Carbohydrates

Physical Properties

- Taste = sweet

Table 17.2 The Relative Sweetness of Sugars (Sucrose = 1.00)		
Sugar	**Relative Sweetness**	**Type**
Lactose	0.16	Disaccharide
Galactose	0.22	Monosaccharide
Maltose	0.32	Disaccharide
Xylose	0.40	Monosaccharide
Glucose	0.74	Monosaccharide
Sucrose	1.00	Disaccharide
Invert sugar	1.30	Mixture of glucose and fructose
Fructose	1.73	Monosaccharide

- Solids at room temperature
- Water soluble (H-bonding)

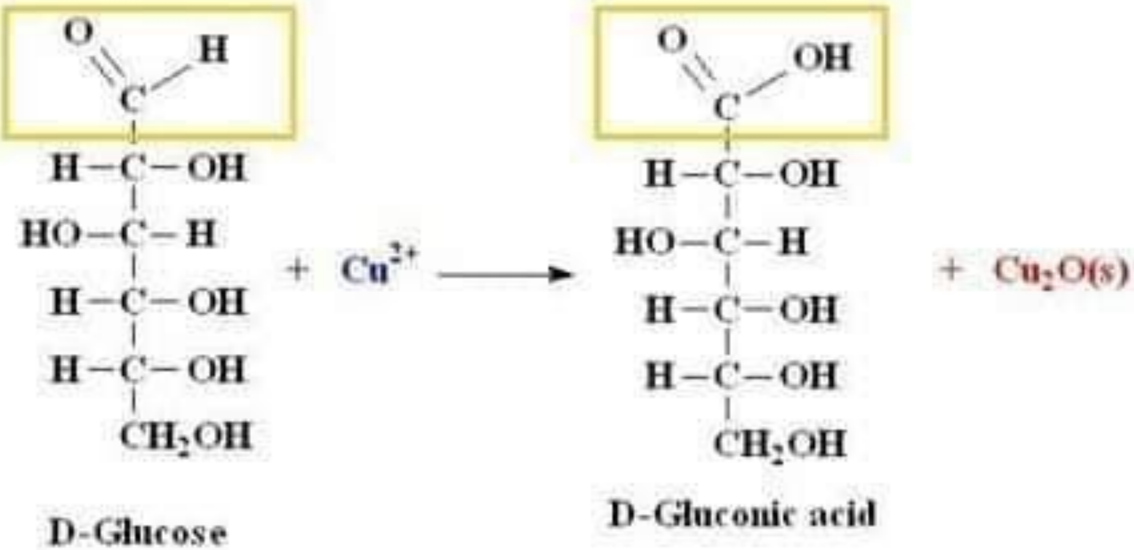
Chemical Properties

- Review: Reactions of aldehydes and ketones
  1. Oxidation (aldehydes) to form carboxylic acids
  2. Reduction to form alcohols
  3. Formation of hemiacetal/hemiketal
  4. Hemiacetal/hemiketal + alcohol → acetal/ketal

- Now we'll see all of these with monosaccharides...

1. Oxidation of Monosaccharides

- Monosaccharides are reducing sugars if their carbonyl groups oxidize to give carboxylic acids
- Benedict's reagent can oxidize aldehydes adjacent to -OH group



- In the Benedict's text, D-glucose is oxidized to D-gluconic acid. Glucose is a reducing sugar.

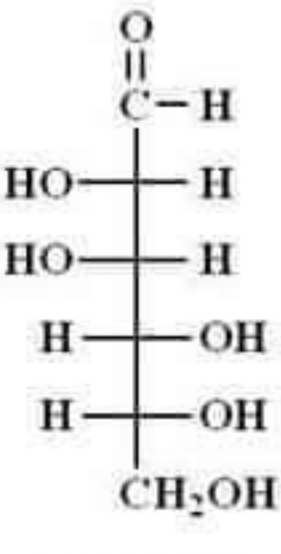
2. Reduction of Monosaccharides

- The reduction of the carbonyl group produces sugar alcohols, or *alditols*
- D-Glucose is reduced to D-glucitol (also called sorbitol)
- Used in sugar-free products

D-Sorbitol

Learning Check

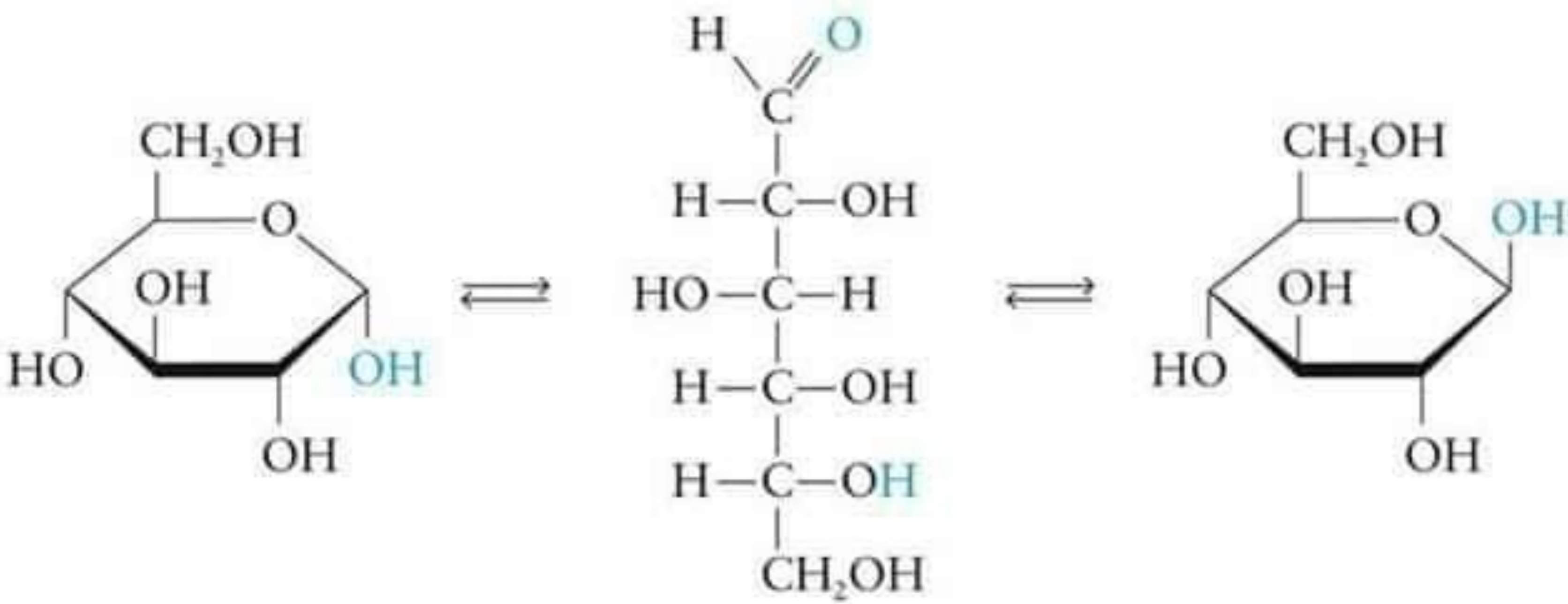
Write the products of the oxidation and reduction of D-mannose.



D-Mannose

3. Monosaccharides + alcohol

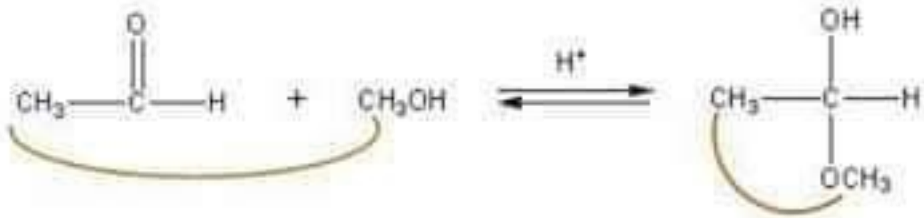
- Formation of hemiacetal/hemiketal (cyclic structures)



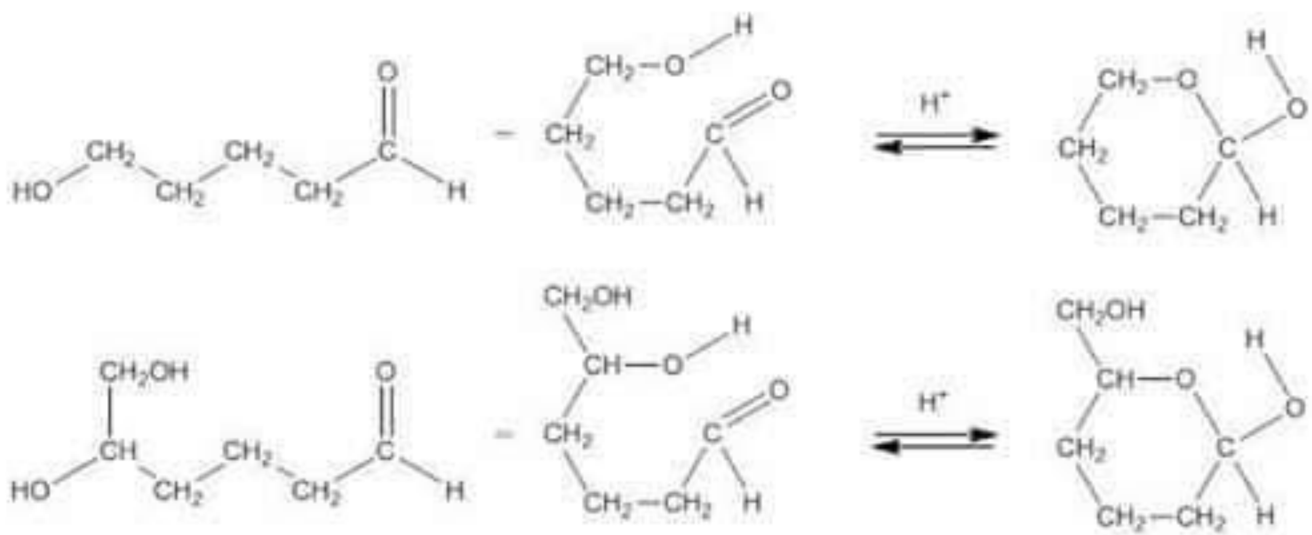
α-D-glucose (36%) D-glucose (0.02%) β-D-glucose (64%)

Hemiacetal Review

- What is a hemiacetal?
- How is a hemiacetal formed?

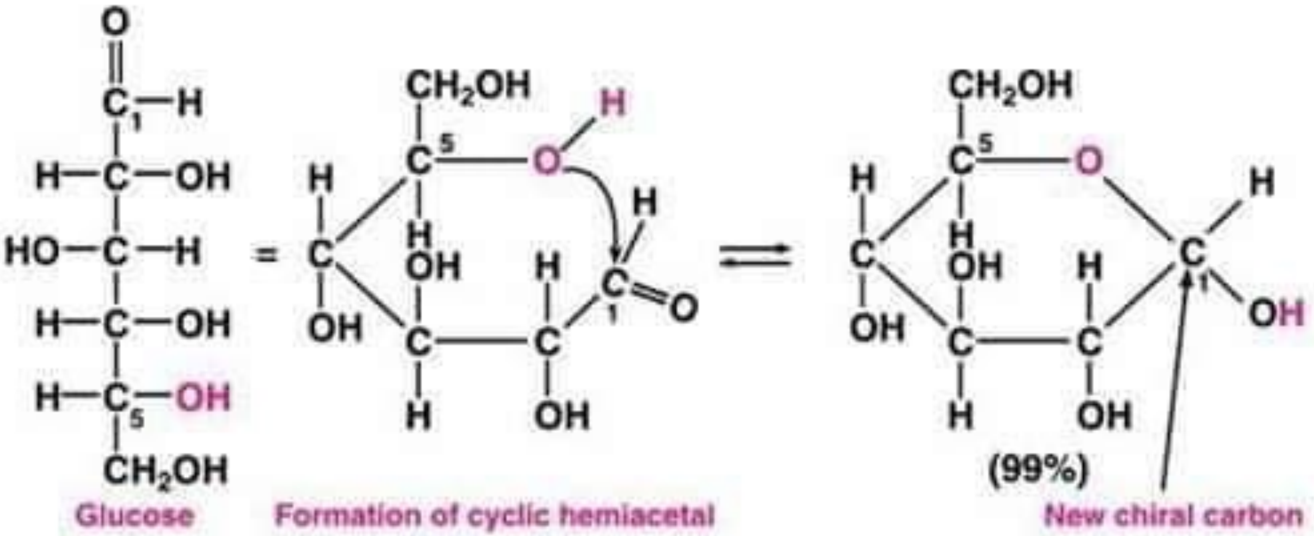


- What if the alcohol and carbonyl are attached?



Hexose hemiacetals

- Favor formation of 5- or 6-membered rings
- Hydroxyl group on C5 reacts with the aldehyde or ketone



- The Haworth structure can be written from the Fischer projection
  - The D-isomer has the last CH_2OH group located above the ring
  - The –OH group on the left (C3) is drawn up
  - The –OH groups on the right (C2, C4) are drawn down
  - Carbonyl C becomes chiral (anomeric carbon); drawn on the right

α and β Anomers for D-Glucose

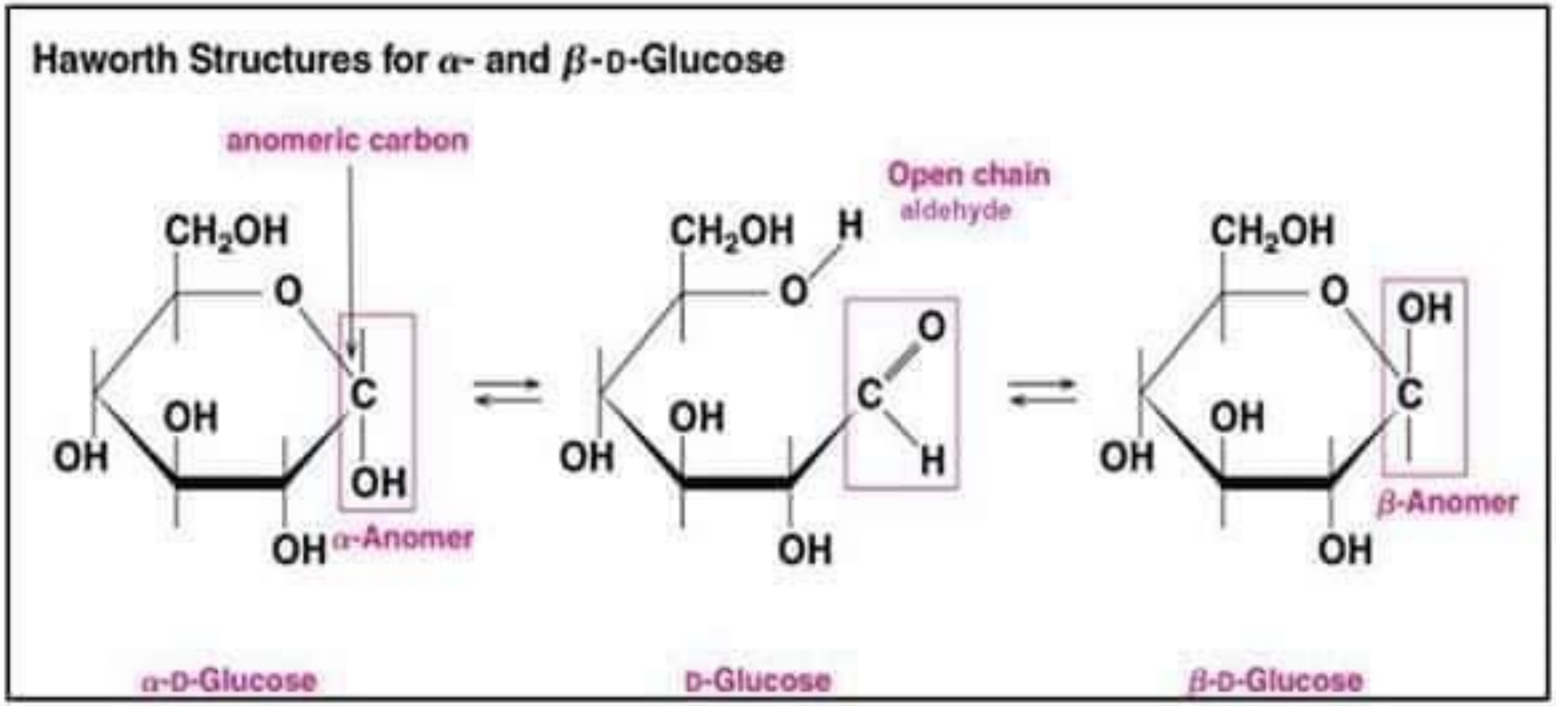
- Anomers are isomers which differ in placement of hydroxyl on anomeric C
- The –OH is drawn down for the α-anomer, and up for the β-anomer

α-D-Glucose β-D-Glucose

- Mashed potatoes or mashed paper?

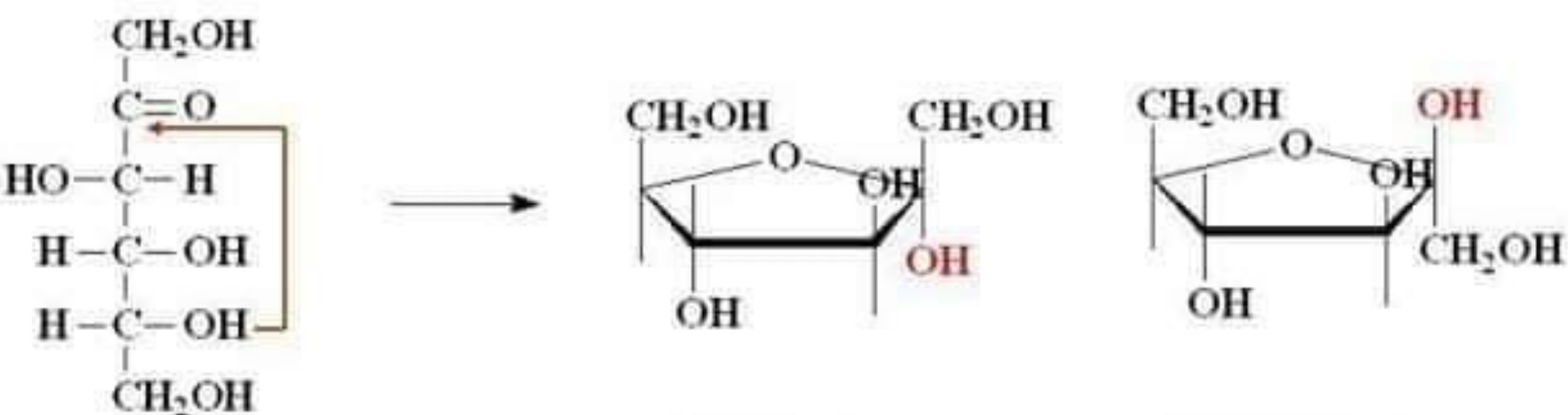
Mutarotation

- In solution, α-D-glucose is in equilibrium with β-D-glucose
- Mutarotation involves the conversion of the cyclic anomers into the open chain
- At any time, there is only a small amount of open chain



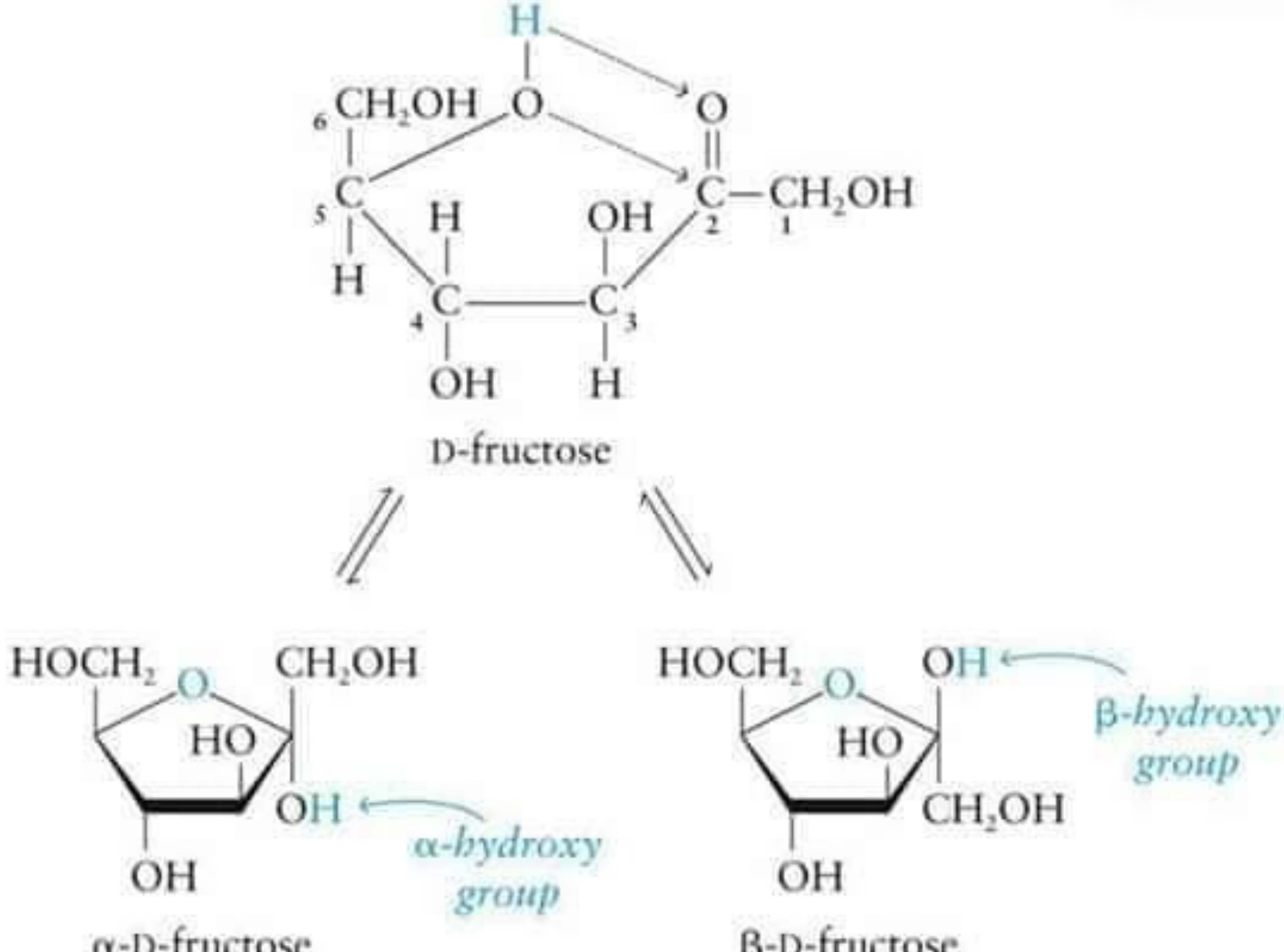
Cyclic Structure of Fructose

- As a ketohexose, fructose forms a cyclic structure when the —OH on C5 reacts with the ketone on C2
- Result is 5-atom ring
- Anomeric carbon is C2



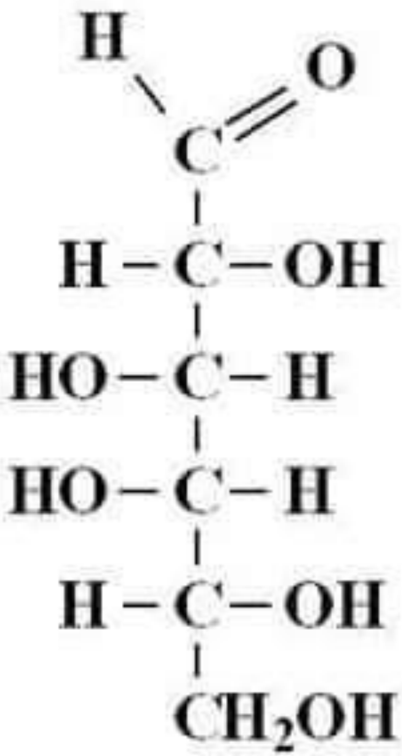
D-Fructose α-D-Fructose β-D-Fructose

α and β Anomers for D-Fructose



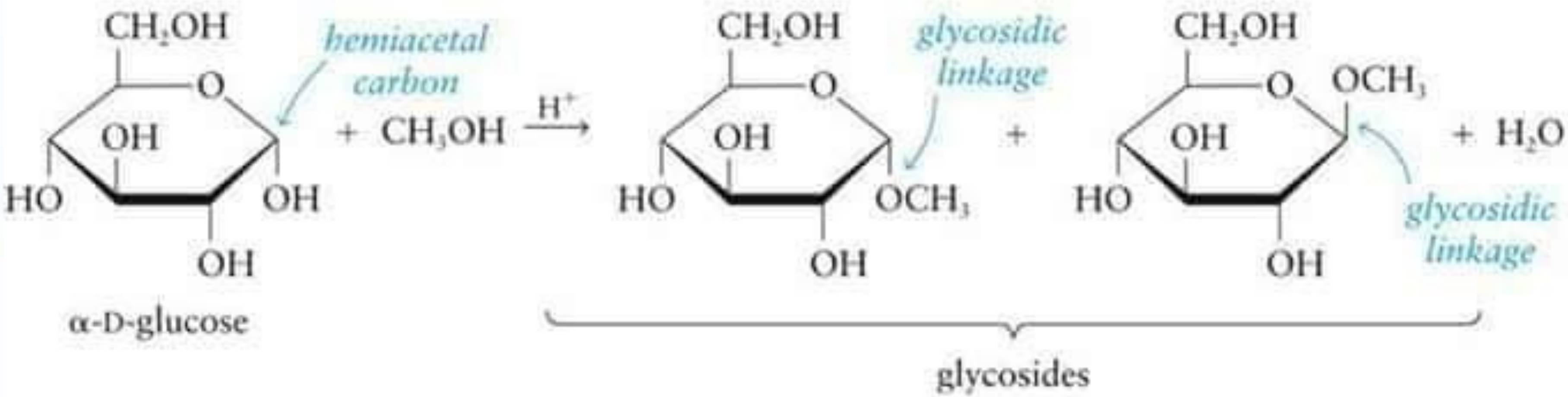
Learning Check

Write the cyclic form of α-D-galactose:



4. Monosaccharide hemiacetals/ hemiketals + alcohol

- When a cyclic monosaccharide reacts with an alcohol:
  - A glycoside is produced (acetal/ketal)
  - The bond is a glycosidic bond or glycosidic linkage



  - Glycosides do not exhibit open chain forms
  - Glycosides are not reducing sugars

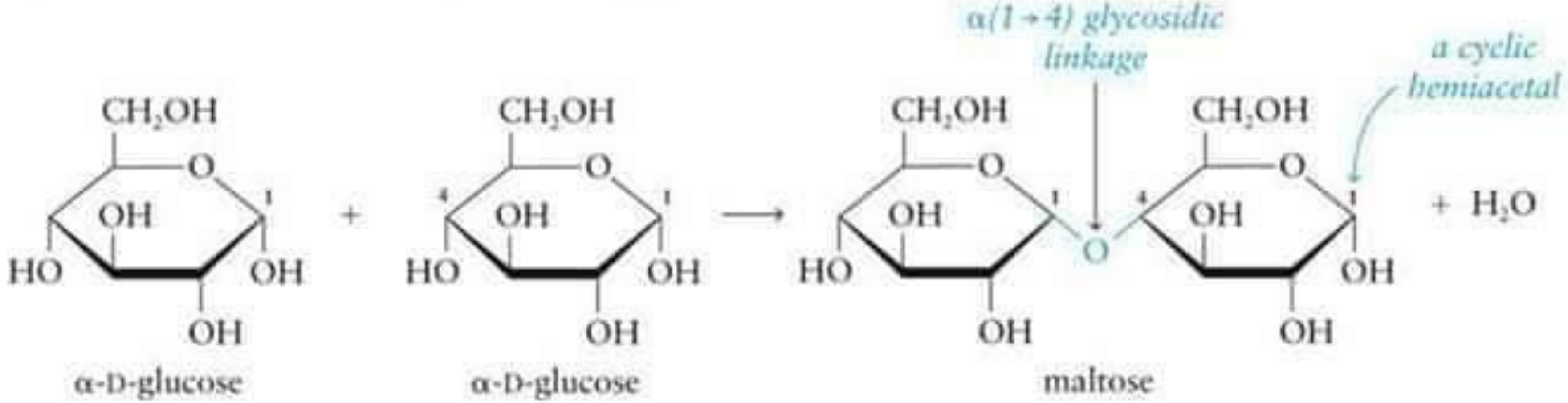
Disaccharides

- A disaccharide consists of two monosaccharides

Disaccharide		Monosaccharides
Maltose + H_2O	$\overset{H^+}{\rightleftharpoons}$	Glucose + Glucose
Lactose + H_2O	$\rightleftharpoons$	Glucose + Galactose
Sucrose + H_2O	$\rightleftharpoons$	Glucose + Fructose

Maltose

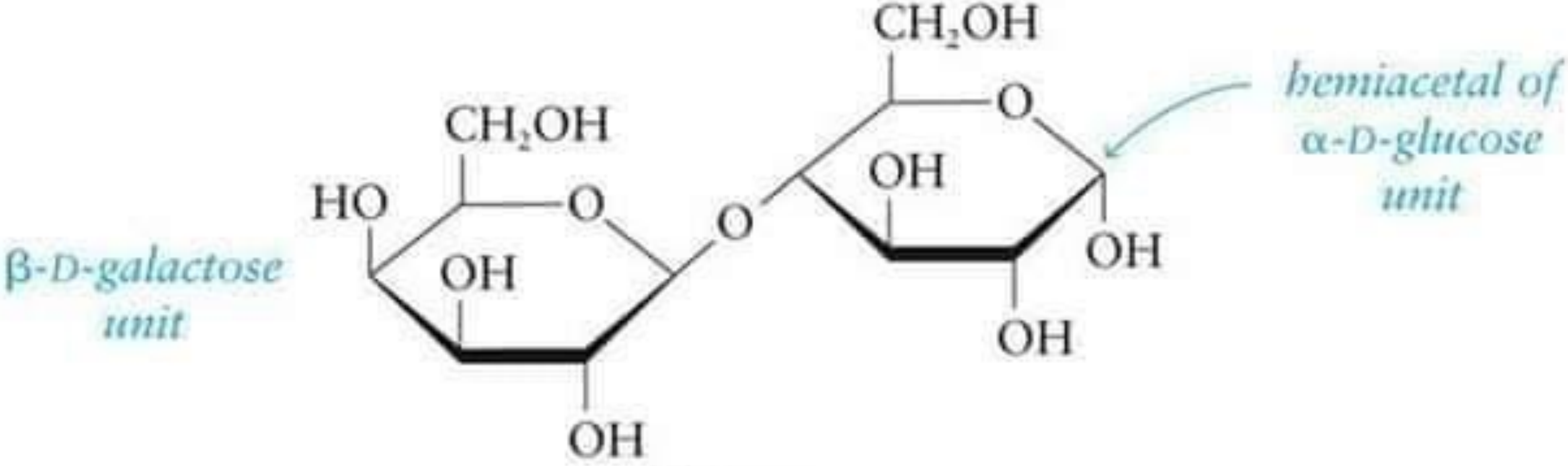
- Malt sugar
- Obtained from starch
- Used in cereals, candies, and brewing
- A disaccharide in which two D-glucose molecules are joined by an $\alpha(1 \longrightarrow 4)$glycosidic bond



- A reducing sugar (has a hemiacetal)

Lactose

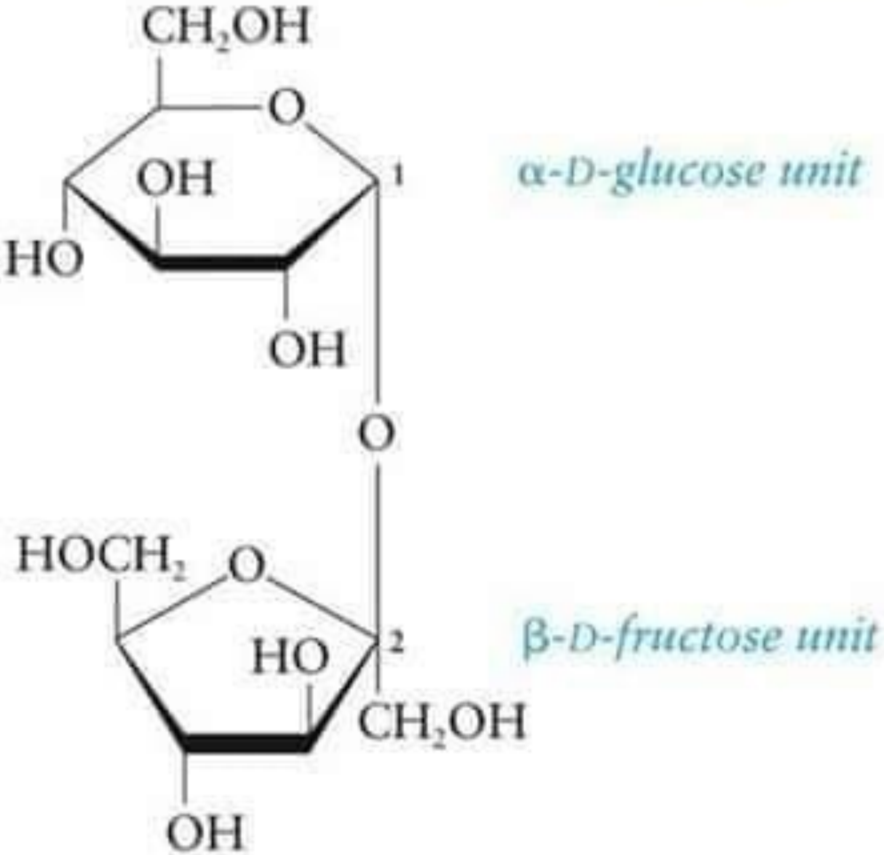
- Milk sugar
- Composed of galactose and glucose linked by a $\beta(1 \rightarrow 4)$ glycosidic bond
- Lactose intolerance
- A reducing sugar



lactose

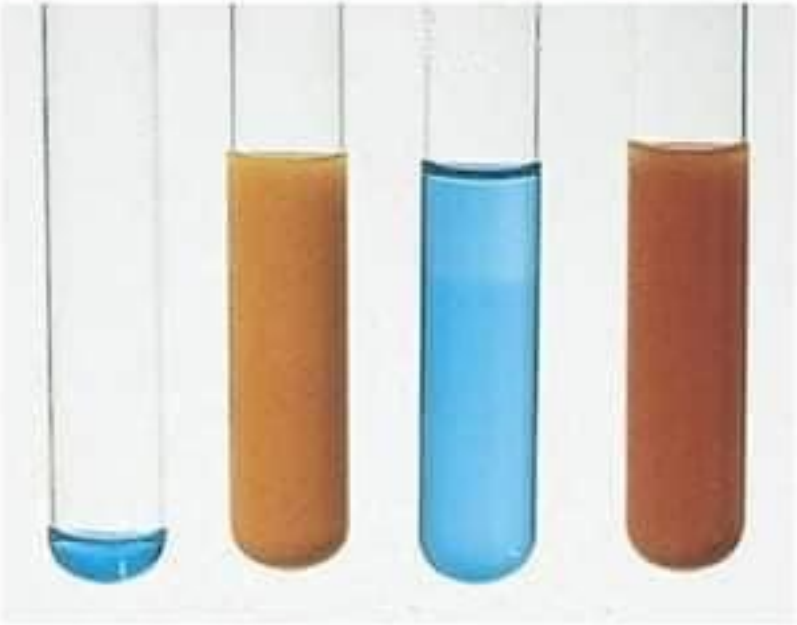
Sucrose

- Table sugar
- Composed of glucose and fructose joined by $\alpha 1 \longrightarrow \beta 2$-glycosidic bond
- Has no isomers because mutarotation is blocked
- Not a reducing sugar (no hemiacetal)



sucrose

Benedict's Test on Disaccharides



1

From left to right, the four test Tubes contain Benedict's reagent, 2% maltose solution, 2% sucrose solution, and 2% lactose solution.

2

Both maltose and lactose are reducing sugars. The sucrose has remained unreacted.

Disaccharides Summary

Table 17.3 Some Important Disaccharides

Name	Monosaccharide Constituents	Glycoside Linkage	Source
Maltose	Two glucose units	$\alpha(1 \rightarrow 4)$	Hydrolysis of starch
Lactose	Galactose and glucose	$\beta(1 \rightarrow 4)$	Mammalian milk
Sucrose	Glucose and fructose	$\alpha\text{-}1 \rightarrow \beta\text{-}2$	Sugar cane and sugar beet juices

Learning Check

Identify the monosaccharides in lactose, maltose, and sucrose as glucose, fructose, and/or galactose:

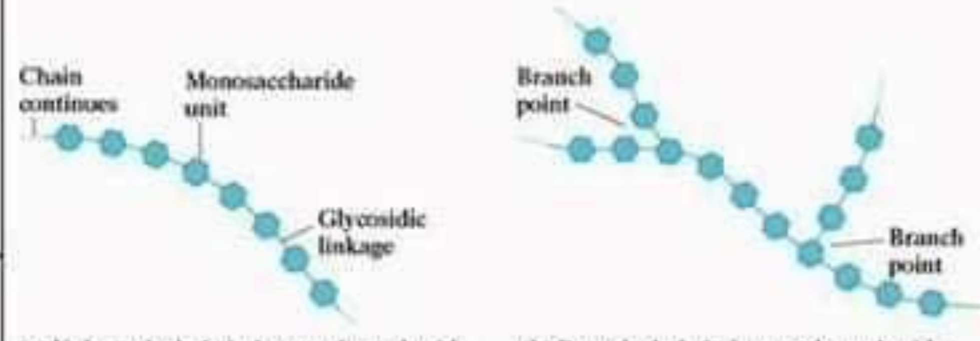
A. Lactose

B. Maltose

C. Sucrose

Polysaccharides

- Polysaccharides are polymers of monosaccharides
- "Complex" carbohydrates
- Important polysaccharides of D-glucose are:
  - Starch (Amylose and Amylopectin)
  - Glycogen
  - Cellulose



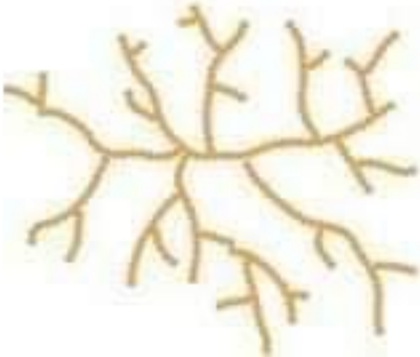
(a) Unbranched-chain homopolysaccharide (b) Branched-chain homopolysaccharide
(c) Unbranched-chain heteropolysaccharide (d) Branched-chain heteropolysaccharide

Table 17.4 Properties of Polysaccharides Compared with Those of Monosaccharides and Disaccharides

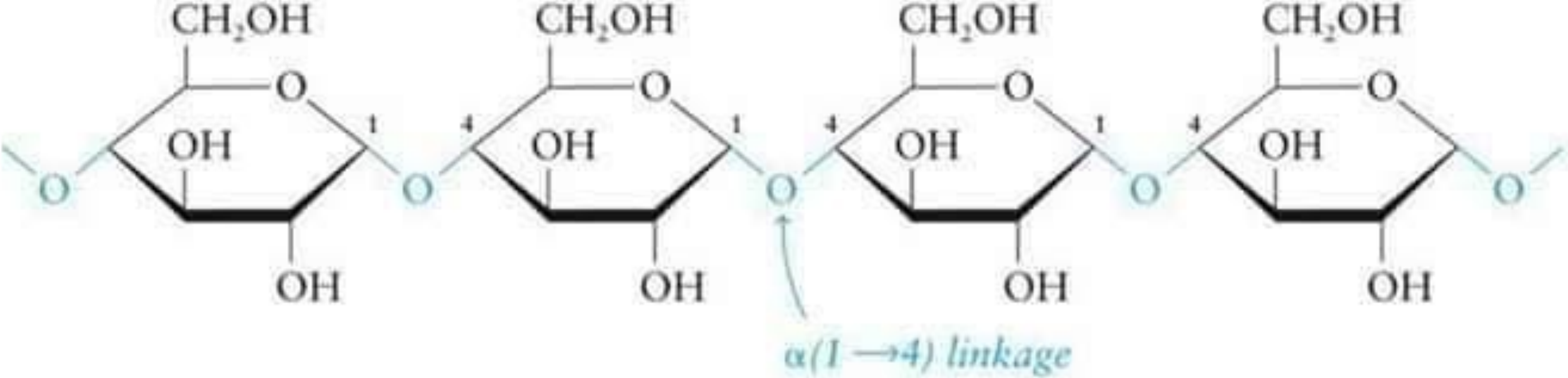
Property	Monosaccharides and Disaccharides	Polysaccharides
Molecular weight	Low	Very high
Taste	Sweet	Tasteless
Solubility in water	Soluble	Insoluble or form colloidal dispersions
Size of particles	Pass through a membrane	Do not pass through a membrane
Test with Cu^{2+} for reducing sugars	Positive (except for sucrose)	Negative

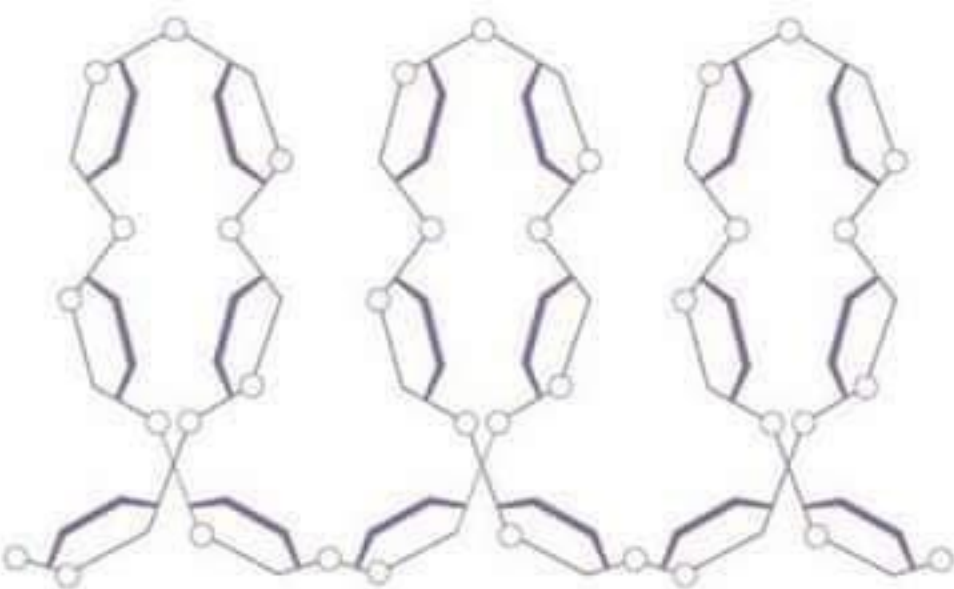
Starch and Glycogen

- Storage polysaccharides
  - Form monosaccharides used for energy
- Starch
  - Plants
  - Amylose is a continuous chain of D-glucose molecules linked by $\alpha(1 \rightarrow 4)$-glycosidic bonds.
  - Amylopectin is a branched chain of D-glucose molecules linked by $\alpha(1 \rightarrow 4)$- and $\alpha(1 \rightarrow 6)$-glycosidic bonds.
- Glycogen
  - Humans, animals
  - Similar to amylopectin, but more highly branched.

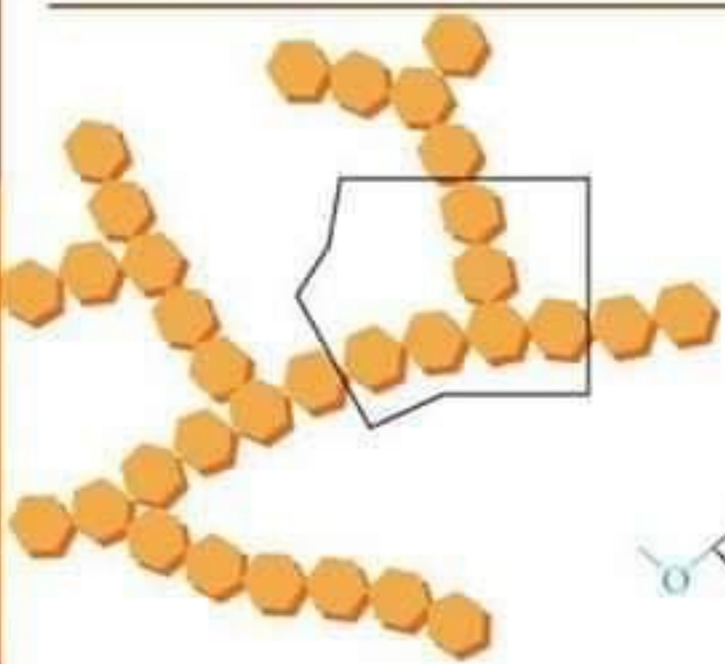


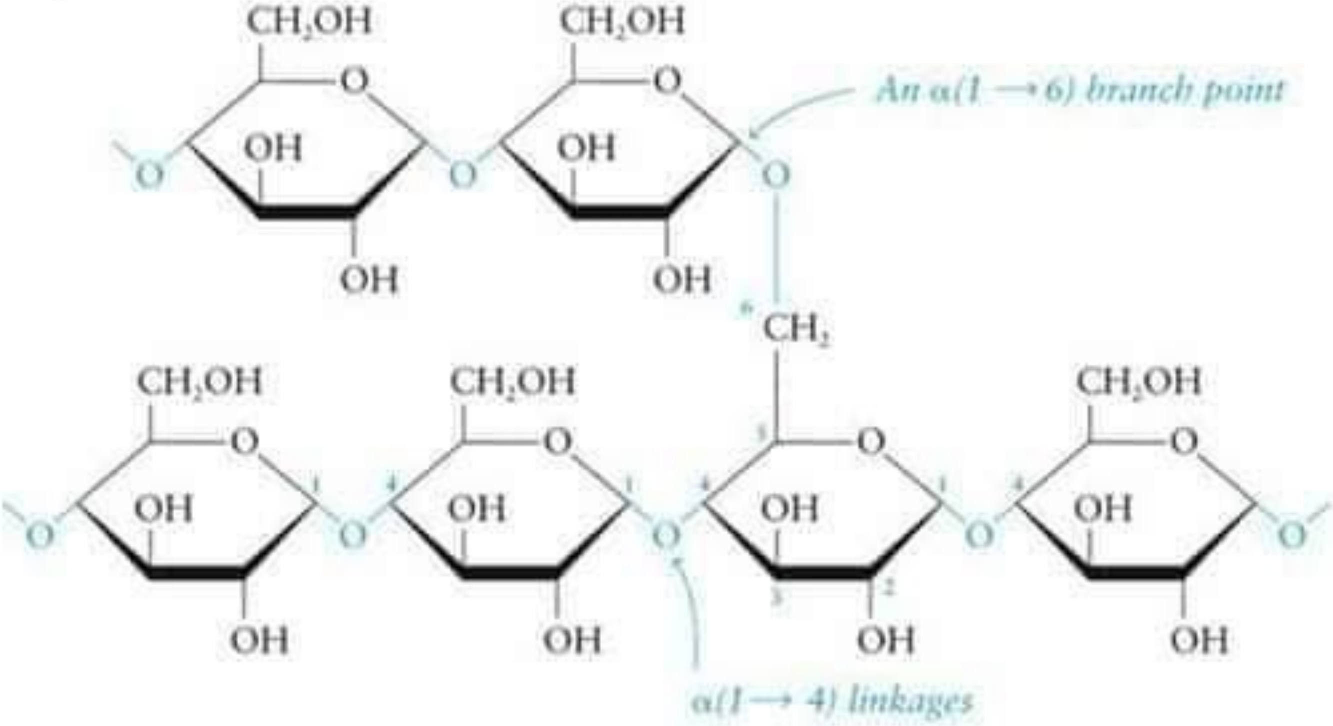
Structure of Amylose





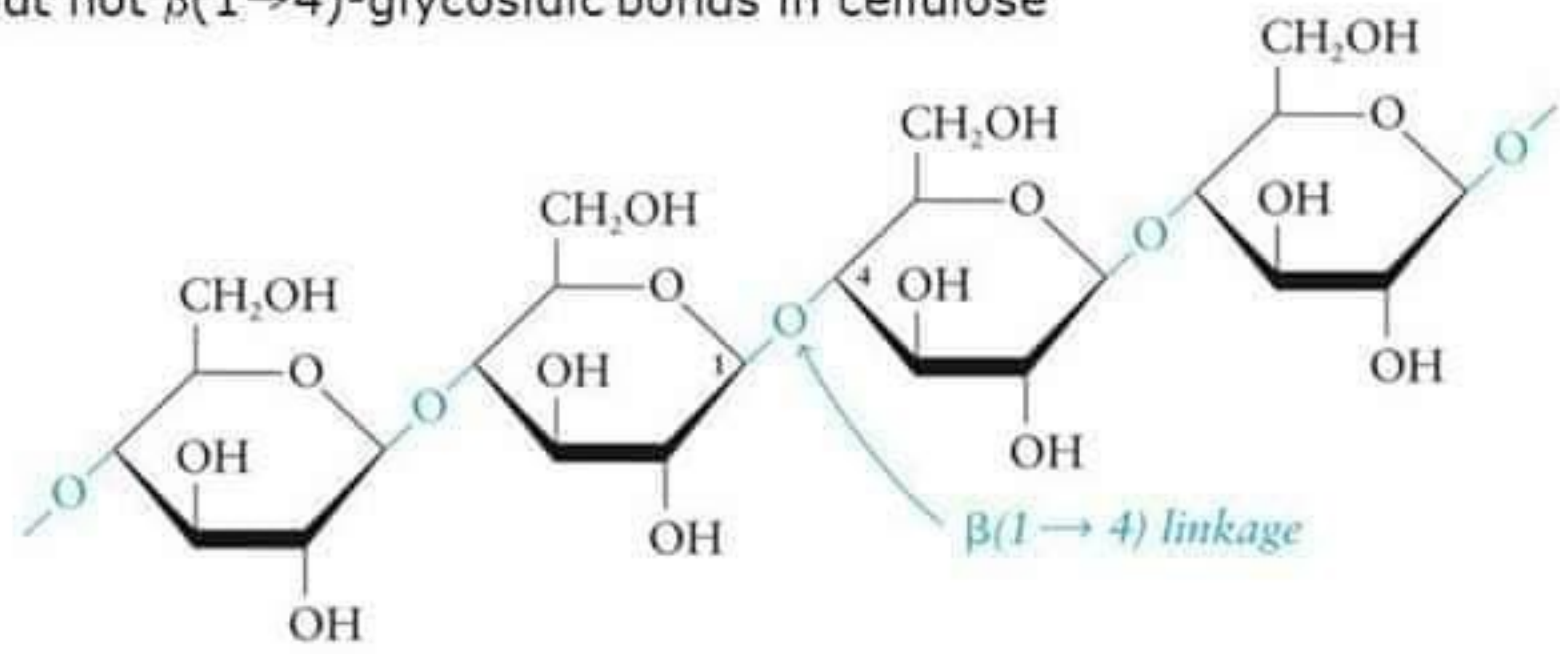
Structure of Amylopectin





Cellulose

- Structural polysaccharide
  - Plant cell walls (cellulose) and animal exoskeletons (chitin)
- Cellulose is a linear polymer of glucose molecules linked by $\beta(1\rightarrow4)$-glycosidic bonds
- Enzymes in saliva can hydrolyze $\alpha(1\rightarrow4)$-glycosidic bonds in starch, but not $\beta(1\rightarrow4)$-glycosidic bonds in cellulose



Learning Check

Identify the types of glycosidic bonds in:

1) Amylose

2) Glycogen

3) Cellulose