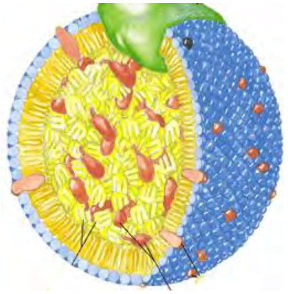



BIOCHEMISTRY REVIEW

Overview of Biomolecules

Chapter 7

Carbohydrates




Classification of Carbohydrates

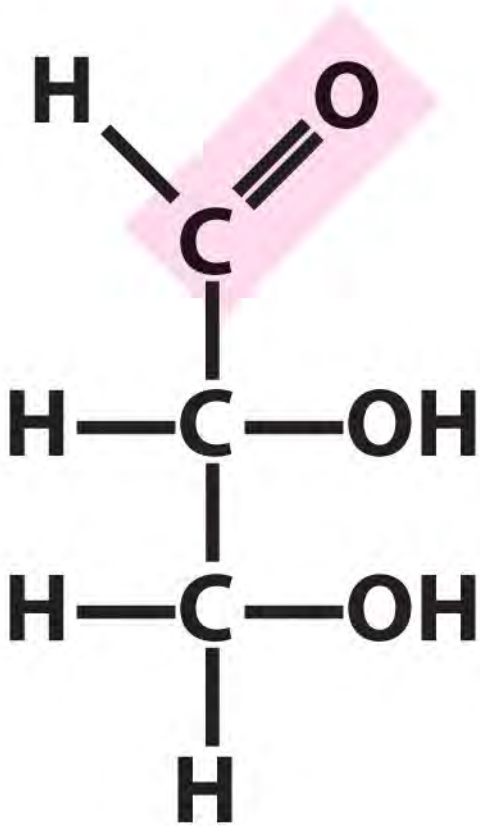
Monosaccharide- one sugar residue. Most well known is glucose, $C_6H_{12}O_6$

Oligosaccharide- a few (2-9) sugar residues . Most well known is cane sugar or sucrose, $C_{12}H_{22}O_{11}$.

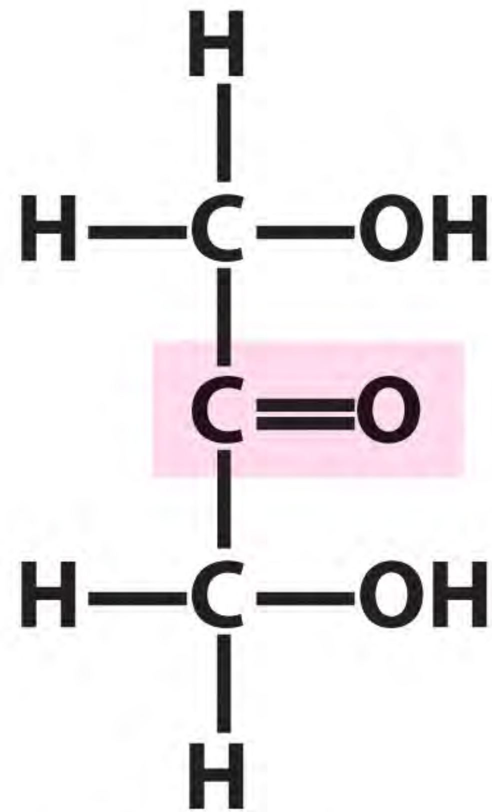
Polysaccharide- many sugar residues. Most common are glycogen, starch and cellulose, from animals, plants and plants.

MONOSACCHARIDE PROPERTIES

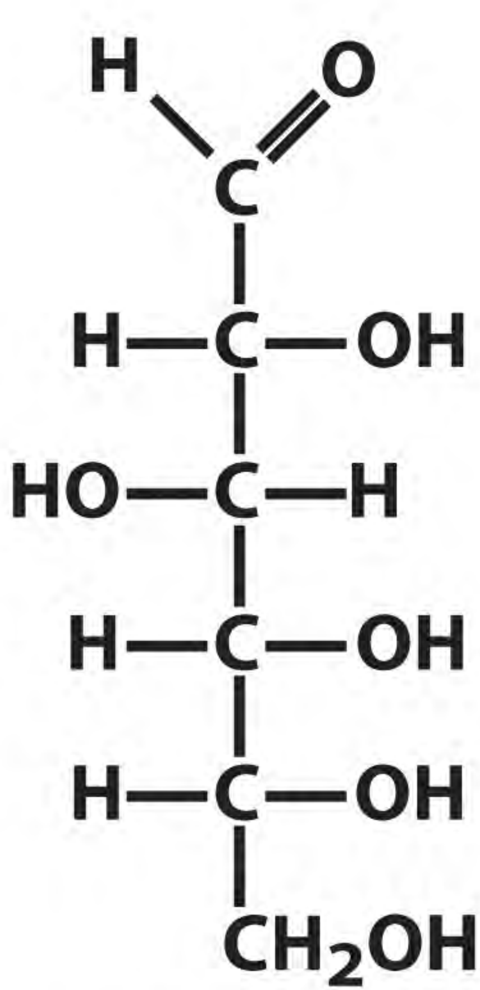
- **WHITE SOLIDS**
- **POLAR- SOLUBLE IN WATER**
- **FORMULA = $(CH_2O)_n$ where n = 3-7**
- **UNBRANCHED CARBON SKELETON**
- **ONE CARBONYL GROUP**
- **ALL OTHER CARBONS HAVE HYDROXYL**
- **CLASSIFIED AS ALDOSE OR KETOSE**
- **CLASSIFIED BY NUMBER OF CARBONS**



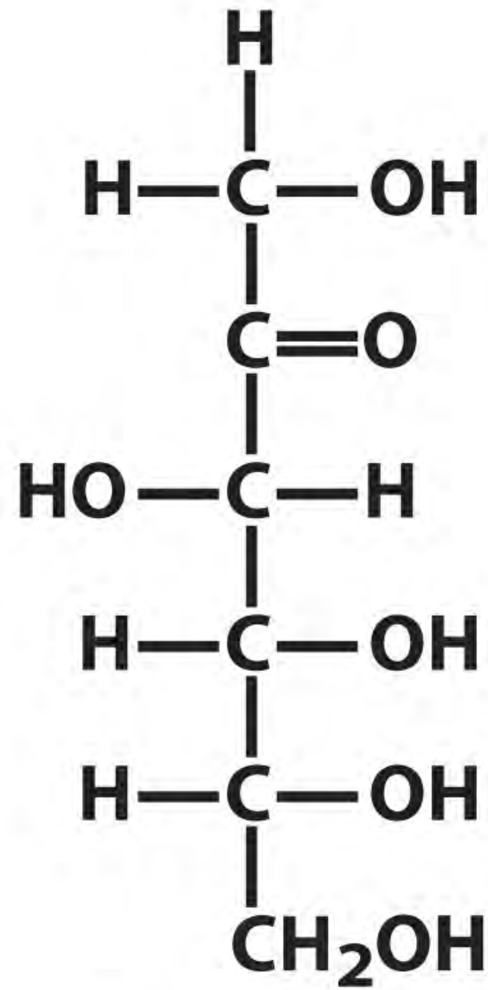
Glyceraldehyde, an aldotriose



Dihydroxyacetone, a ketotriose



D-Glucose,
an aldohexose



D-Fructose,
a ketohexose

Are You Getting It??

Which of the following structures are monosaccharides?

(multiple answers)

a)

CHO
|
CHOH
|
CHOH
|
CH_2OH

b)

CHO
|
CHOH
|
CHOH
|
COOH

c)

CH_2OH
|
C = O
|
CHOH
|
CH_2OH

d)

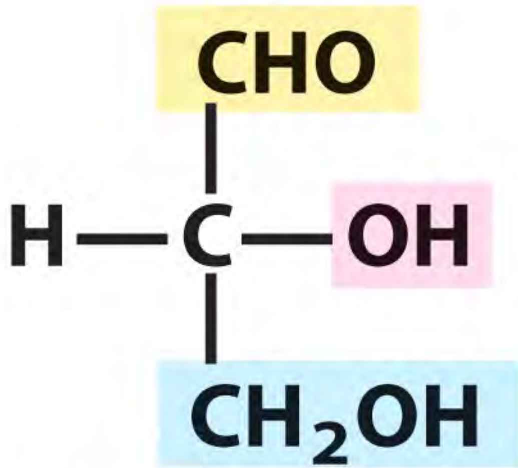
CHO
|
CH_2
|
CHOH
|
CH_2OH

Are You Getting It??

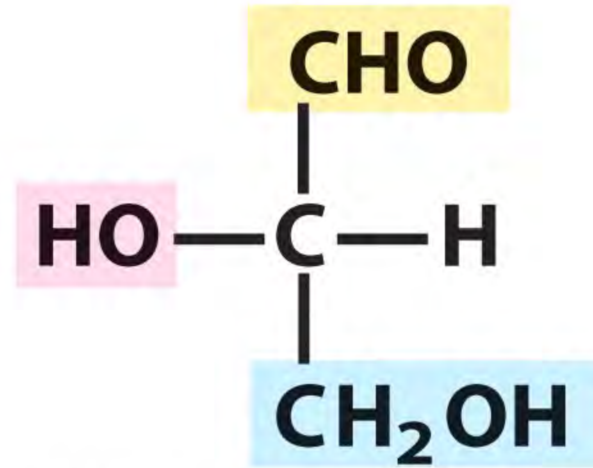
Answer

Which of the following structures are monosaccharides?

a)	b)	c)	d)
CHO	CHO	CH_2OH	CHO
|	|	|	|
CHOH	CHOH	C = O	CH_2
|	|	|	|
CHOH	CHOH	CHOH	CHOH
|	|	|	|
CH_2OH	COOH	CH_2OH	CH_2OH

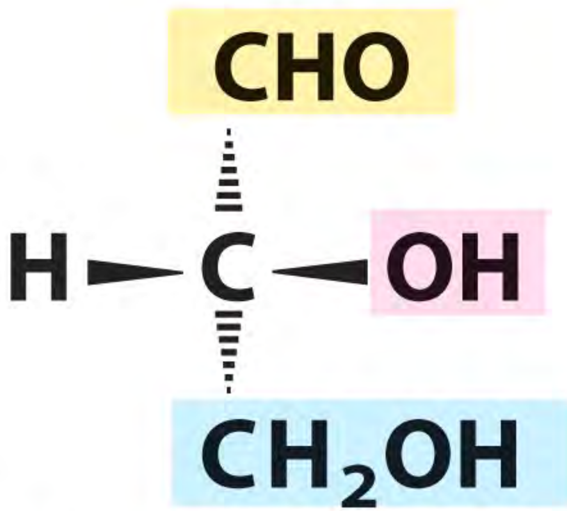


D-Glyceraldehyde

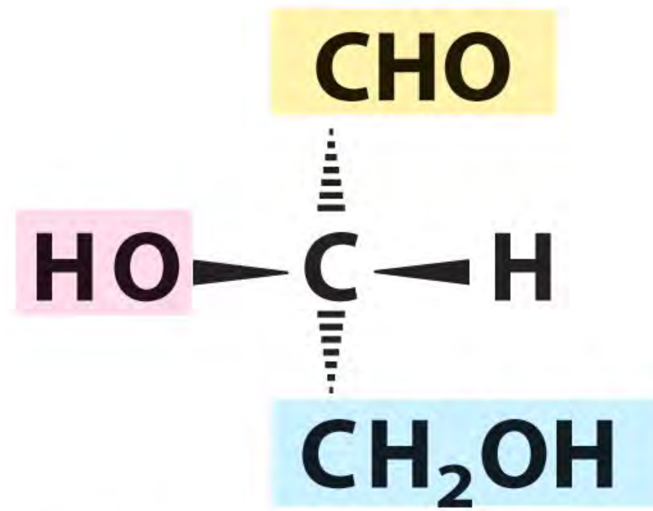


L-Glyceraldehyde

Fischer projection formulas



D-Glyceraldehyde

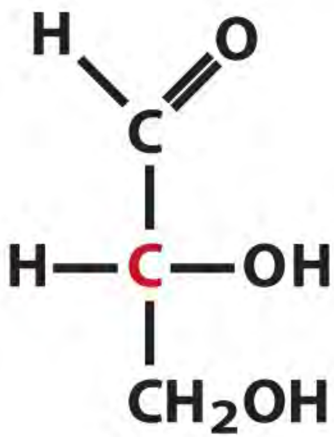


L-Glyceraldehyde

Perspective formulas

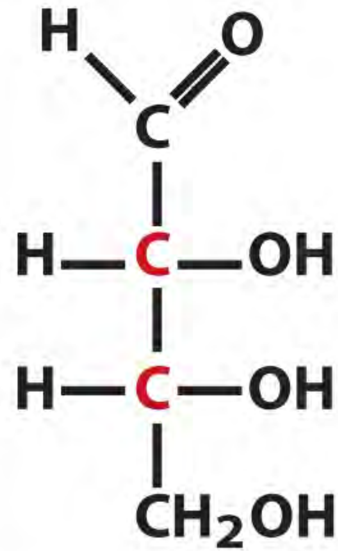
D-Aldoses

Three carbons

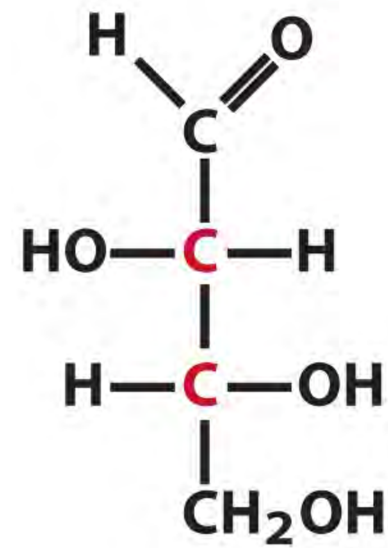


D-Glyceraldehyde

Four carbons



D-Erythrose



D-Threose

D-erythrose

CHO
|
H – C – OH
|
H – C – OH
|
CH_2OH

D-threose

CHO
|
HO – C – H
|
H – C – OH
|
CH_2OH

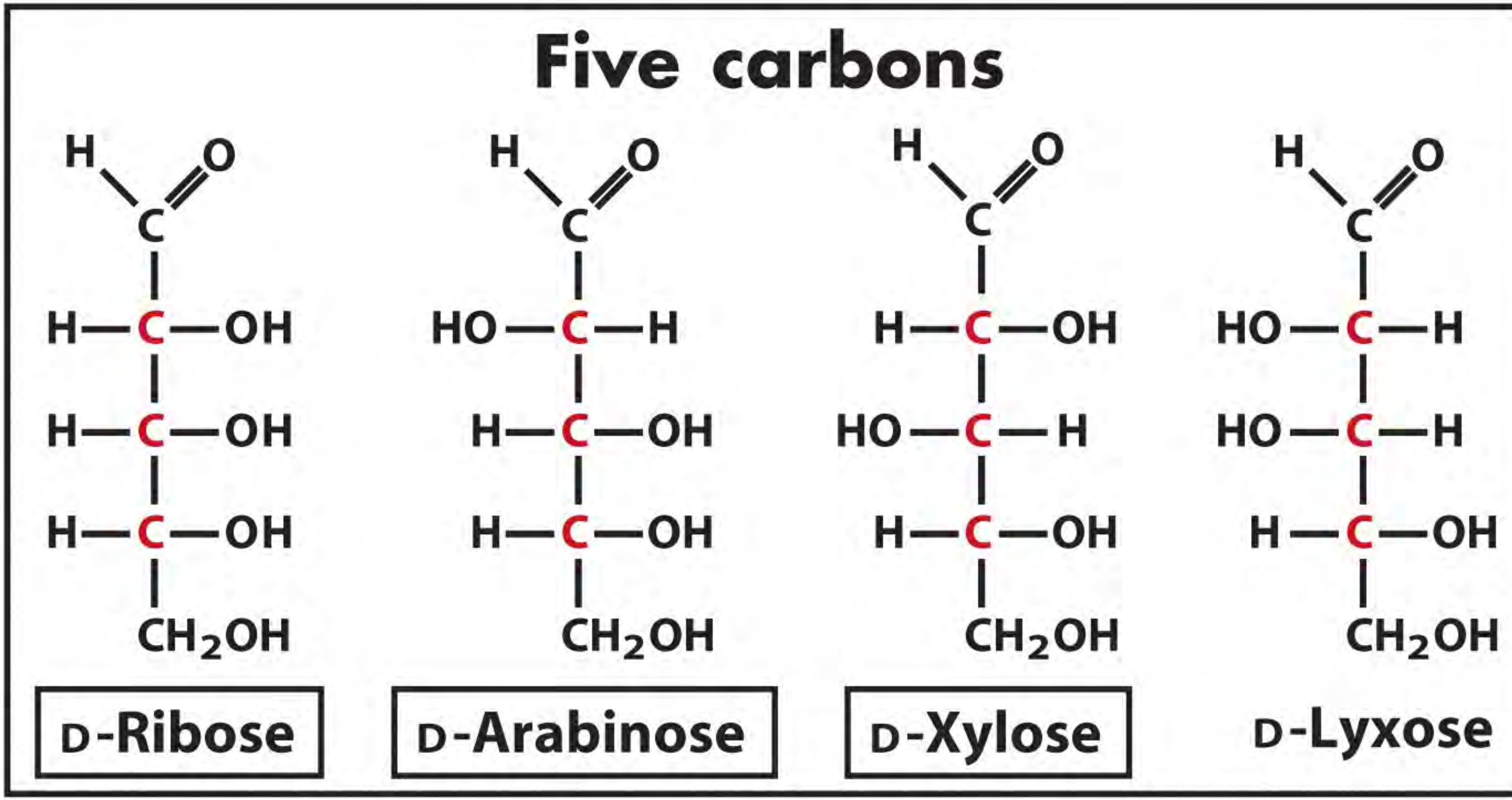
L-threose

CHO
|
H – C – OH
|
HO – C – H
|
CH_2OH

L-erythrose

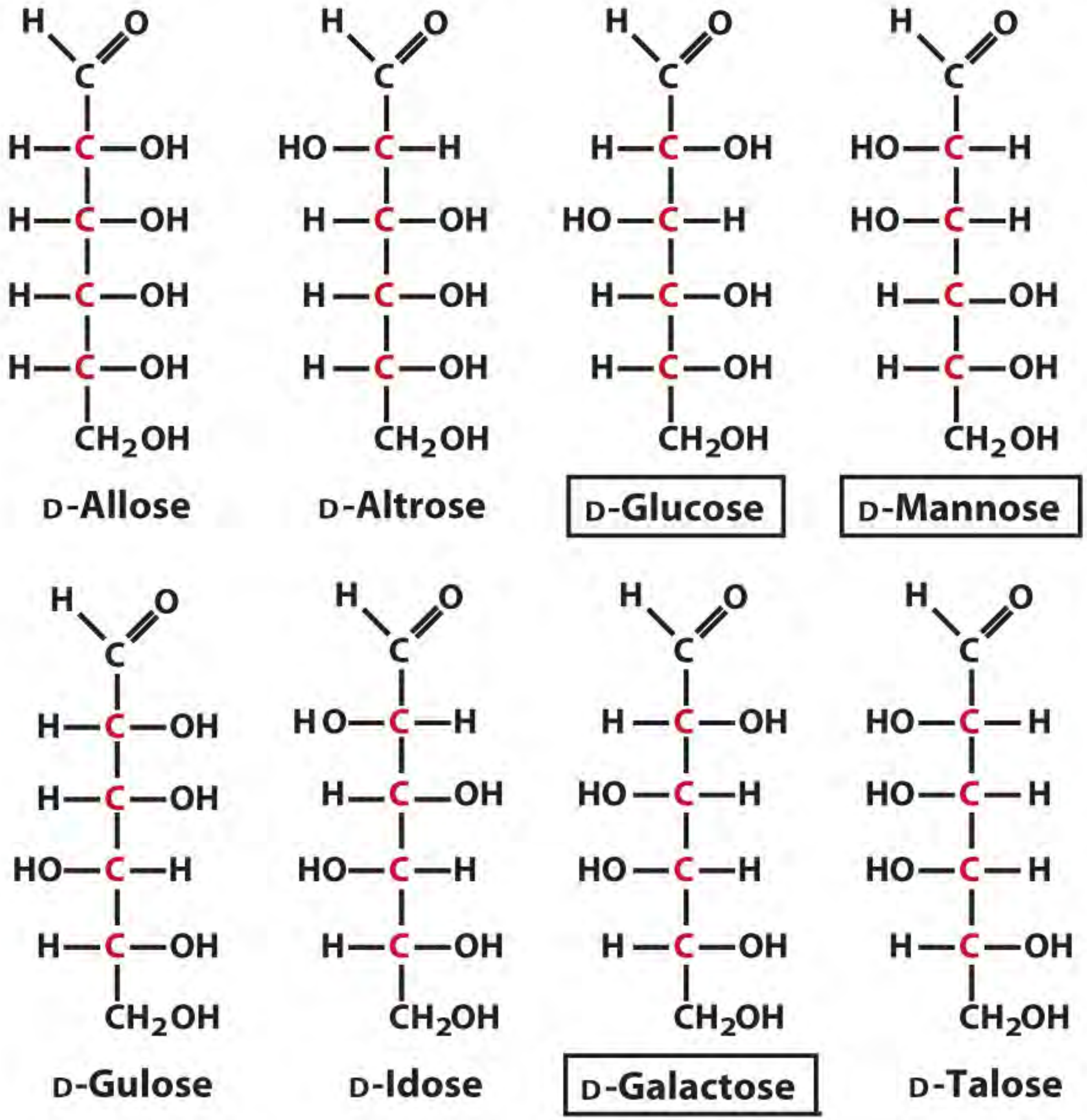
CHO
|
HO – C – H
|
HO – C – H
|
CH_2OH

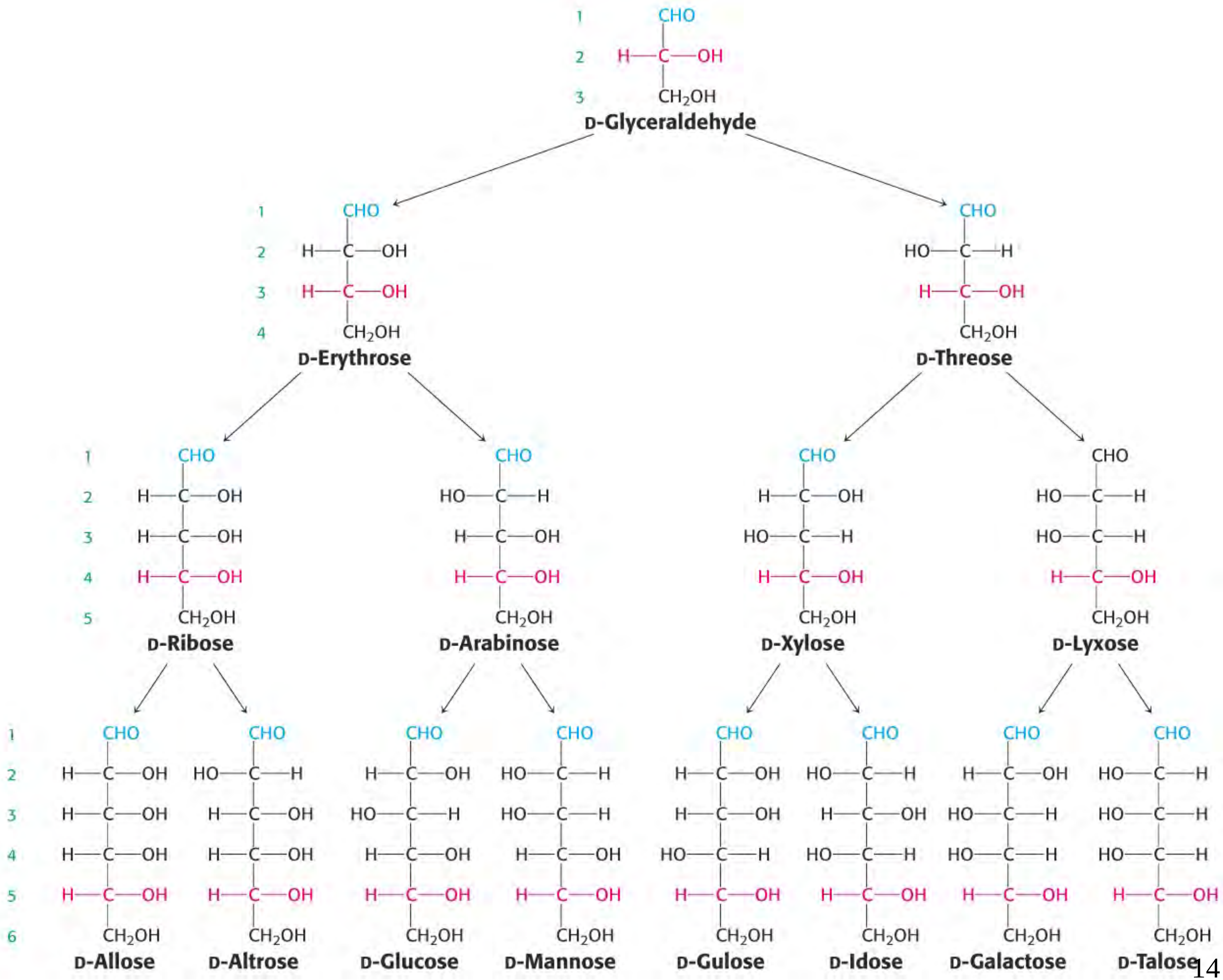
D-Aldoses

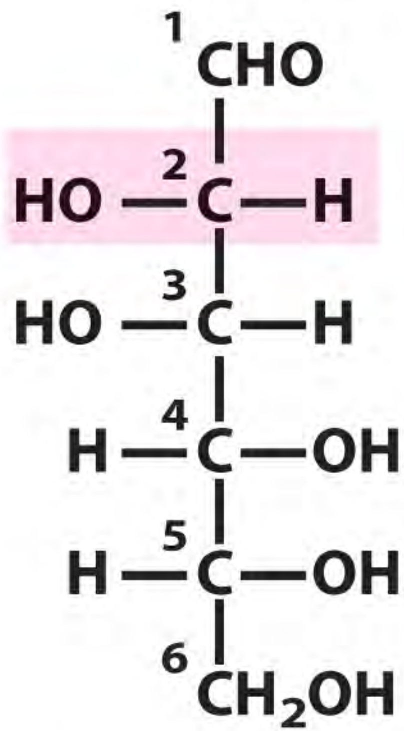


D-Aldoses

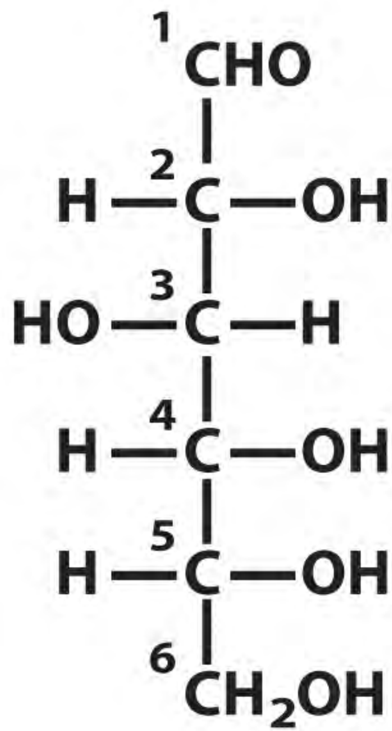
Six carbons



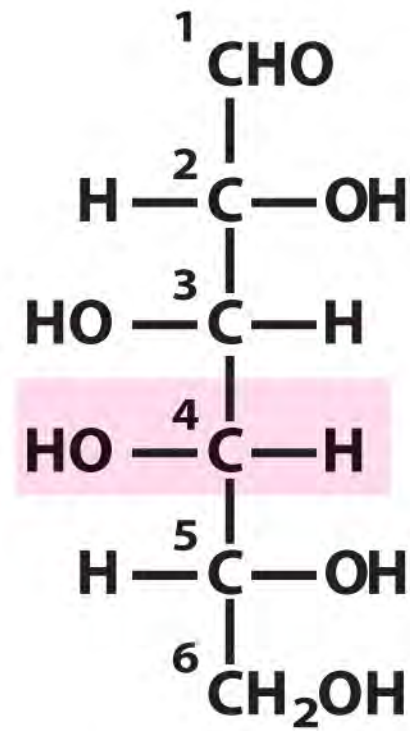

D-Glyceraldehyde
D-Erythrose
D-Threose
D-Ribose
D-Arabinose
D-Xylose
D-Lyxose
D-Allose
D-Altrose
D-Glucose
D-Mannose
D-Gulose
D-Idose
D-Galactose
D-Talose



D-Mannose
(epimer at C-2)



D-Glucose



D-Galactose
(epimer at C-4)

Are You Getting It??

Consider an aldopentose: $HOH_2C - (CHOH)_3 - CHO$

a) How many carbonyl groups does it contain?
b) How many primary alcohols does it contain?
c) How many stereogenic centers does it contain?
d) How many aldopentoses exist?
e) How many D-aldopentoses exist?
f) How many L-aldopentoses exist?

Are You Getting It??

Answer

Consider an aldopentose: $HOH_2C - (CHOH)_3 - CHO$

a) **How many carbonyl groups does it contain?** *1*

b) **How many primary alcohols does it contain?** *1*

c) **How many stereogenic centers does it contain?** *3*

d) **How many aldopentoses exist?** *8*

e) **How many D-aldopentoses exist?** *4*

f) **How many L-aldopentoses exist?** *4*

Are You Getting It??

D-ribose is an aldopentose.
The C-3 epimer of D-ribose is
(multiple answers)

a) another aldopentose
b) a ketopentose
c) an enantiomer of D-ribose
d) a diastereomer of D-ribose
e) an L-pentose
f) a D-hexose

CHO
|
H – C – OH
|
H – C – OH
|
H – C – OH
|
CH_2OH

Are You Getting It??

Answer

D-ribose is an aldopentose.

The C-3 epimer of D-ribose is

a) another aldopentose

b) a ketopentose

c) an enantiomer of D-ribose

d) a diastereomer of D-ribose

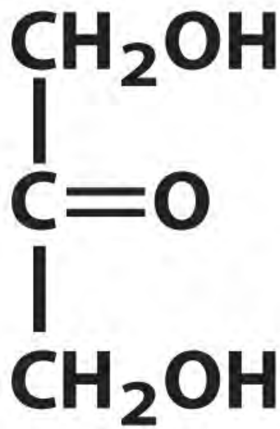
e) an L-pentose

f) a D-hexose

CHO
|
H – C – OH
|
H – C – OH
|
H – C – OH
|
CH_2OH

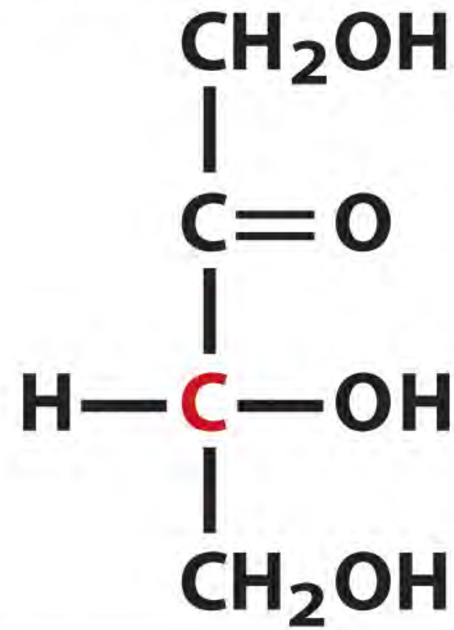
D-Ketoses

Three carbons



Dihydroxyacetone

Four carbons



D-Erythrulose

D-erythrulose

CH_2OH

|

C = O

|

H – C – OH

|

CH_2OH

L-erythrulose

CH_2OH

|

C = O

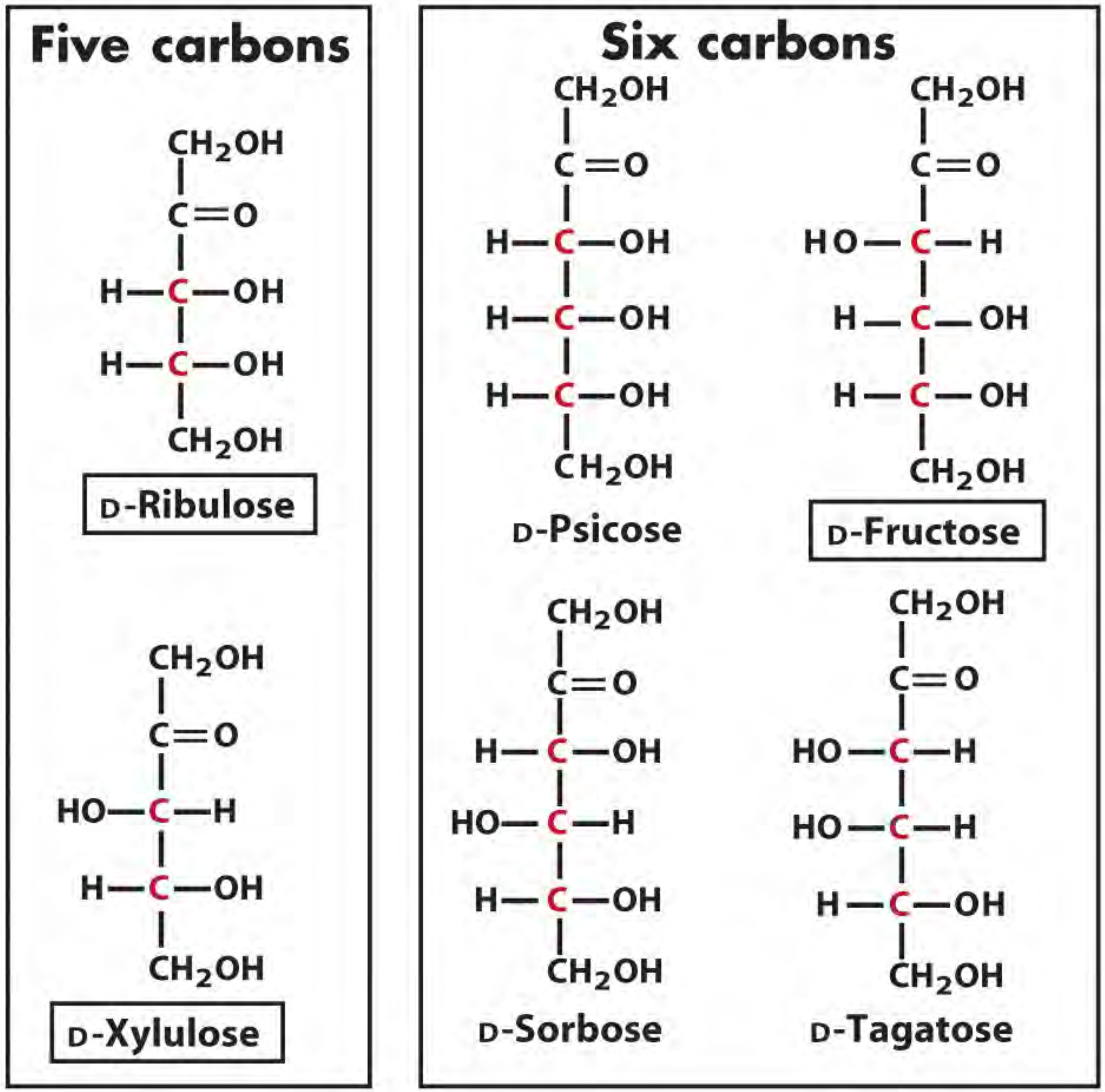
|

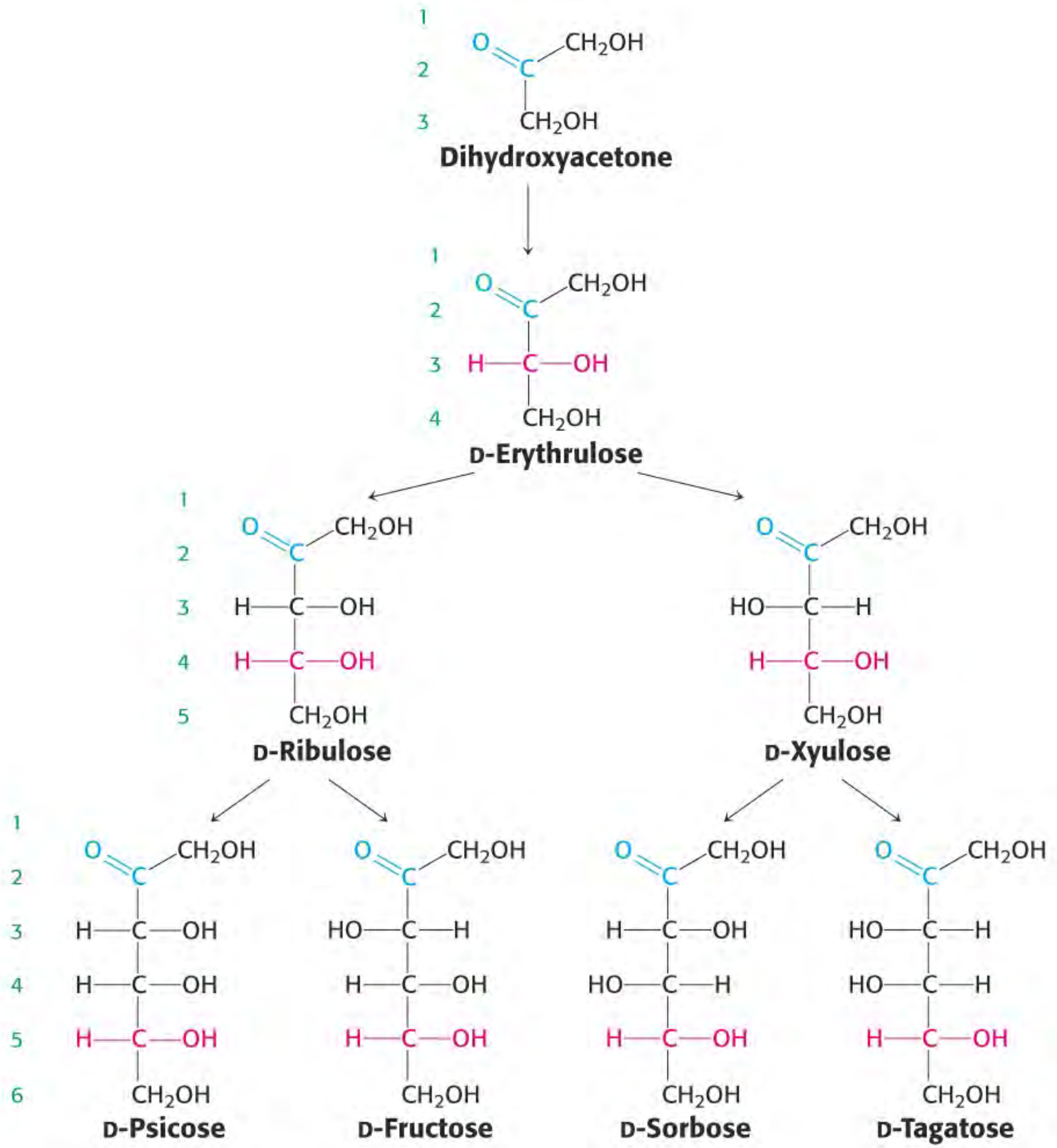
HO – C – H

|

CH_2OH

D-Ketoses


Five carbons
D-Ribulose
D-Xylulose
Six carbons
D-Psicose
D-Fructose
D-Sorbose
D-Tagatose


1
2
3
4
5
6
O
C
CH_2OH
H—C—OH
HO—C—H
Dihydroxyacetone
D-Erythrulose
D-Ribulose
D-Xylose
D-Psicose
D-Fructose
D-Sorbose
D-Tagatose

Are You Getting It??

Consider a ketohexose: $HOH_2C - (CHOH)_3 - C - CH_2OH$

$$\begin{array}{c} \| \\ O \end{array}$$

a) How many carbonyl groups does it contain?

b) How many primary alcohols does it contain?

c) How many stereogenic centers does it contain?

d) How many ketohexoses exist?

e) How many D-ketohexoses exist?

Are You Getting It??

Answer

Consider a ketohexose: $HOH_2C - (CHOH)_3 - C - CH_2OH$

$\| \; O$ (C=O on the central C)

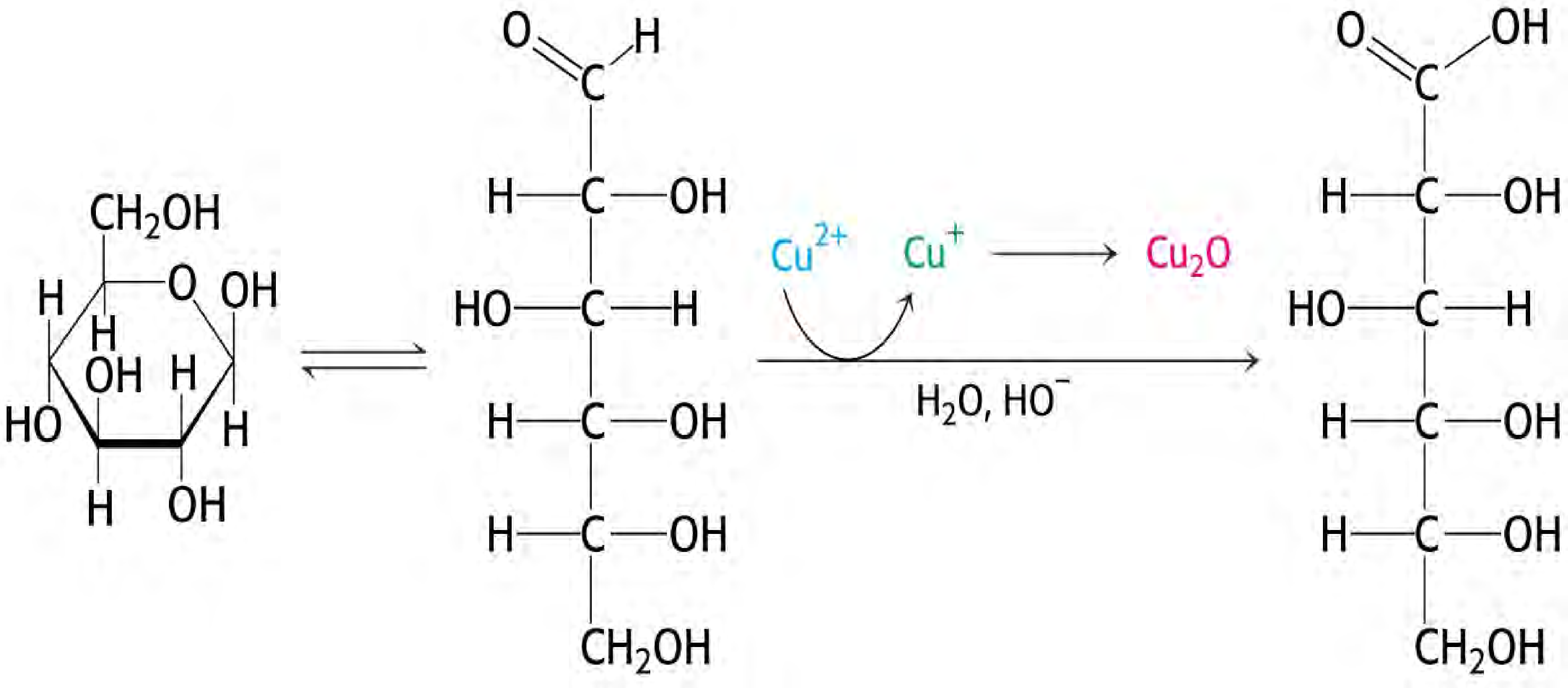
a) How many carbonyl groups does it contain? *1*

b) How many primary alcohols does it contain? *2*

c) How many stereogenic centers does it contain? *3*

d) How many ketohexoses exist? *8*

e) How many D-ketohexoses exist? *4*


CH2OH
O
OH
H
H
OH
H
HO
H
H
OH
O
H
C
H—C—OH
HO—C—H
H—C—OH
H—C—OH
CH2OH
Cu2+
Cu+
Cu2O
H2O, HO−
O
OH
C
H—C—OH
HO—C—H
H—C—OH
H—C—OH
CH2OH

OXIDIZING AGENTS

- **Benedict's Reagent- alkaline Cu^{2+} + citrate**

- **Fehling's Reagent- alkaline Cu^{2+} + tartrate**

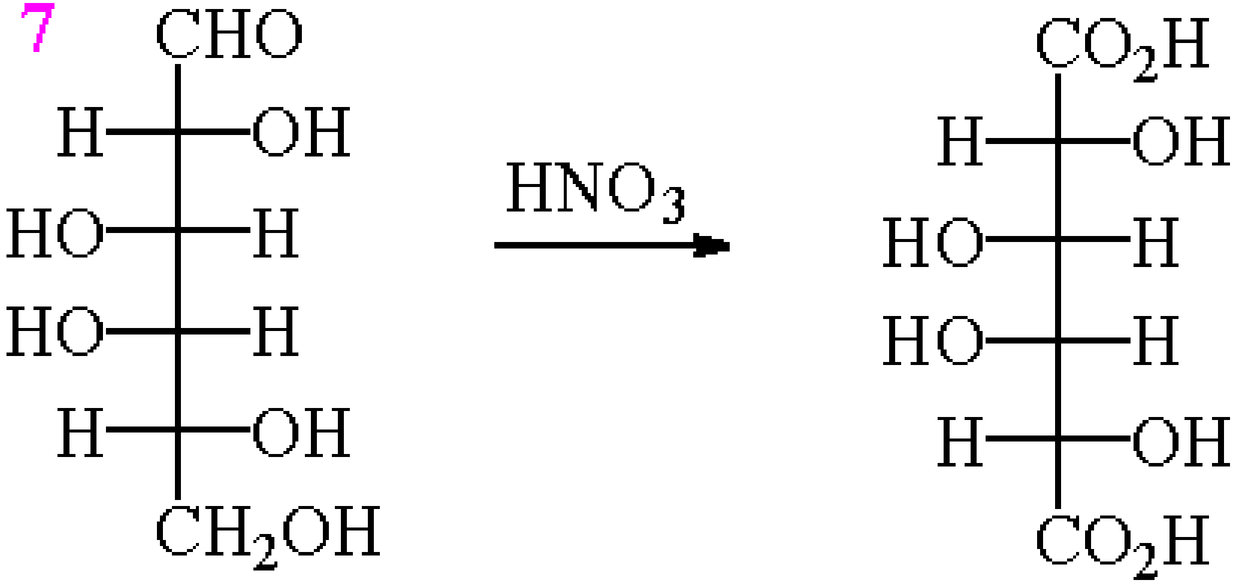
- **Tollen's Reagent- alkaline Ag^{+}**

OXIDATION BY BROMINE WATER

$$\begin{array}{ccc} CHO & & COOH \\ | & & | \\ (CHOH)_n & \xrightarrow{Br_2 + H_2O} & (CHOH)_n \\ | & & | \\ CH_2OH & & CH_2OH \end{array}$$

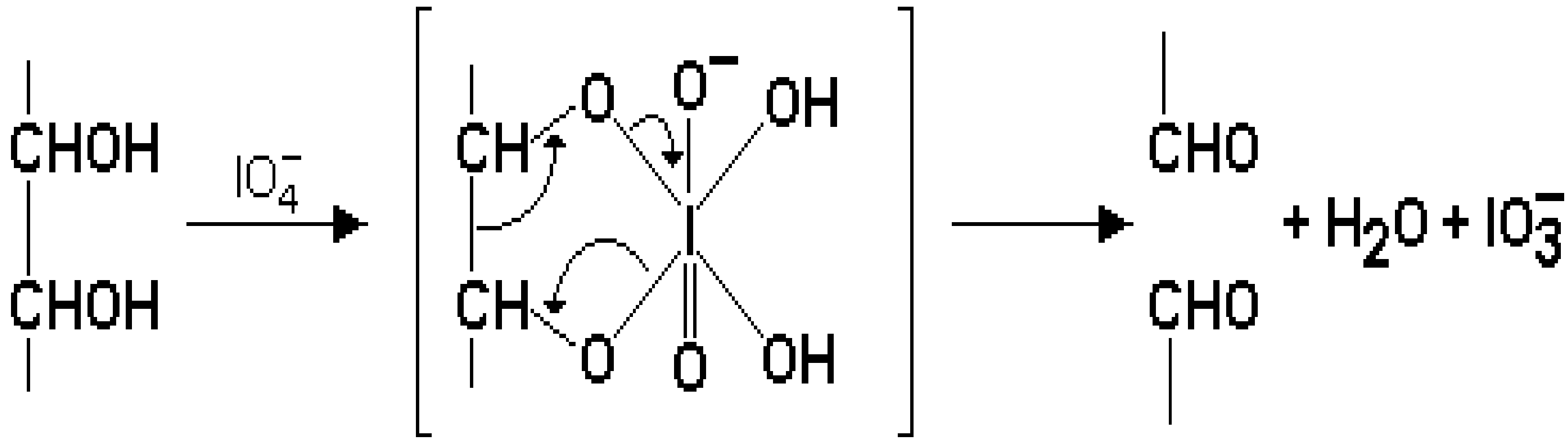
Nitric Acid Oxidation of 7

7

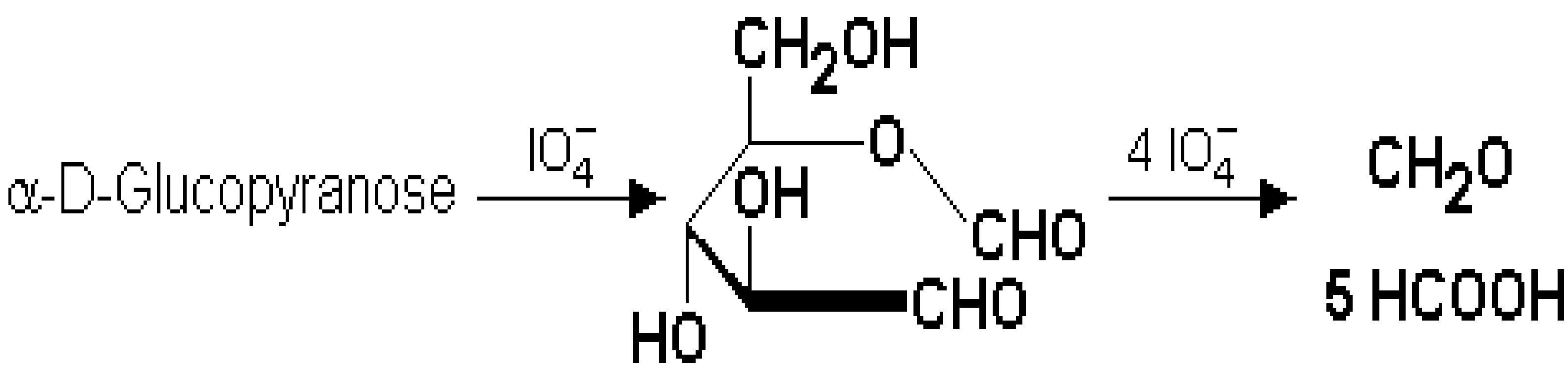


meso

Therefore, neither (+)-glucose nor (+)-mannose can be 7 and must be 3 and 4.



$$\text{Mannitol} \xrightarrow{5\ IO_4^-} 2\ CH_2O + 4\ HCOOH$$

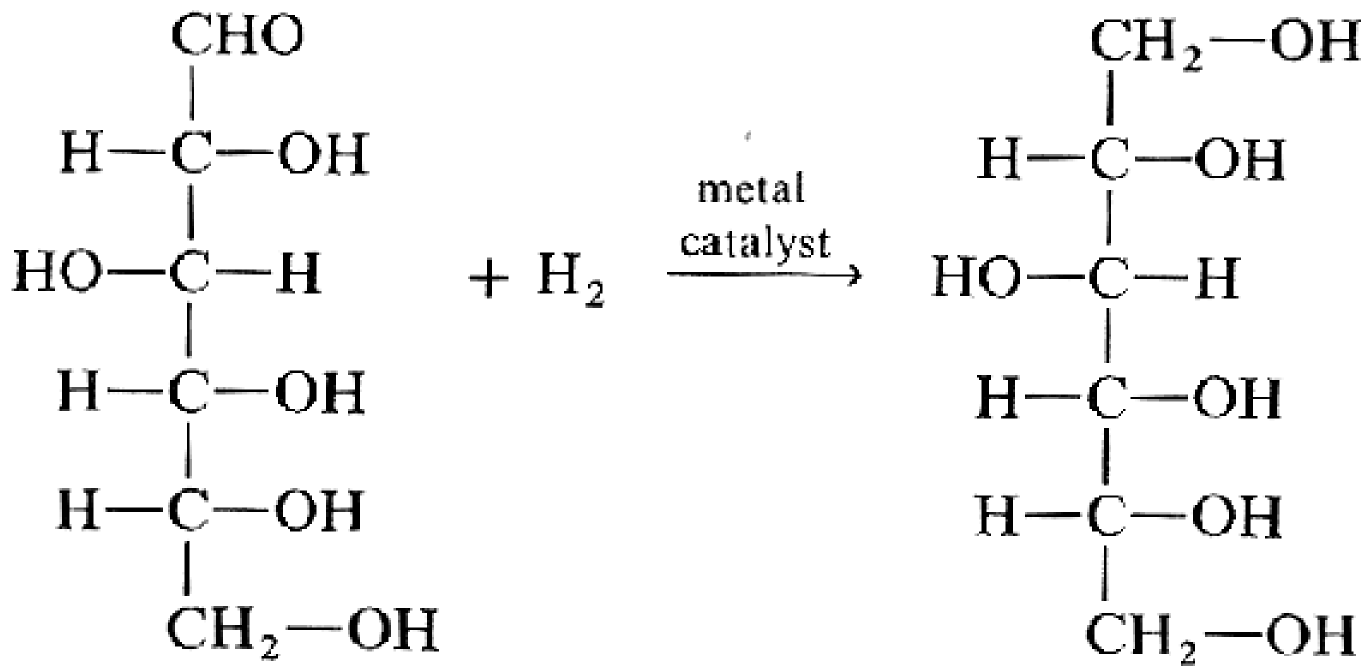


PERIODATE OXIDATION

GROUPS	MONOSACCHARIDES
OH $\rightarrow$ C=O	ONE HIO_4 PER C-C BOND
C=O $\rightarrow$ COOH	ONE HCHO PER 1^{O} OH
COOH $\rightarrow$ CO_2	ONE HCOOH PER 2^{O} OH
	ONE HCOOH PER ALDEHYDE
	ONE CO_2 PER KETONE

PERIODATE OXIDATION OF GLUCOSE

Glucose	Reagents	Products
CHO		HCOOH
|		
H – C – OH		HCOOH
|		
HO – C – H		HCOOH
|	$5\ IO_4^-$ → $5\ IO_3^-$	
H – C – OH	⟶	HCOOH
|		
H – C – OH		HCOOH
|		
CH_2OH		HCHO



D-glucose

D-glucitol (sorbitol)

Are You Getting It??

Which oxidations and reductions can occur with monosaccharides? ***(multiple answers)***

a) **Primary alcohols can be oxidized into aldehydes.**
b) **Aldehydes can be reduced into acids.**
c) **Secondary alcohols can be oxidized into acids.**
d) **Ketones can be oxidized into alcohols.**
e) **Aldehydes can be reduced into alcohols.**

Are You Getting It??

Answer

Which oxidations and reductions can occur with monosaccharides?

a) Primary alcohols can be oxidized into aldehydes.

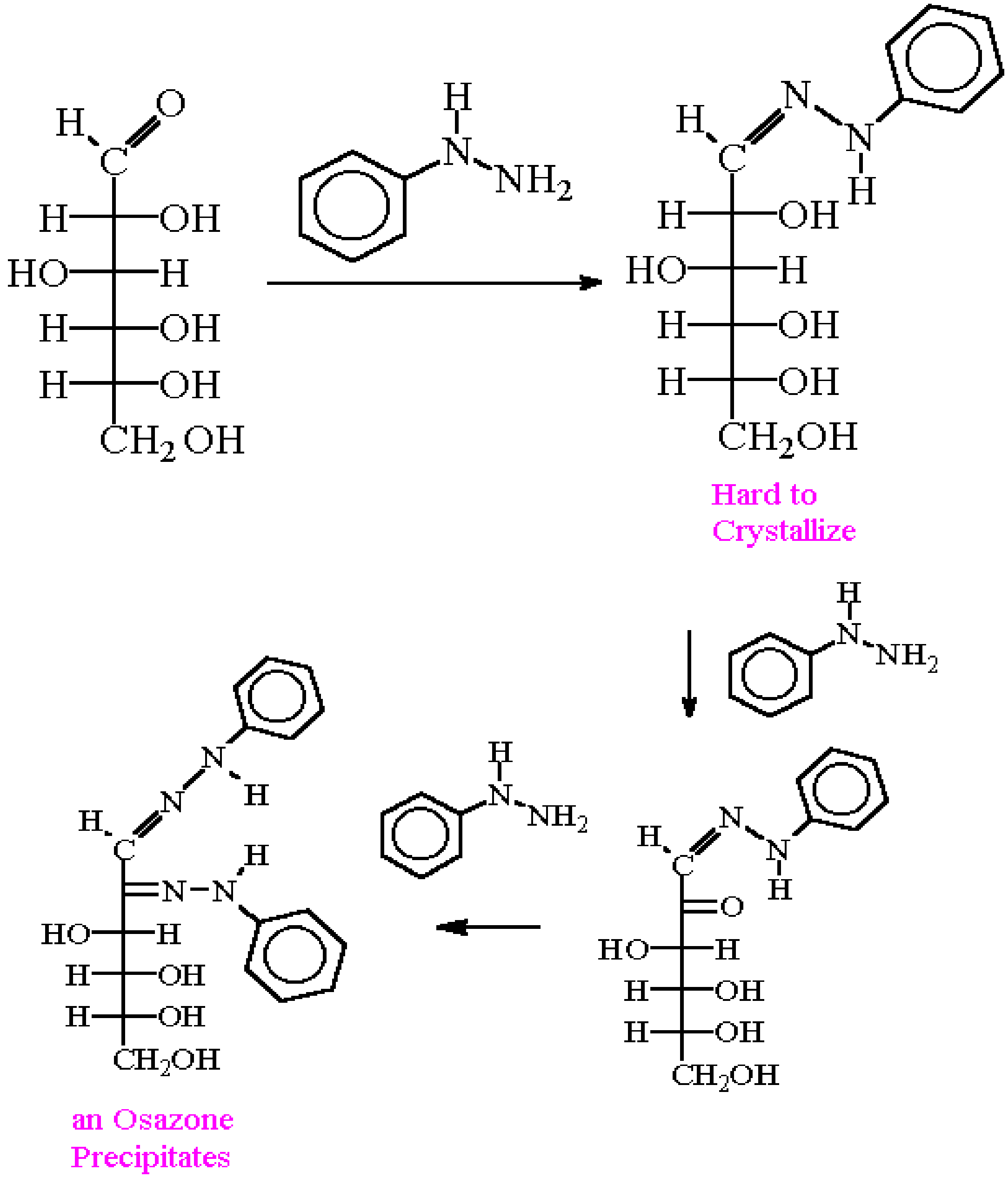
b) Aldehydes can be reduced into acids.

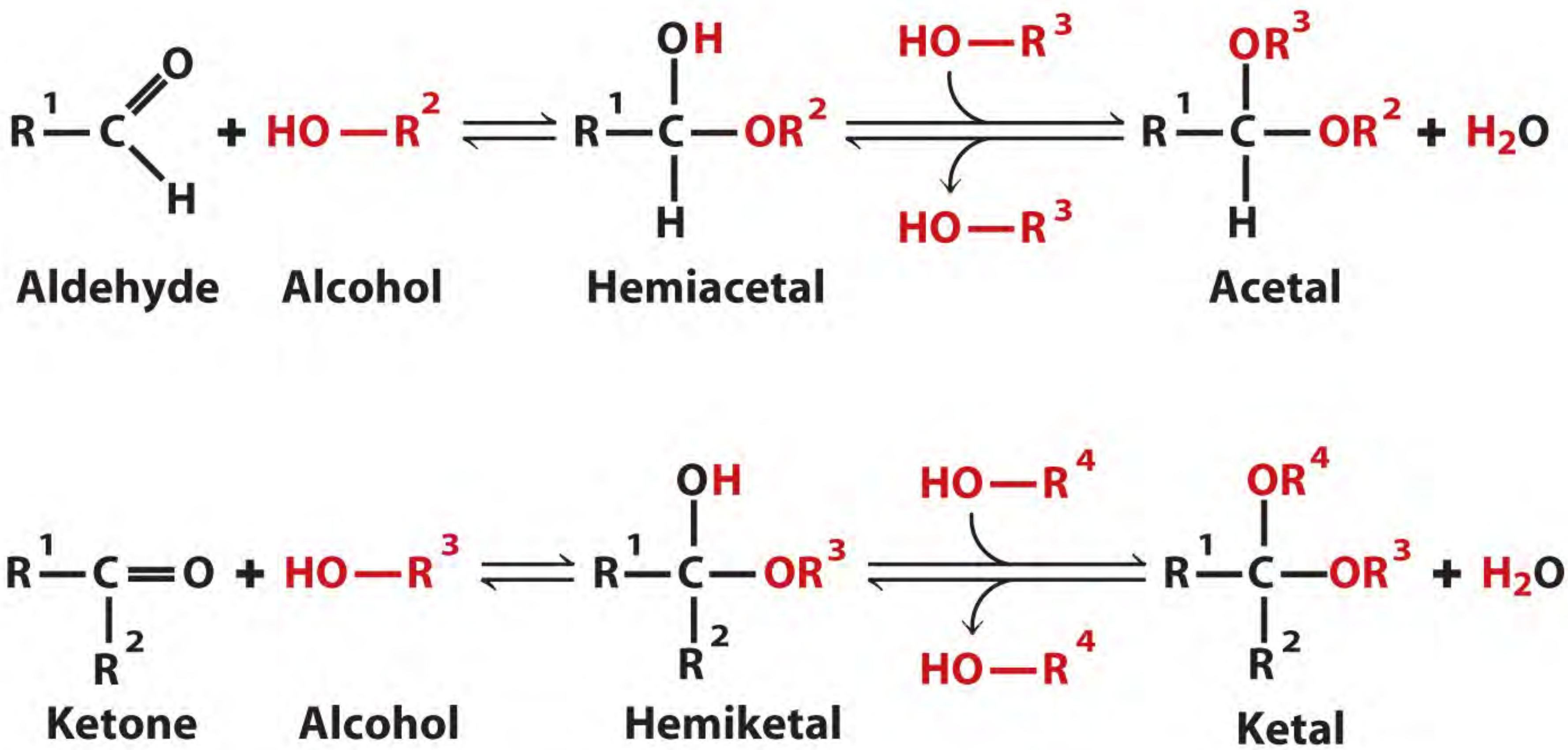
c) Secondary alcohols can be oxidized into acids.

d) Ketones can be oxidized into alcohols.

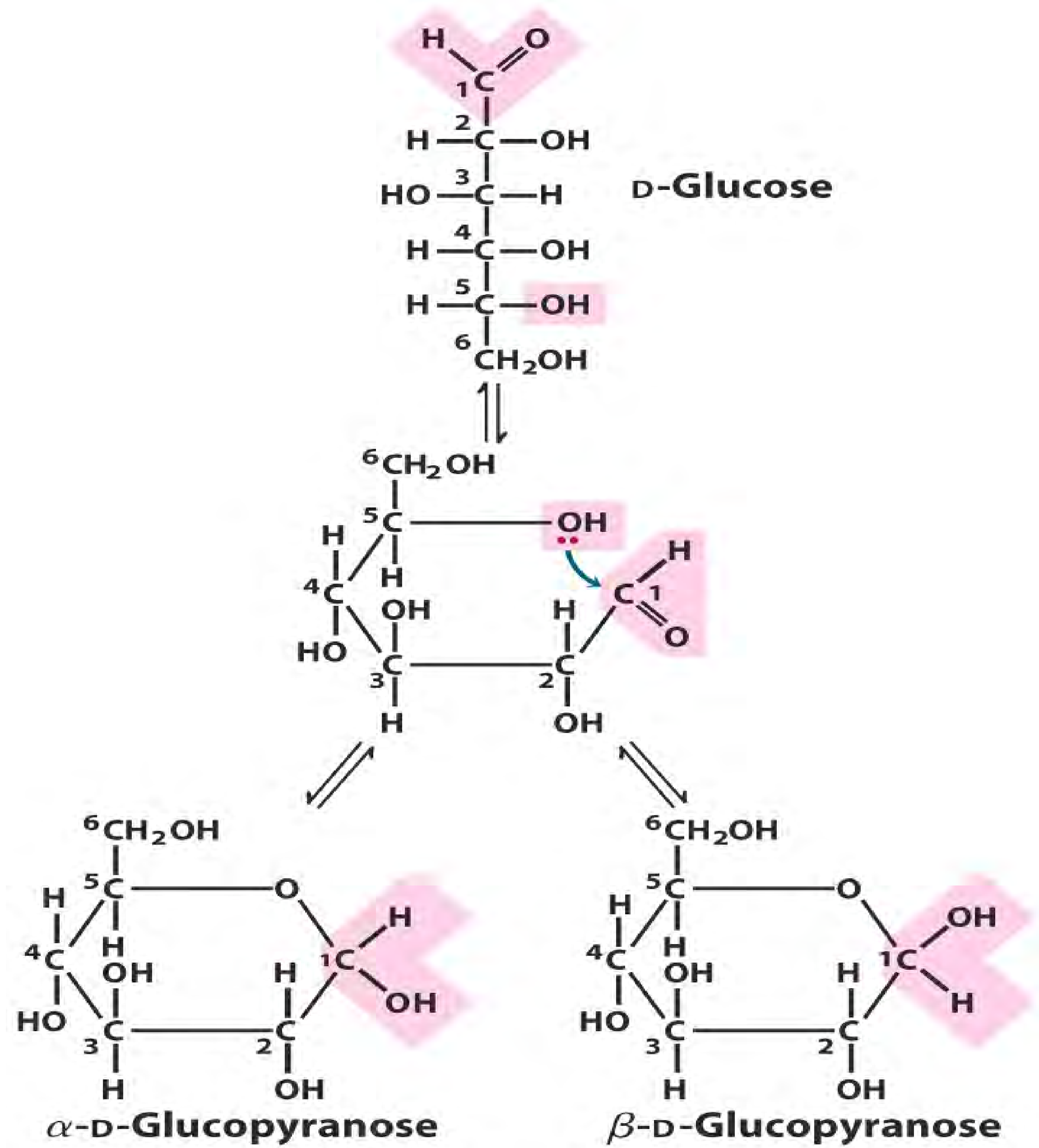
e) Aldehydes can be reduced into alcohols.

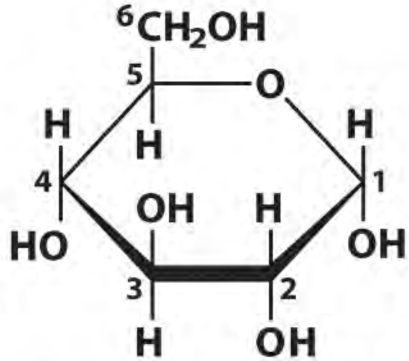
Reactions with Phenylhydrazine



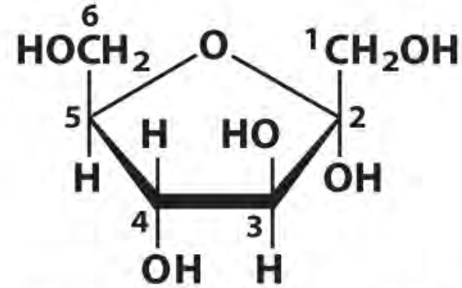


Aldehyde
Alcohol
Hemiacetal
Acetal
Ketone
Alcohol
Hemiketal
Ketal

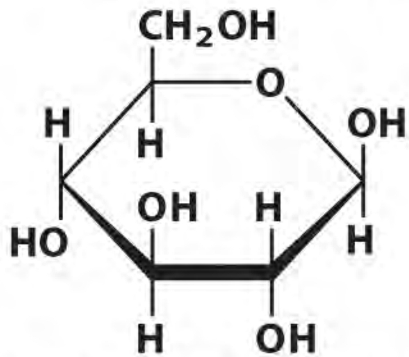

D-Glucose
α-D-Glucopyranose
β-D-Glucopyranose



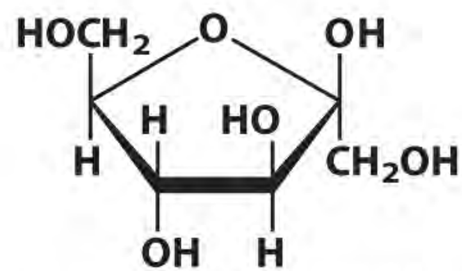
α-D-Glucopyranose



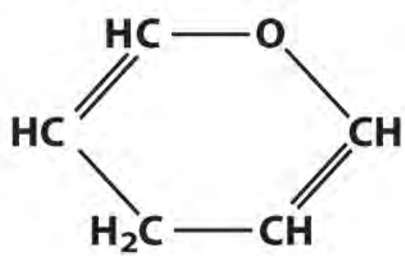
α-D-Fructofuranose



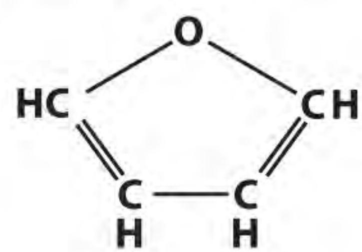
β-D-Glucopyranose



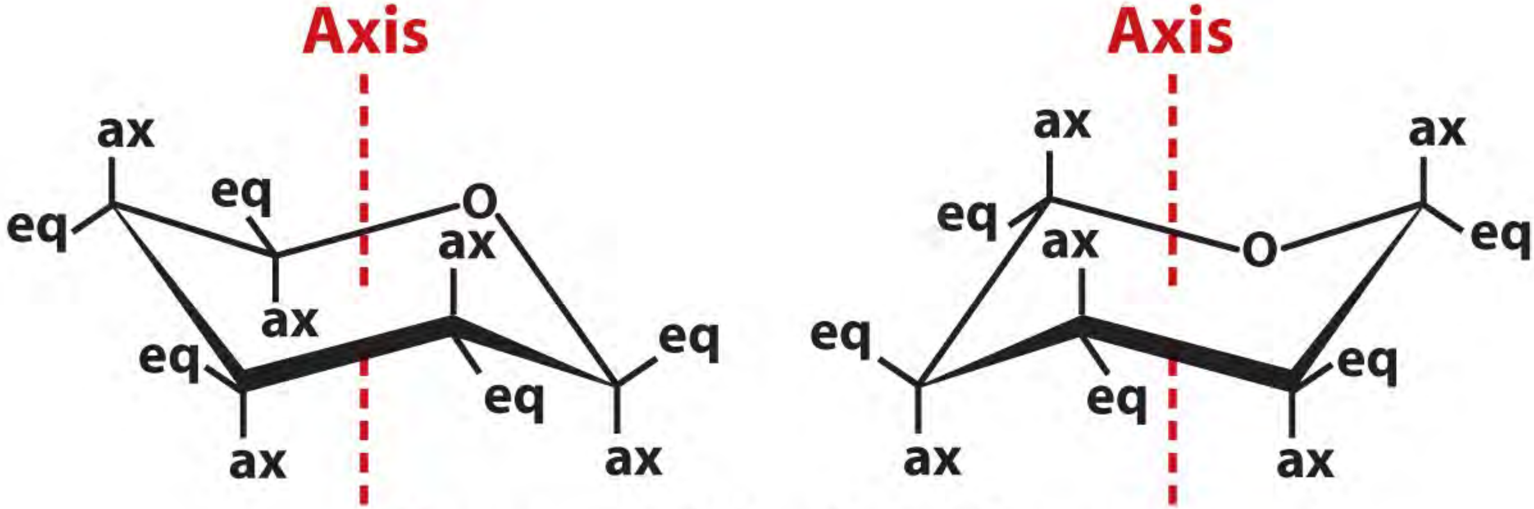
β-D-Fructofuranose



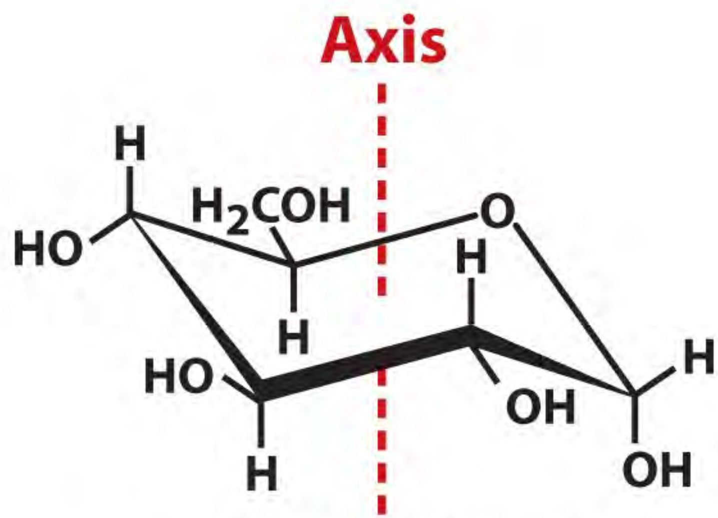
Pyran



Furan

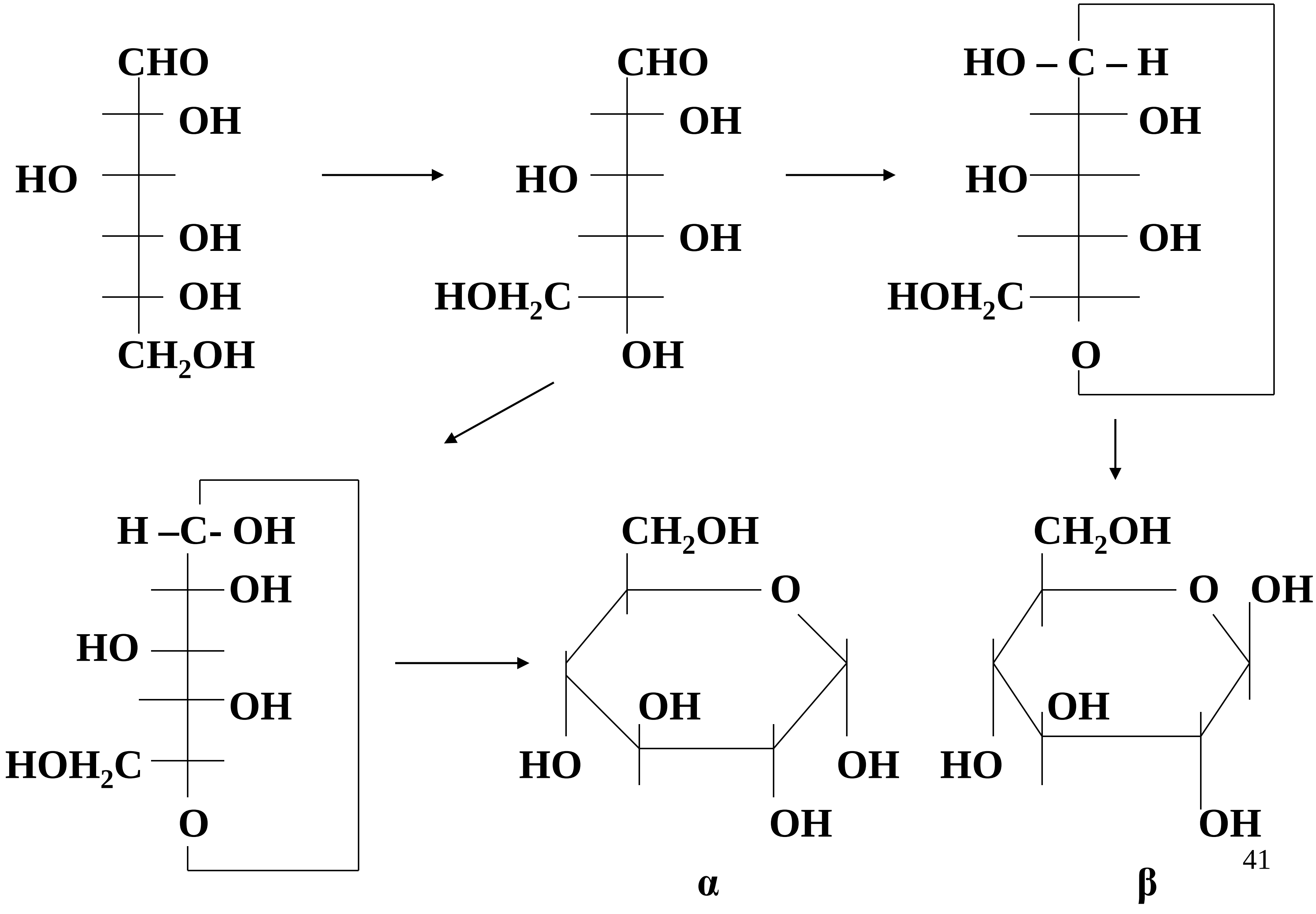


Two possible chair forms



α-D-**Glucopyranose**

HAWORTH STRUCTURES



Are You Getting It??

When an aldohexose forms a ring structure,

(multiple answers)

a) the ring contains 5 carbons and 1 oxygen.
b) the hemiacetal bond is stable.
c) the ring is planar.
d) C-1 becomes chiral.
e) the reaction is between two alcohols.
f) the two anomeric forms are mirror images.

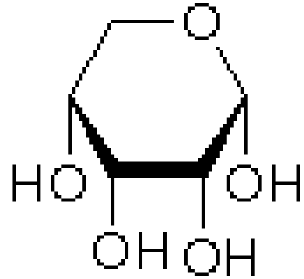
Are You Getting It??

Answer

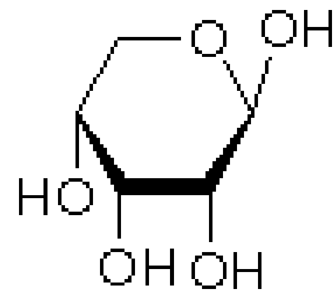
When an aldohexose forms a ring structure,

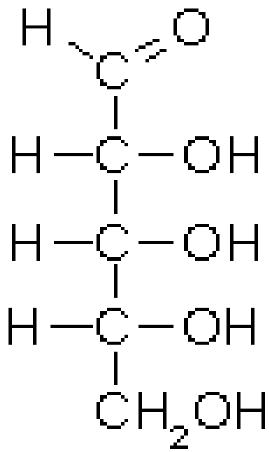
- ***a) the ring contains 5 carbons and 1 oxygen.***
- **b) the hemiacetal bond is stable.**
- **c) the ring is planar.**
- ***d) C-1 becomes chiral.***
- **e) the reaction is between two alcohols.**
- **f) the two anomeric forms are mirror images.**

alpha pyranose

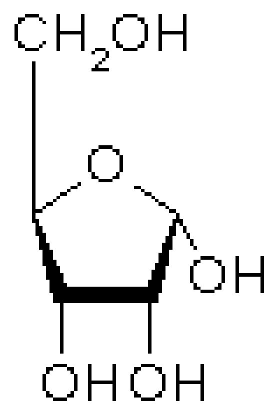


beta pyranose

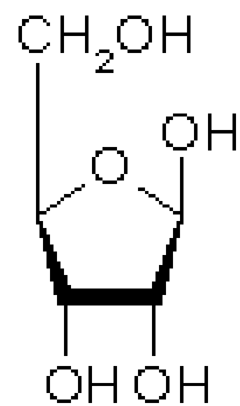




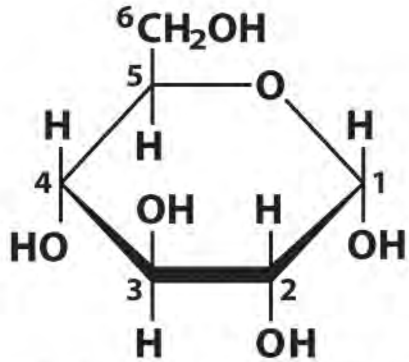
Fischer
open-chain



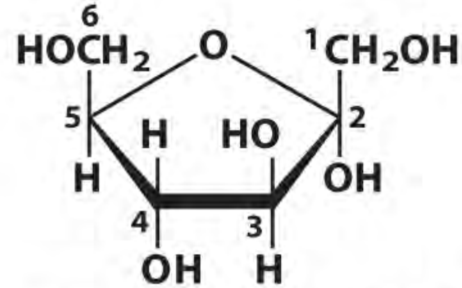
alpha furanose



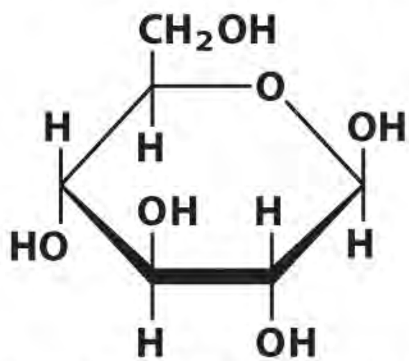
beta furanose



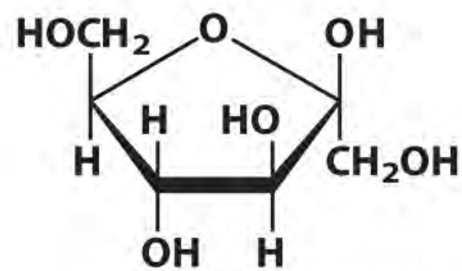
α-D-Glucopyranose



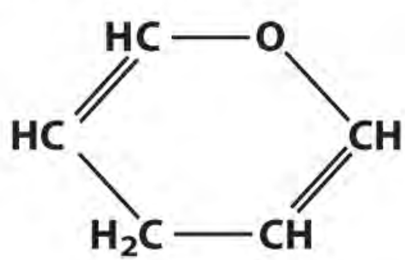
α-D-Fructofuranose



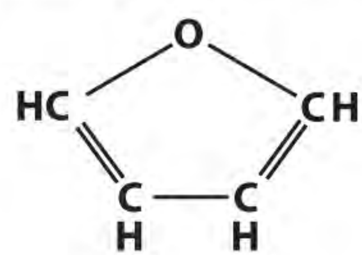
β-D-Glucopyranose



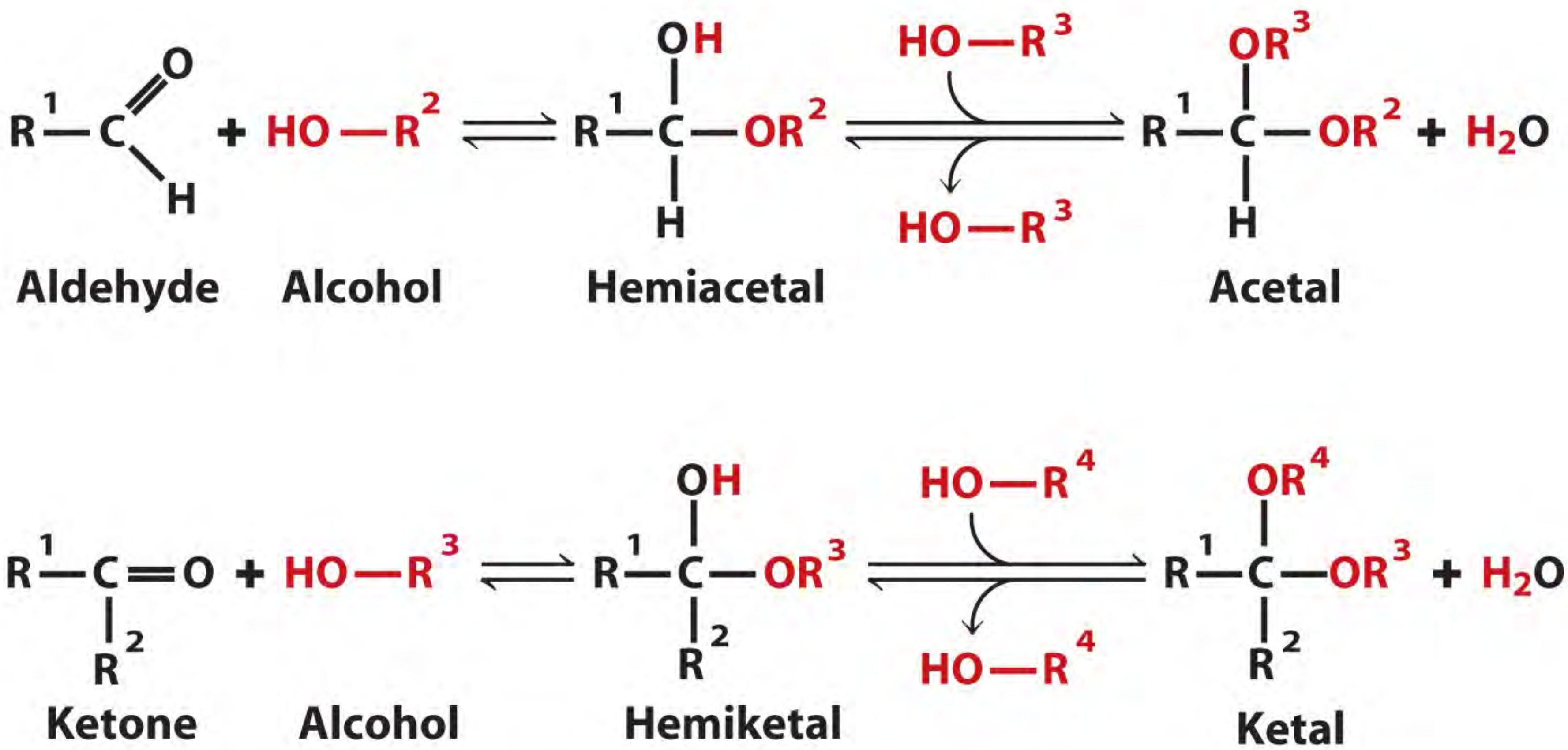
β-D-Fructofuranose



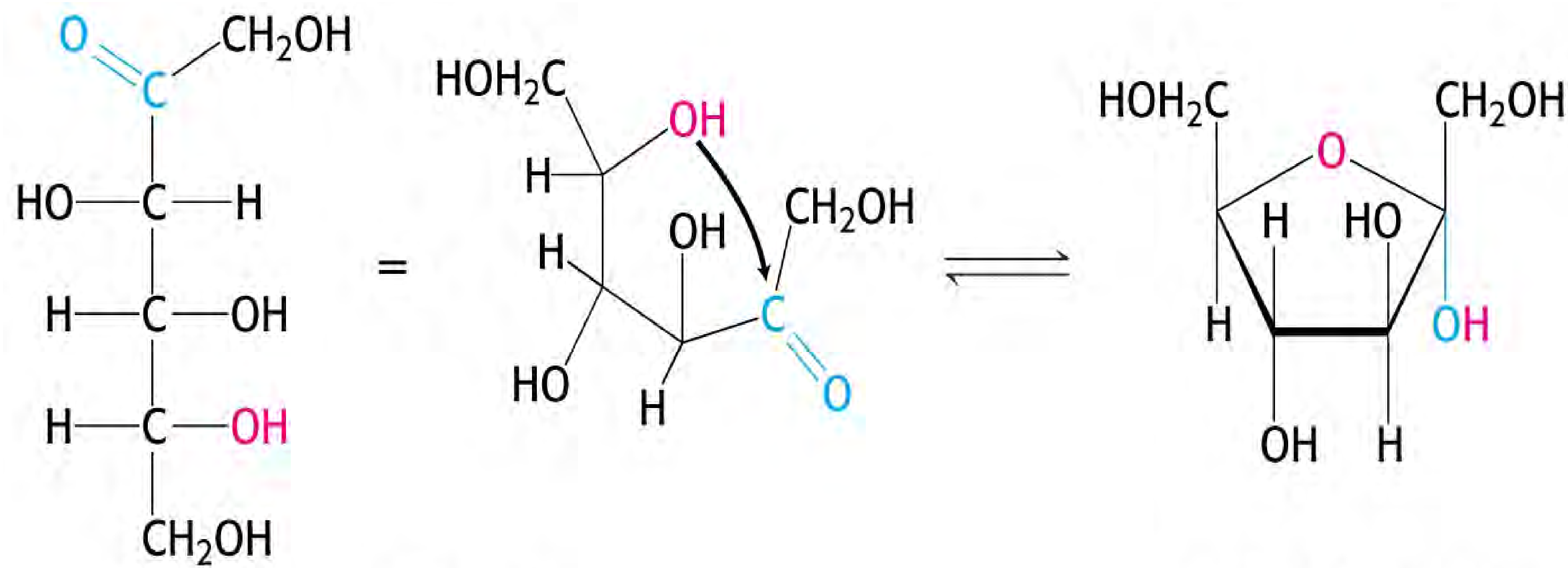
Pyran



Furan



Aldehyde
Alcohol
Hemiacetal
Acetal
Ketone
Alcohol
Hemiketal
Ketal



D-Fructose
(open-chain form)

α-D-Fructofuranose
(a cyclic form of fructose)

Are You Getting It??

When a ketohexose forms a ring structure,
(multiple answers)

a) the ring is a furanose.
b) the bond formed is a hemiketal.
c) the reaction involves the ketone group.
d) the orientation of all the OH groups changes.
e) a new stereogenic center is created.

Are You Getting It??

Answer

When a ketohexose forms a ring structure,

a) the ring is a furanose.
b) the bond formed is a hemiketal.
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d) the orientation of all the OH groups changes.
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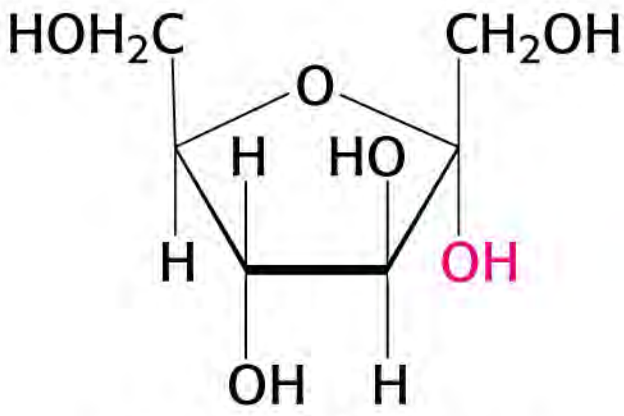
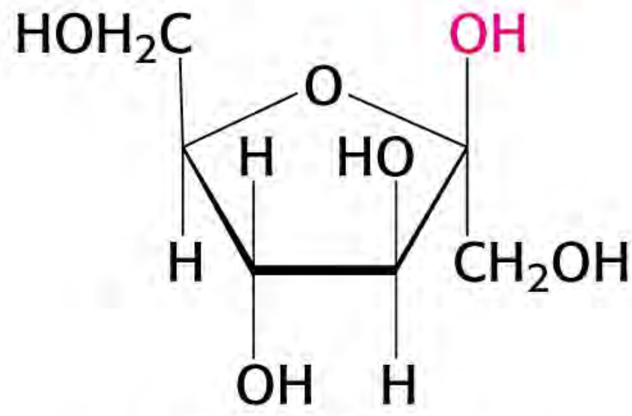
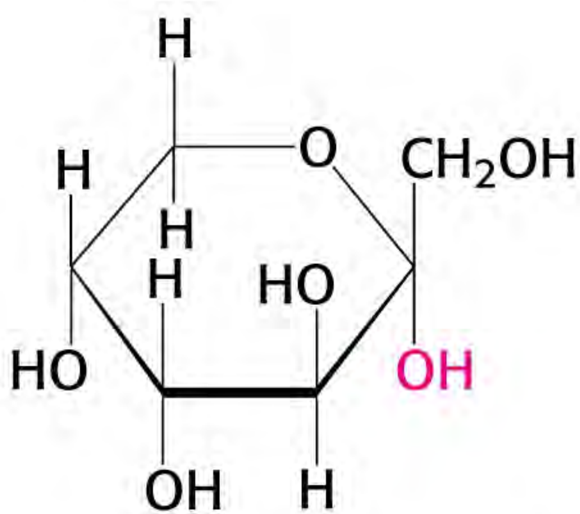


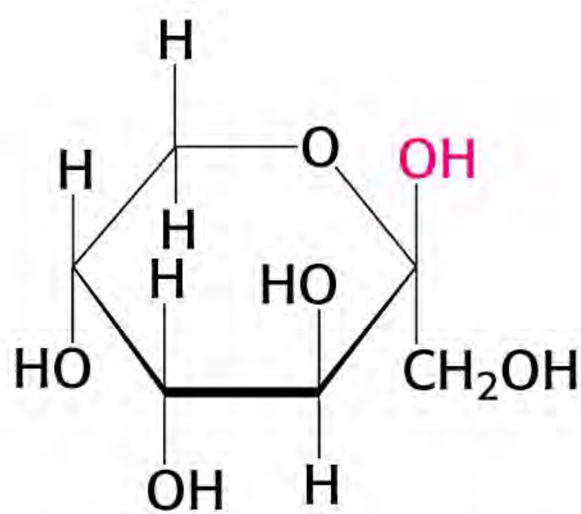
α-D-Fructofuranose



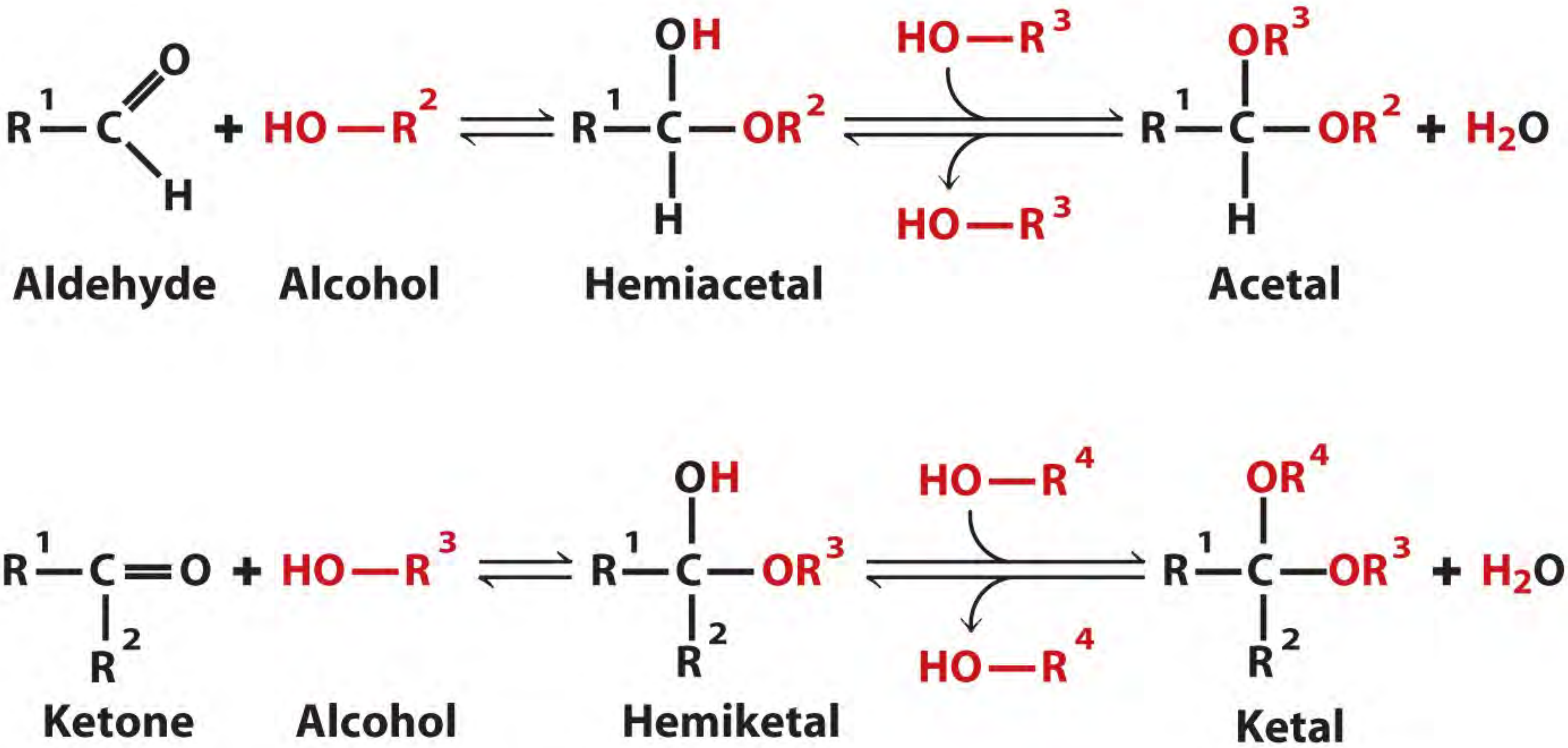
β-D-Fructofuranose

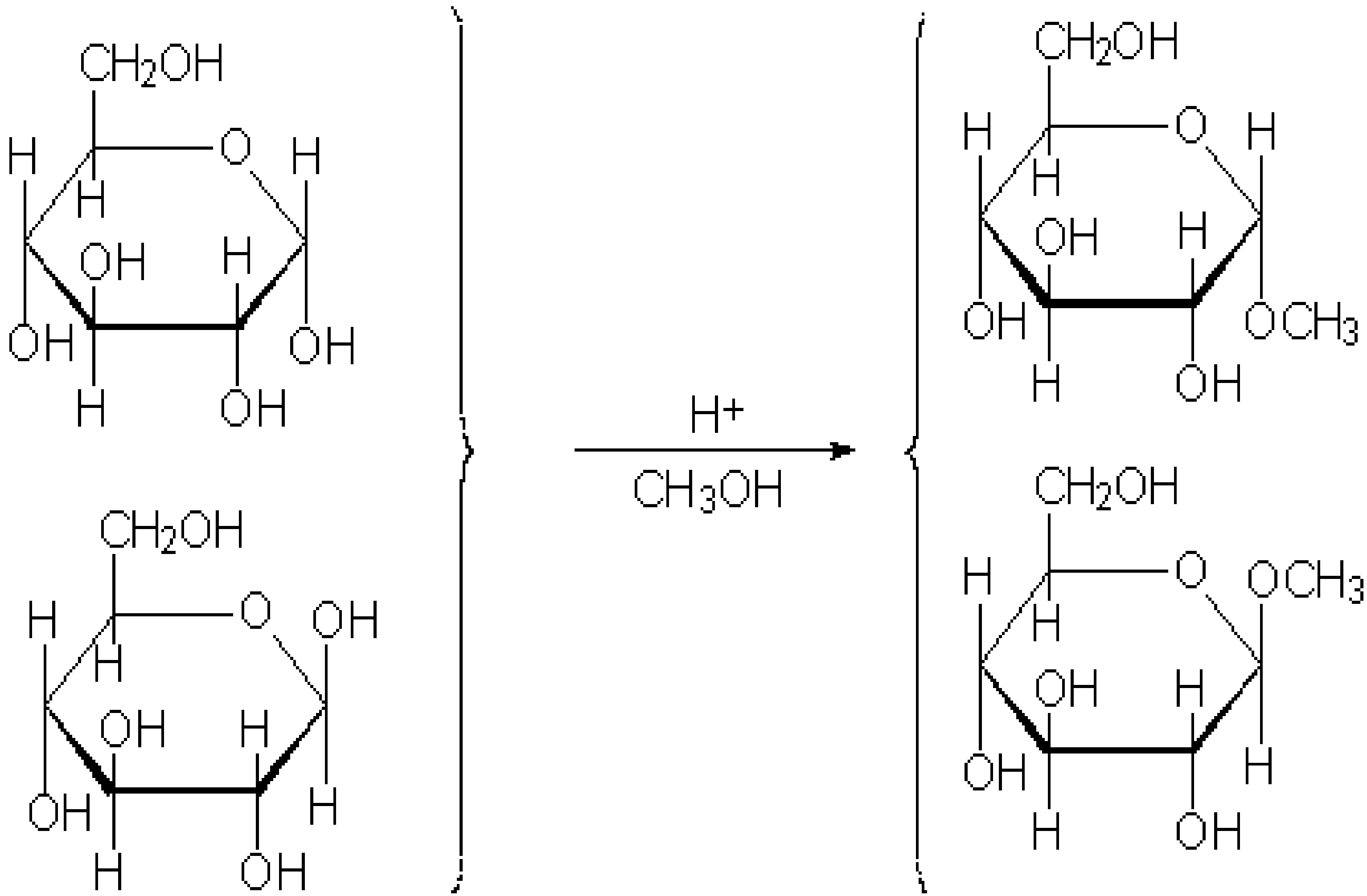


α-D-Fructopyranose



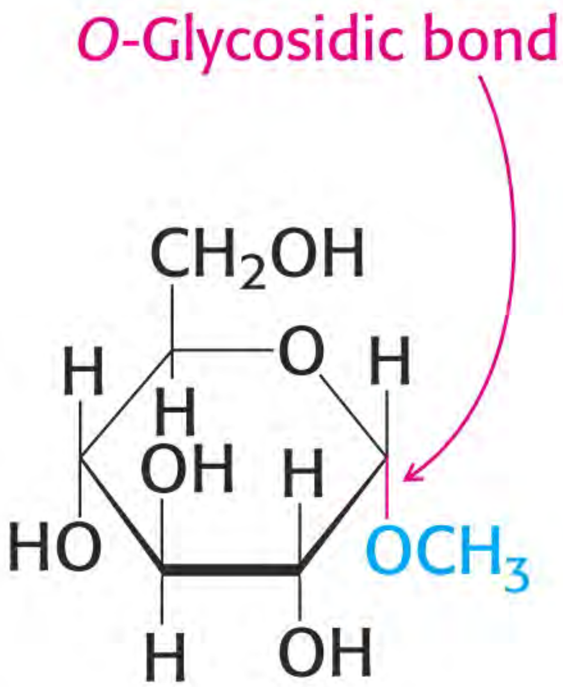
β-D-Fructopyranose


Aldehyde
Alcohol
Hemiacetal
Acetal
Ketone
Alcohol
Hemiketal
Ketal

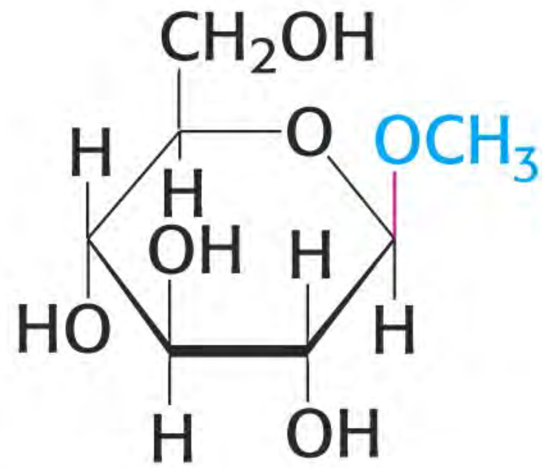


A

B



Methyl α-D-glucopyranoside



Methyl β-D-glucopyranoside

Are You Getting It??

Which are properties of an acetal/ketal bond?
(multiple answers)

a) The bond is stable at neutral pH.
b) The bond is stable at acidic pH.
c) The bond forms when an alcohol reacts with a hemiacetal/hemiketal.
d) The bond can mutarotate.
e) The bond can be part of a monosaccharide.
f) The bond can be part of an oligosaccharide.

Are You Getting It??

Answer

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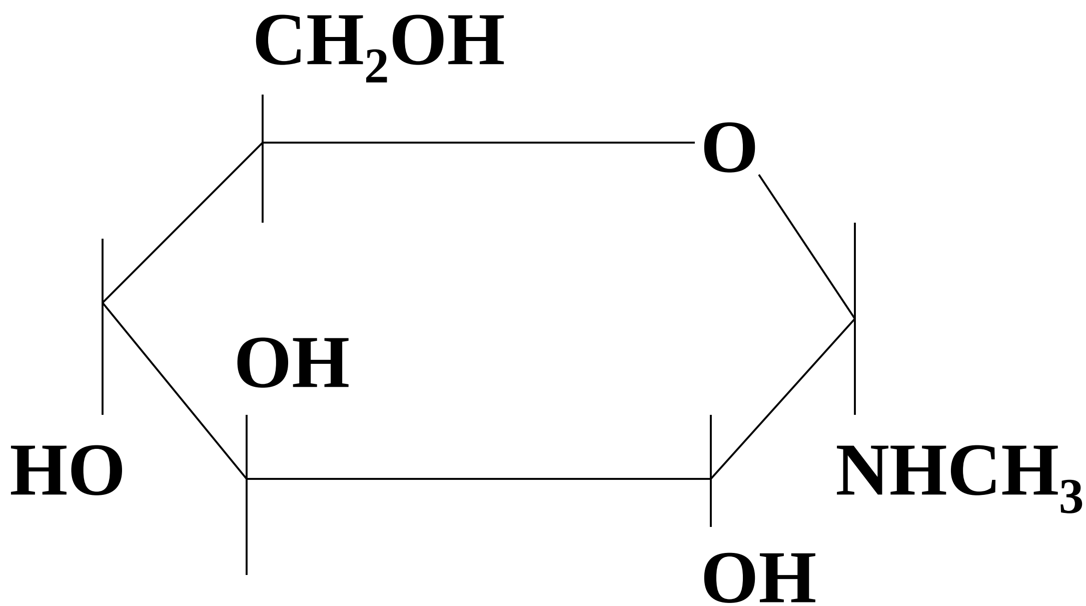
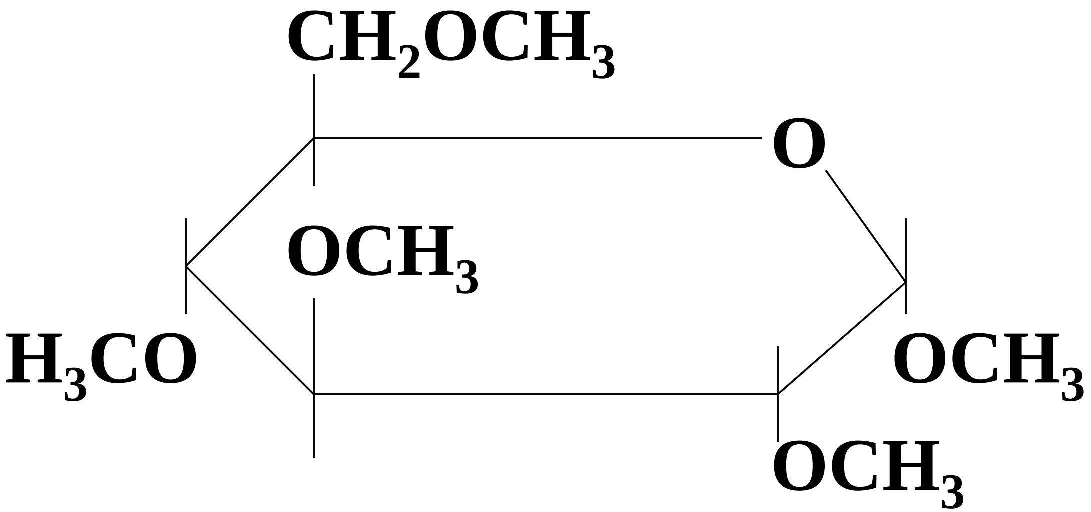
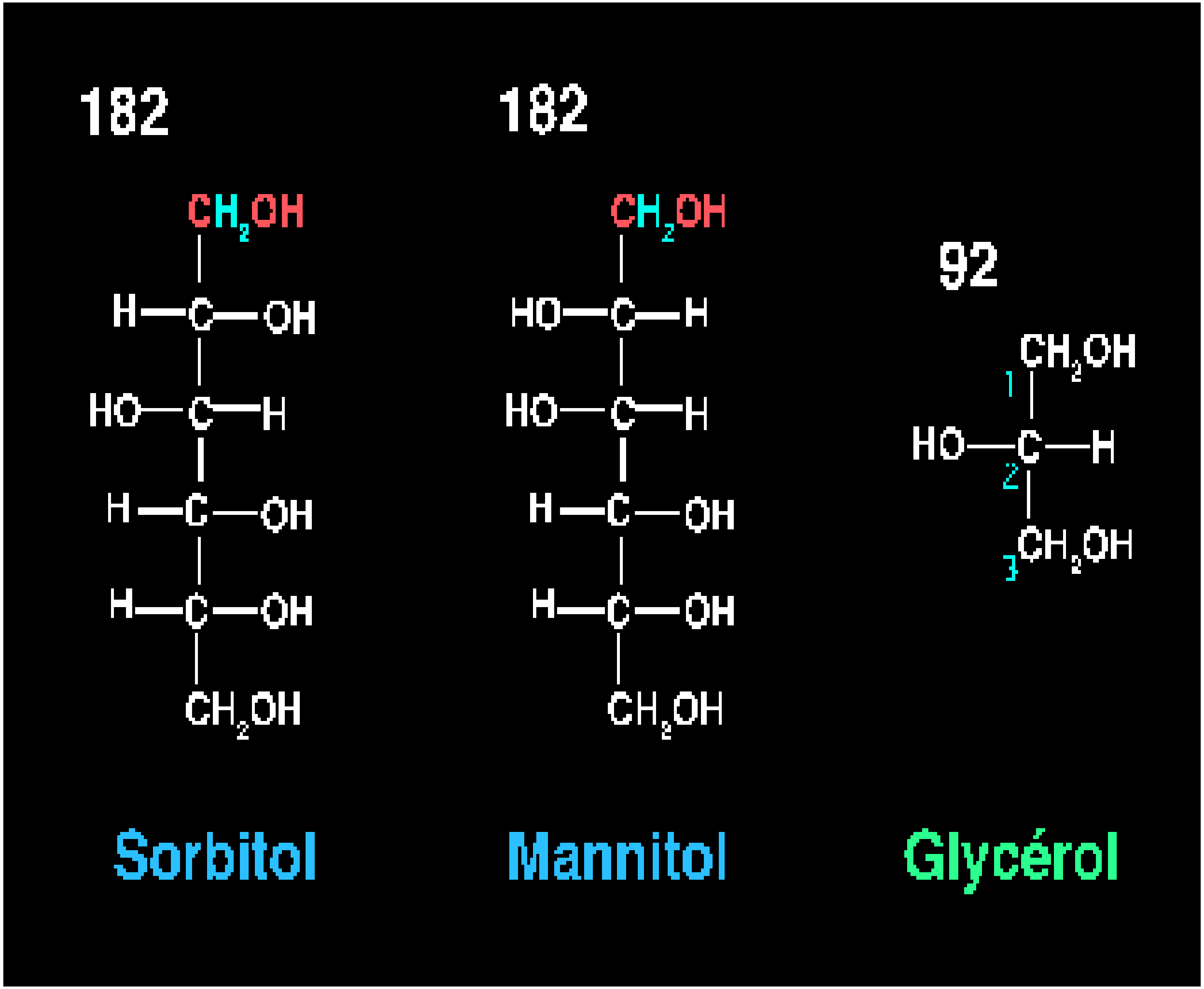
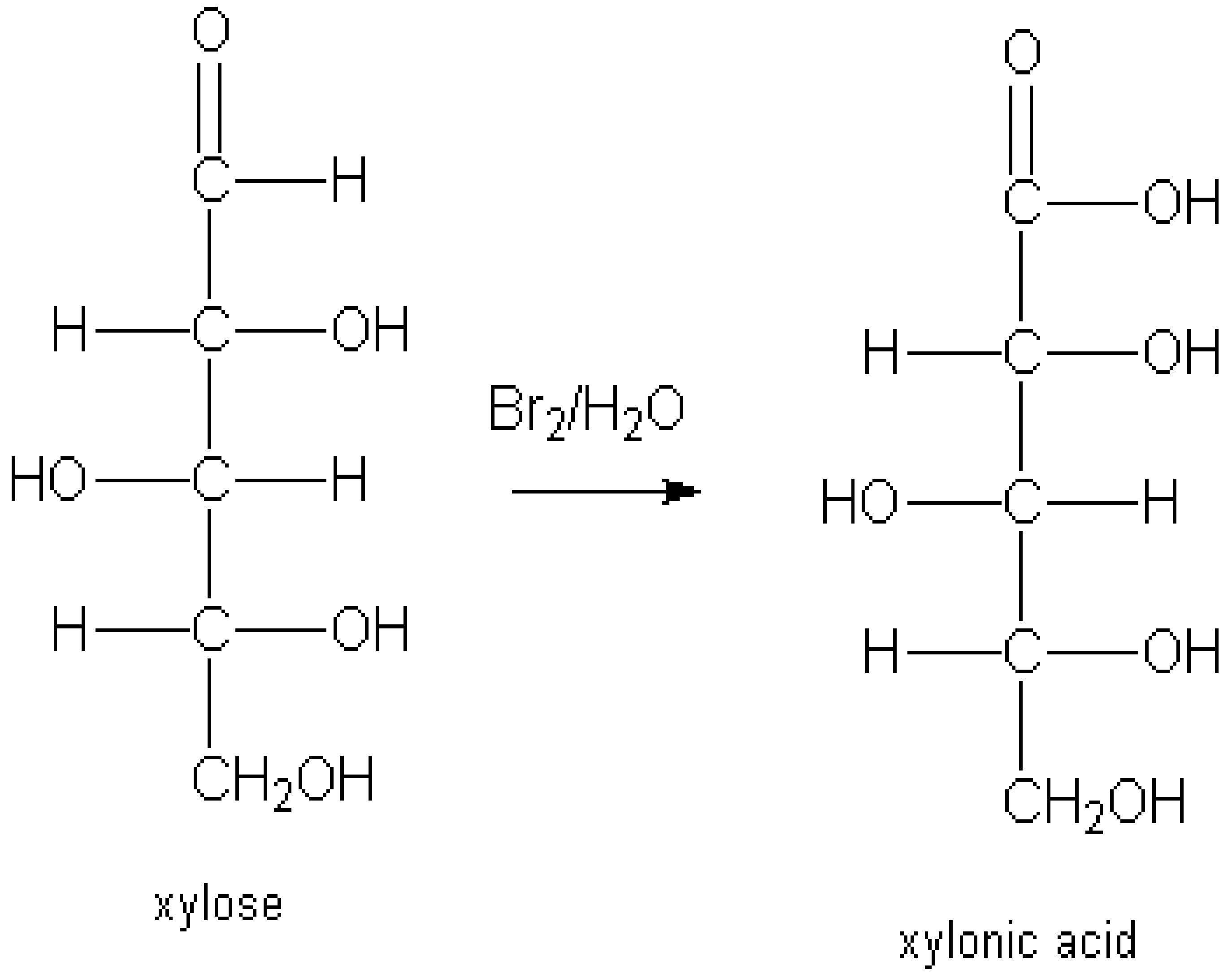
N-GLYCOSIDE



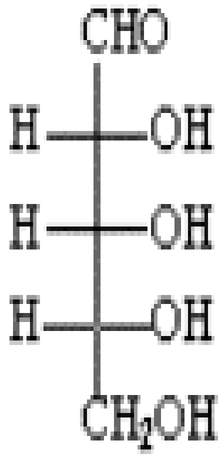
O-ACYL DERIVATIVE



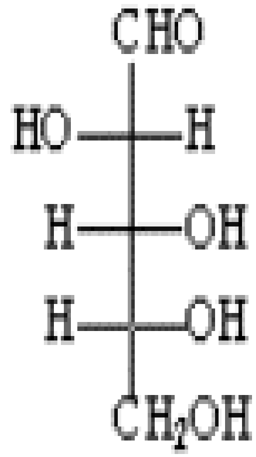

182
182
92
Sorbitol
Mannitol
Glycérol



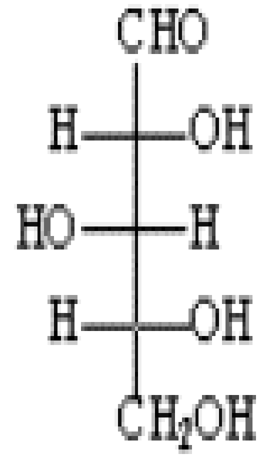
O
C
H
H
C
OH
HO
C
H
H
C
OH
CH2OH
xylose
Br2/H2O
O
C
OH
H
C
OH
HO
C
H
H
C
OH
CH2OH
xylonic acid



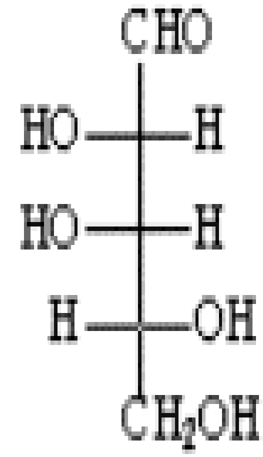
A



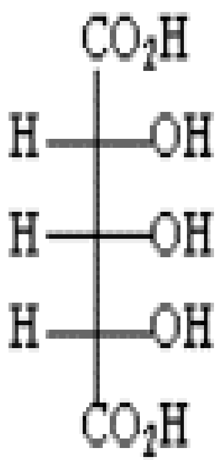
B

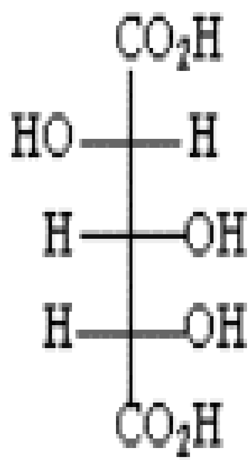


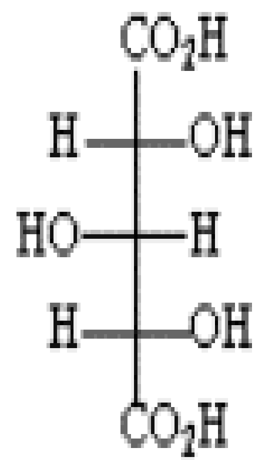
C

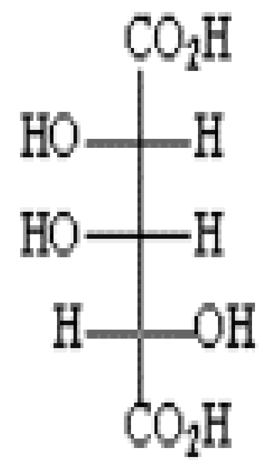


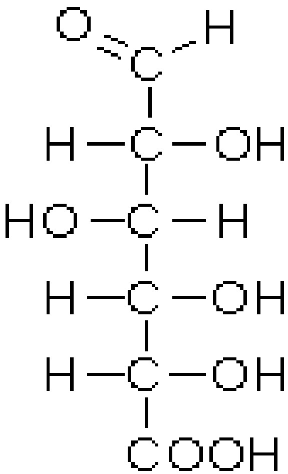
D





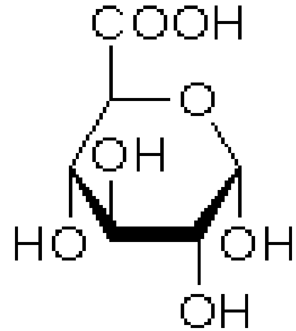




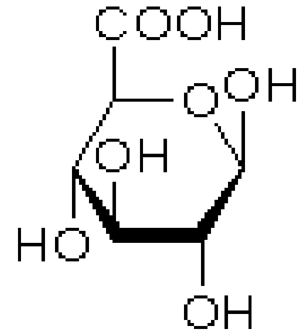


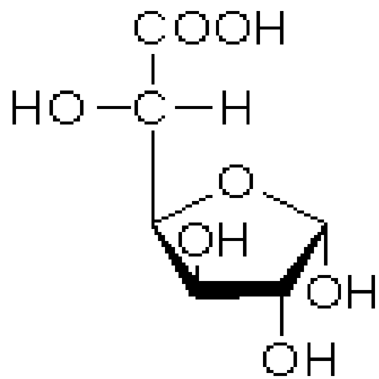
Fischer
open-chain

alpha pyranose

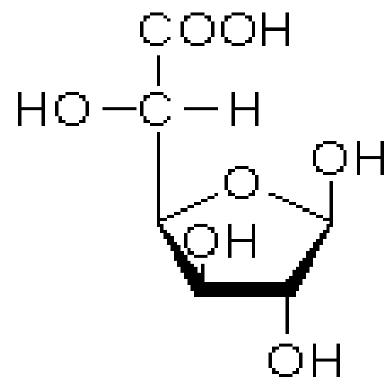


beta pyranose

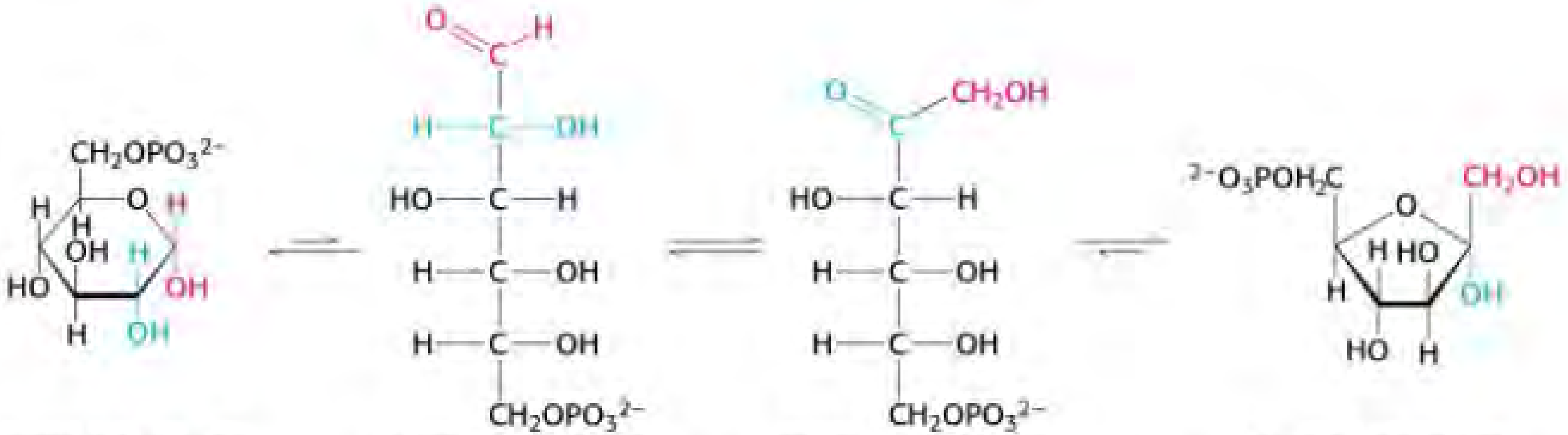




alpha furanose

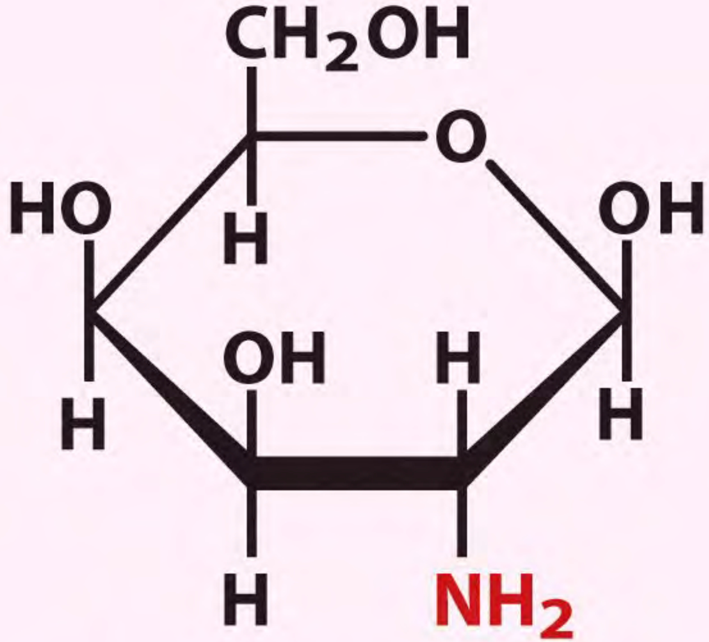


beta furanose

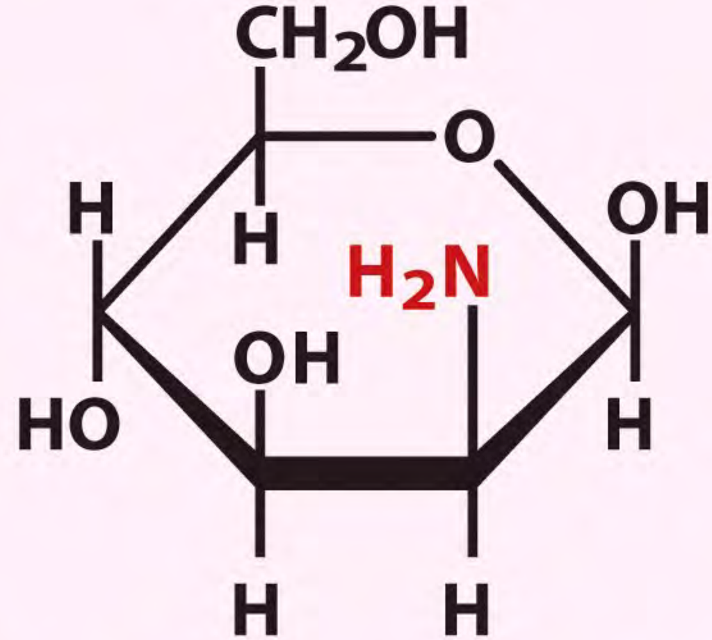


Glucose 6-phosphate (G-6P) — **Glucose 6-phosphate** (Open chain form) — **Fructose 6-phosphate** (Open chain form) — **Fructose 6-phosphate (F-6P)**

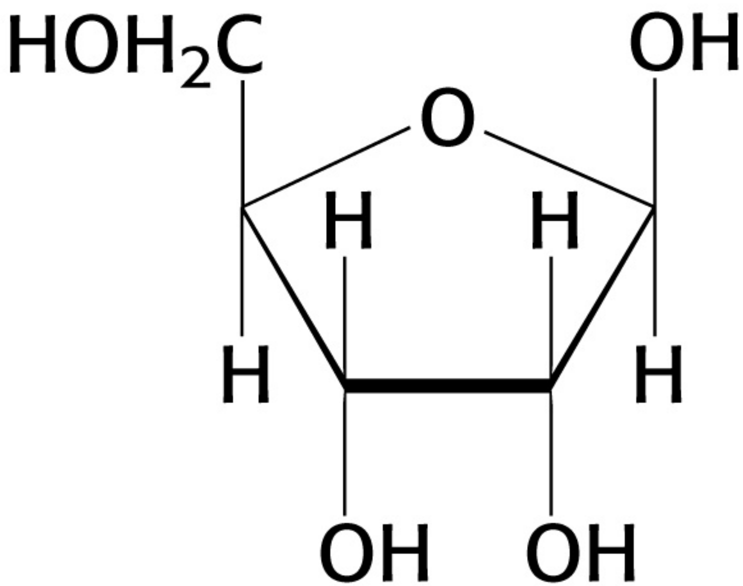
Amino sugars



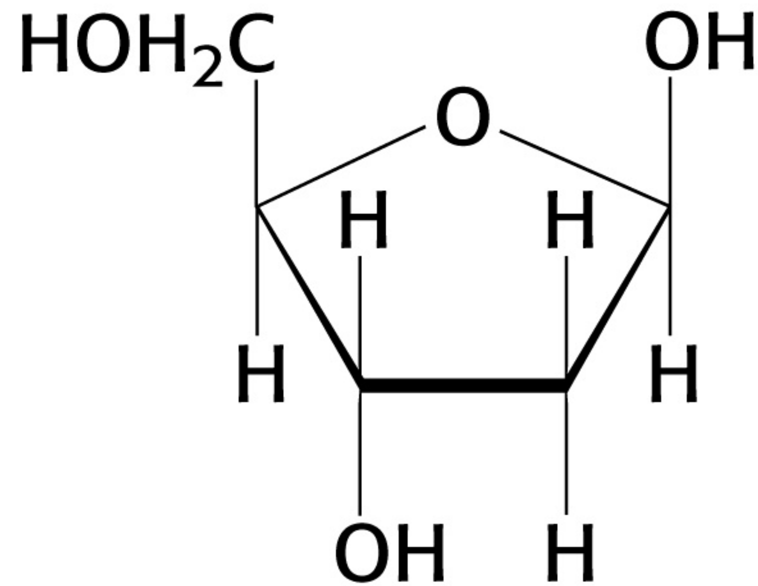
β-D-Galactosamine



β-D-Mannosamine

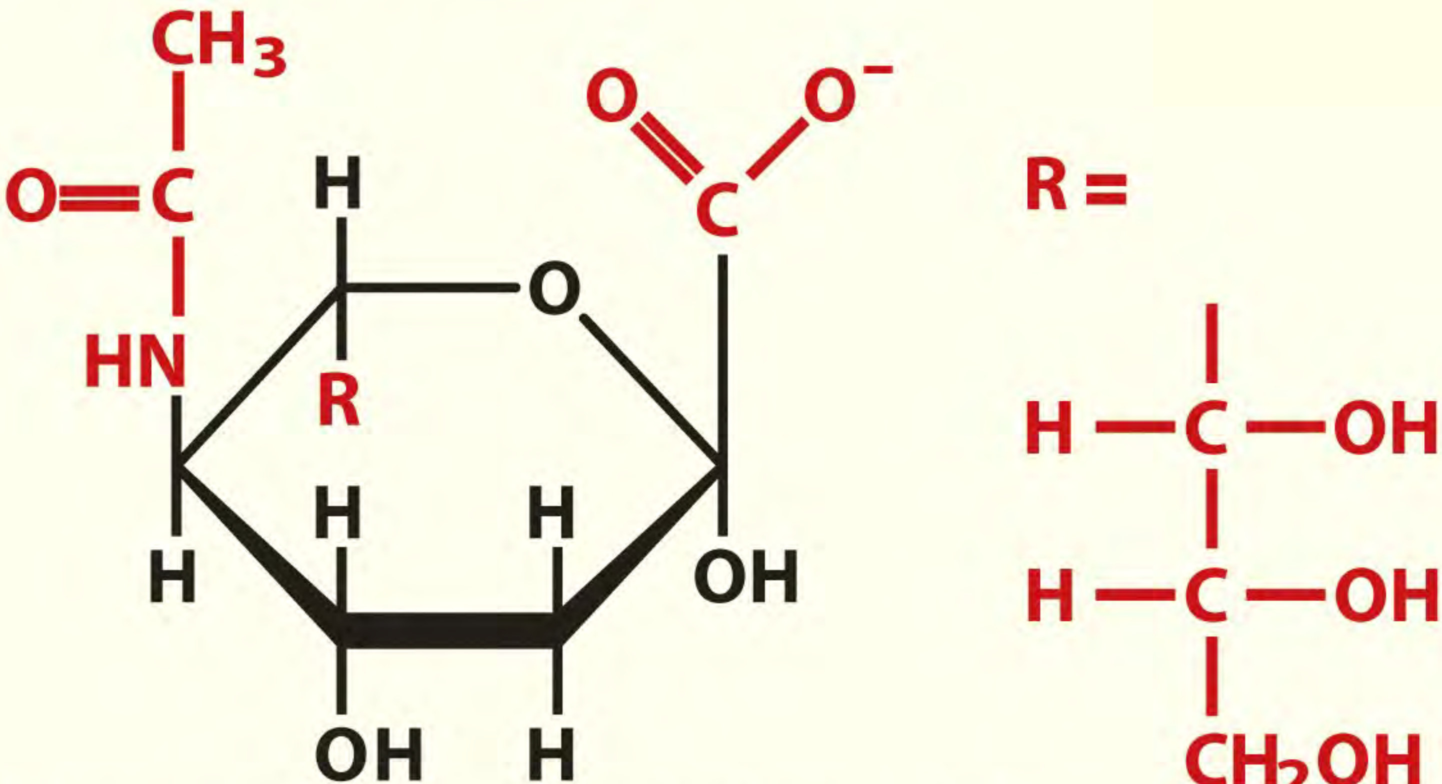


D-Ribose



2-Deoxy-D-ribose

Acidic sugars



***N*-Acetylneuraminic acid**
(a sialic acid)

Are You Getting It??

Which characteristics are found in monosaccharide derivatives? ***(multiple answers)***

a) They can contain nitrogen.
b) They have the formula $(CH_2O)_n$.
c) They can be negatively charged.
d) They always are ring structures.
e) They can be formed by oxidizing or reducing monosaccharides.

Are You Getting It??

Answer

Which characteristics are found in monosaccharide derivatives?

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b) They have the formula $(CH_2O)_n$.
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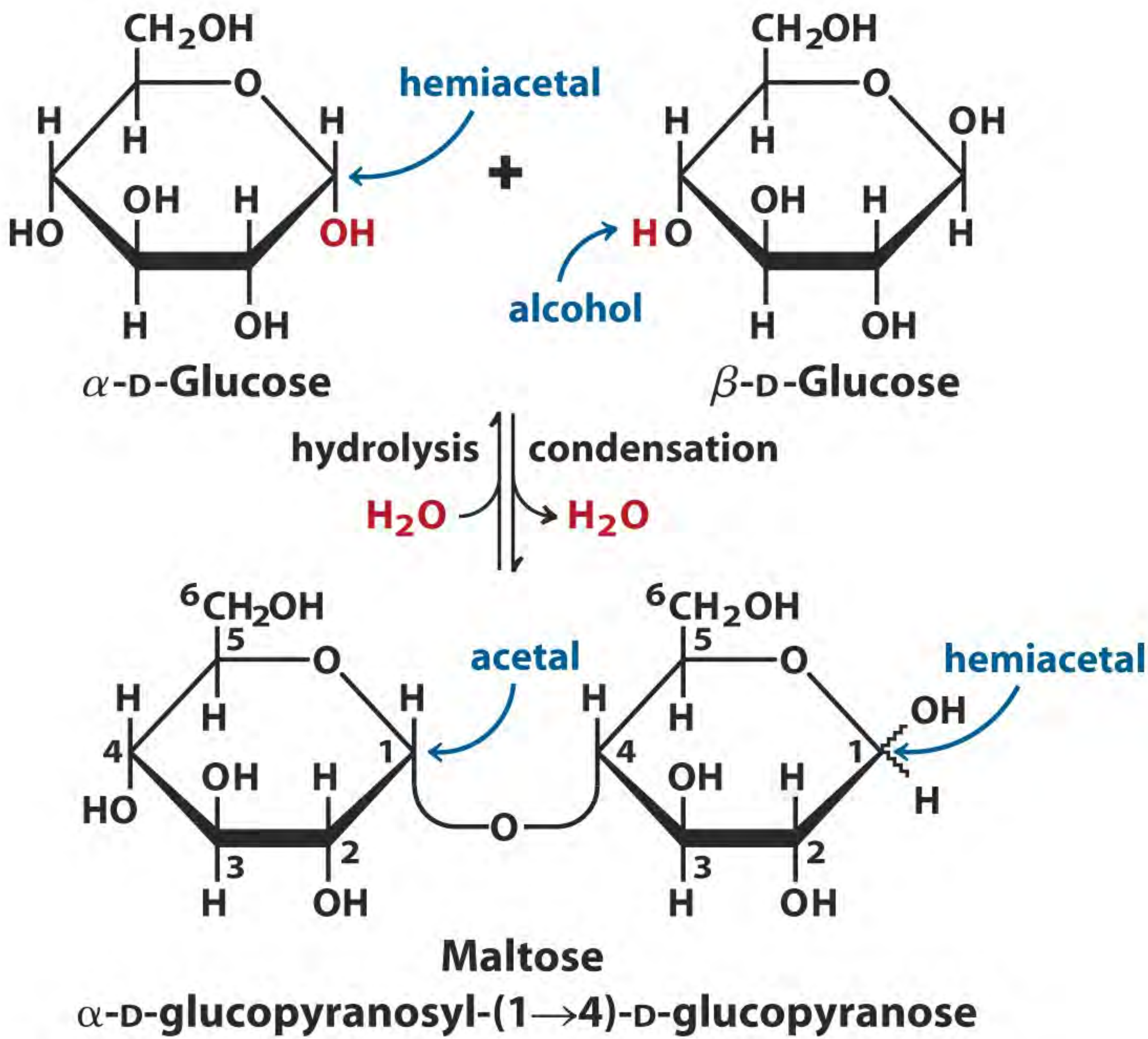
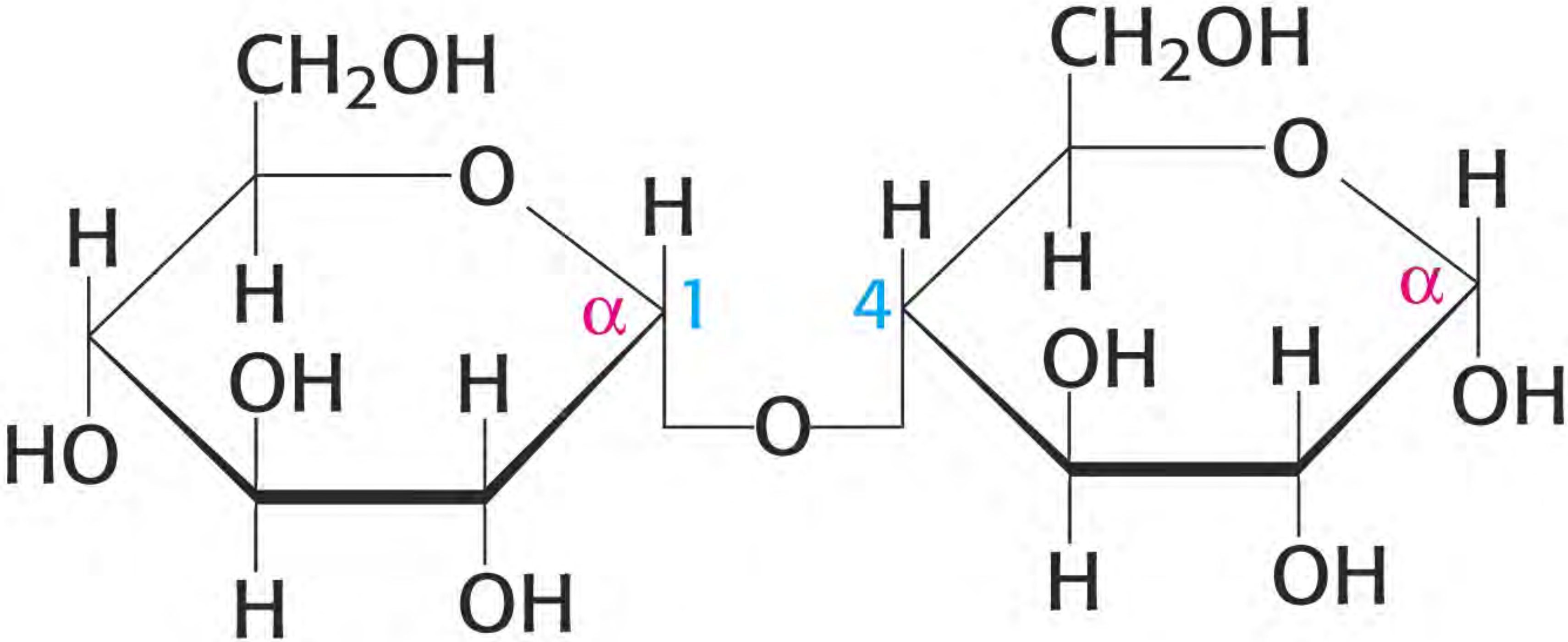
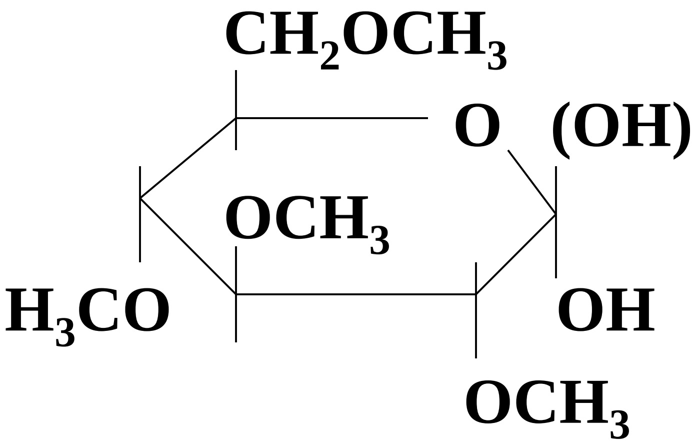

hemiacetal
alcohol
α-D-Glucose
β-D-Glucose
hydrolysis
condensation
H₂O
H₂O
acetal
hemiacetal
Maltose
α-D-glucopyranosyl-(1→4)-D-glucopyranose

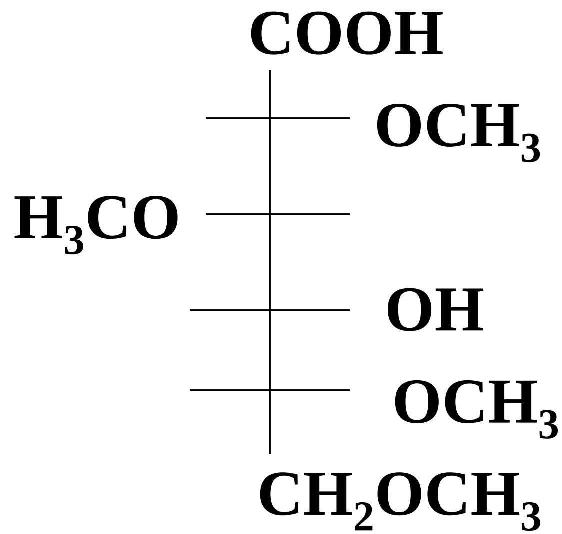


Maltose
(α-D-Glucopyranosyl-(1 → 4)-α-D-glucopyranose

STRUCTURAL DETERMINATION OF MALTOSE

BROMINE WATER / DIMETHYL SULFATE / ACID





Are You Getting It??

Which are properties of maltose?

(multiple answers)

a) It is composed of two aldohexoses.
b) It is a non-reducing sugar.
c) It can mutarotate.
d) It can exist as α-maltose or β-maltose.
e) It can have an α-glycosidic bond or a β-glycosidic bond.
f) It contains a hemiacetal bond.
g) It contains an acetal bond.

Are You Getting It??

Answer

Which are properties of maltose?

a) It is composed of two aldohexoses.

b) It is a non-reducing sugar.

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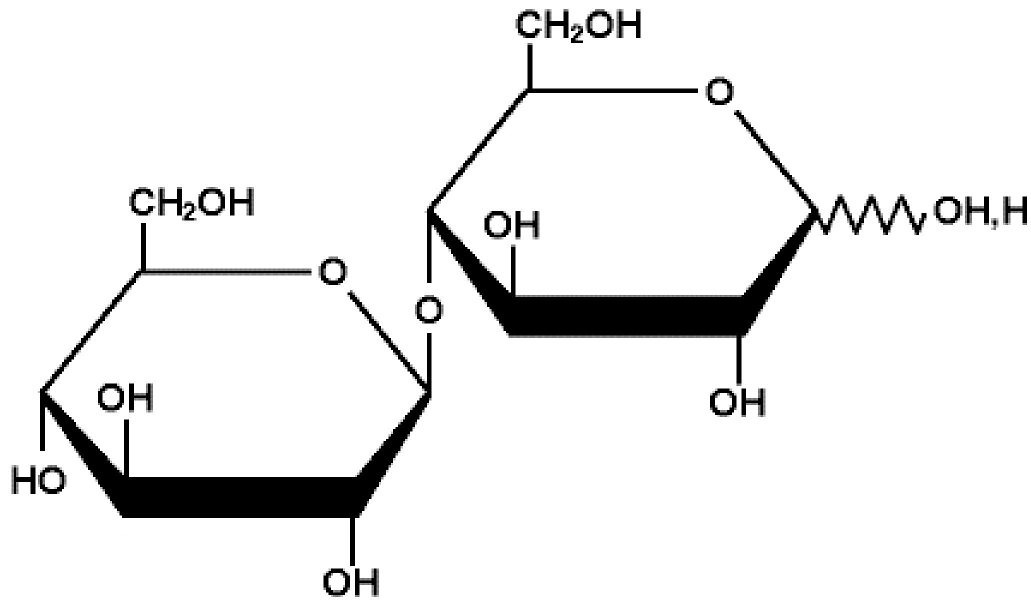
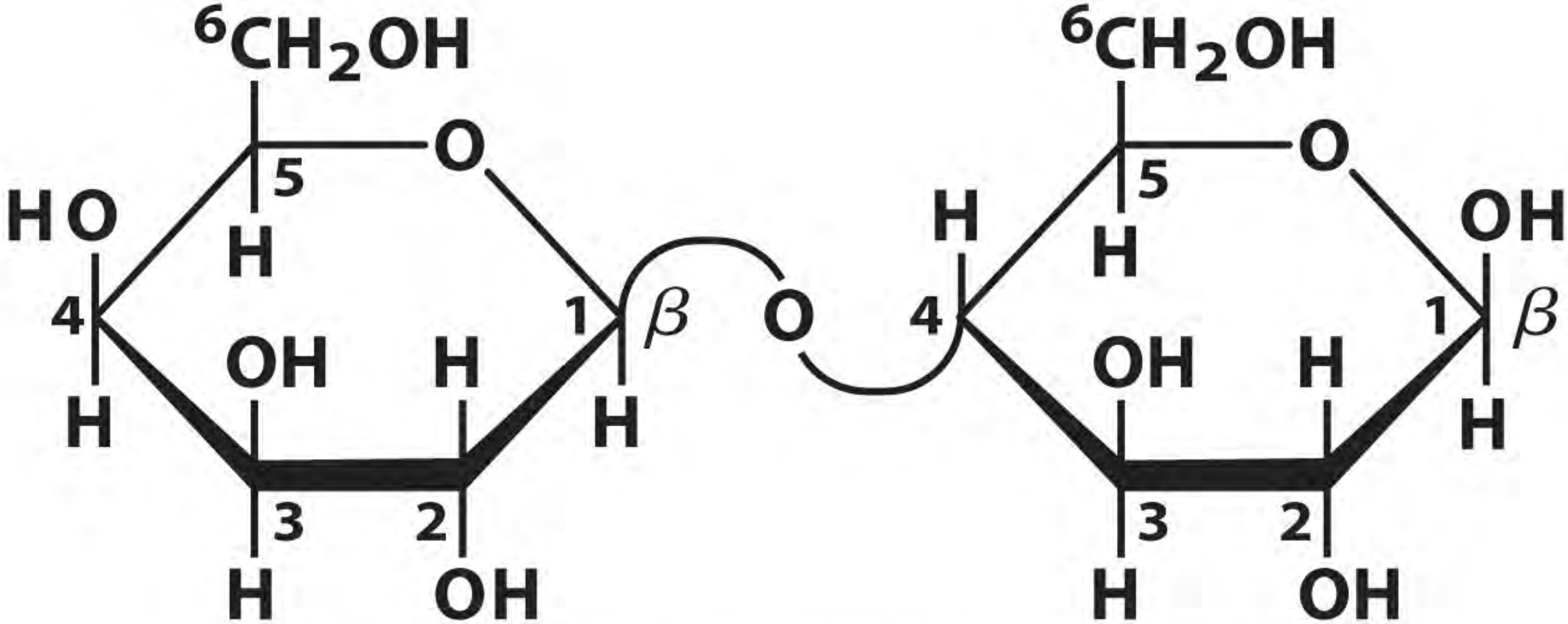
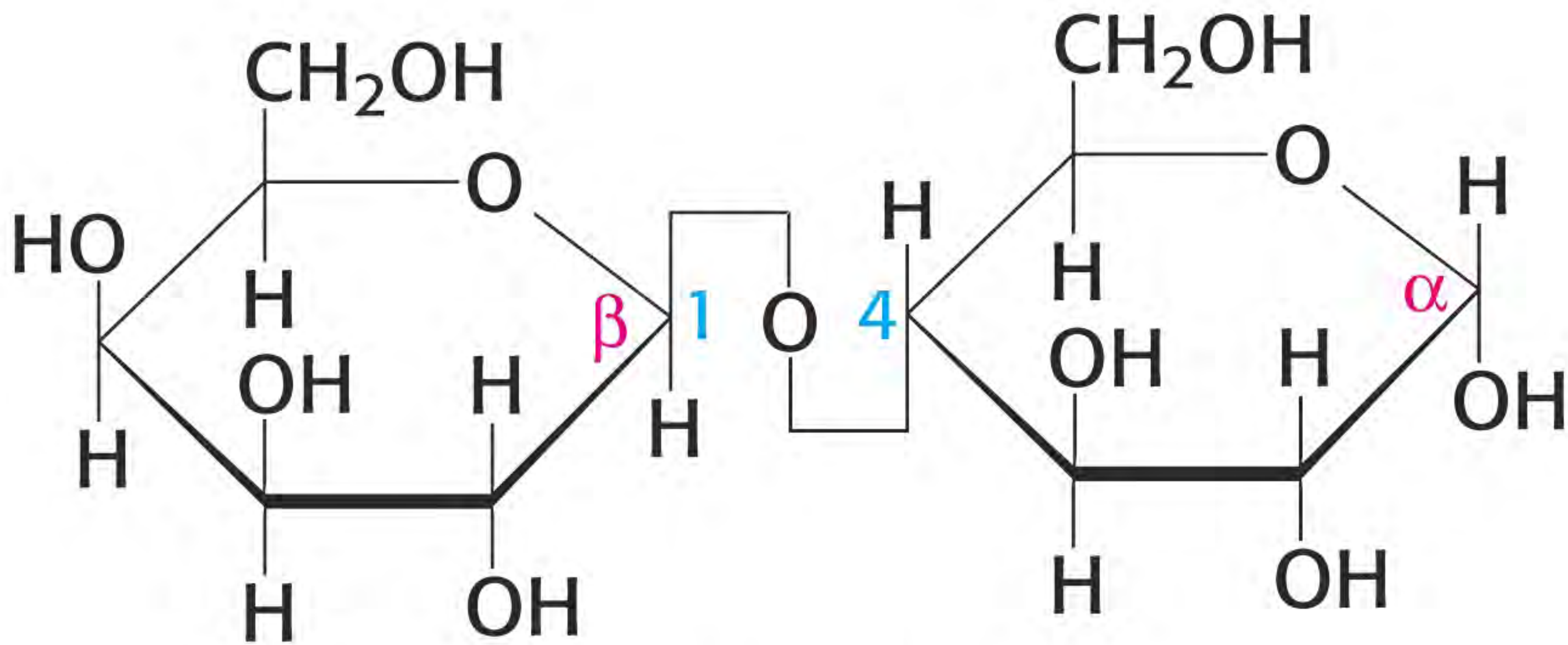

CH2OH
O
OH
HO
OH
O
CH2OH
O
OH
OH,H
OH



Lactose (β form)

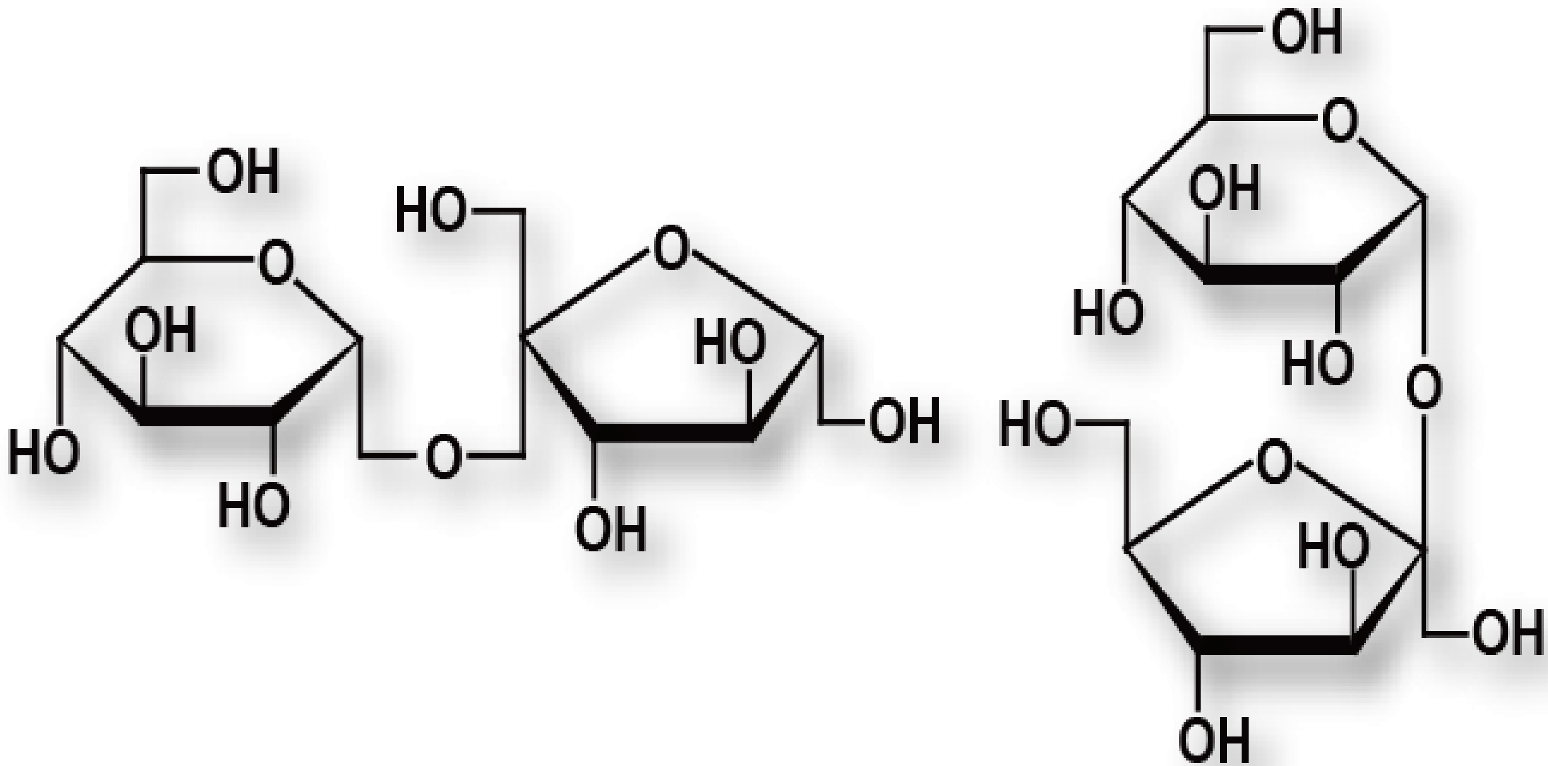
β-D-galactopyranosyl-(1→4)-β-D-glucopyranose

Gal(β1→4)Glc



Lactose

(β-D-Galactopyranosyl-(1→4)-α-D-glucopyranose



Sucrose

Are You Getting It??

Which are properties of disaccharides?

(multiple answers)

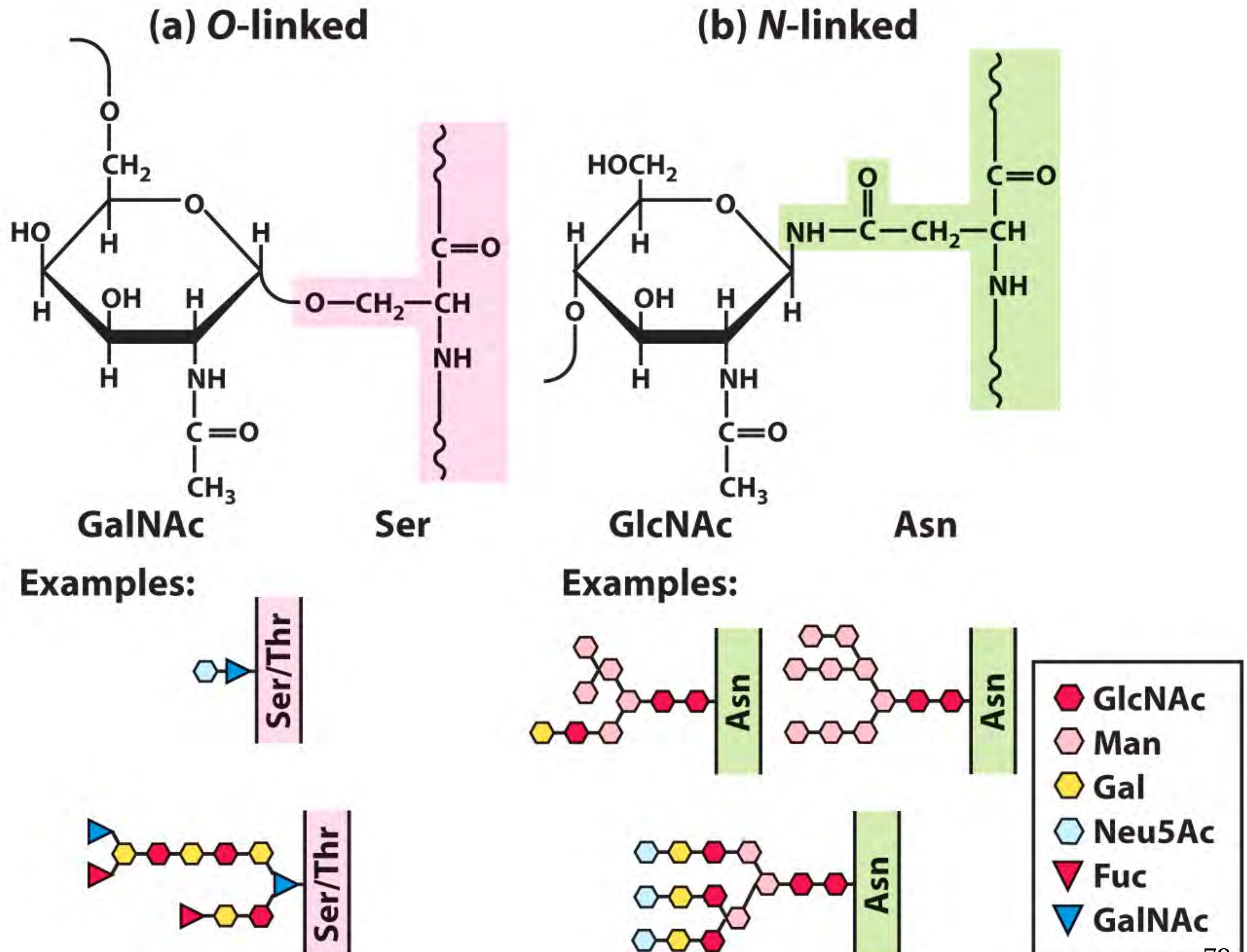
a) **They are all reducing sugars.**
b) **They are all composed of aldoses.**
c) **They all contain a glycosidic bond.**
d) **They all have anomeric forms.**
e) **They all have 1,4 bonds.**
f) **The two monosaccharide components can be the same or different.**

Are You Getting It??

Answer

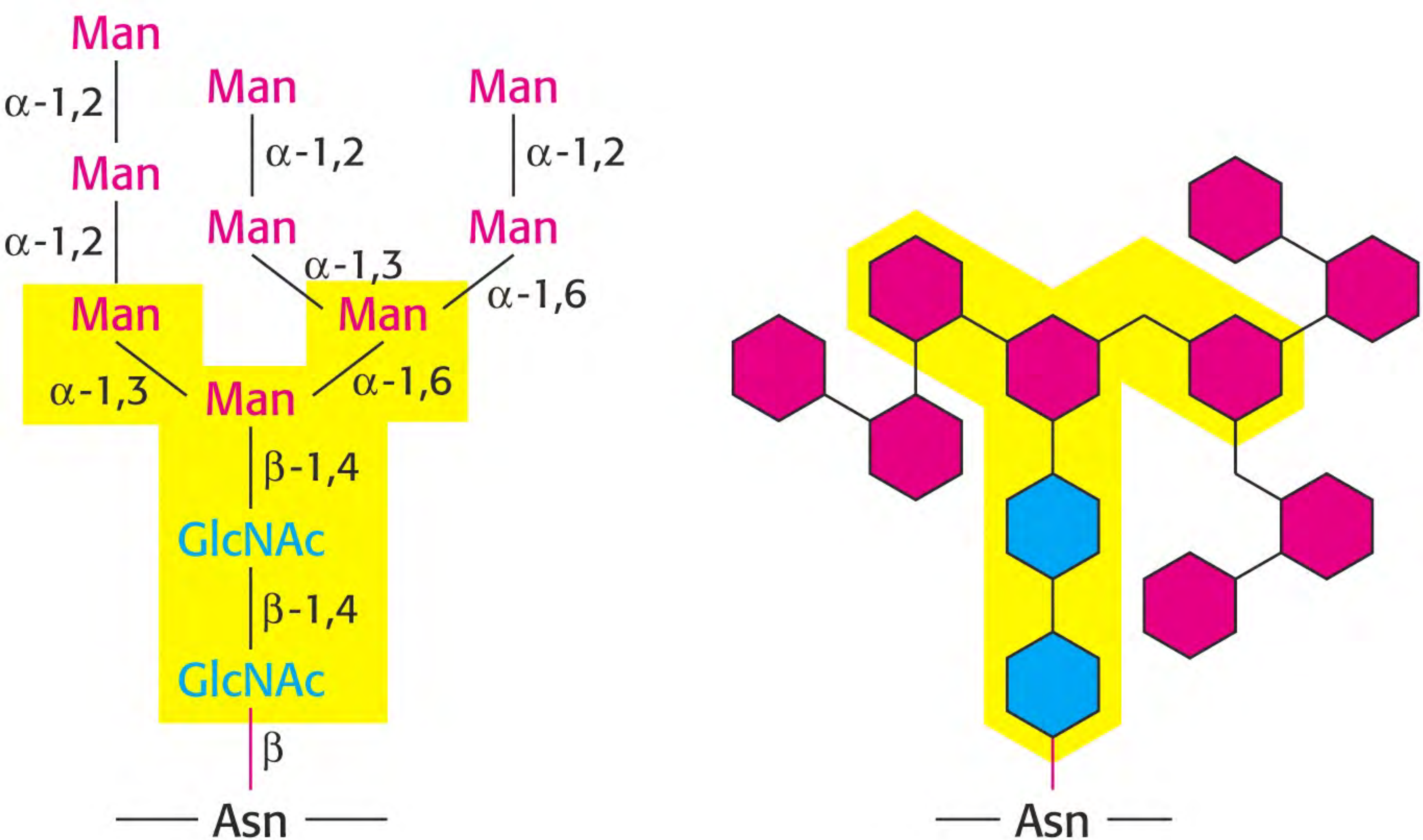
Which are properties of disaccharides?

a) **They are all reducing sugars.**
b) **They are all composed of aldoses.**
c) ***They all contain a glycosidic bond.***
d) **They all have anomeric forms.**
e) **They all have 1,4 bonds.**
f) ***The two monosaccharide components can be the same or different.***



(a) O-linked
(b) N-linked
GalNAc
Ser
GlcNAc
Asn
Examples:
Ser/Thr
Examples:
Asn
GlcNAc
Man
Gal
Neu5Ac
Fuc
GalNAc

(A)


Man
α-1,2
Man
Man
α-1,2
α-1,2
Man
Man
α-1,2
Man
Man
α-1,3
α-1,6
Man
Man
α-1,3
Man
α-1,6
β-1,4
GlcNAc
β-1,4
GlcNAc
β
Asn
Asn

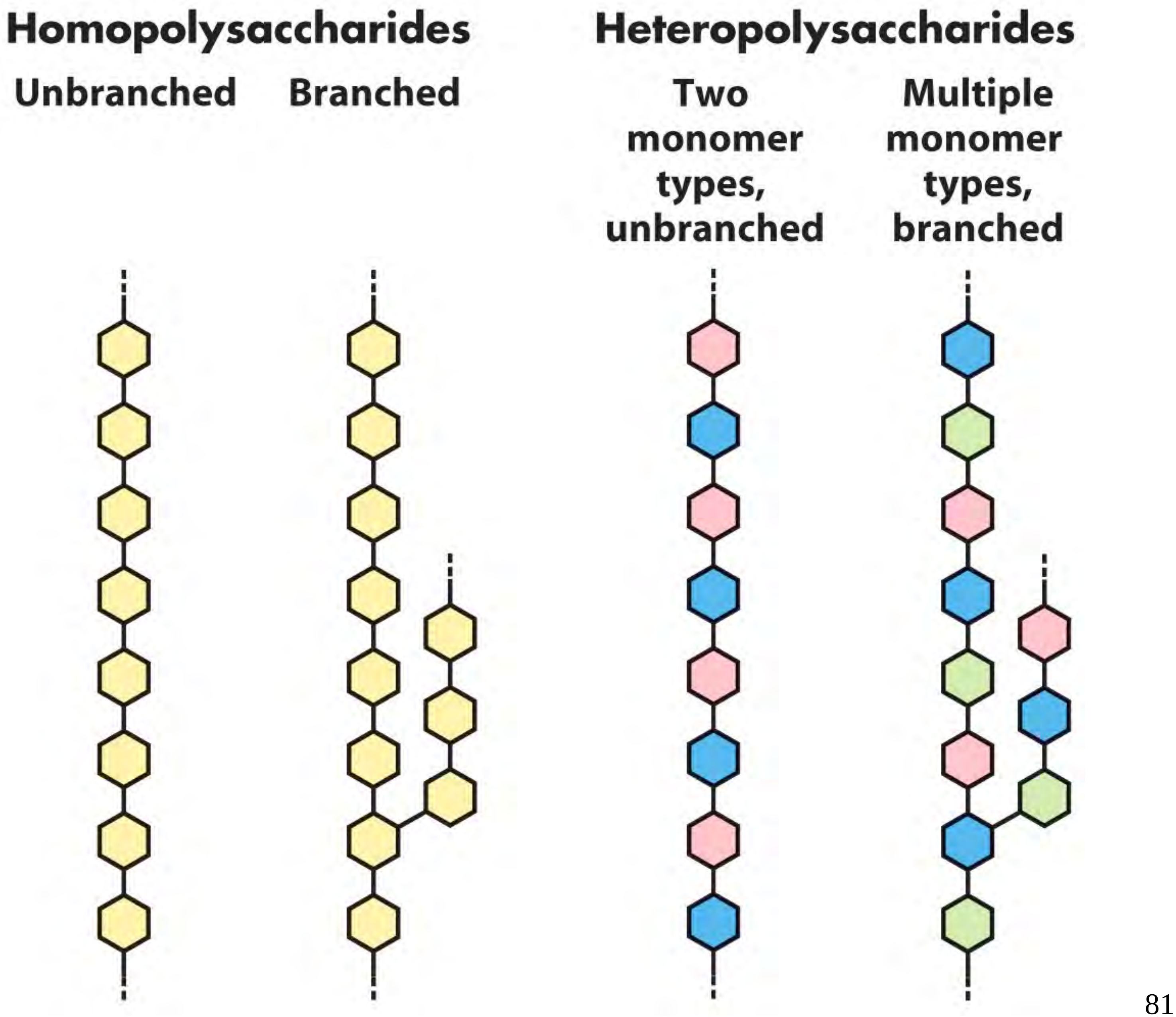

Homopolysaccharides
Unbranched
Branched
Heteropolysaccharides
Two monomer types, unbranched
Multiple monomer types, branched

TABLE 7–2 **Structures and Roles of Some Polysaccharides**

Polymer	*Type**	*Repeating unit*†	*Size (number of monosaccharide units)*	*Roles/significance*
Starch				Energy storage: in plants
Amylose	Homo-	(α1→4)Glc, linear	50–5,000	
Amylopectin	Homo-	(α1→4)Glc, with (α1→6)Glc branches every 24–30 residues	Up to 10^6	
Glycogen	Homo-	(α1→4)Glc, with (α1→6)Glc branches every 8–12 residues	Up to 50,000	Energy storage: in bacteria and animal cells
Cellulose	Homo-	(β1→4)Glc	Up to 15,000	Structural: in plants, gives rigidity and strength to cell walls
Chitin	Homo-	(β1→4)GlcNAc	Very large	Structural: in insects, spiders, crustaceans, gives rigidity and strength to exoskeletons
Dextran	Homo-	(α1→6)Glc, with (α1→3) branches	Wide range	Structural: in bacteria, extracellular adhesive
Peptidoglycan	Hetero-; peptides attached	4)Mur2Ac(β1→4) GlcNAc(β1	Very large	Structural: in bacteria, gives rigidity and strength to cell envelope
Agarose	Hetero-	3)D-Gal(β1→4)3,6-anhydro-L-Gal(α1	1,000	Structural: in algae, cell wall material
Hyaluronate (a glycosamino-glycan)	Hetero-; acidic	4)GlcA(β1→3) GlcNAc(β1	Up to 100,000	Structural: in vertebrates, extracellular matrix of skin and connective tissue; viscosity and lubrication in joints

*Each polymer is classified as a homopolysaccharide (homo-) or heteropolysaccharide (hetero-).

†The abbreviated names for the peptidoglycan, agarose, and hyaluronate repeating units indicate that the polymer contains repeats of this disaccharide unit. For example, in peptidoglycan, the GlcNAc of one disaccharide unit is (β1→4)-linked to the first residue of the next disaccharide unit.

Are You Getting It??

Which can be a characteristic of a polysaccharide?
(multiple answers)

a) It can contain one type of monosaccharide component.
b) It can contain different types of glycosidic bonds.
c) It can contain monosaccharide derivatives.
d) It can have an unbranched structure.
e) It can function in energy storage.
f) It will have a precise molecular weight.

Are You Getting It??

Answer

Which can be a characteristic of a polysaccharide?

a) It can contain one type of monosaccharide component.

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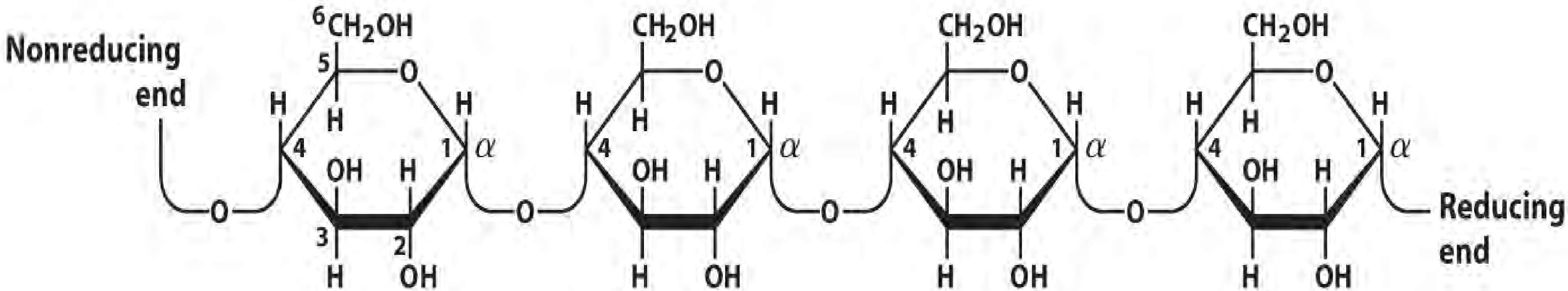
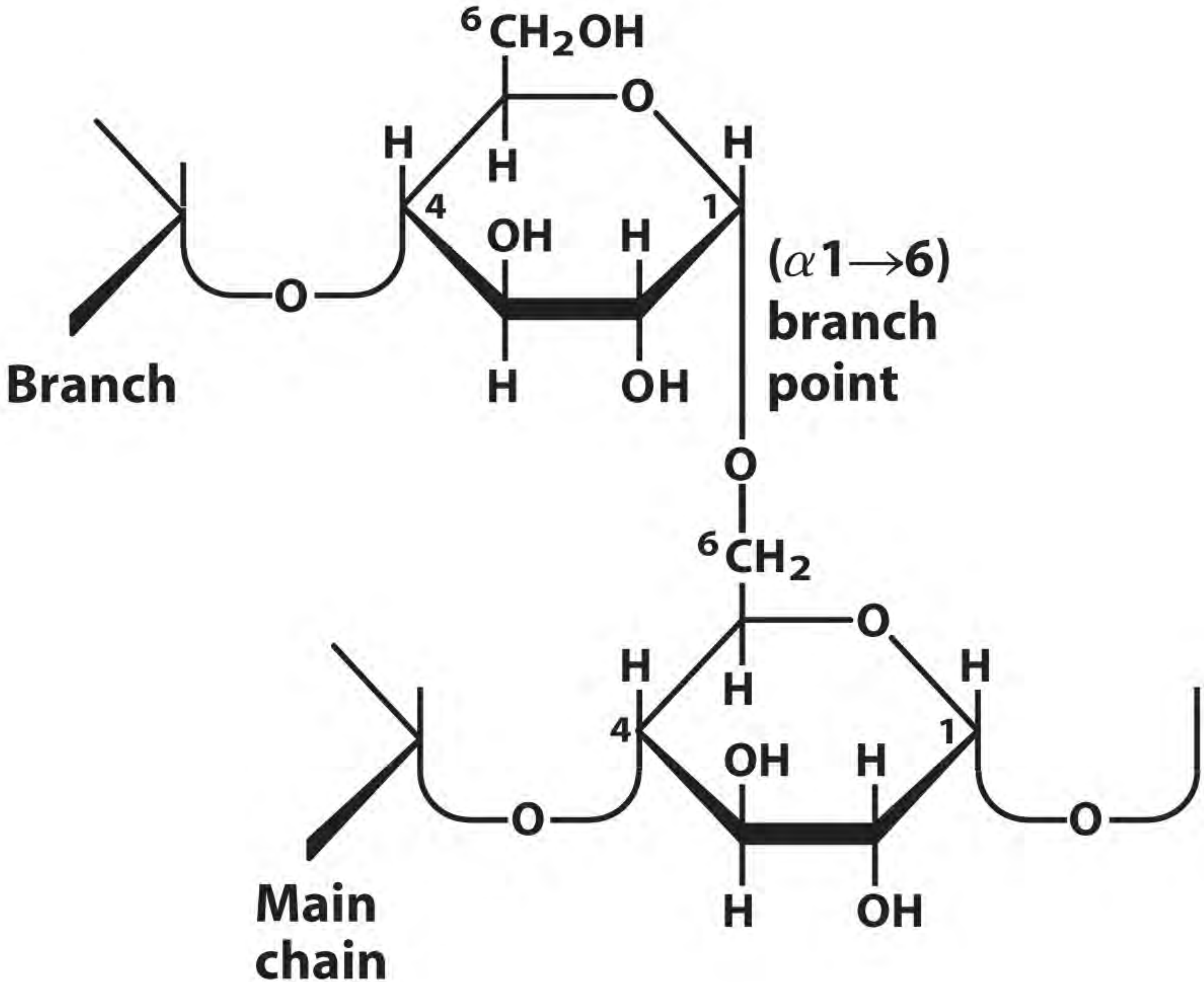
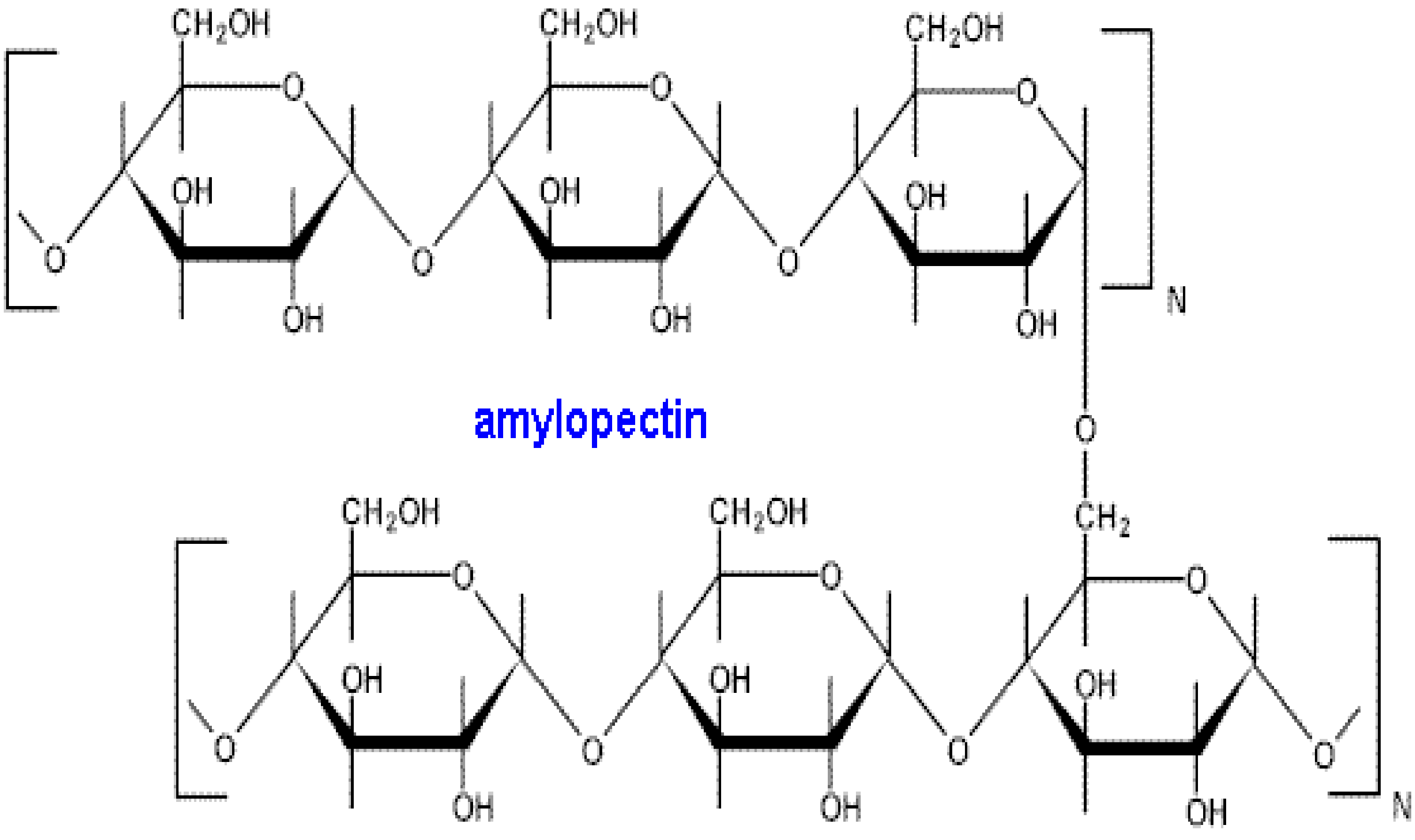


amylose



6 CH2OH
O
H
H
4
1
OH
H
H
(α1→6)
branch
point
Branch
H
OH
O
O
6 CH2
O
H
H
H
4
1
OH
H
O
Main
chain
H
OH


CH₂OH
O
OH
OH
N
amylopectin
CH₂

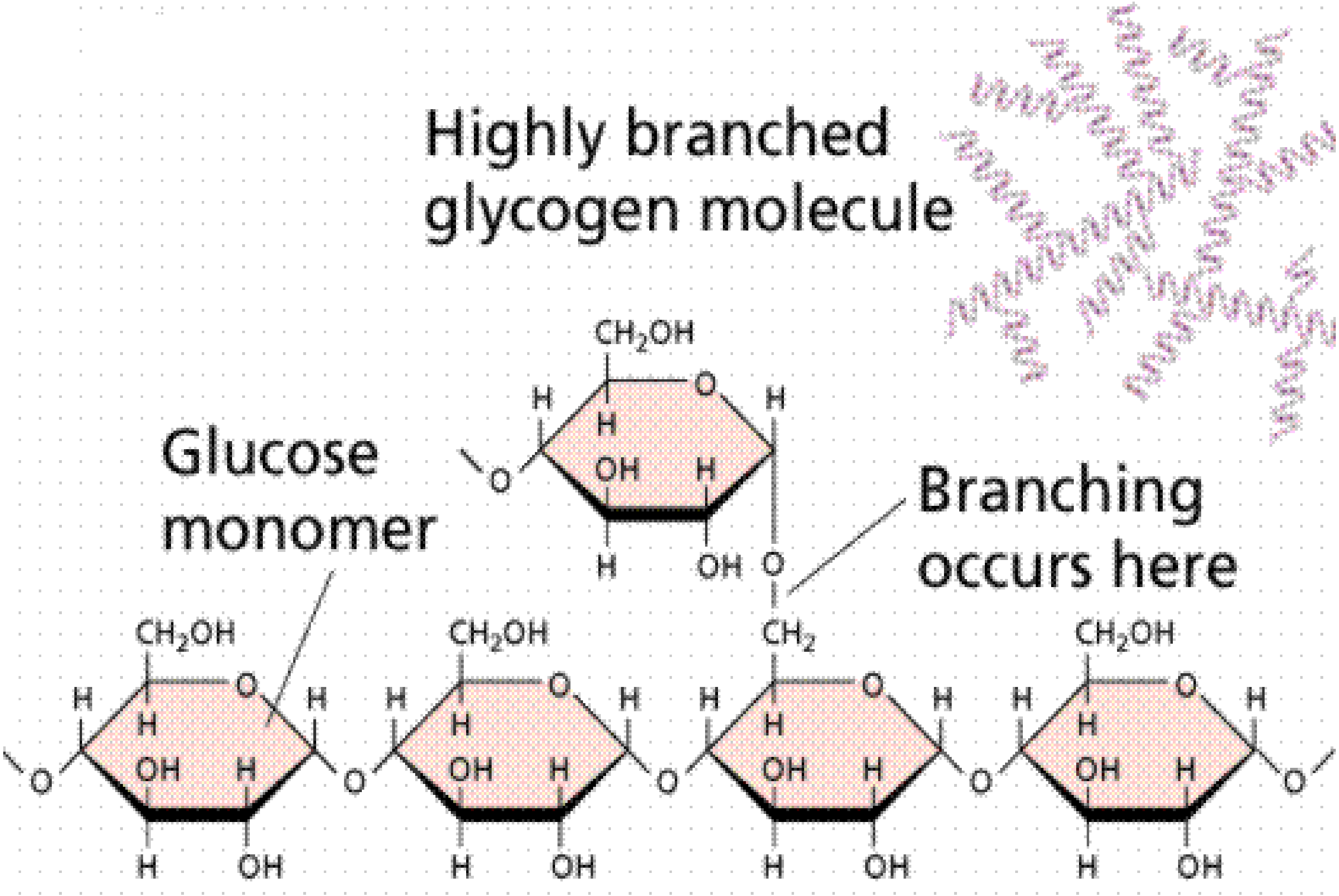
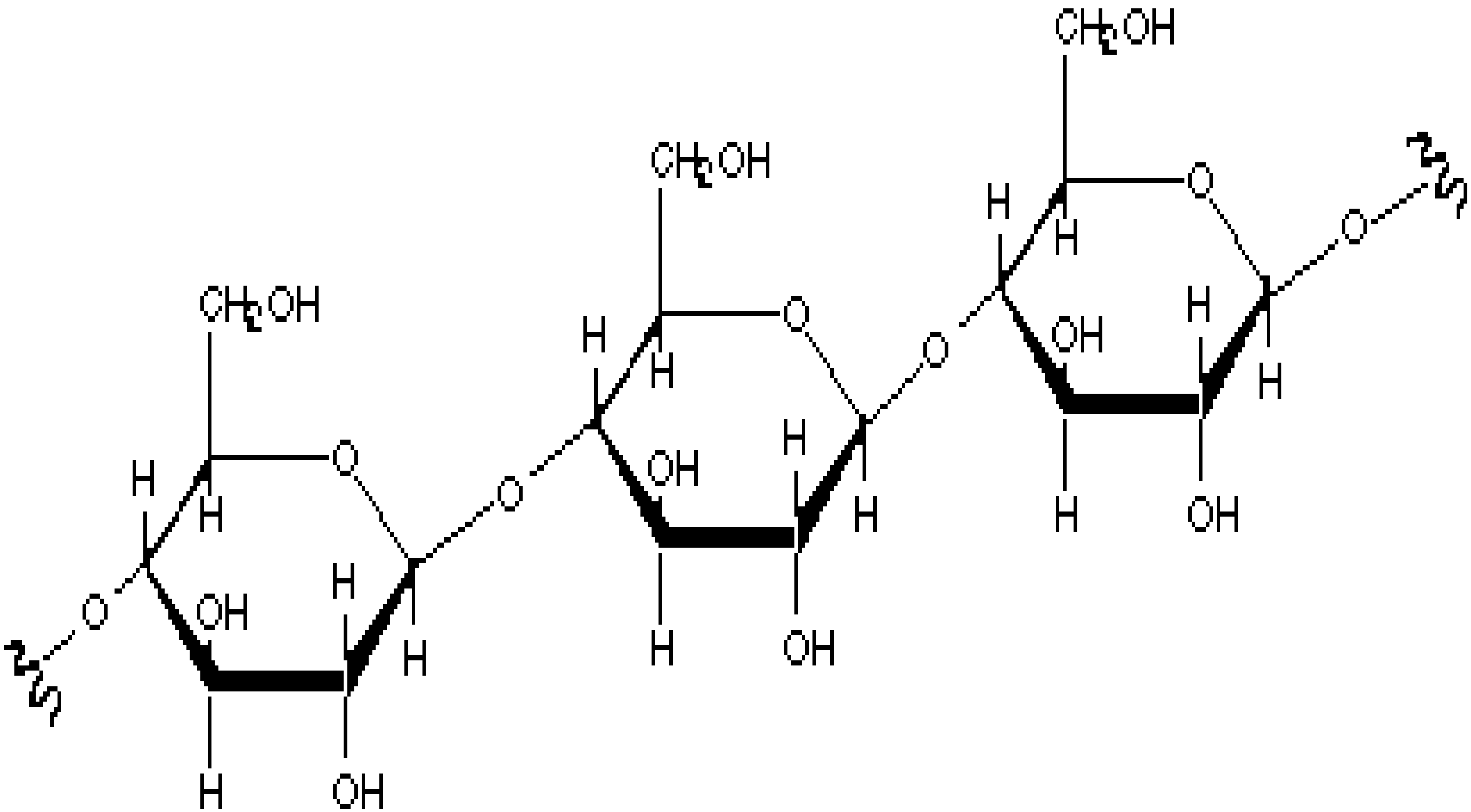
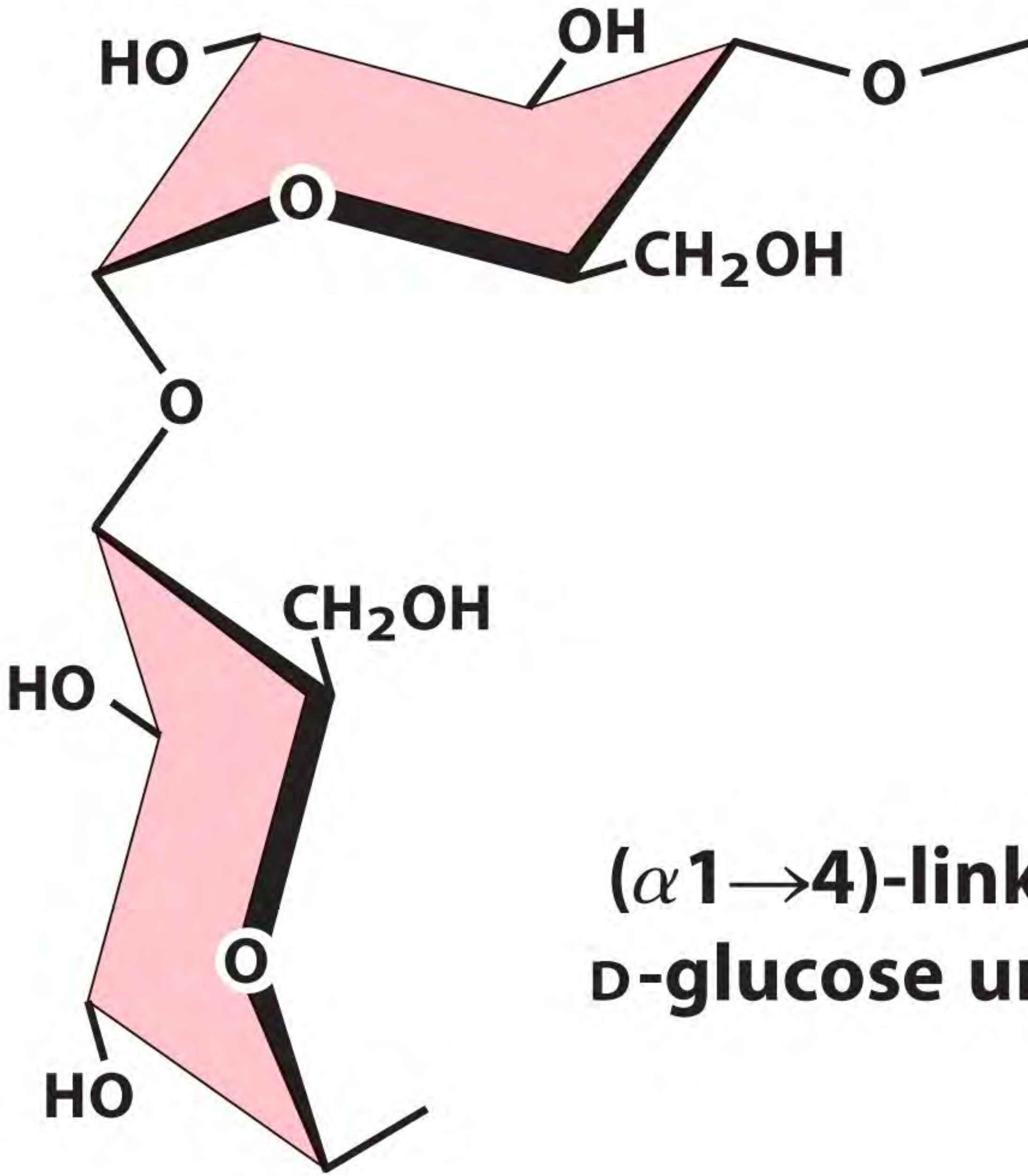

Highly branched
glycogen molecule
Glucose
monomer
Branching
occurs here
CH₂OH
O
H
OH
CH₂

Figure 3.12 (3)

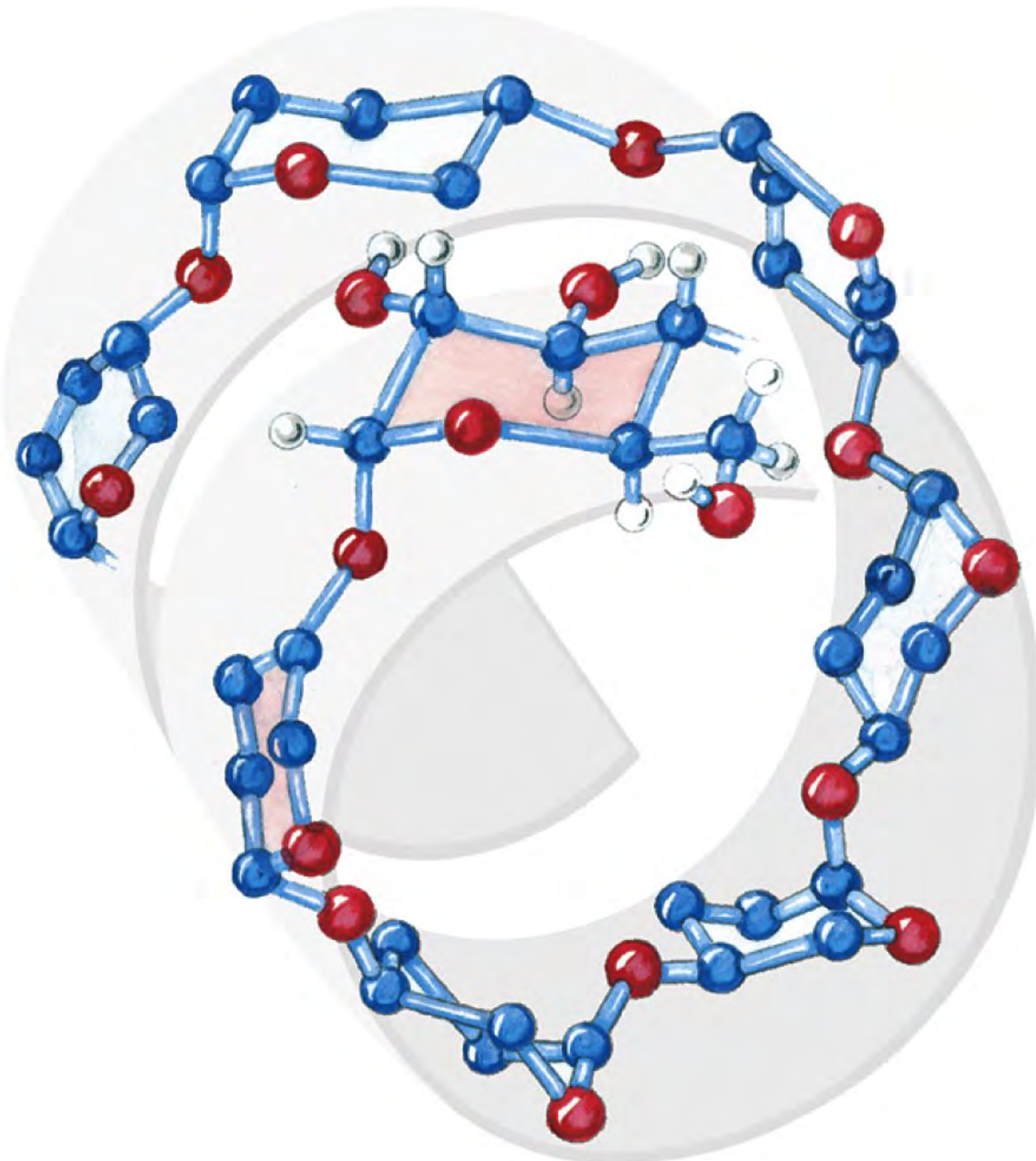


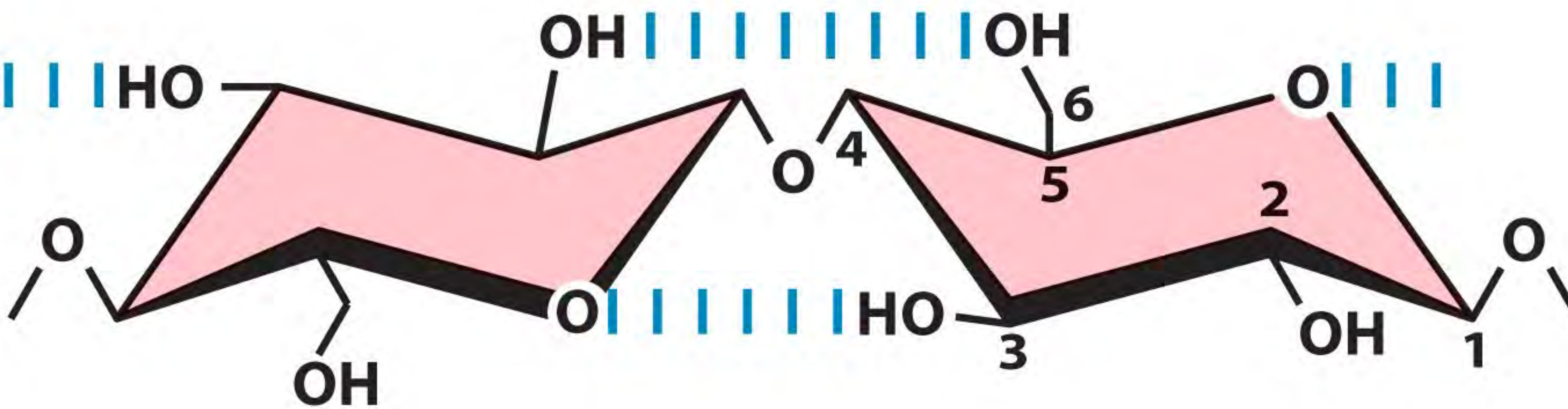
Cellulose

poly (1,4'-O-β-D-glucopyranoside)

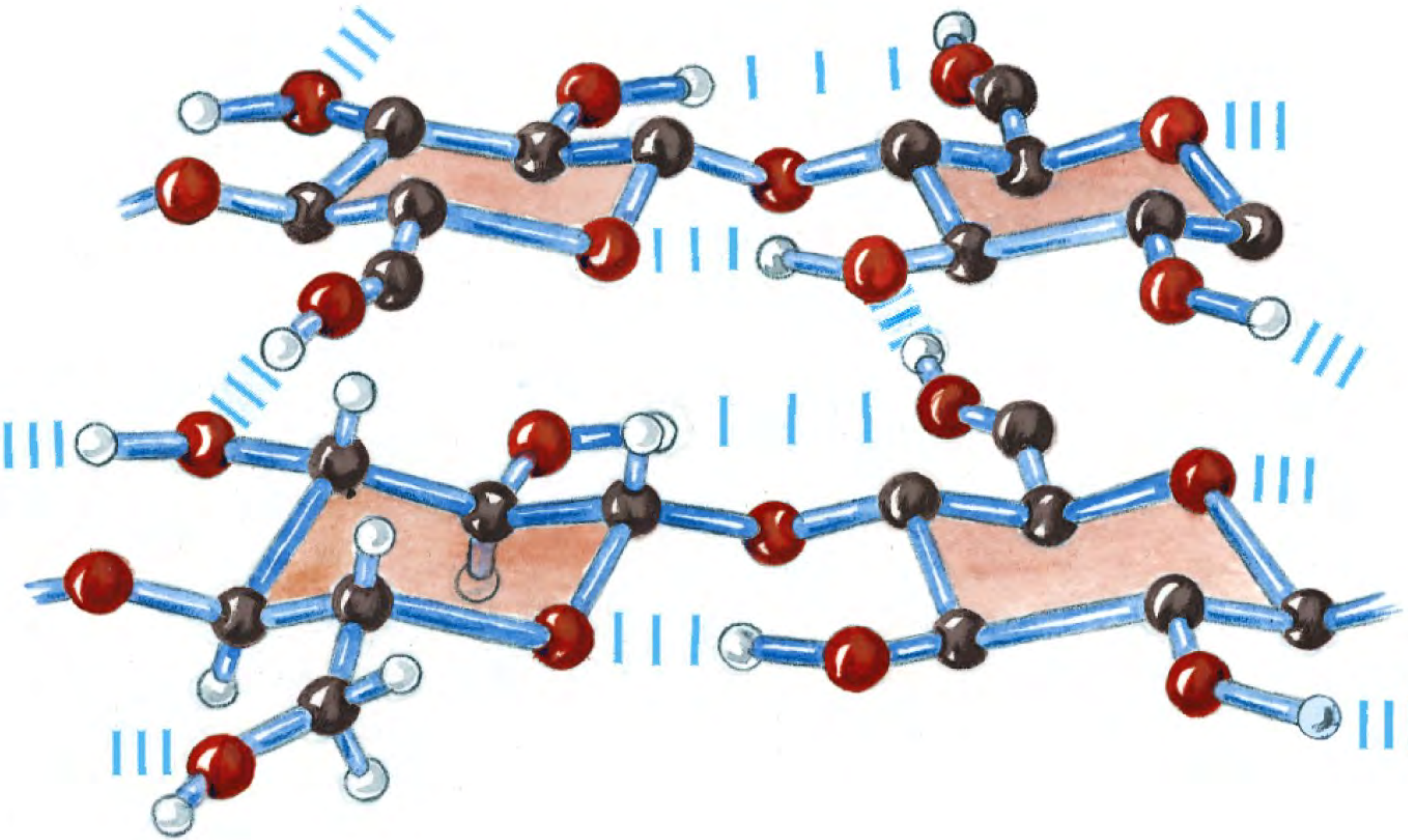


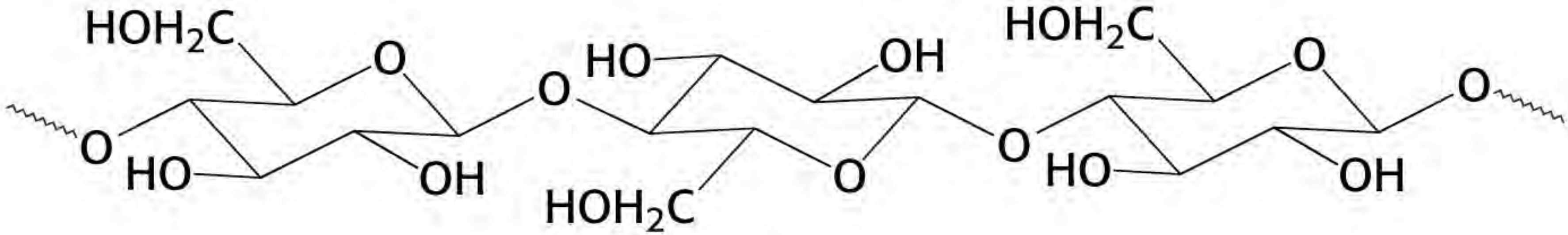
(α1→4)-linked
D-glucose units



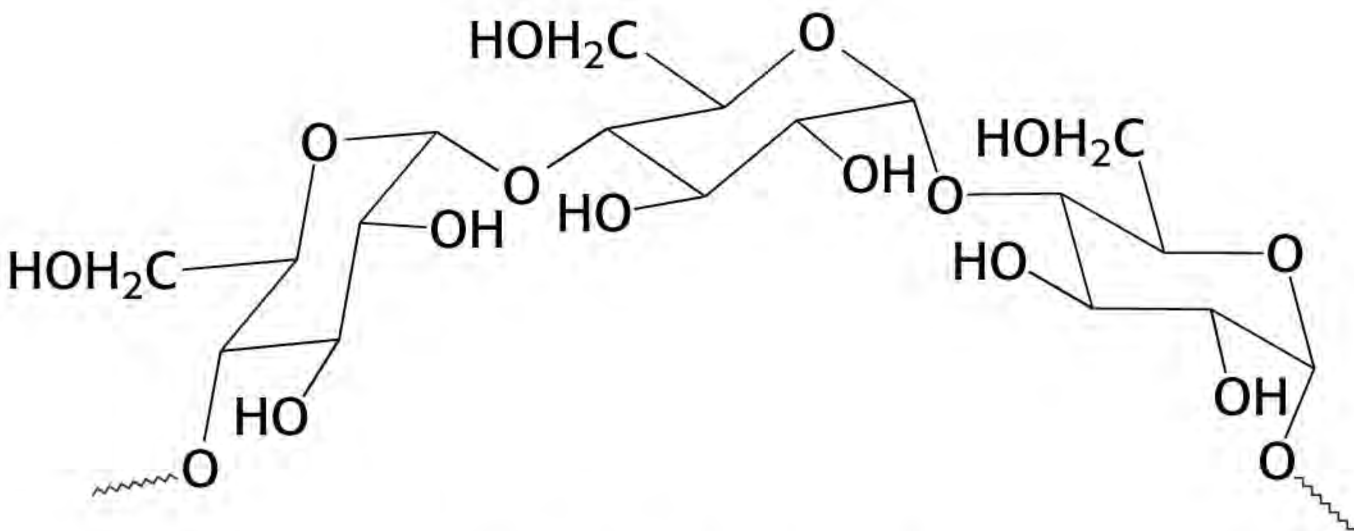


(β1→4)-linked D-glucose units





Cellulose
(β-1,4 linkages)



Starch and Glycogen
(α-1,4 linkages)

Are You Getting It??

Which characteristics are found in glycogen, cellulose, or both?

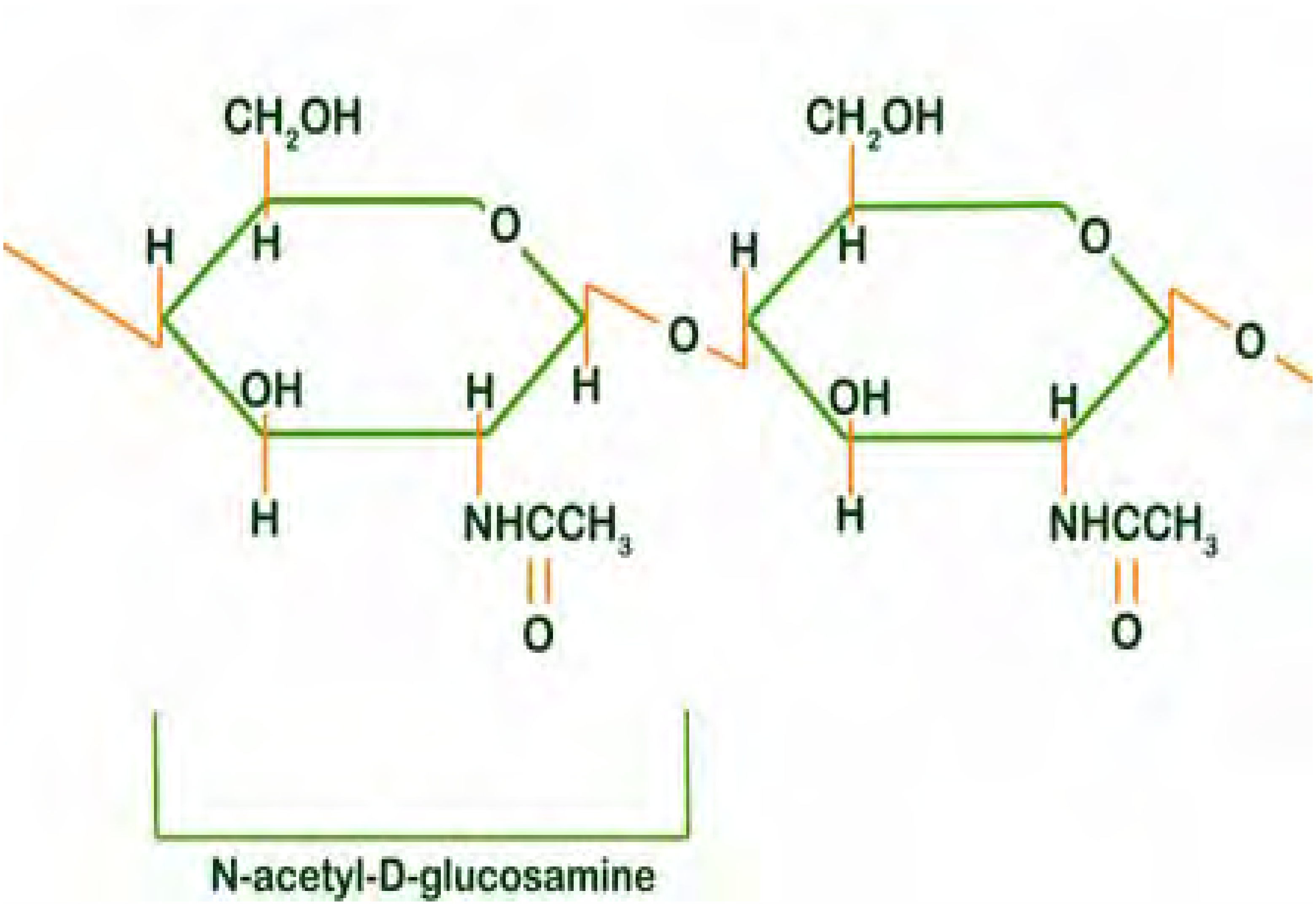
a) It contains α-glycosidic bonds.
b) It contains β-glycosidic bonds.
c) It contains 1,4-glycosidic bonds.
d) It contains hydrogen bonds.
e) It has a fibrous structure.
f) It has a branched structure.

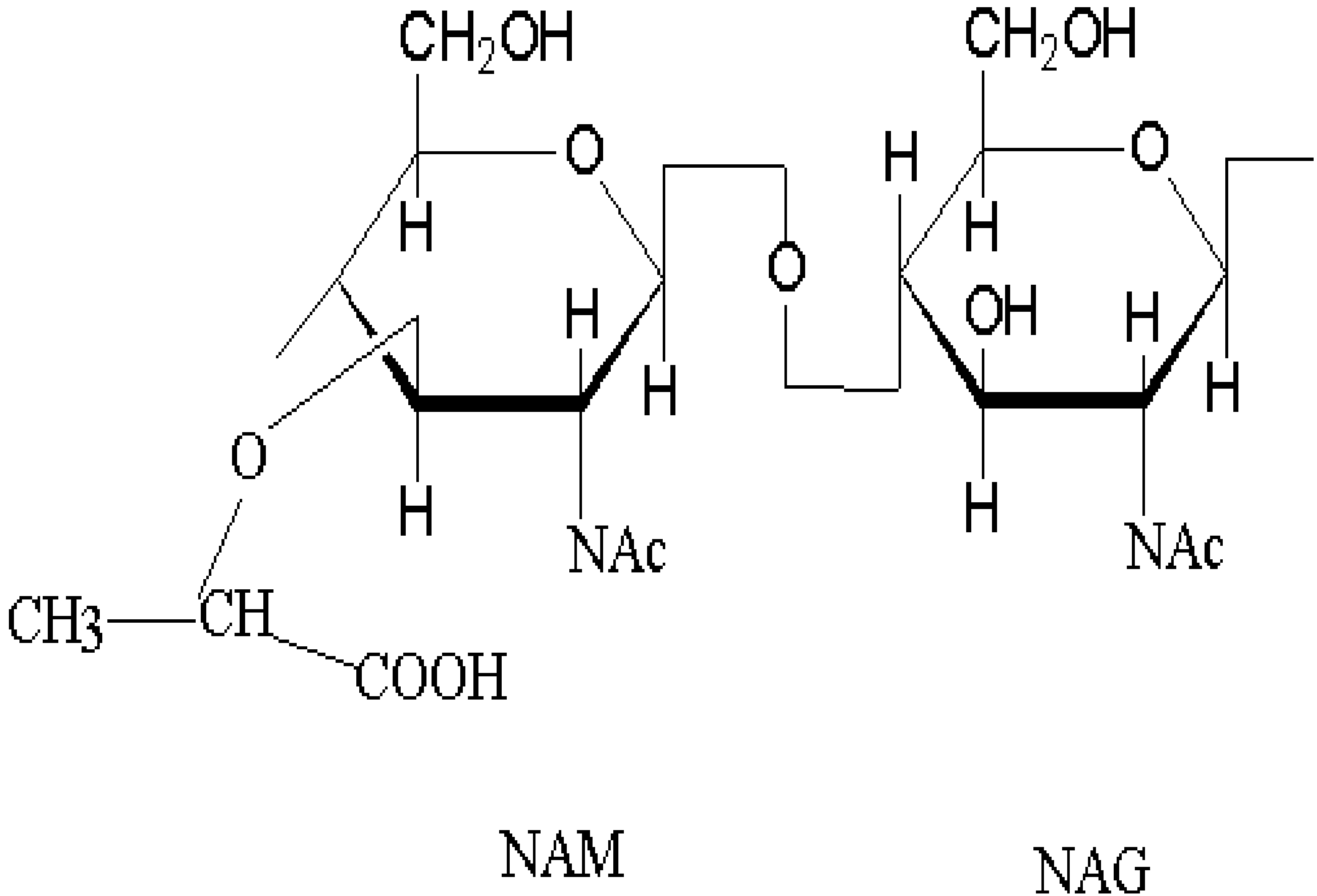
Are You Getting It??

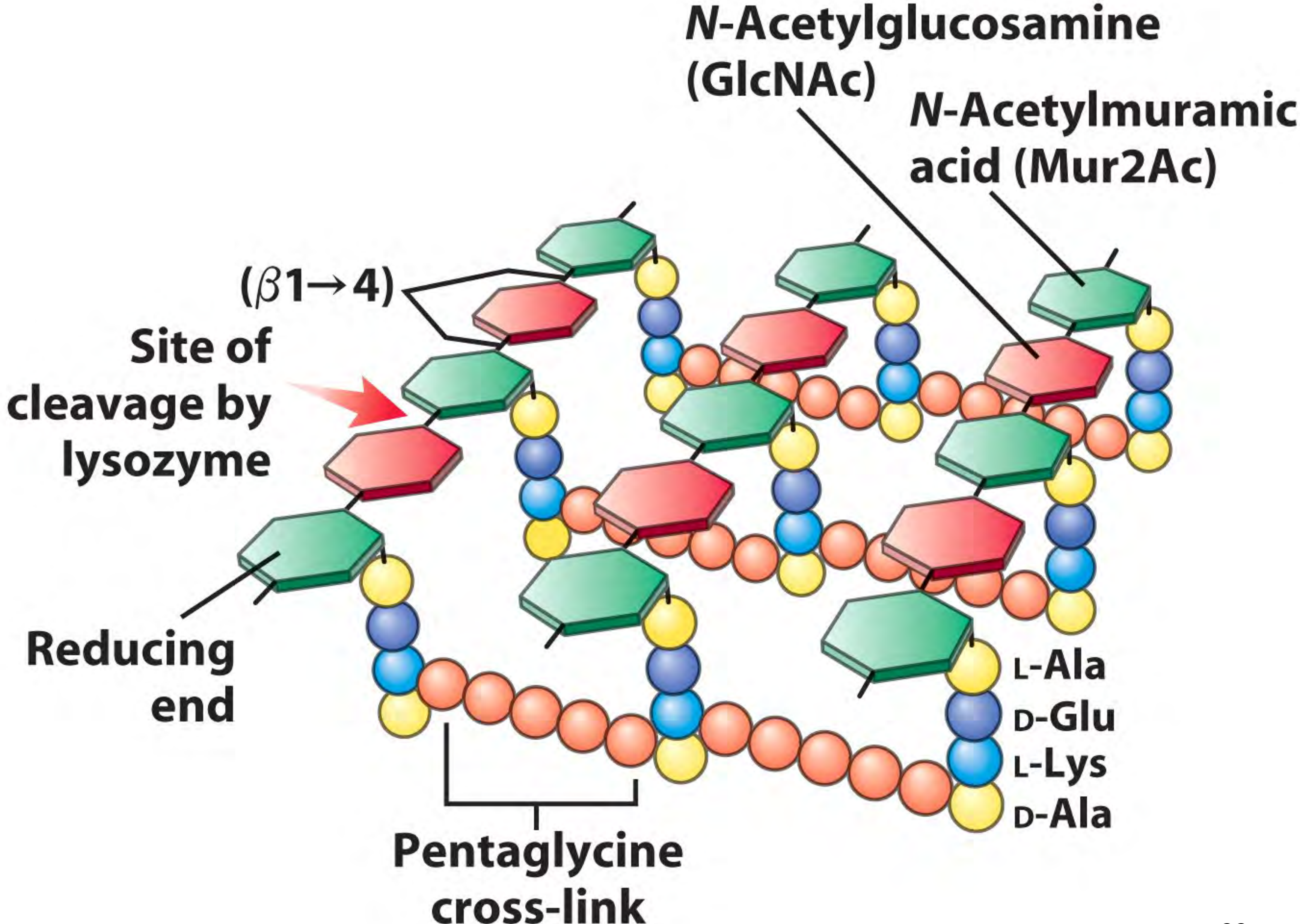
Answer

Which characteristics are found in glycogen, cellulose, or both?

a) It contains α-glycosidic bonds. *glycogen*
b) It contains β-glycosidic bonds. *cellulose*
c) It contains 1,4-glycosidic bonds. *both*
d) It contains hydrogen bonds. *both*
e) It has a fibrous structure. *cellulose*
f) It has a branched structure. *glycogen*


CH2OH
O
H
H
OH
H
H
H
NHCCH3
O
O
CH2OH
O
H
H
OH
H
H
NHCCH3
O
O
N-acetyl-D-glucosamine


CH2OH
O
H
H
H
H
NAc
H
O
CH2OH
O
H
H
OH
H
H
H
NAc
O
CH3
CH
COOH
NAM
NAG


N-Acetylglucosamine (GlcNAc)
N-Acetylmuramic acid (Mur2Ac)
(β1→4)
Site of cleavage by lysozyme
Reducing end
Pentaglycine cross-link
L-Ala
D-Glu
L-Lys
D-Ala

Glycosaminoglycan	Repeating disaccharide
Number of disaccharides per chain	
Hyaluronate ~50,000