouellette, R (2018). Organic Chemistry: Structure, Mechanism, Synthesis, Second Edition, Academic Press, USA.

Module 4 Polysaccharides

Unit 2: Homopolysacharides; deals with cellulose and derivatives of cellulose, they are also polysaccharides that gives only one kind of monosaccharides on hydrolysis.

Unit 2: Homopolysaccharides; Cellulose and derivatives

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1.0 Introduction

Cellulose are polysaccharides that contain many linked monosaccharides that may vary in chain length and molecular weight. Cellulose gives a single monosaccharide (homopolysaccharide) on complete hydrolysis.

2.0 Intended learning Outcomes (ILOs)

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

i. understand the term cellulose,

ii. Sources of cellulosic materials,

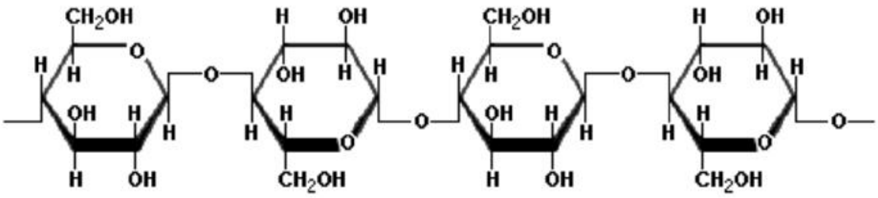
iii. Some derivatives of cellulose.

3.0 Main content

3.1 Cellulose

Cellulose is a polymer of β-D-Glucose, which in contrast to starch, is oriented with -CH_2OH 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 (-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.

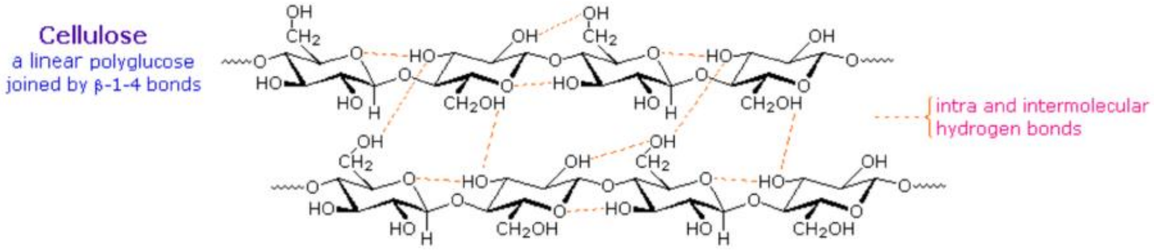
Over half of the total organic carbon in the earth's biosphere is in cellulose. Cotton fibers are essentially pure cellulose, and the wood of bushes and trees is about 50% cellulose. As a polymer of glucose, cellulose has the formula $(C_6H_{10}O_5)_n$ where n ranges from 500 to 5,000, depending on the 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

3.1.1 Cellulose Gum or **Carboxymethyl Cellulose (CMC)** is a chemical derivative of cellulose where some of the hydroxyl groups (-OH) are substituted with carboxymethyl groups (- CH_2COOH). 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.



Between α-glycosidic and β-glycosidic bonds which can the human digestive system hydrolyzed?

Solution: The human digestive system contains enzymes that can catalyze the hydrolysis of α-glycosidic bonds but lacks the enzyme necessary to hydrolyze β-glycosidic bonds.

3.1.2 Synthetic Modification of Cellulose

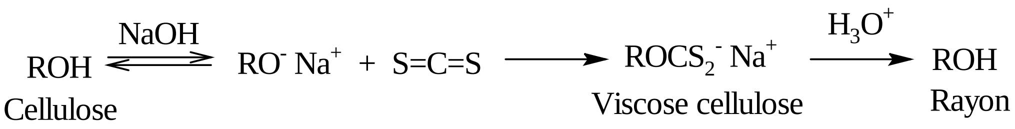
Cotton, probably the most useful natural fiber, is nearly pure cellulose. The manufacture of textiles from cotton involves physical manipulation of the raw material by carding, combing and spinning selected fibers. For fabrics the best cotton has long fibers, and short fibers or cotton dust are removed. 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.

3.1.3 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.

3.1.4 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.

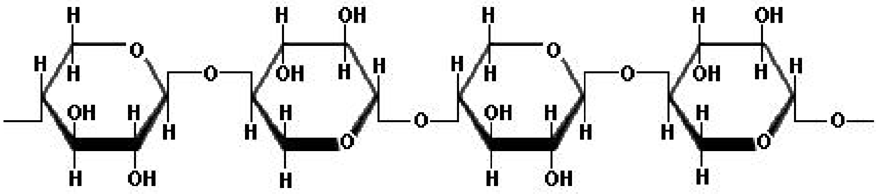
3.1.5 Viscose Rayon is prepared by formation of an alkali soluble xanthate derivative that can be spun into a fiber that reforms the cellulose polymer by acid quenching. The following general equation illustrates these transformations. The product fiber is called *viscose rayon*.



$$\underset{\text{Cellulose}}{ROH} \xrightleftharpoons{NaOH} RO^- Na^+ + S{=}C{=}S \longrightarrow \underset{\text{Viscose cellulose}}{ROCS_2^- Na^+} \xrightarrow{H_3O^+} \underset{\text{Rayon}}{ROH}$$

3.1.6 Hemicellulose

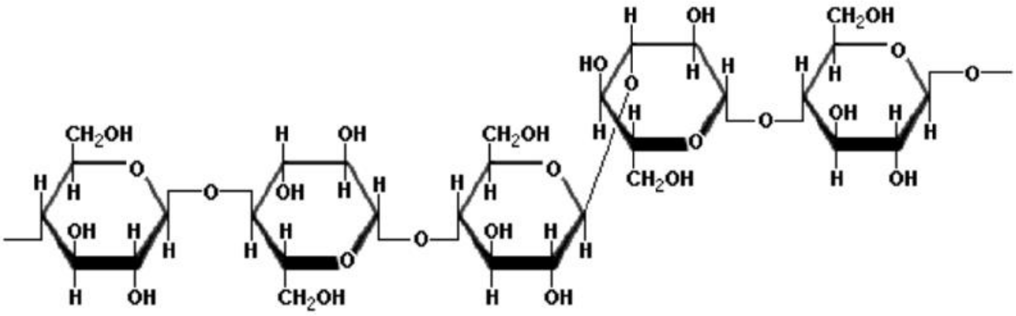
The term "hemicellulose" is applied to the polysaccharide components of plant cell walls other than cellulose, or to polysaccharides in plant cell walls which are extractable by dilute alkaline solutions. Hemicelluloses comprise almost one-third of the carbohydrates in woody plant tissue. The chemical 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 1β → 4 linkages.



Xylan

3.1.7 Beta-Glucan

Beta-glucans consist of linear unbranched polysaccharides of β-D-Glucose like cellulose, but with one 1β→3 linkage for every three or four 1β→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 comercially to modify food texture and as fat substitutes.



β-Glucan

4.0 Self-assessment exercise 6

i. How does cellulose differ from starch structurally?

ii. Using equations only write the general conversion of cellulose to rayon

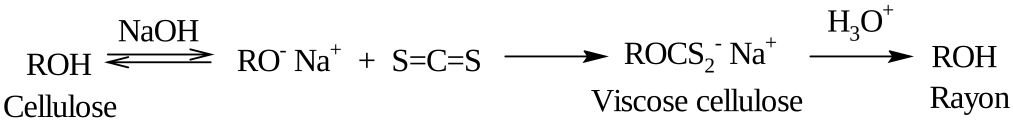
iii. Give one (1) reason why humans cannot digest cellulose but animals such as cattle's digest cellulose easily.

iv. Cellulose compound, guncotton is an explosive flammable compound. It is prepared by treating cellulose with what?

Answers to self-assessment exercise 6

i. cellulose consist of β-D-glucose in which the –CH_2OH groups are alternating above and below the plane of the molecule, thus producing long unbranched chain. Unlike starch which does not have alternating –CH_2OH group.

ii. the general conversion of cellulose to rayon



$$\underset{\text{Cellulose}}{ROH} \xrightleftharpoons{NaOH} RO^- Na^+ + S{=}C{=}S \longrightarrow \underset{\text{Viscose cellulose}}{ROCS_2^- Na^+} \xrightarrow{H_3O^+} \underset{\text{Rayon}}{ROH}$$

iii. Human cannot digest cellulose directly because they lack the enzyme beta-glycosidase needed to breakdown cellulose, unlike animals such as cattle's that have such enzyme.

iv. Cellulose compound, guncotton is made by treating cellulose with nitric acid.

5.0 Conclusion

Cellulose is a homopolysaccharide consisting of an unbranched chain of glucose monosaccharides joined by glycosidic bonds. X-ray examination of cellulose shows that it consists of linear chains of cellobiose units, in which the ring oxygens alternate in forward and backward positions.

6.0 Summary

In this unit, we have learnt that;

i. Cellulose is a homopolysaccharides, which consist of glucose units in a linear chain.

ii. Cellulose undergo chemical reactions to form different types of derivatives.

iii. Examples of cellulose derivatives include cellulose acetate, cellulose nitrates etc.

7.0 Further reading

Rawn, J. D and Ouellette, R (2018). Organic Chemistry: Structure, Mechanism, Synthesis, Second Edition, Academic Press, USA.

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Module 4 Polysaccharides

Unit 3: Heteropolysaccharides, this unit deals with polysaccharides that gives more than one type of monosaccharide on hydrolysis.

Unit 2: Heteropolysacchardes

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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 Intended learning Outcomes (ILOs)

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

i. Define heteropolysaccharides.

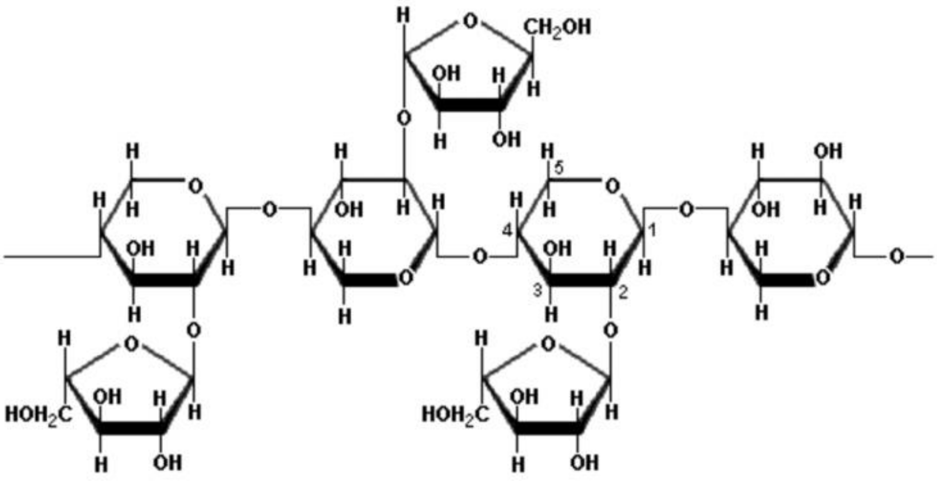
ii. Highlight specific examples of heteropolysaccharides. iii. Describe chitin, caragenaan and agar.

3.0 Main content

3.1 Types of heteropolysaccharides

3.1.1 Arabinoxylan

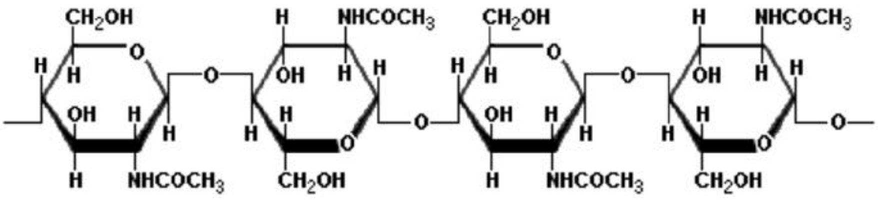
Arabinoxylans are polysaccharides found in the bran of grasses and grains such as wheat, rye, and barley. Arabinoxylans consist of a xylan backbone with L-arabinofuranose (L-arabinose in its 5-atom ring form) attached randomly by 1α→2 and/or 1α→3 linkages to the xylose units throughout the chain. Since 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

3.1.2 Chitin

Chitin is a nitrogen-containing polysaccharide that forms the shells of crustaceans and the exoskeletons of insects. It is similar to cellulose, except that the hydroxyl group at C-2 of each glucose unit is replaced by an acetylamino group, CH_3CONH-.



Chitin

3.1.3 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.

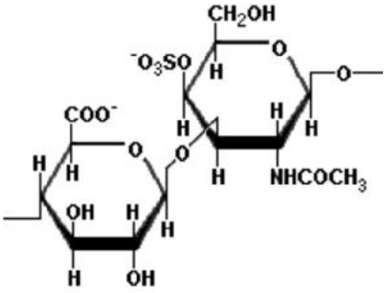
i. Xylose and arabinose are classified as?

ii. What carbohydrate is present in sea shell?

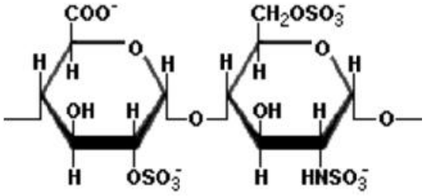
Solution:

i. Pentosans because they are both pentose

ii. Chitin

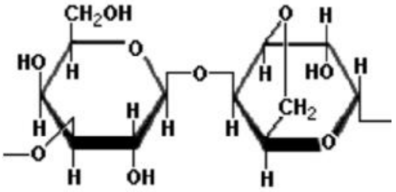


Chondroitin Sulfate



Heparin

3.1.4 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.

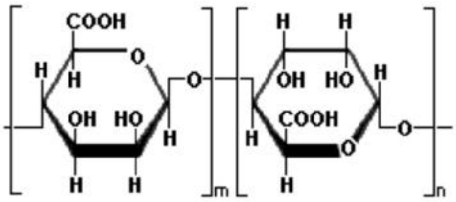


Agarobiose

3.1.5 Carrageenan is a generic term for several polysaccharides also extracted from seaweed. Carrageenan compounds differ from agar in that they have sulfate groups ($-OSO_3^-$) in place of some hydroxyl groups. Carrageenan is also used for thickening, suspending, and gelling food products.

3.1.6 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→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 suppresants. In dentistry, alginates are used to make dental impressions.



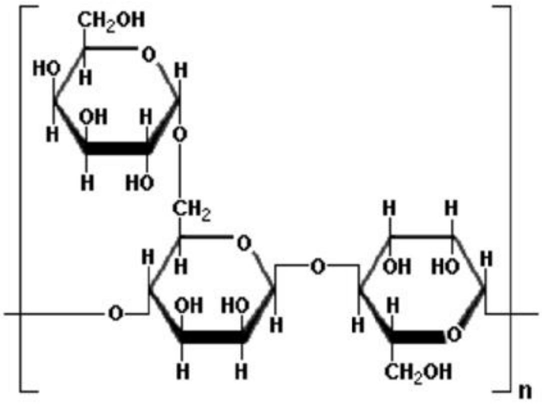
Alginic acid

3.1.7 Galactomannan

Galactomannans are polysaccharides consisting of a mannose backbone with galactose side groups. The mannopyranose units are linked with 1β→4 linkages to which galactopyranose units are attached with 1α→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)

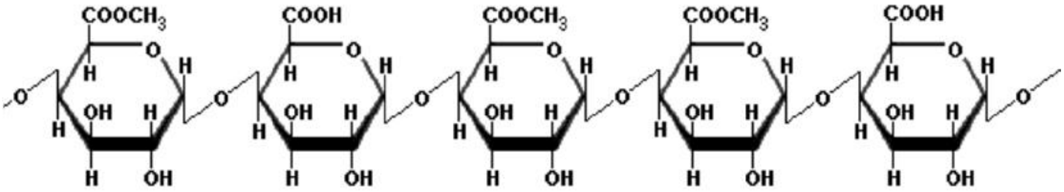
Guar is a legume that has been traditionally cultivated as livestock feed. Guar gum is also known by the name *cyamopsis tetragonoloba* which is the Latin taxonomy for the guar bean or cluster bean. *Guar gum* is the ground endosperm of the seeds. Approximately 85% of guar gum is *guaran*, a water soluble polysaccharide consisting of linear chains of mannose with 1β→4 linkages to which galactose units are attached with 1α→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.

3.1.8 Pectin

Pectin is a polysaccharide that are obtained from fruits and berries, they act 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 1α→4 linkages. The Degree of Esterification (DE) affects the gelling properties of pectin. The structure shown here has three methyl ester forms (**$-COOCH_3$**) for every two carboxyl groups (**$-COOH$**), hence it is has a 60% degree of esterification, normally called a DE-60 pectin. Pectin is an important ingredient of fruit used in making jellies, and jams.

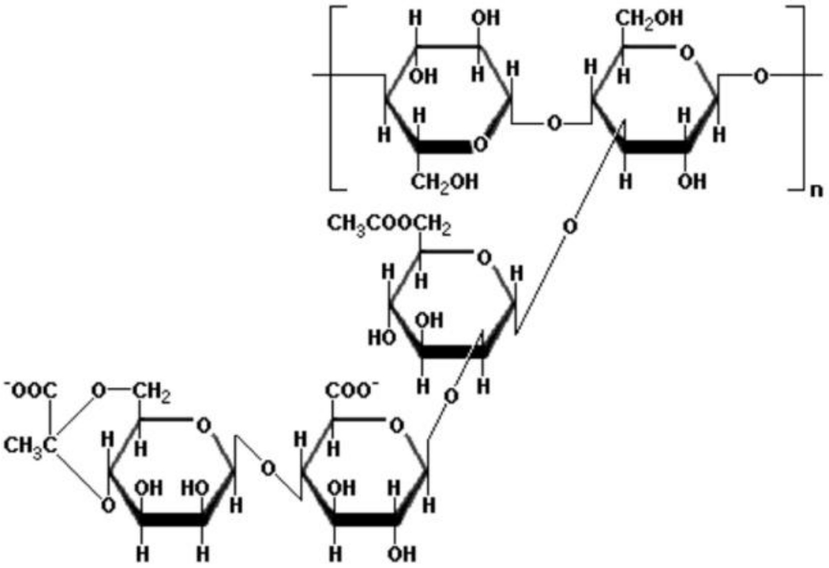


Pectin is a polymer of α-Galacturonic acid with a variable number of methyl ester groups.

3.1.9 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.

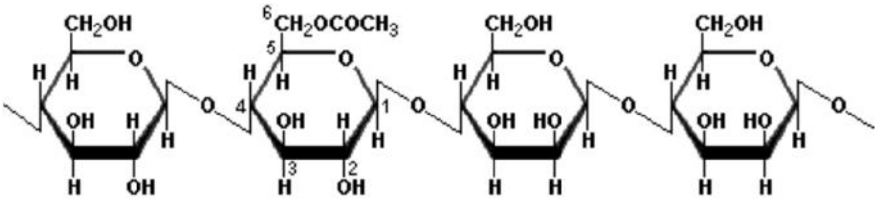
Xanthan Gum is produced by the bacterium *Xanthomonas campestris*, which is found on cruciferous vegetables such as cabbage and cauliflower. The negatively charged carboxyl groups on the side chains cause the molecules to form very viscous fluids when mixed with water. Xanthan gum is used as a thickener 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

3.10 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 1β→4 linkages. The basic polymeric repeating unit has the pattern: GGMMGMMMMMGGM. Short side chains of 11-16 monosaccharides occur at intervals of 50-60 units of the main chain attached by 1β→3 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.

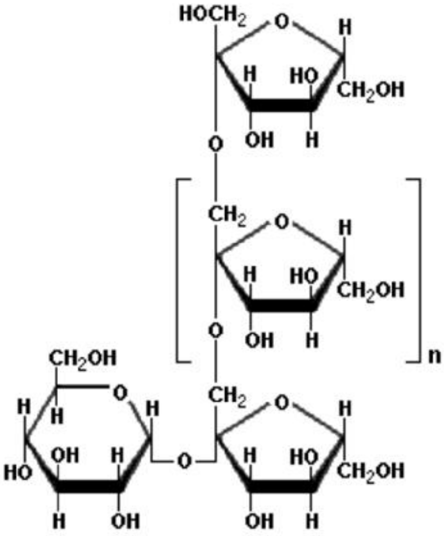


A portion (GGMM) of the glucomannan repeating unit.

The second glucose has an acetate group.

3.11 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.



Inulin (n = approx.. 35)

4.0 Self- Assessment Exercise 7

i. Describe the structure and function of chitin.

ii. Distinguish between agar and carrageenan

iii. What are the polysaccharides and monosaccharides present in the following;
   (a) Onions (b) Berry (c) Guar gum (d) Seashells

iv. Give four examples of heteropolysaccharides

v. Draw the structure of Chitin and state how it differ to that of Cellulose

vi. What polysaccharide is present in jellies and jams?

Answers to self-assessment exercise 7

Answers to question iii-vi is hereby provided, attempt i & ii

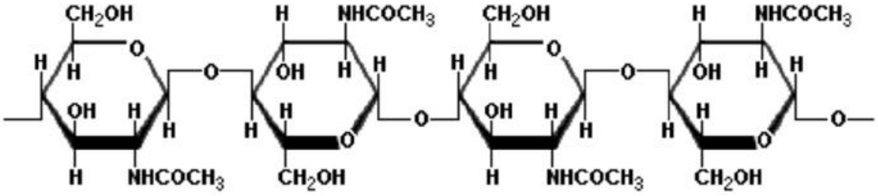
iii. polysaccharides and monosaccharides present in the following;

Question	Material	Polysaccharide	Monosaccharide
a	Onion	Inulin	Fructose & glucose
b	Berry	Pectin	Galacturonic acid
c	Guar gum	Galactomannan	Mannose& galactose
d	Seashell	Chitin	Acetylaminoglucose

iv. four examples of heteropolysaccharides;

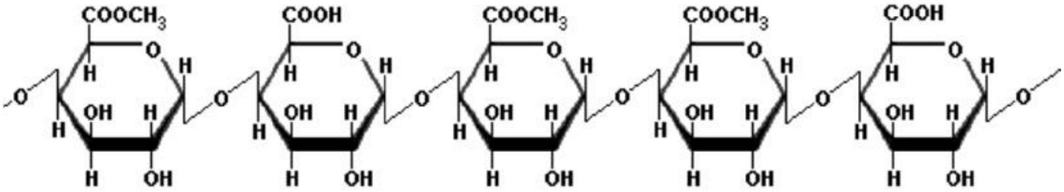
(a) Chitin (b) Pectin (c) Inulin (d) Glucomannan (e) Xanthan (f) Galactomann (g) Glycosaminoglycans (any 4)

v. structure of Chitin



It is similar to cellulose, except that the hydroxyl group at C-2 of each glucose unit is replaced by an acetylamino group (CH_3CONH-) in Chitin.

vi. polysaccharide is present in jellies and jams is Pectin and the structure is;



5.0 Conclusion

Heteropolysaccharides are polysaccharides which are characterised by more than one unit of monosaccharides. Examples of heteropolysaccharides include chitin, agar, caragenaan, pectin and inulin. Chitin is a nitrogen-containing polysaccharide that forms the shells of crustaceans and the exoskeletons of insects. Pectin is a polysaccharide that are obtained from fruits and berries, they act as a cementing material in the cell walls of all plant tissues.

6.0 Summary

In this Unit, we have learnt that

i. Heteropolysaccharides are made up of more than one type of monosaccharides.

ii. Heteropolysaccharides are present naturally in plants, animals and micro-organisms

iii. Examples of heteropoysaccharides include chitin, pectin and inulin.

7.0 Further reading

Rawn, J. D and Ouellette, R (2018). Organic Chemistry: Structure, Mechanism, Synthesis, Second Edition, Academic Press, USA.

CHM315: Carbohydrates Chemistry

Answers to Tutorial Questions

Module 1

Unit 1

i. Give four (4) different classes of carbohydrates with at least two examples each.

ii. Differentiate between disaccharides and oligosaccharides.
iii. What are the two important functional groups present in a carbohydrate?

Answers

i. Carbohydrates can be classified into four;

a. Monosaccharides- eg glucose, fructose, galactose (any 2)

b. Disaccharides- eg sucrose, lactose, maltose (any 2)

c. Oligosaccharides-eg raffinose and stachyose

d. Polysaccharides-eg starch, glucogen, cellulose (any 2)

ii. Disaccharides differ from oligosaccharide; disaccharide consist of only two monosaccharide units while oligosaccharide can content 2 to 10 monosaccharides units

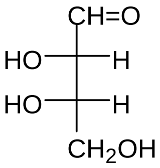
iii. The two most important functional groups present in a carbohydrates are hydroxyl (-OH) and ether (-O-)

Module 2
Unit 1

i. Using the Fisher projection formula, write the structural formula for L-aldotetrose
ii. Convert the fisher projection formula for D-erythrose to a 3-D structural formula.
iii. What is the special name given to diastereomers that differ in configuration at the one stereogenic center? Use D-(-)-erythrose and D-(-)-threose as examples.
iv. Draw the Haworth projection of the α and β forms of D-glucofuranose.

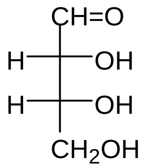
Answer

i. L- aldotetrose is the enantiomer of D-aldotetrose. Since both hydroxyl (-OH) group are on the right in D-aldotetrose, they will both be on the left in its mirror image (L-aldotetrose) i.e



L-aldotetrose

ii. Fisher projection formula for D-erythrose to a 3-D structural formula.



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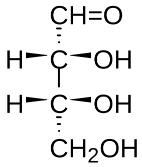
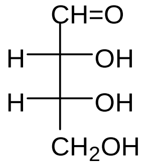
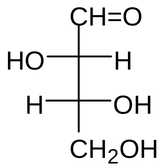


D-erythrose 3D form

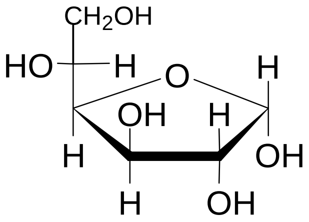
iii. They are called epimers e.g



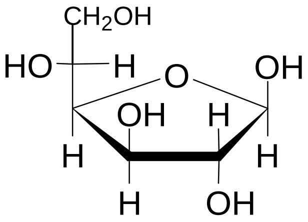


D-(-)-erythrose D-(-)-threose

iv. Haworth projection of the α and β forms of D-glucofuranose.



α-D-glucofuranose



β-D-glucofuranose

Module 2
Unit 2
self-assessment exercise

i. Show the conversion of D-glucose to D -gluconic acid

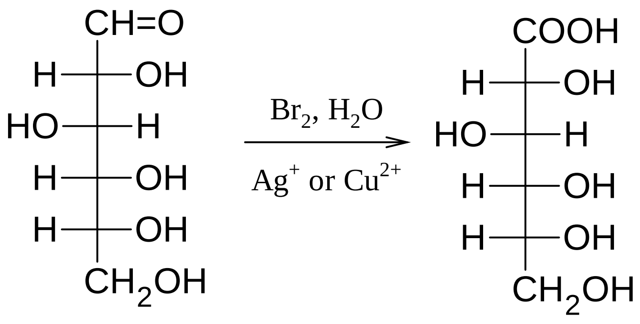
ii. Show the formation of sorbitol from D-glucose

iii. What is the difference between gluconic and glucaric acid?

iv. Draw the structure of salicin (β-D-glucoside of salicyl alcohol)

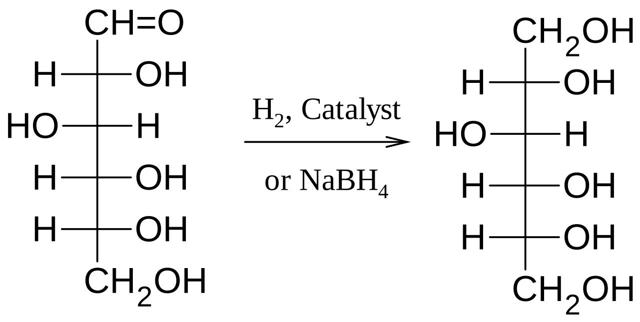
Answers

i. Conversion of D-glucose to gluconic acid.



D-glucose D-gluconic acid

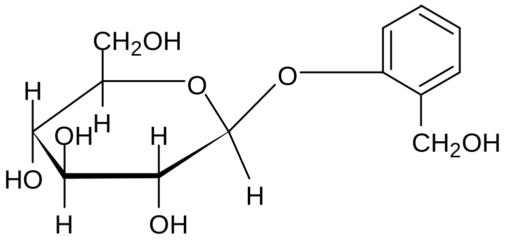
ii. formation of sorbitol from D-glucose



D-glucose Sorbitol (D-glucitol

iii. the difference between gluconic and glucaric acid is that gluconic acid has only one carboxylic functional group whereas glucaric acid has two.

iv. the structure of salicin



Salicin

Tutor Marked Assignment

i. When cyclic D-glucose react with methanol, what class of compound is formed? Illustrate with appropriate equation of reaction.

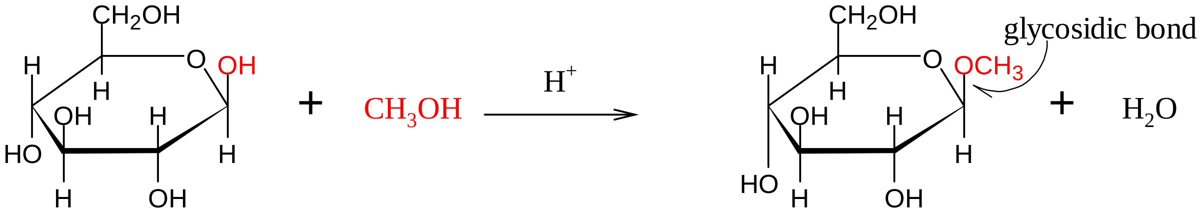
ii. Outline the Williamson synthesis of α-glucopyranose

iii. Oxidation of D-glucose with bromine water in the presence of silver ion gives what product? Show the reaction.

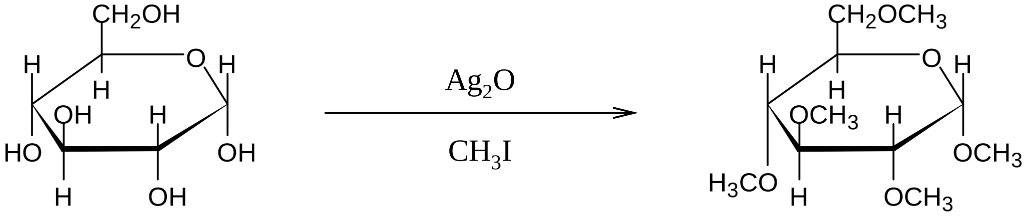
iv. Reduction of D-glucose leads to the formation of Sorbitol, outline the reaction.

Answers

i. Glycoside is the class of compound that is formed

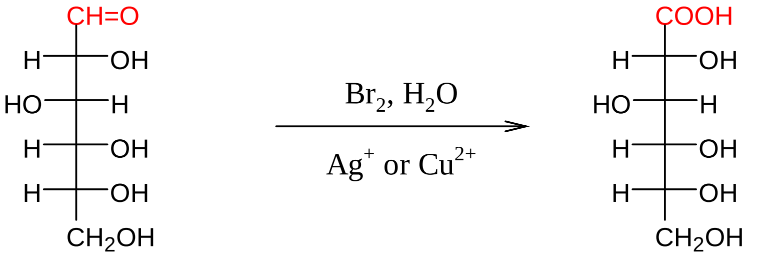


ii. Williamson synthesis of α-glucopyranose



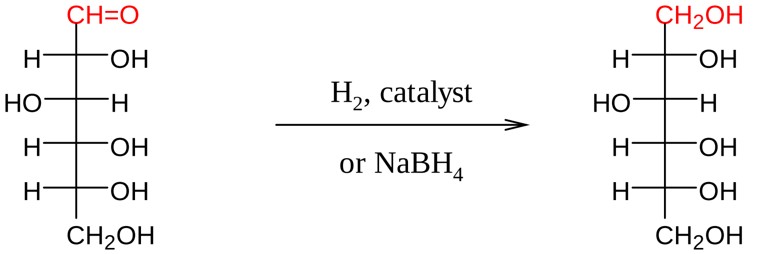
α-glucopyranose **α-glucopyranose pentamethyl ether**

iii. Oxidation of D-glucose with bromine water in the presence of silver ion gives D-gluconic acid.



D-glucose D-gluconic acid

iv. Reduction of D-glucose leads to the formation of Sorbitol as shown;



D-glucose **D-glucitol (sorbitol)**

Module 3
Unit 1
Tutor marked assignment

i. Give five examples of disaccharides and state the composition of each.

ii. Write the structures of sucrose, trehalose and maltose.

iii. Kindly explain the infant disease called galactosemia and how it can be avoided.

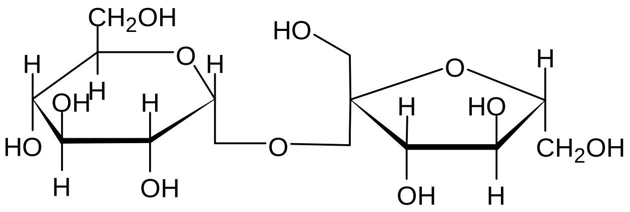
iv. Draw the structure of lactose indicating the monosaccharides present.

Answer

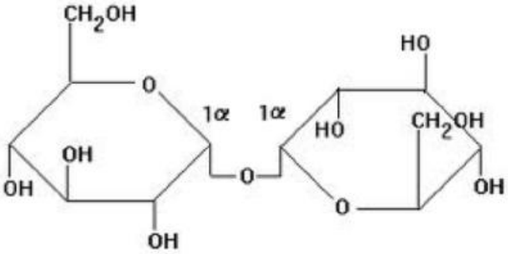
i. Five examples of Disaccharides and their compositions

Disaccharide	**Description**	**Component monosaccharides**
sucrose	common table sugar	glucose and fructose
maltose	product of starch hydrolysis	glucose and glucose
trehalose	found in fungi	glucose and glucose
lactose	main sugar in milk	galactose and glucose
melibiose	found in legumes	galactose and glucose

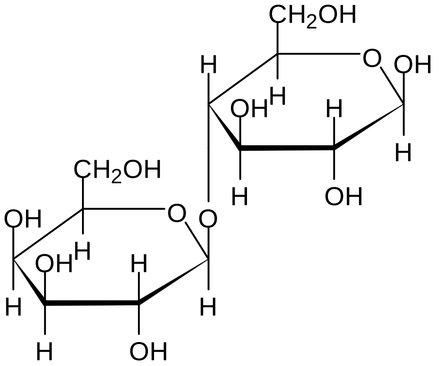
ii. the structures of sucrose, trehalose and maltose.



Sucrose



Trehalose

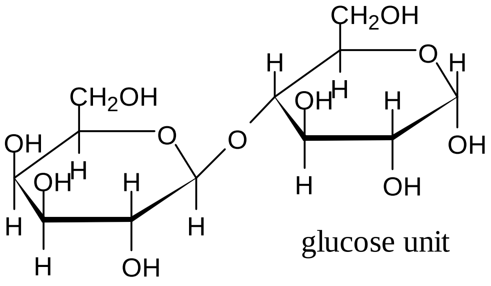


Maltose

iii. galactosemia and how it can be avoided

Some human infants are born with a disease called galctosemia which arises as a result of lack of the enzyme that isomerizes galactose to glucose, hence the baby cannot digest milk. If therefore milk is excluded from such infant's diet, the disease symptoms caused by accumulation of galactose can be avoided.

iv. the structure of lactose indicating the monosaccharides present



glucose unit

galactose unit

Module 4
Unit 1
Tutor-marked Assignment

i. What are Homopolysaccharides?

ii. Give three examples of homopolysaccharides and state the composition of each.

iii. Using equations only write the general conversion of cellulose to rayon

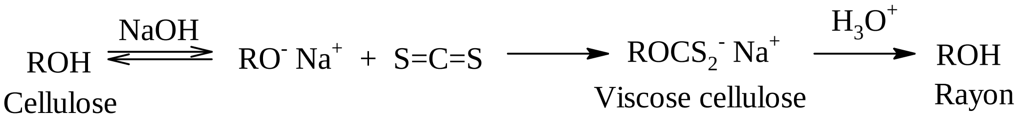
iv. Draw the structure of amylose and how does it differ from that of amylopectin

Answers

i. These are polysaccharides that gives a single type of monosaccharides on complete hydrolysis.

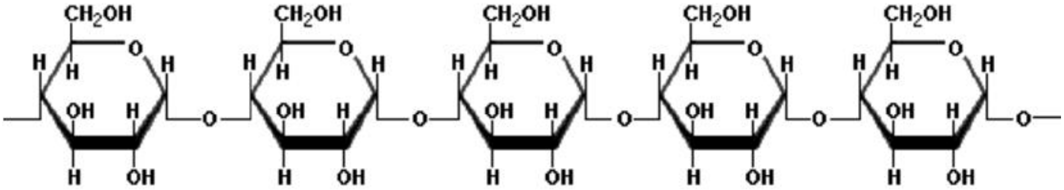
ii. Three examples of homopolysaccharides are starch, glycogen and cellulose, they are all composed of glucose units.

iii. the general conversion of cellulose to rayon



$$\underset{\text{Cellulose}}{ROH} \overset{NaOH}{\rightleftharpoons} RO^- Na^+ + S{=}C{=}S \longrightarrow \underset{\text{Viscose cellulose}}{ROCS_2^- Na^+} \xrightarrow{H_3O^+} \underset{\text{Rayon}}{ROH}$$

iv. the structure of amylose and how it differ from that of amylopectin



The structure of amylose consist of glucose units arranged in a linear form, whereas that of amylopectin has some branches.

Module 4
Unit 2
Tutor marked assignment

i. What are the polysaccharides and monosaccharides present in the following;
(b) Onions (b) Berry (c) Guar gum (d) Seashells

ii. Give four examples of heteropolysaccharides

iii. Draw the structure of Chitin and state how it differ to that of Cellulose

iv. What polysaccharide is present in jellies and jams. Draw its structure.

Answers

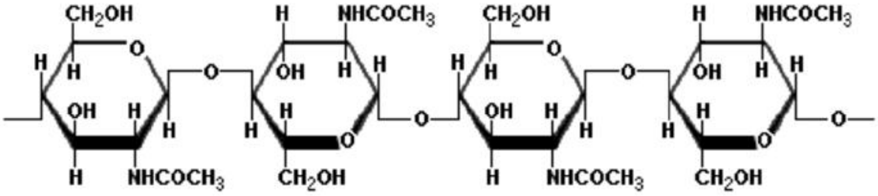
i. polysaccharides and monosaccharides present in the following;

Question	**Material**	**Polysaccharide**	**Monosaccharide**
a	Onion	Inulin	Fructose & glucose
b	Berry	Pectin	Galacturonic acid
c	Guar gum	Galactomannan	Mannose& galactose
d	Seashell	Chitin	Acetylaminoglucose

ii. four examples of heteropolysaccharides;

(b) Chitin (b) Pectin (c) Inulin (d) Glucomannan (e) Xanthan (f) Galactomann (g) Glycosaminoglycans (any 4)

iii. structure of Chitin



It is similar to cellulose, except that the hydroxyl group at C-2 of each glucose unit is replaced by an acetylamino group (CH_3CONH-) in Chitin.

iv. polysaccharide is present in jellies and jams is Pectin and the structure is;