Carbohydrates

Definion:*Carbohydrates are defined as Polyhydroxyaldehydes, Polyhydroxyketones or substances that gives such compounds on hydrolysis*

Because carbohydrates contain a carbonyl and hydroxyl group, they exist ,primarily, as *hemiacetals* and *acetals* or as *hemiketals* and *ketals*

Classification: Carbohydrates are usually classified according to the number of subunits that make them up to: a 3 types of carbohydrates

1)Monosaccharides

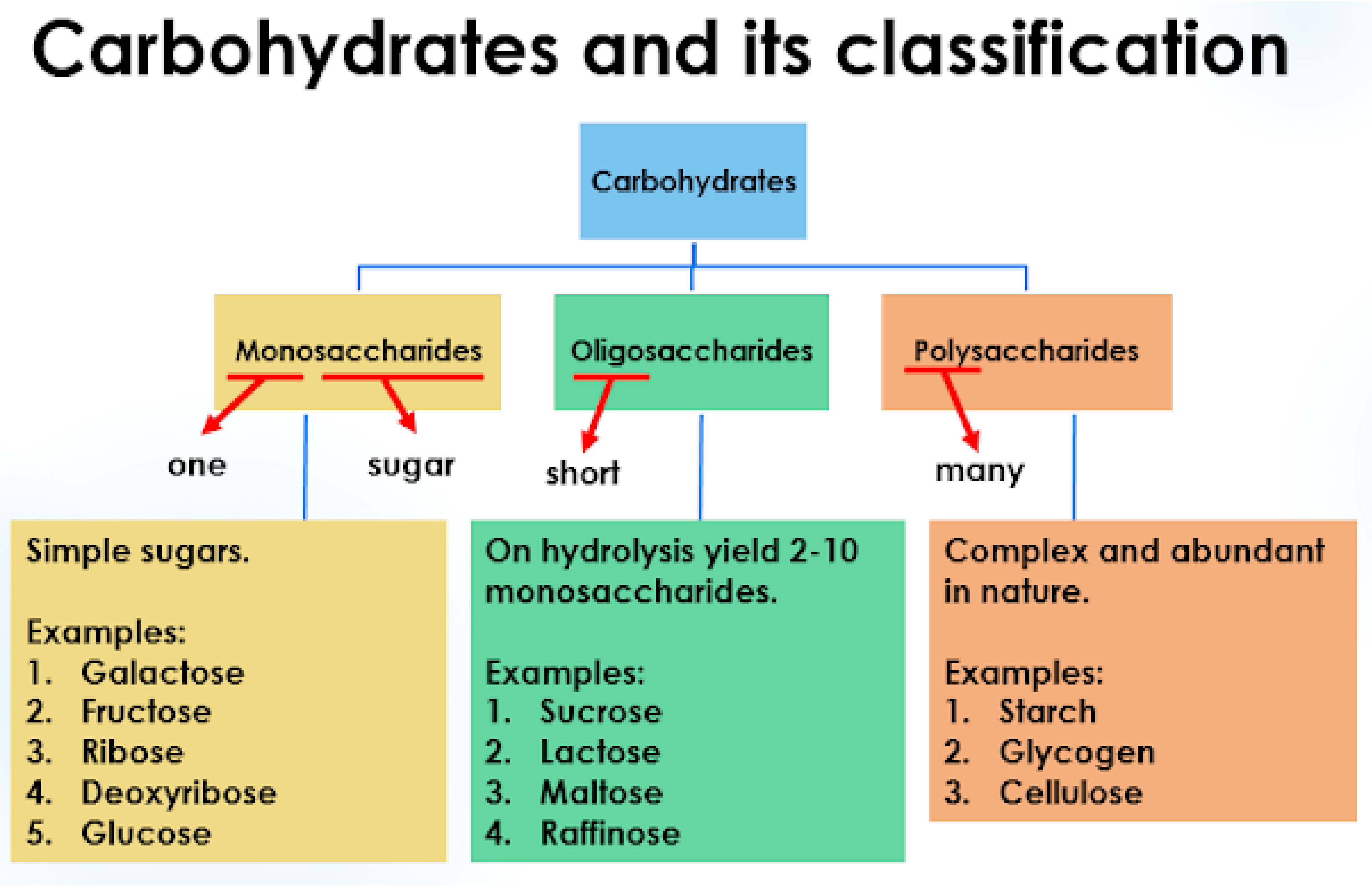
2)Oligosaccharides (2-10 units)

Disaccharides (2 units), Trisaccharides (3 units)

Tertasaccharides (4 units)

3)Polysaccharides (> 10 units)

Carbohydrates



Carbohydrates and its classification

Carbohydrates

Monosaccharides

Simple sugars.

Examples:

1. Galactose
2. Fructose
3. Ribose
4. Deoxyribose
5. Glucose

Oligosaccharides

On hydrolysis yield 2-10 monosaccharides.

Examples:

1. Sucrose
2. Lactose
3. Maltose
4. Raffinose

Polysaccharides

Complex and abundant in nature.

Examples:

1. Starch
2. Glycogen
3. Cellulose

Carbohydrates

The three types of carbohydrates are related to each other through hydrolysis

$$\text{Polysaccharide} \xrightarrow[H^+]{H_2O} \text{Oligosaccharides} \xrightarrow[H^+]{H_2O} \text{Monosaccharides}$$

Carbohydrates can be expressed as *hydrates* of *carbon* they often have the formula $C_x(H_2O)_y$

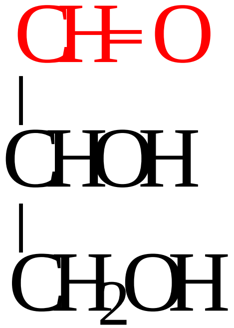
Carbohydrates are composed of Carbon, Hydrogen and Oxygen and the most abundant of all the organic compounds (especially polysaccharides) in nature; they occur in all plants and animals and are essential to life.

Plants convert carbon dioxide to carbohydrate, mainly cellulose, starch and sugars

About 60% of the foods in our diet (rice , pasta , potatoes, bread, table sugar, lactose in milk ….) consist of carbohydrate

Monosaccharides

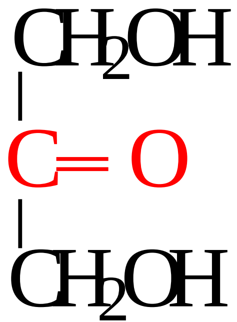
Monosaccharides are the simplest sugars can not be hydrolyzed further into smaller units. Thy have a general formula of $(CH_2O)_n$; n = 3- 7 or more. This means that monosaccharides must have at least 3 carbon atoms. Compounds which possess an aldehyde or ketone group and two or more hydroxyl groups; they can be classified as Aldoses or Ketoses depending upon their functional group and can also be classified according to the number of carbon atoms present as triose, tetroses, pentoses, hexoses and so on, there are only two triose: glyceraldehyde and dihydroxyacetone



$$\begin{array}{l} CH{=}O \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

glyceraldehyde

an aldose



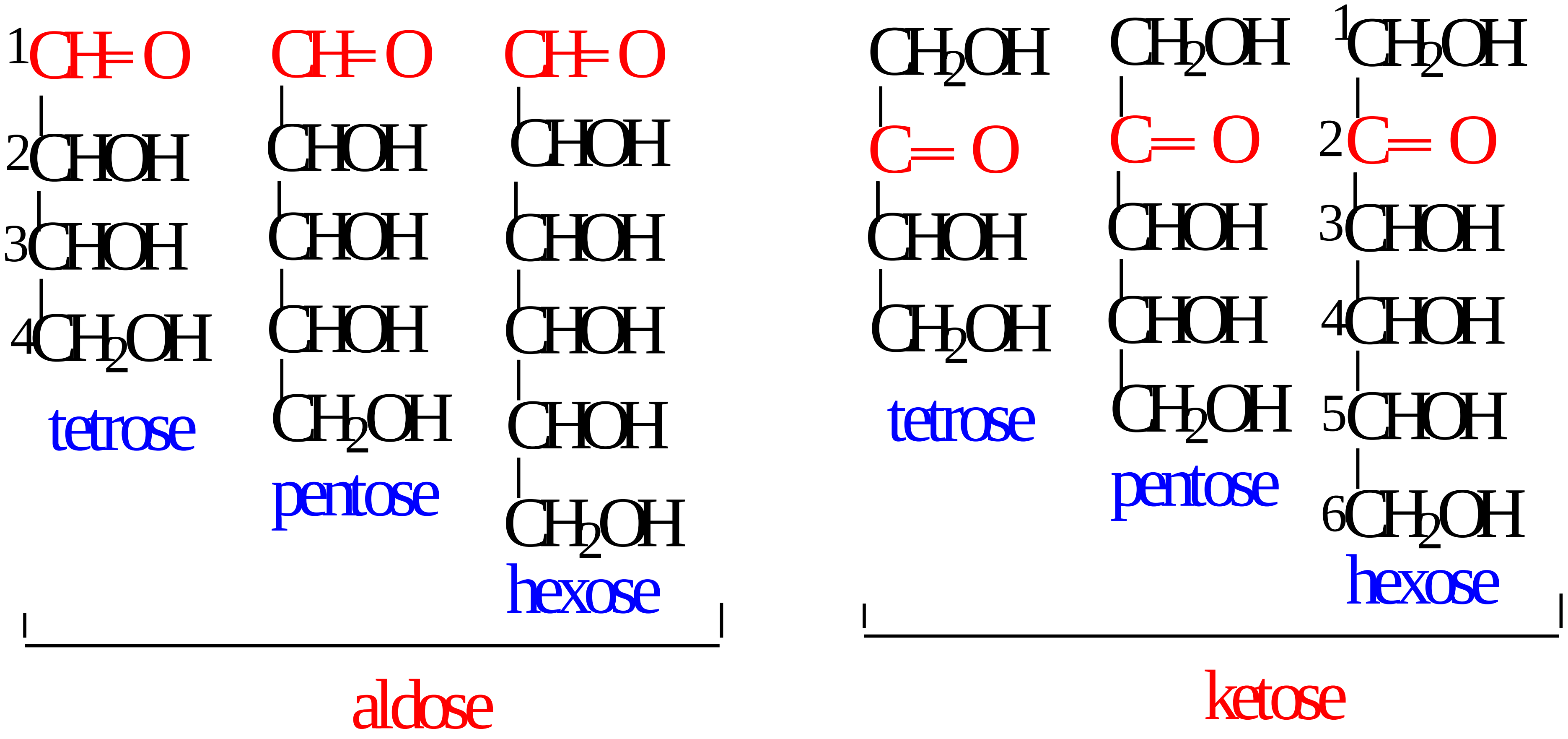
$$\begin{array}{l} CH_2OH \\ | \\ C{=}O \\ | \\ CH_2OH \end{array}$$

dihydroxyacetone

a ketose

Monosaccharides

In Aldose the chain is numbered from the aldehyde carbon, In most Ketose , the carbonyl group is located at C-2



1 $CH=O$
2 $CHOH$
3 $CHOH$
4 CH_2OH
tetrose

$CH=O$
$CHOH$
$CHOH$
$CHOH$
CH_2OH
pentose

$CH=O$
$CHOH$
$CHOH$
$CHOH$
$CHOH$
CH_2OH
hexose

aldose

CH_2OH
$C=O$
$CHOH$
CH_2OH
tetrose

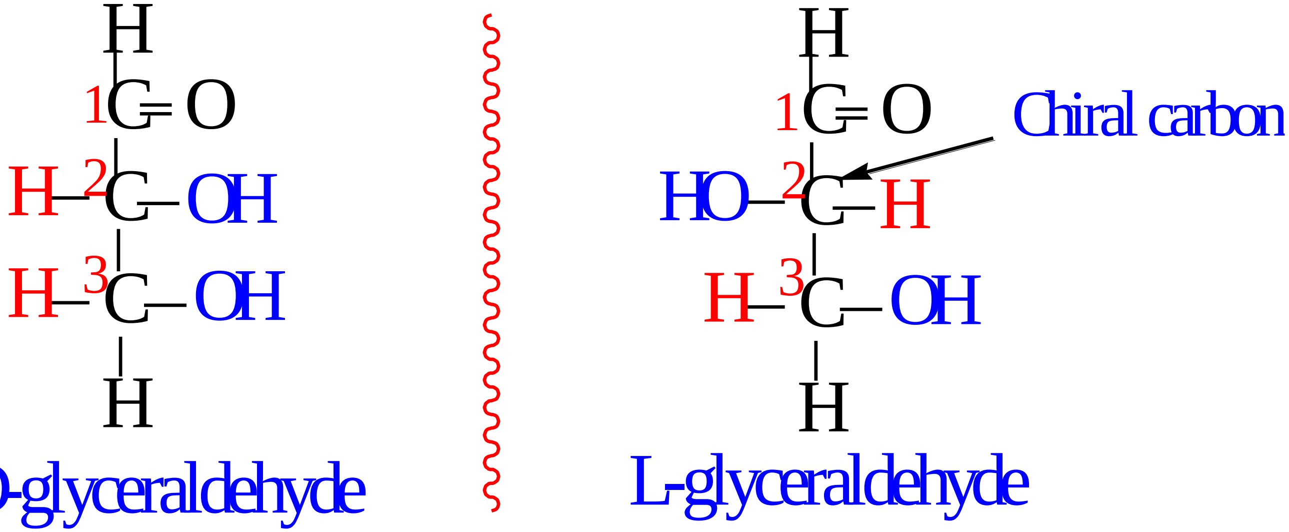
CH_2OH
$C=O$
$CHOH$
$CHOH$
CH_2OH
pentose

1 CH_2OH
2 $C=O$
3 $CHOH$
4 $CHOH$
5 $CHOH$
6 CH_2OH
hexose

ketose

Steriochemistry, Chiral Molecules

Optical isomers (Enantiomers) are a pair of molecules that are a mirror images of each other but not superimposed. they differ only in the arrangement of their atoms in space around the chiral (asymmetric) center. Thus glyceraldehyde which has one chiral carbon exist in two forms which differ only on the orientation of H atom and OH group on the chiral carbon (C-2), if the OH group is on the right side the form is designated as D isomer whereas if the OH group is on the left the form is designated as L isomer It is important to note that Monosaccharides found in nature belong to D series



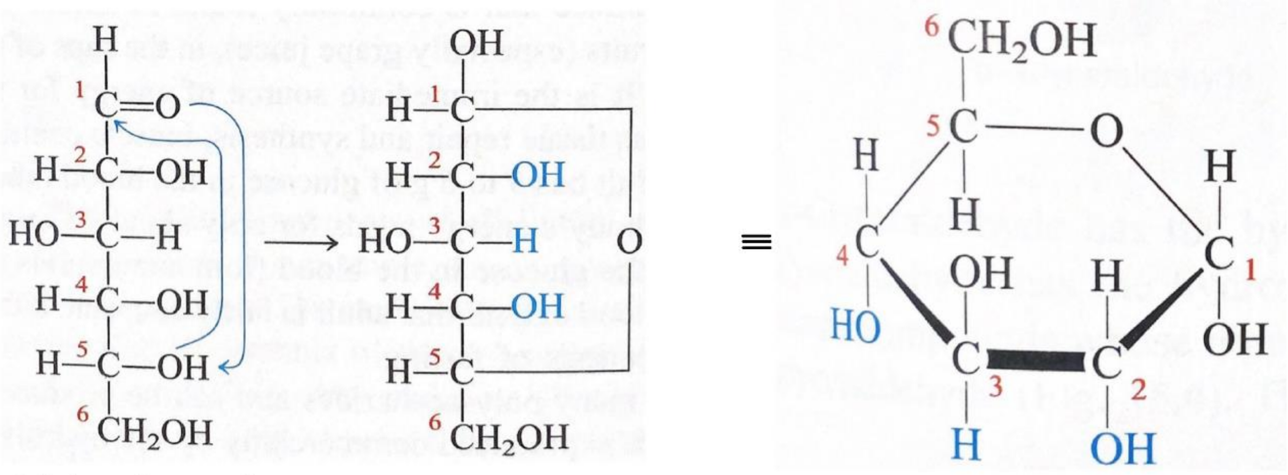
D-glyceraldehyde

L-glyceraldehyde

Mirror

Cyclic hemiacetal structures of Monosaccharides

You learned earlier that 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 to form cyclic structure,thus, many monosaccharides exist mainly in cyclic hemiacetal forms in equilibrium with traces of the straight-chain form of the carbonyl compound. The cyclic hemiacetal forms are represented by Haworth formula



Fisher formula

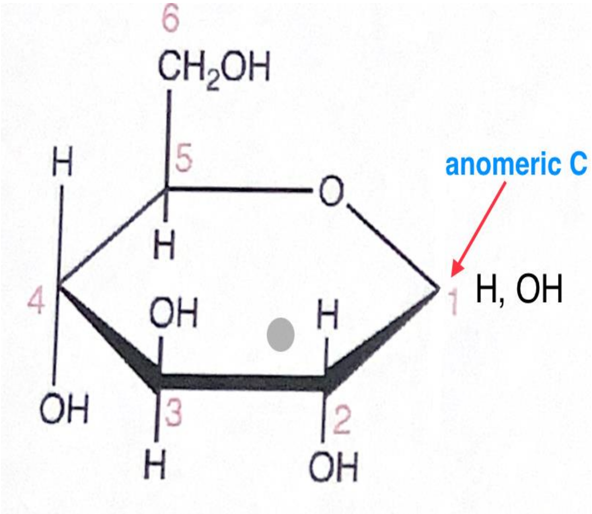
Haworth formula

Glucose form a cyclic hemiacetal

Haworth Formula of Monosaccharides

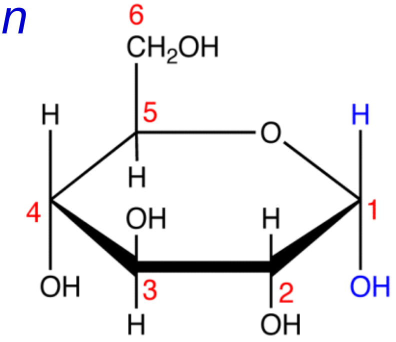
In going from Fisher formula of glucose to Haworth formula the following important features should be noticed.

- In a **Haworth projection** , the hemiacetal ring is represented as it is were planar and viewed from the side rather than looking down from above the ring; with the oxygen at the upper right.
- The carbons are arranged clockwise numerically, with C-1 at the right side; substituents attached to the ring above or below the plane. any atoms or group in the right of carbons 2,3,and 4 in Fisher projection are placed below the ring.
- C-1 through C-5 are part of the ring structure, but carbon 6 (the CH_2OH group) is a substituent on the ring.
- Finally *achiral* C-1 in Fisher projection is converted in the cyclic hemiacetal form to *chiral* carbon (attached to four different groups) and called **anomeric**

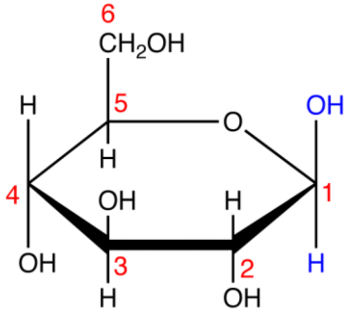


Haworth Formula of Monosaccharides

The newly created chiral carbon in the cyclic structure C-1 allowing the possibility of a pair of configurational isomers to be formed. Two monosaccharides that differ only in configuration at the anomeric center are *anomers;* which are called α and β depending on the position of the hydroxyl group. A hydroxyl group on C-1below the plane of the ring is the alpha (α) form; one that appear above the ring is the beta(β) form. *The α and β forms of D-glucose have identical confuiguration at every chiral center except at C-1, the anomeric carbon*

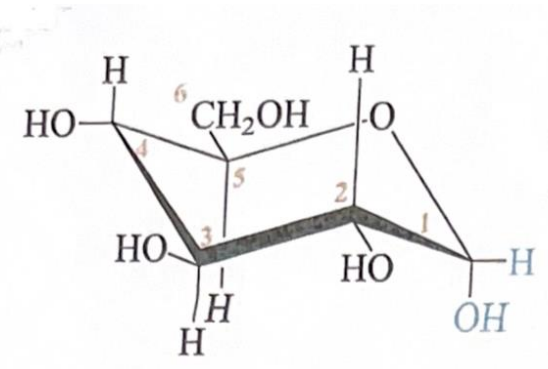


α-D-glucose, mp 146 °C, [α] +112 °

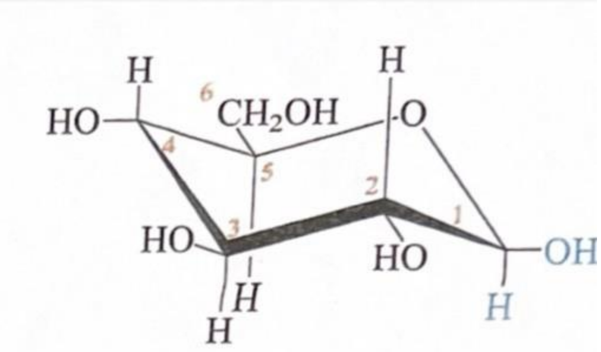


β-D-glucose, mp 150 °C , [α] +90 °

Although Haworth Formulas are easy to draw , they do not accurately represent the true shape of the ring, thus it can be replaced by chair conformations as shown below for glucose.



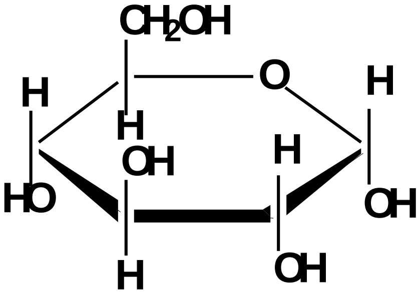
α-glucose



β-glucose

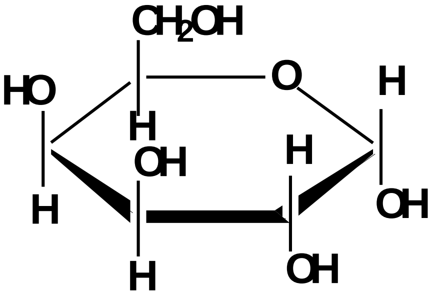
Monosaccharides

Examples of Haworth projection for some Monosaccharides and their properties

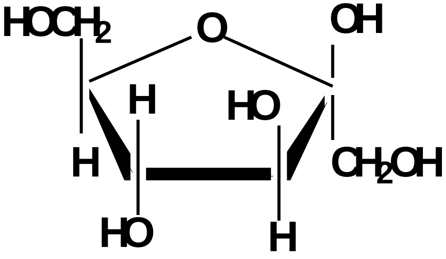


D-Glucose

Blood sugar



D-Galactose



D-Fructose

Fruit sugar

-The essentiai energy source fo rall body functions

- A component of each disacchride

-Seldom occures freely in nature

-Once absorbed by the body it convert to Glucose to provide energy

-The sweetest of all sugars

-Occurs naturally in fruits and honey

Physical properties & functions of Monosaccharides

In pure form, Monosaccharides such as glucose and fructose are crystalline colorless solids at room temperature and quite soluble in water, each molecule having several OH groups that readily engage in hydrogen bonding.

They have a sweet flavor because the orientation of the OH group interacts with the taste receptor on the tongue.Sorbitol is used commercially as a sweetener and sugar substitute.

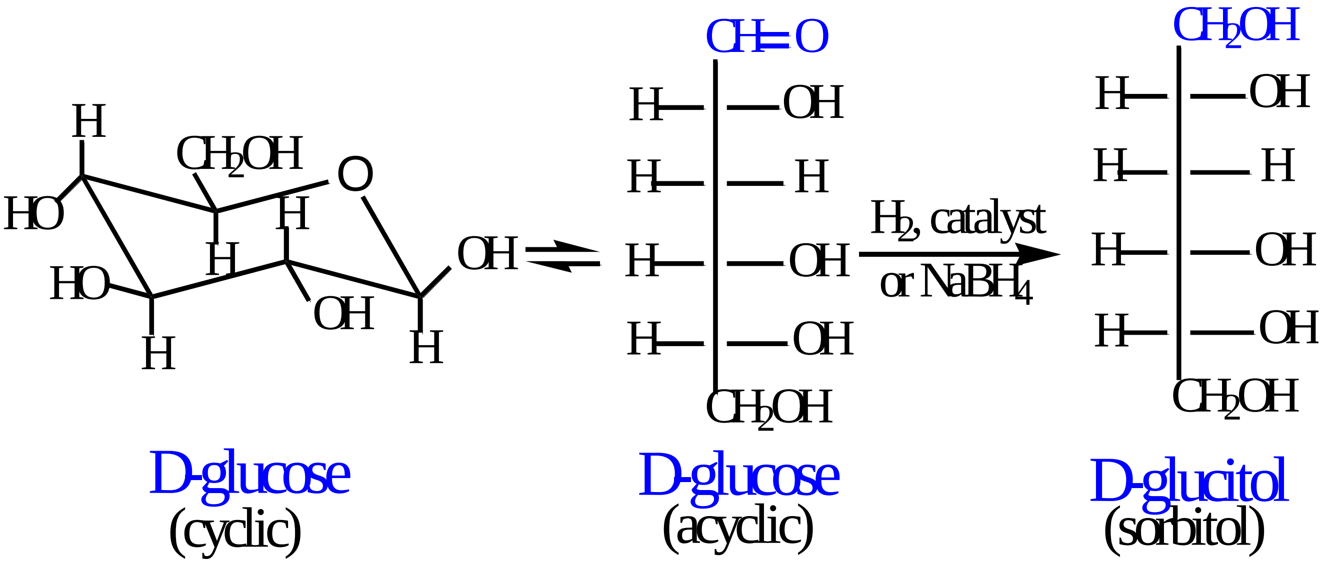
Monosaccharides have many functions within cells. First and foremost, they are used to produce and store energy.

Most organisms create energy by breaking down glucose, and harvesting the energy released from the bonds braking.

Reaction of Monosaccharides

Reduction of Monosaccharides

The chemical behavior of Monosaccharides is determined by their functional groups.The carbonyl group aldose and ketoses can be reduced by various reagents to give polyols called alditols. Catalytic hydrogenation or reduction with sodium borohydride($NaBH_4$) converts D- glucose to D- glucitol

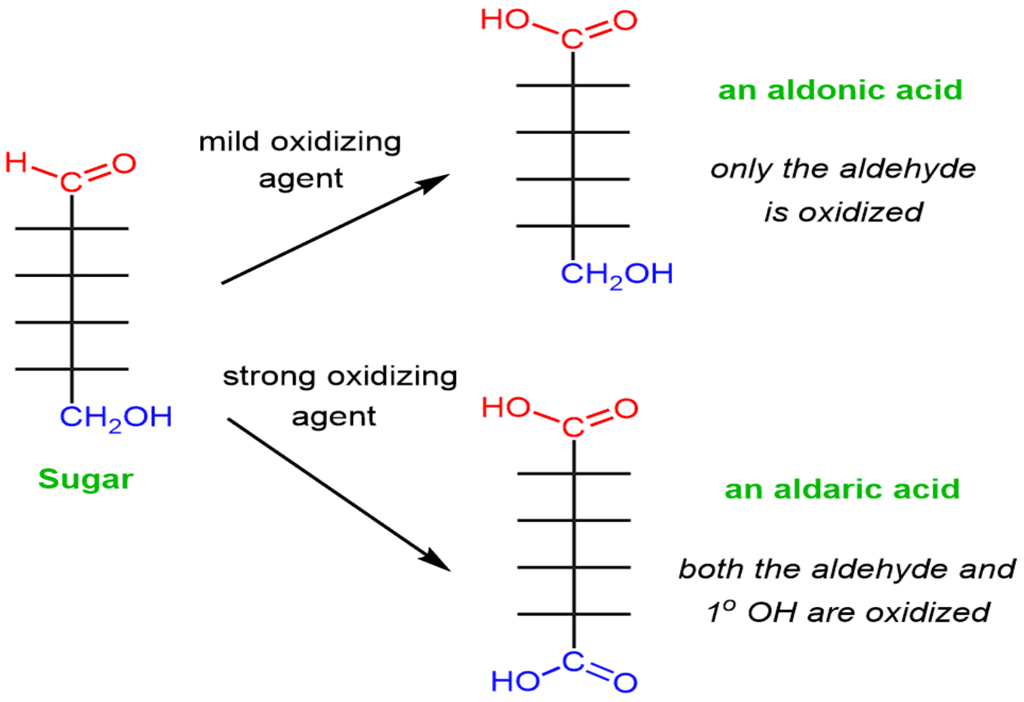


Reduction occurs by reduction of the small amount of aldehyde in equilibrium with the cyclic hemiacetal. As the aldehyde is reduced the equilibrium shifts to the right, so that eventually all of the sugar is converted. Sorbitol is used commercially as sweetner and sugar substitute.

Reactions of Monosaccharides

Oxidation of Monosaccharides

An important reaction of Monosaccharides is the oxidation of the aldehyde group. Oxidation of the aldehyde group can be accomplished with any mild oxidizing agent, such as Tollen’s, Fehing’s or Benedict’s reagents. to give an **aldonic** acid. Strong oxidizing agent oxidize both the aldehyde group and the primary alcohol to give an **aldaric** acid.



Mild oxidizing agents

Tollen’s reagent

Ag^+ *in aqueous ammonia*

Benedict’s reagent

(*Cu^{2+} in aqueous sodium citrate*).

Fehling's reagent

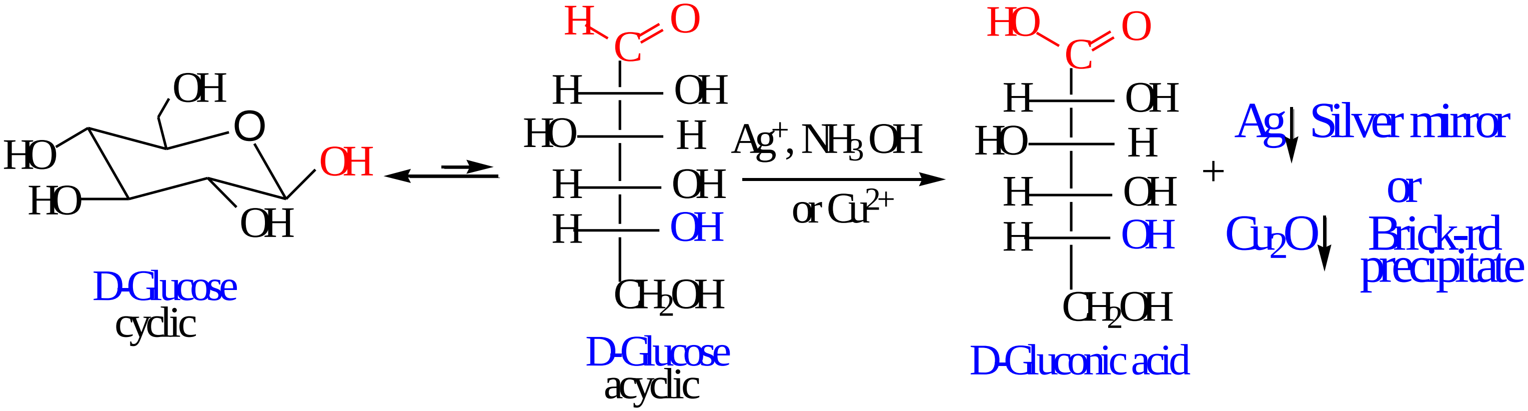
(*Cu^{2+} in aqueous sodium tartrate*)

Strong oxidizing agent

aqueous HNO_3

Reactions of Monosaccharides

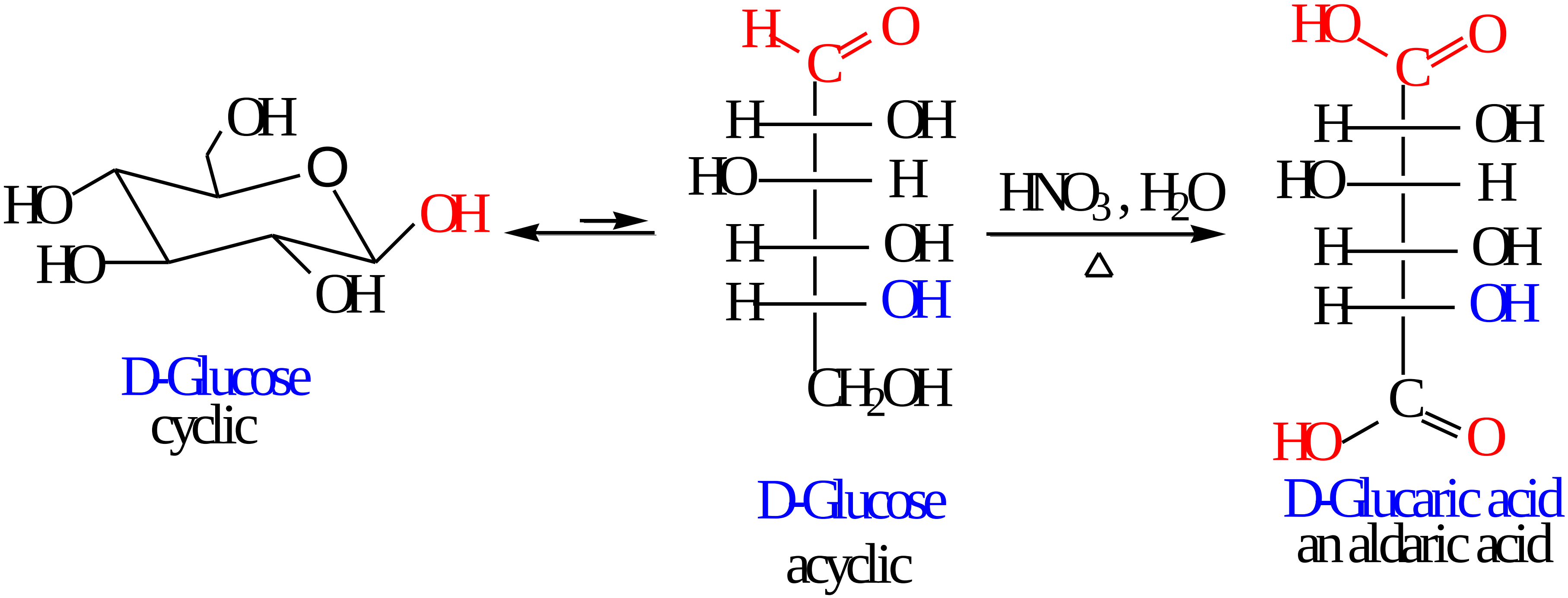
The mild oxidizing agents are used to distinguish between **aldoses and ketoses** since the aldehyde, being more reactive is converted to a carboxylic acid while the ketone and the alcohols present in both are not. The indicator in **Tollens reagent** is the by-product **Ag** which coats the surface of the flask forming a **mirror**. The **Fehling's** and **Benedict's** tests rely on the formation of **Cu_2O as a red precipitate** when the Cu^{2+} salt is reduced by the aldose present in the solution.



Any redox reaction **involves an oxidation and reduction** so if one species is oxidized then the other is reduced, so the oxidation of the carbohydrates by oxidized agent means that the oxidizing agents are **reduced by the carbohydrates,** thus any carbohydrate that **gives a positive test** with Tollens, Benedict's, or Fehling's reagent is called a **reducing sugar.**

Reactions of Monosaccharides

A common way of oxidizing **both the aldehyde and 1º alcohol** groups to carboxylic acids (**aldaric acid**) is using a **stronger oxidizing agent like** nitric acid (HNO_3).



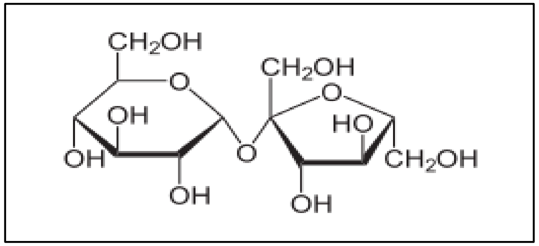
D-Glucose
cyclic

D-Glucose
acyclic

D-Glucaric acid
an aldaric acid

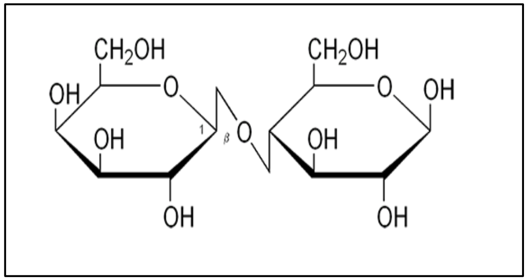
Oligosaccharides

These are carbohydrates that undergo hydrolysis to yield 2 to 10 molecules of the **same** or **different** Monosaccharides. Accordingly, any oligosaccharide yielding two molecules of monosaccharide on hydrolysis is designated as a disaccharide, and the one yielding three molecules of monosaccharide is trisaccharide and so on. Disaccharides is the most common oligosaccharides, two Monosaccharides are liked by glycosidic bond between the anomeric carbon of one monosaccharide and a hydroxyl group of the other. Disaccharides like Sucrose, Lactose, Maltose, are composed of 2 of the **same** or **different** monosaccharides



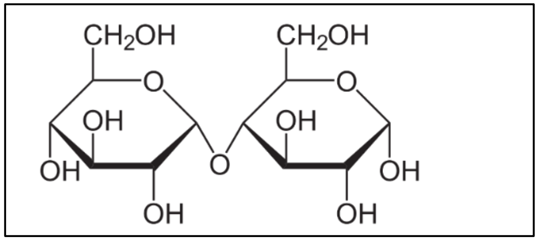
Sucrose = Glucose + Fructose

- Table sugar
- Found naturally in plants
- May be purified from plant sources into Brown



Lactose = Glucose + Galactose

- The primary sugar in milk and milk products
- Many people have problems digesting large
- amounts of Lactose



Maltose = Glucose + Glucose

- Produced when starch break down

Polysaccharides

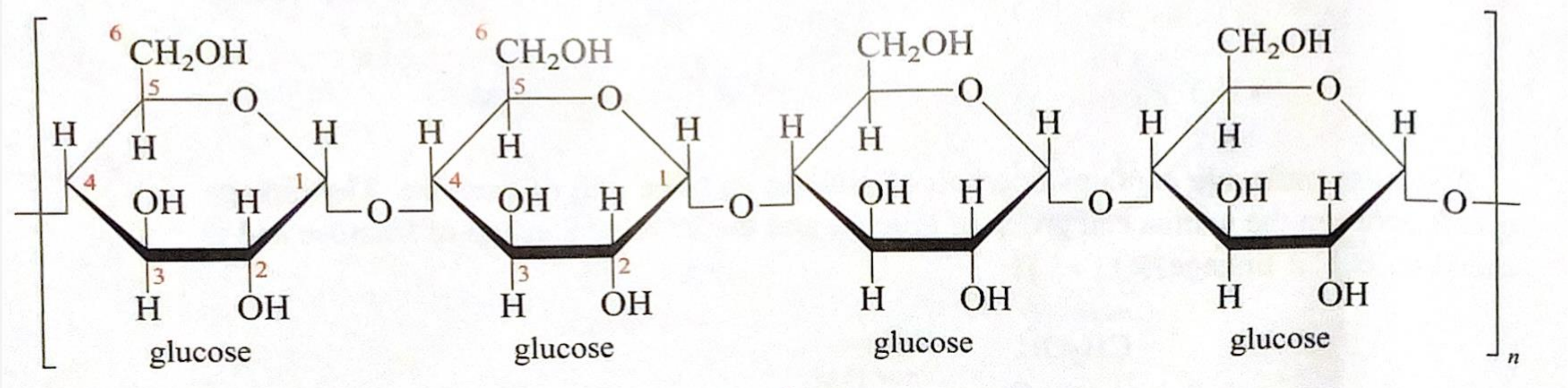
Polysaccharides contain many linked Monosaccharides and vary in chain length and molecular weight. Most polysaccharides give a single monosaccharide on complete hydrolysis . The monosaccharide units may be linked in linearly or in branched chain. Starch, Glycogen and Cellulose are a few of the more important polysaccharides.

1) Starch:

- The major digestible polysaccharides in our diet (wheat, rice, corn , potatoes ….)
- The storage form of carbohydrates in plants

Natural starches are a mixture of two types of polysaccharides; amylose and amylopectin.

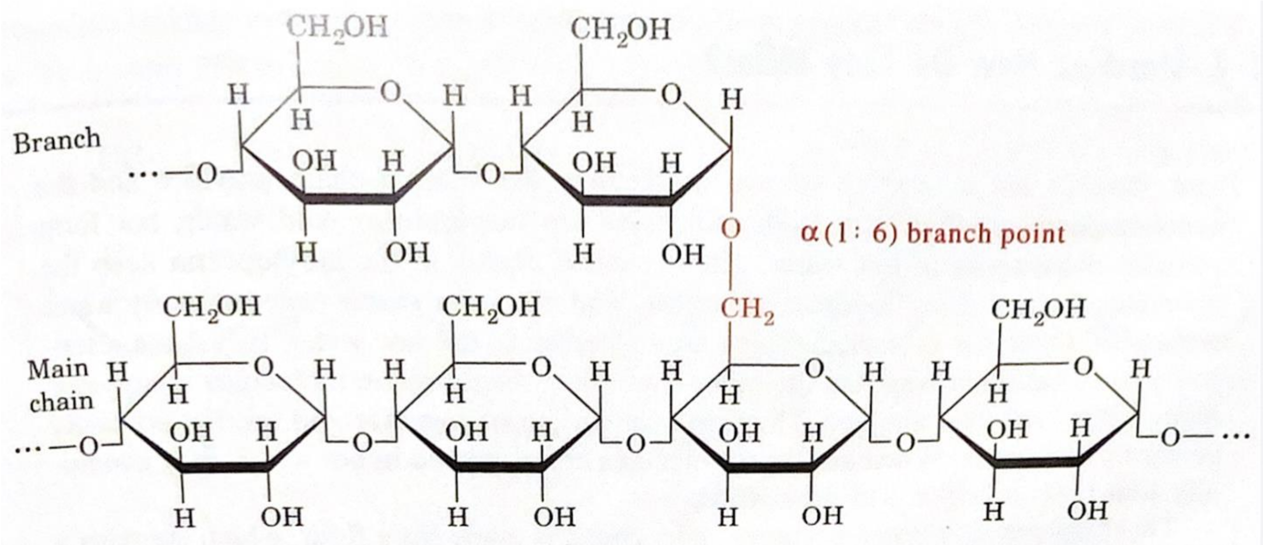
Amylose: is a large linear glucose polysaccharide whose glucose units are connected by 1,4- α-glycosidic bonds



amylose

Polysaccharides

Amylopectin: is highly branched glucose polymer. The glucose units of the nonbranching portion of the molecule are connected by 1,4- α-glycosidic bonds. The branching occurs every 20 to 24 glucose units as a result of 1,6- α-glycosidic bonds between C-1 on the glucose in the alpha form and C-6 on another glucose



2) Glycogen is:

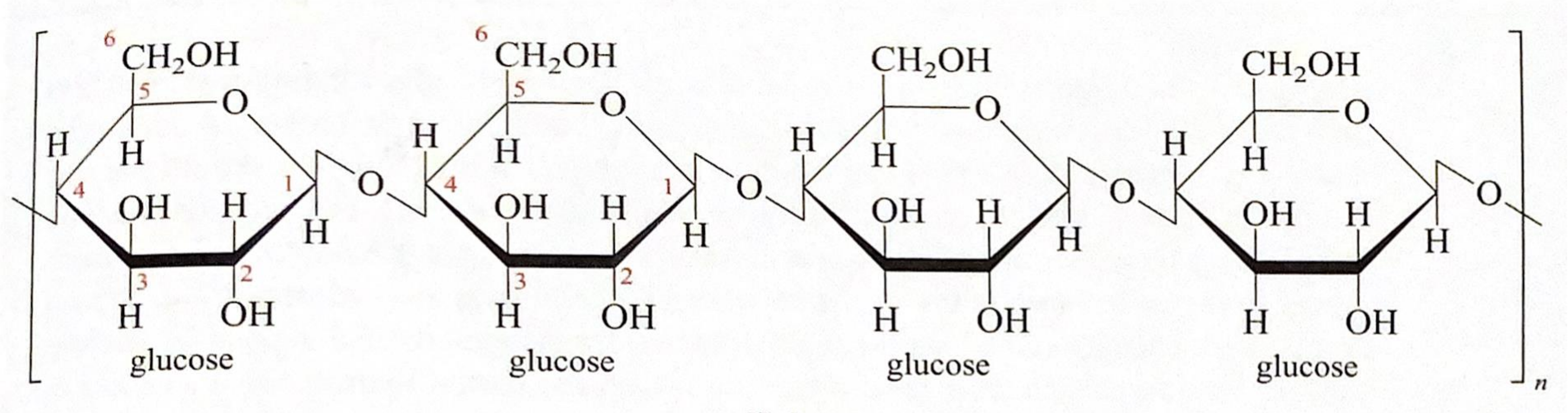
- A heavy branched molecule
- The storage form of glucose in animal
- Stored in the liver and muscles
- Found in tiny amounts in meat sources
- Not found in plants
- Not a significant food sourse of carbohydrate

Polysaccharides

The structure of glycogen molecule is similar to that of amylopectin, it consists of straight chains of glucose units connecting by α ,1:4 linkages. The branching that results from α,1:6 linkages in glycogen molecule occurs every 8 to 12 glucose units, which is more frequent than that in amylopectin. The ability of the body to form glycogen from glucose is extremely important because glucose is the main source of energy for all cells. When we eat a meal, glucose (resulting from the breakdown of carbohydrates) enter the bloodstream to provide cells with needed energy and the excess glucose is converted to glycogen stored in the liver for farther energy supply.

3) Cellulose:

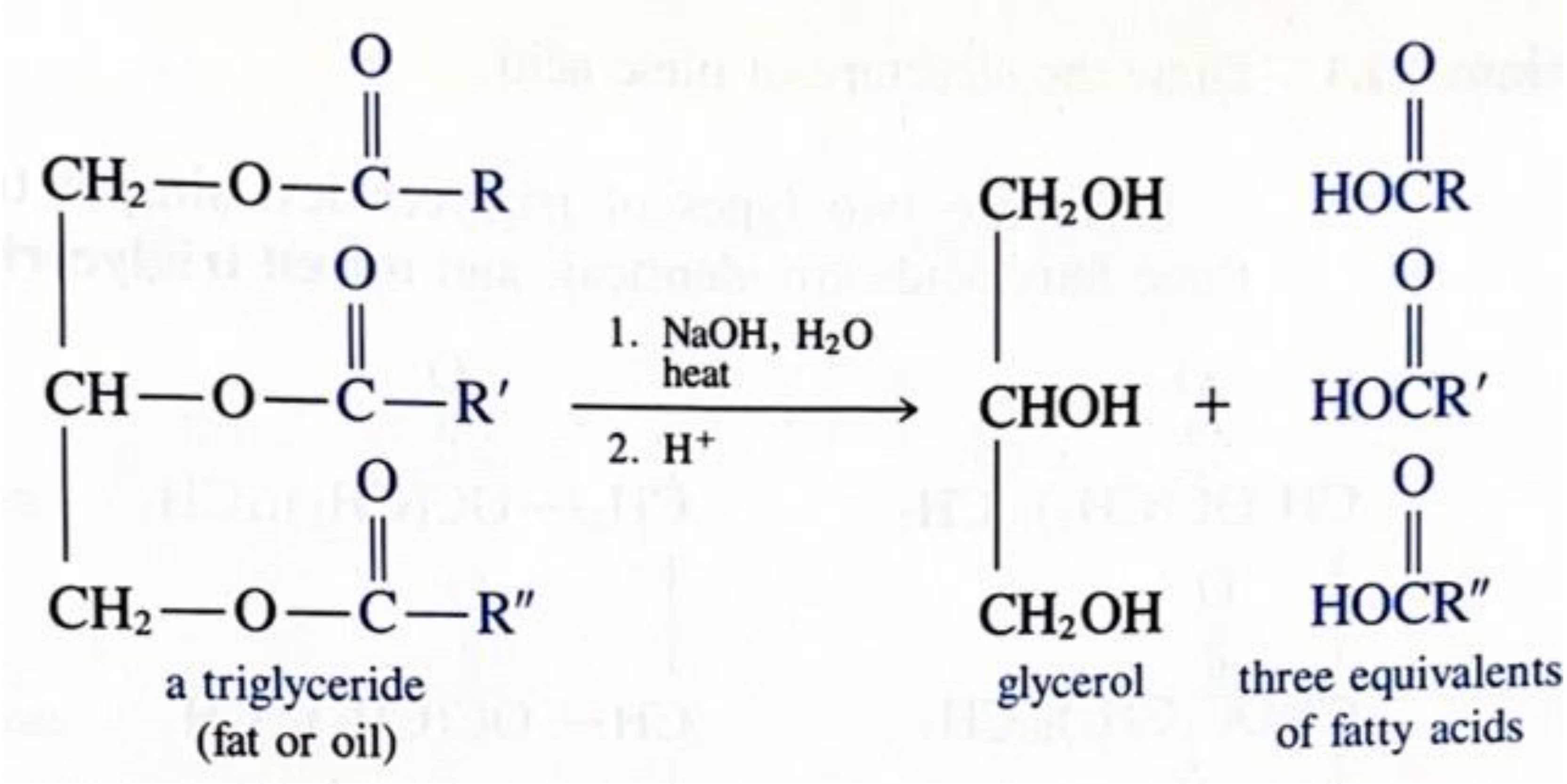
- A glucose polymer produced by plants .
- Makes up the main structural support for plants
- Indigestible by humans
- Insoluble in water



cellulose

Fats and Oils

Fats and oils belong to a class of compound called **Lipids** which include all biological compounds that are insoluble in water but are soluble in organic solvents like ether, chloroform, benzene etc…Fats and oils are *triesters of glycerol and are called triglycerides.* Boiling fat or oil with alkali then acidify the resulting solution produce glycerol and a mixture of **fatty acids** are formed.



Fats and Oils

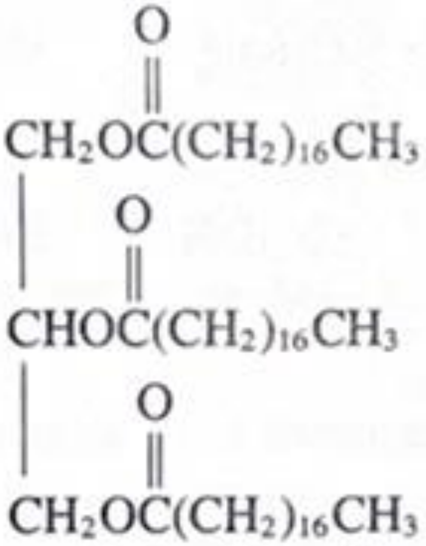
Fatty acid is a carboxylic acid with an aliphatic chain, which is saturated or unsaturated. Most naturally occurring fatty acids have unsaturated chain of an even number of carbon atom from 4 to 28. The unsaturated naturally occurring fatty acids have cis configuration.

Common acids obtained from fats

	Common name	**No. of C**	**Structural formula**	**m p °C**
Saturated	lauric	12	$CH_3(CH_2)_{10}COOH$	44
	myristic	14	$CH_3(CH_2)_{12}COOH$	58
	palmatic	16	$CH_3(CH_2)_{14}COOH$	63
	stearic	18	$CH_3(CH_2)_{16}COOH$	70
	arachidic	20	$CH_3(CH_2)_{18}COOH$	77
Unsaturated				
	oleic	18	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ (*cis*)	13
	linoleic	18	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	-5
	linolenic	18	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$	-11

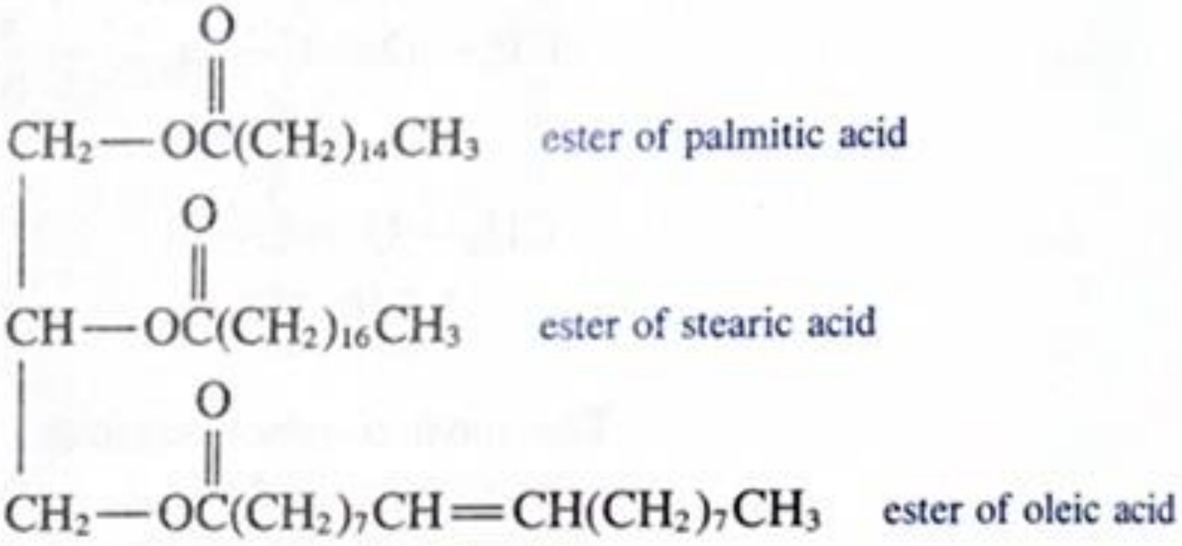
Fats and Oils

Triglycerides are two types: ***simple triglycerides*** *in which all three fatty acids are identical and* ***mixed triglycerides,*** *which contain two or more different fatty acids*



$$\begin{array}{l} \mathrm{CH_2O\overset{\overset{O}{\|}}{C}(CH_2)_{16}CH_3} \\ | \\ \mathrm{CHO\overset{\overset{O}{\|}}{C}(CH_2)_{16}CH_3} \\ | \\ \mathrm{CH_2O\overset{\overset{O}{\|}}{C}(CH_2)_{16}CH_3} \end{array}$$

a simple triglyceride
(glyceryl tristearate or tristearin)



$$\begin{array}{l} \mathrm{CH_2{-}O\overset{\overset{O}{\|}}{C}(CH_2)_{14}CH_3} \\ | \\ \mathrm{CH{-}O\overset{\overset{O}{\|}}{C}(CH_2)_{16}CH_3} \\ | \\ \mathrm{CH_2{-}O\overset{\overset{O}{\|}}{C}(CH_2)_7CH{=}CH(CH_2)_7CH_3} \end{array}$$

a mixed triglyceride
(glyceryl palmitostearoöleate)

Physical properties of Fats and Oils

Fats and oils are **solids** or **liquids** with **a greasy feel**, but when pure they are **colorless, odorless and tasteless.** They **are insoluble in water** but **soluble in organic solvent** like ethers , chloroform and benzene. They have **low density** than water and consequently float on surface win mixed with each other.

Differences between Fats and Oils

Fats	Oils
1) Solid at room temperature, due to a large % of saturated fatty acids 2) High melting point (above 20 °C) 3) Vander waal`s forces between molecules are stronger 4) Source: mainly animals 5) No double bonds	1) Liquid at room temperature, due to a large % of unsaturated fatty acids 2) Low melting point (below 20 °C) 3) Vander waal`s forces between molecules are weaker 4) Source: mainly plants 5) Have double bonds

Chemical properties of Fats and Oils

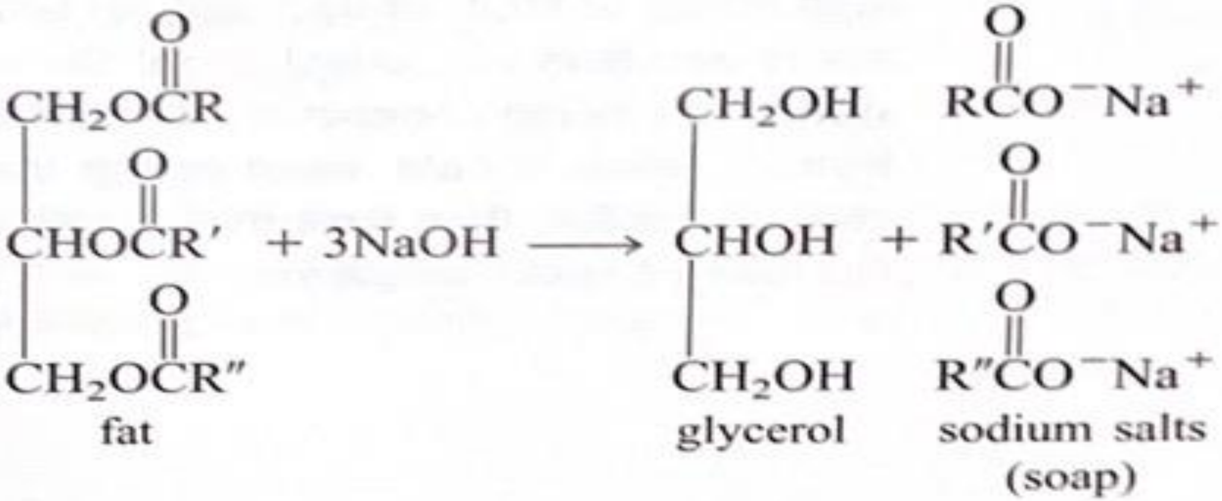
Fats and oils are triesters of glycerol with saturated and unsaturated fatty acids. Their reactions are those of ester group and C = C bonds.

1) Hydrolysis
2) Hydrogenation
3) Hydrogenolysis

Chemical properties of Fats and Oils

1) Hydrolysis:

Fats and oils are hydrolylsed by heating with **acids or alkalis**, when boiled with **sodium or potassium hydroxide solution** gave glycerol and **sodium or potassium salts** which is called **soap** and the alkaline hydrolysis are called as **saponification**



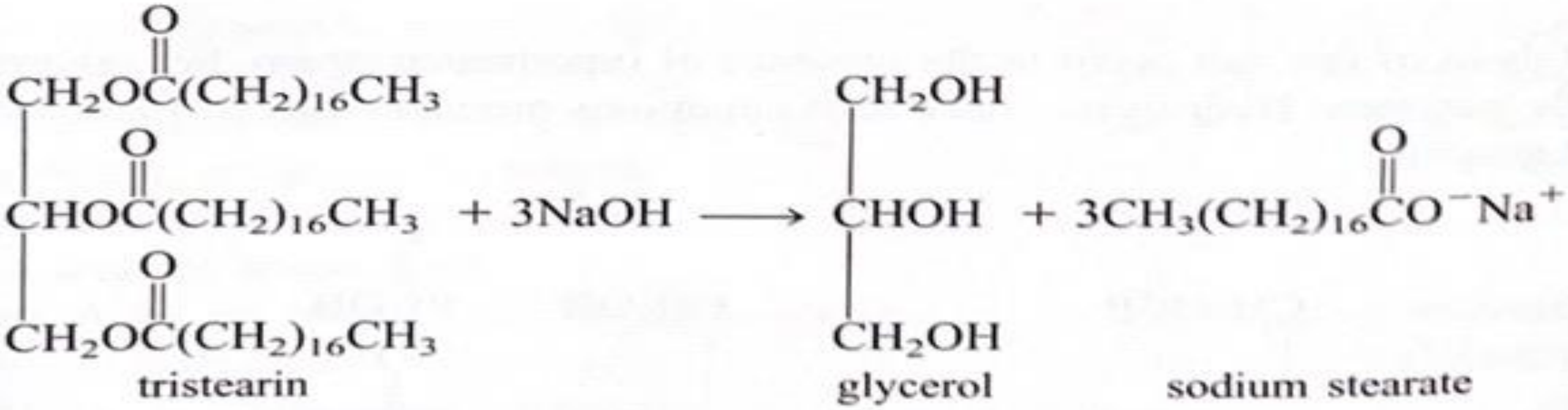
$$\begin{array}{l} CH_2O\overset{O}{\overset{\|}{C}}R \\ | \\ CHO\overset{O}{\overset{\|}{C}}R' \\ | \\ CH_2O\overset{O}{\overset{\|}{C}}R'' \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} R\overset{O}{\overset{\|}{C}}O^-Na^+ \\ R'\overset{O}{\overset{\|}{C}}O^-Na^+ \\ R''\overset{O}{\overset{\|}{C}}O^-Na^+ \end{array}$$

fat

glycerol

sodium salts
(soap)

For example,



$$\begin{array}{l} CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_{16}CH_3 \\ | \\ CHO\overset{O}{\overset{\|}{C}}(CH_2)_{16}CH_3 \\ | \\ CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_{16}CH_3 \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3CH_3(CH_2)_{16}\overset{O}{\overset{\|}{C}}O^-Na^+$$

tristearin

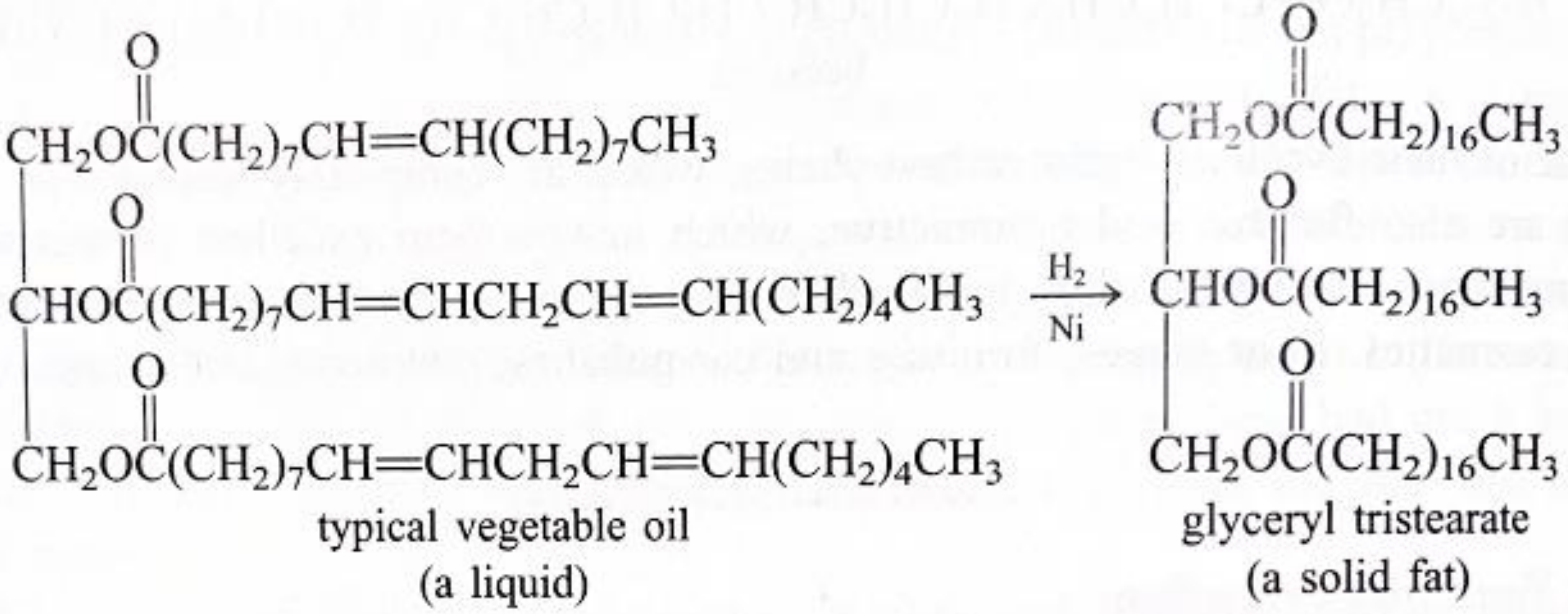
glycerol

sodium stearate

Chemical properties of Fats and Oils

2) Hydrgenation:

Vegetable oils are **triglyceride** of **unsaturated fatty acids** such as oleic acid and linoleic acid. Catalytic hydrogenation at low temperature add hydrogen to the carbon –carbon double bond at the acid component of the triglyceride to form a **saturated triglyceride.** This processes is called Hardening**.**



$$\begin{array}{l} CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ | \\ CHO\overset{O}{\overset{\|}{C}}(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3 \\ | \\ CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3 \end{array} \xrightarrow[Ni]{H_2} \begin{array}{l} CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_{16}CH_3 \\ | \\ CHO\overset{O}{\overset{\|}{C}}(CH_2)_{16}CH_3 \\ | \\ CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_{16}CH_3 \end{array}$$

typical vegetable oil
(a liquid)

glyceryl tristearate
(a solid fat)

Chemical properties of Fats and Oils

3) Hydrogenolysis

The ester group of **triglyceride** (fats or oil) can be reduced in the presence of copper chromite catalyst CuCr2O4 at high temperature to give glycerol and a long chain primary alcohol. This reaction called **Hydrogenolysis** (hydrogenation involving cleavage)