Chem 150, Spring 2015

Unit 11 - Carbohydrates

Introduction

- Biomolecules include
  - Proteins
  - Nucleic acids
  - **Carbohydrates**
  - Lipids
- Some can be quite large and complex, but comprise a limited number of elements (C,H,O) arranged in predictable patterns.
- Simple sugars share a common empirical formula $(CH_2O)_n$

Introduction

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15.1 Monosaccharides

- Carbohydrates are used for fuel in cells..
- Monosaccharides, or simple sugars, are the building blocks of carbohydrates.
- Monosaccharides contain carbon, hydrogen and oxygen in a 1:2:1 ratio and are classified based on the number of carbons.

TABLE 15.1 Formulas of Common Monosaccharides

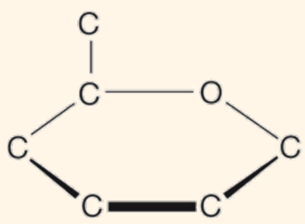
Type of Monosaccharide	Number of Carbon Atoms	Molecular Formula	Examples
Triose	3	$C_3H_6O_3$	Glyceraldehyde
Tetrose	4	$C_4H_8O_4$	Erythrose
Pentose	5	$C_5H_{10}O_5$	Ribose, arabinose, xylose
Hexose	6	$C_6H_{12}O_6$	Glucose, fructose, galactose, mannose

Monosaccharides in Our Bodies

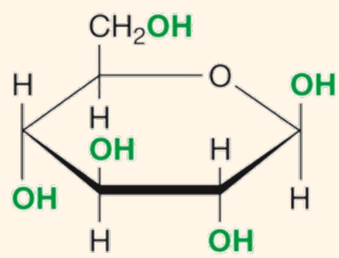
- Most monosaccharides in our bodies:
  - Many exist as a five- or six-membered ring of atoms
  - One of the atoms in the ring is an oxygen and the rest are carbon
  - Any carbon not included in the ring is attached to the ring carbons nearest the oxygen
  - All but one of the carbon atoms are bonded to an hydroxyl group

Haworth Projections

- Haworth projections are a common way to visualize a simple sugar

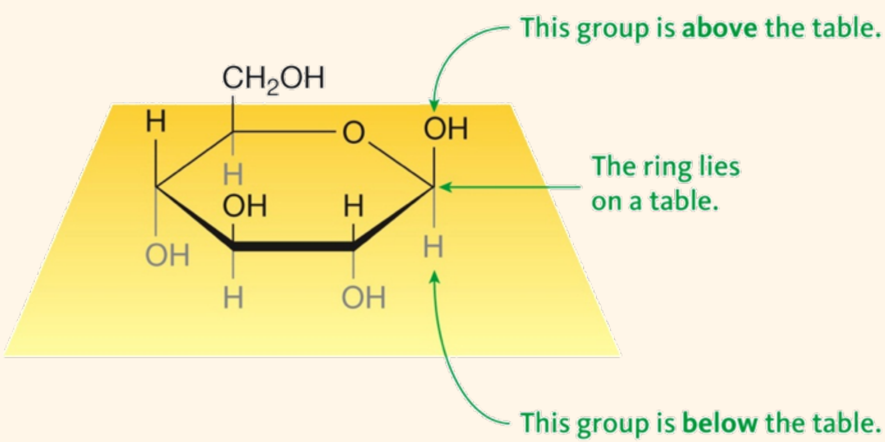


Skeleton structure
of glucose



Full structure of glucose
(Haworth projection)

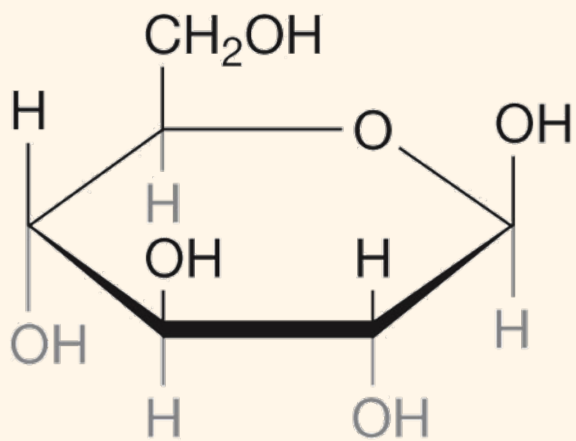
The up or down arrangement of the -OH groups is what make this glucose, and not some other hexose



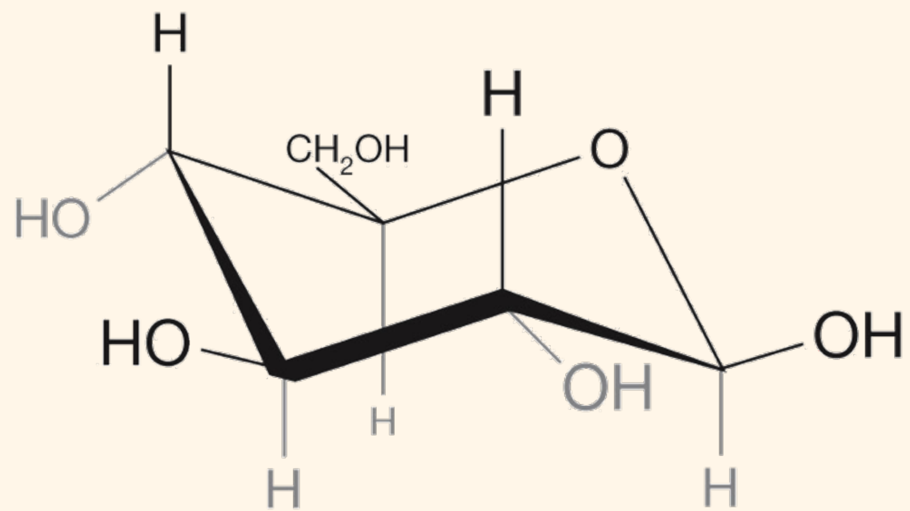
Interpreting the Haworth projection

The Actual Shape of Glucose

- The Haworth projection does not accurately portray the actual shape of a sugar. If the sugar is a 6-membered ring, it actually adopts what is known as the **chair conformation**.



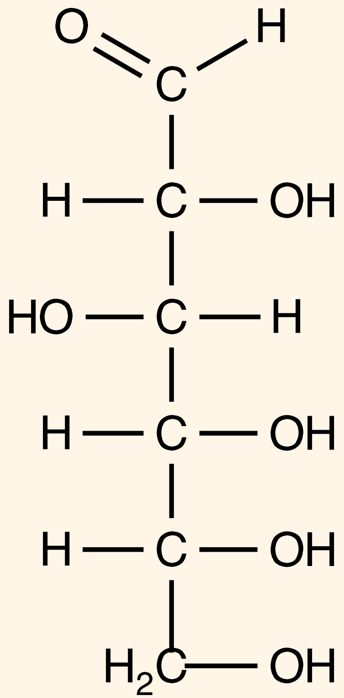
Glucose:
Haworth projection



Glucose:
actual shape of molecule

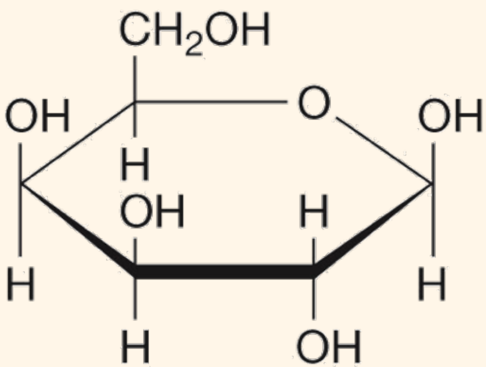
The Actual Shape of Glucose

- Monosaccharides can also have an open structure.

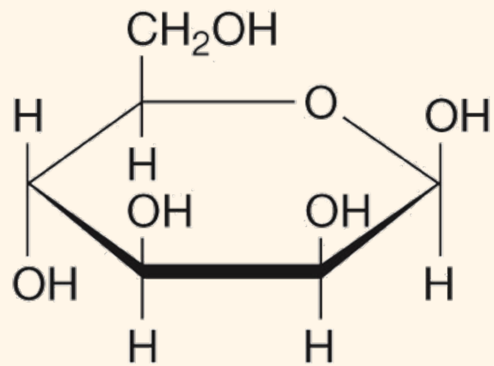


Glucose

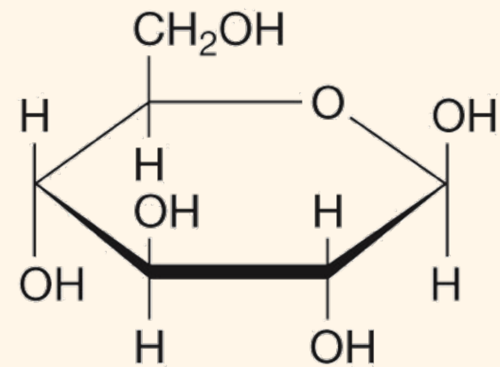
Common Monosaccharides



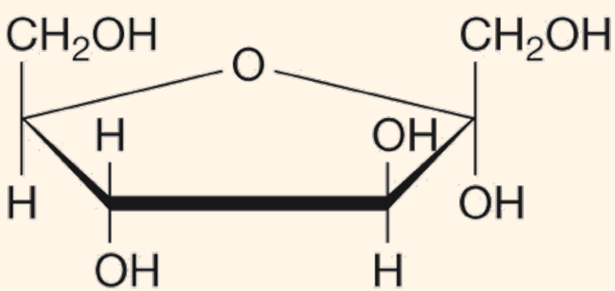
Galactose
(a hexose)



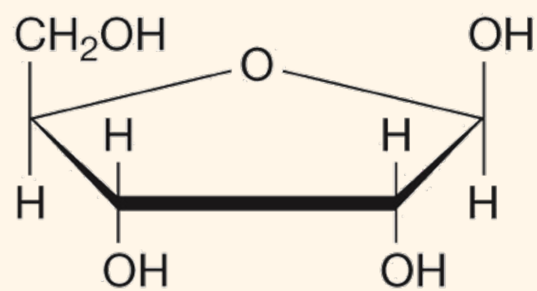
Mannose
(a hexose)



Glucose
(a hexose)



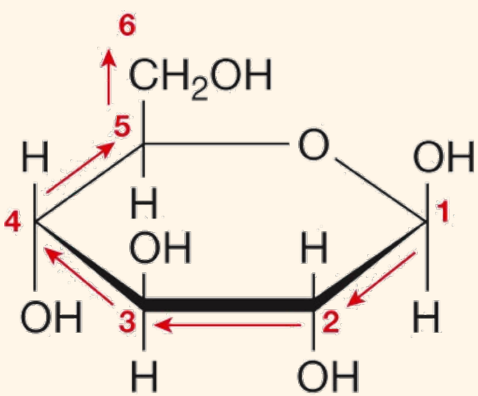
Fructose
(a hexose)



Ribose
(a pentose)

Numbering Carbon Atoms

- Number carbon atoms from the right side beginning with the carbon that is not part of the ring (if any) or beginning with the rightmost carbon in the ring.



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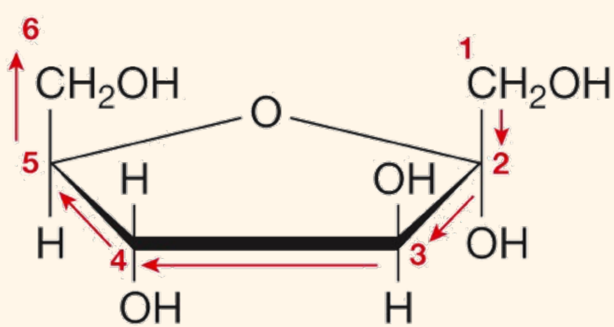

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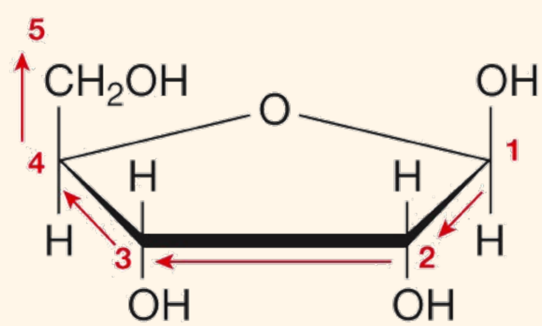


Ribose
(a pentose)

Physical Properties

- Because of the similarity in structures, all of the monosaccharides have similar physical properties, including high melting points, high solubility in water and low solubility in organic solvents.
- The boiling points of sugars are so high that they break down into carbon and water when they are heated rather than boiling.

TABLE 15.2 The Properties of Four Hexoses

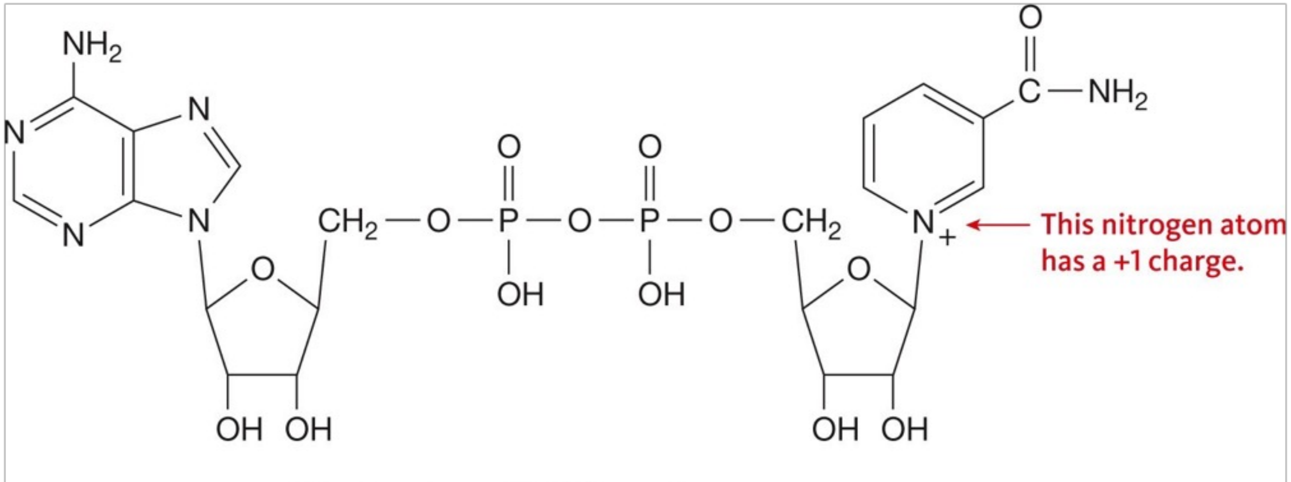
	Glucose	Galactose	Mannose	Fructose
Melting point	150°C	167°C	133°C	103°C
Solubility in water	900 g/L	2000 g/L	2500 g/L	3700 g/L
Heat of combustion	3.72 kcal/g	3.70 kcal/g	3.73 kcal/g	3.73 kcal/g

Energy Sources and Taste

- Our bodies can use any of the common hexoses for energy, but prefer to use glucose. Every cell in our bodies can use glucose for energy
- We also perceive taste differences in the common hexoses. Fructose tastes twice as sweet as glucose and more than five times sweeter than galactose or mannose.

Monosaccharides for Larger Molecules

- Many monosaccharides are found as part of a larger molecule, rather than individually.
  - Galactose and mannose are used to build cell membranes components and are rarely found free.
  - Ribose is used in nucleic acids and a few coenzymes



The structure of NAD^+, a redox coenzyme

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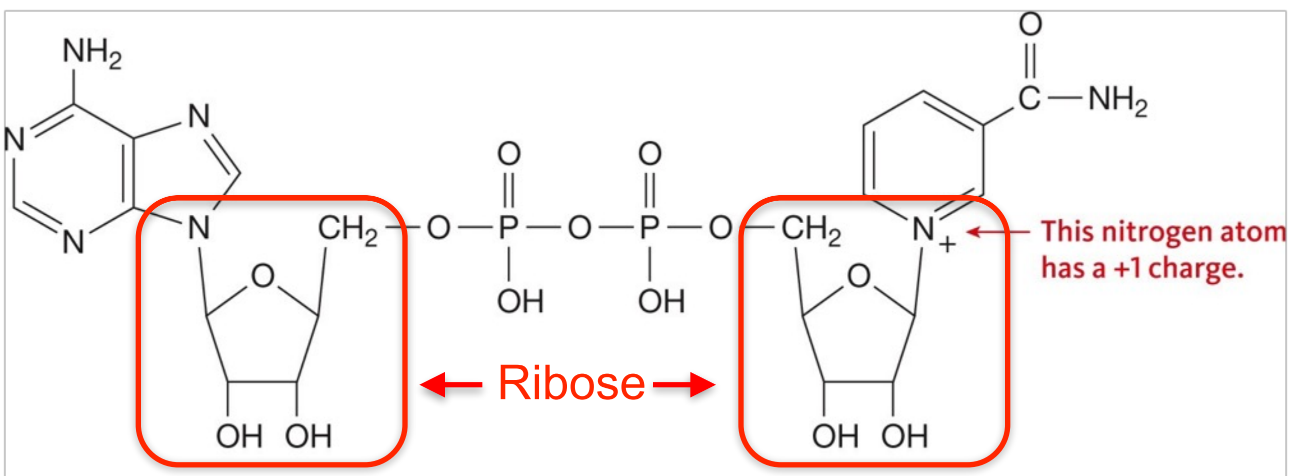
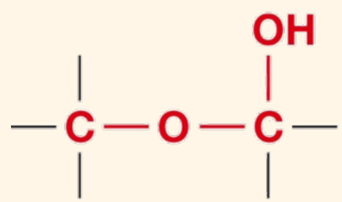


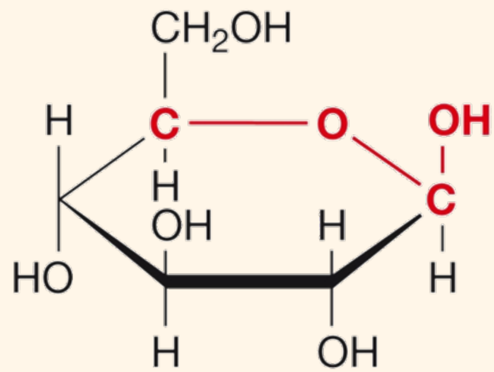
The structure of NAD^+, a redox coenzyme

15.2 Isomeric Forms of Monosaccharides: Anomers and Enantiomers.

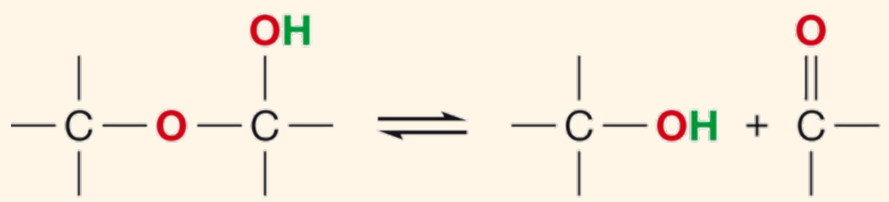
- Monosaccharide rings easily open because they contain a hemiacetal group.



The hemiacetal functional group



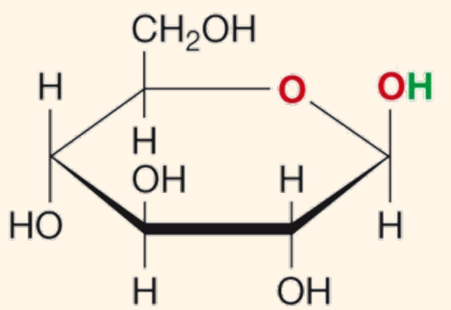
The location of the hemiacetal group in glucose



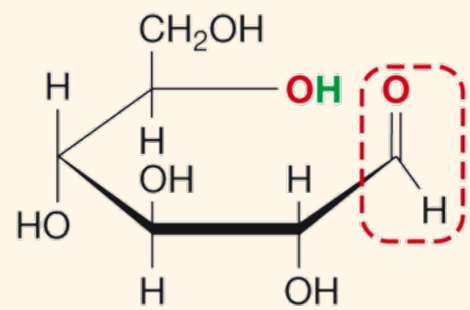
Hemiacetal **Alcohol** **Carbonyl group** (aldehyde or ketone)

Aldoses and Ketoses

- Glucose opens to form an aldehyde, and is thus known as an aldose.



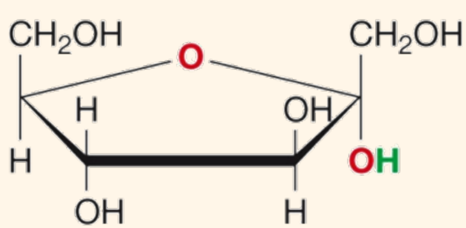
The ring form of glucose



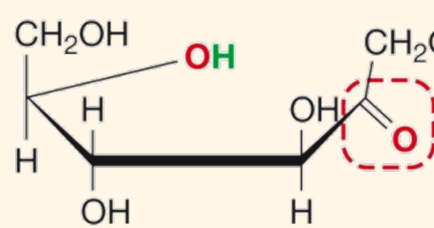
The open-chain form of glucose

The open-chain form of glucose contains an aldehyde group, so glucose is an aldose.

- Fructose opens to form a ketone, and is thus known as a ketose.



The ring form of fructose



The open-chain form of fructose

The open-chain form of fructose contains a ketone group, so fructose is a ketose.

Benedict's Test

- When dissolved in water, there is an equilibrium between the ring and the open form of the sugar.

- Open chain aldoses oxidize easily using Benedict's reagent:

$$\underset{\text{glucose}}{C_6H_{12}O_{6\,(aq)}} + \underset{\text{Benedict's solution (blue)}}{2\,Cu^{2+}_{(aq)} + 5\,OH^-_{(aq)}} \longrightarrow \underset{\text{gluconate}}{C_6H_{11}O_7^-{}_{(aq)}} + \underset{\text{brick red ppt.}}{Cu_2O_{(s)}} + 3\,H_2O_{(l)}$$

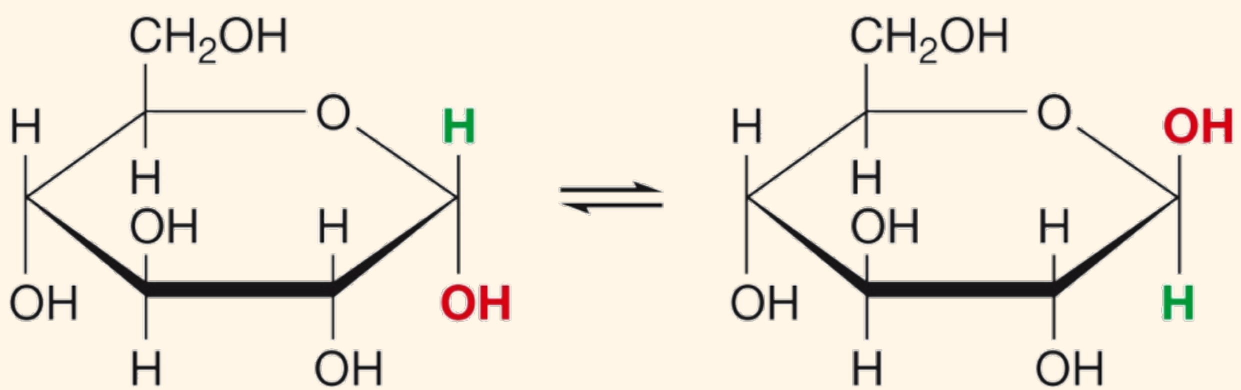
  - ✦ This reaction is used to test for the presences of sugar in the urine of diabetics.

- Sugars that react in the Benedict's test are called reducing sugars.

- All aldoses react; also fructose (a ketone) reacts because it easily converts into glucose in a basic solution.

Anomers

- D-glucose is the naturally occurring form of glucose and is present as a mixture of anomers.
- Anomers are sugars that differ in the position of the OH in the hemiacetal group.



α-D-Glucose
(the OH in the hemiacetal group is **down**)

β-D-Glucose
(the OH in the hemiacetal group is **up**)

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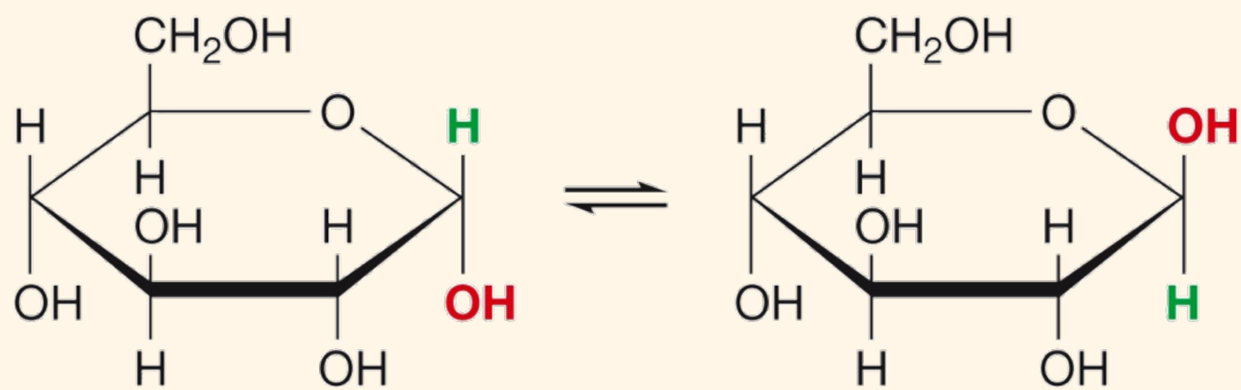


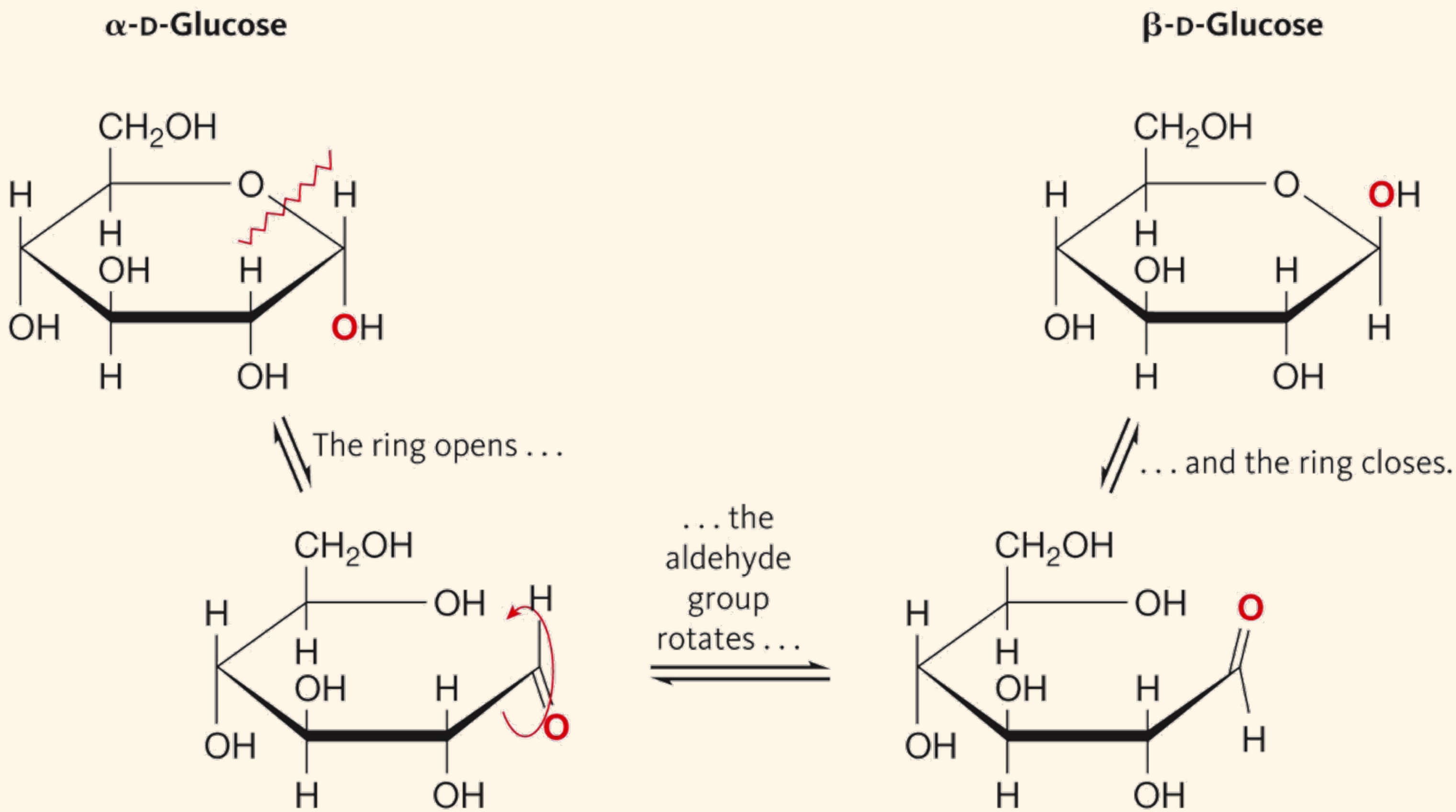
anomeric carbon

α-D-Glucose
(the OH in the hemiacetal group is **down**)

β-D-Glucose
(the OH in the hemiacetal group is **up**)

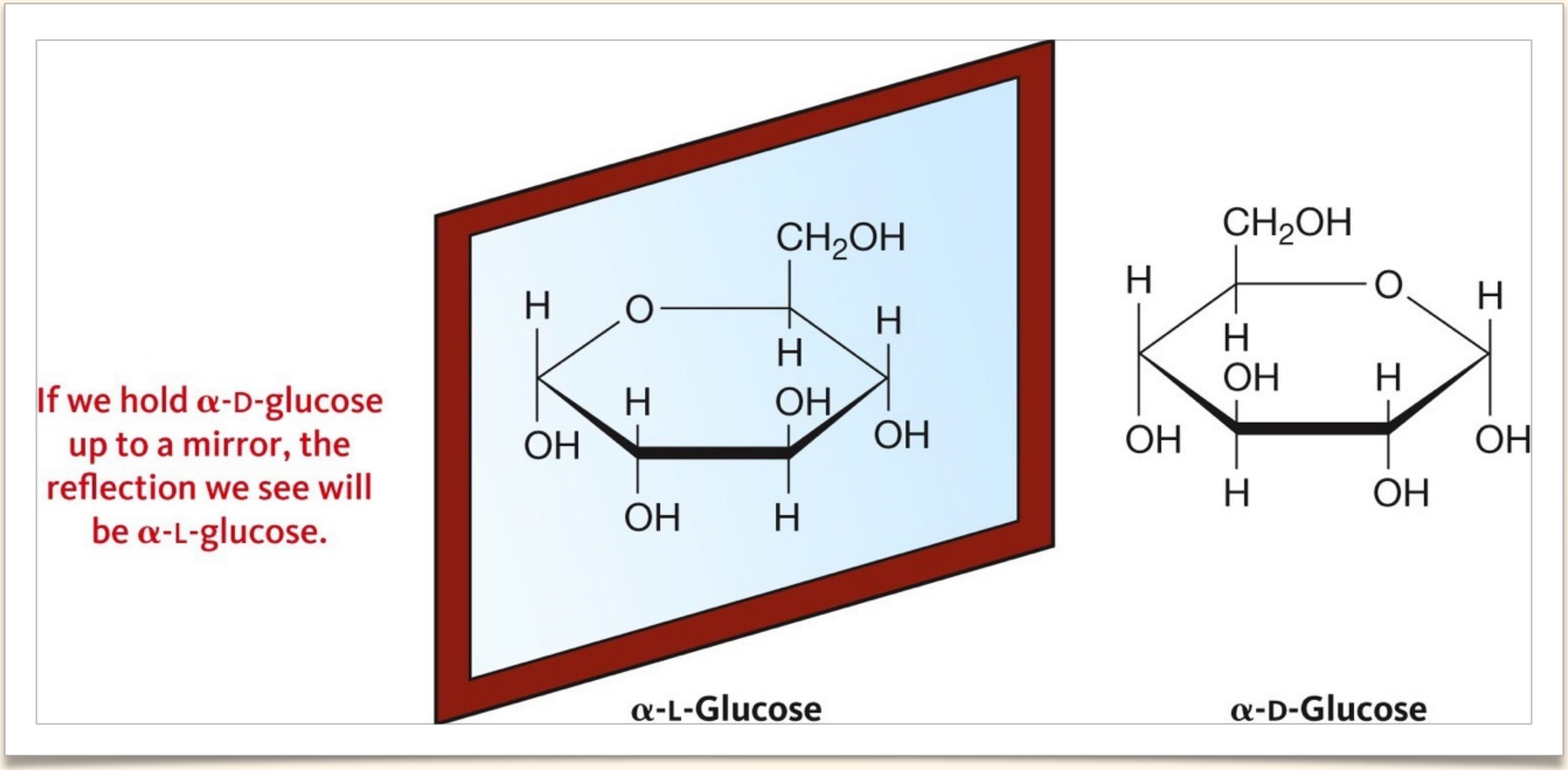
Mutarotation

- The α- and β-anomers interconvert because the hemiacetal opens and closes rapidly in an aqueous solution.



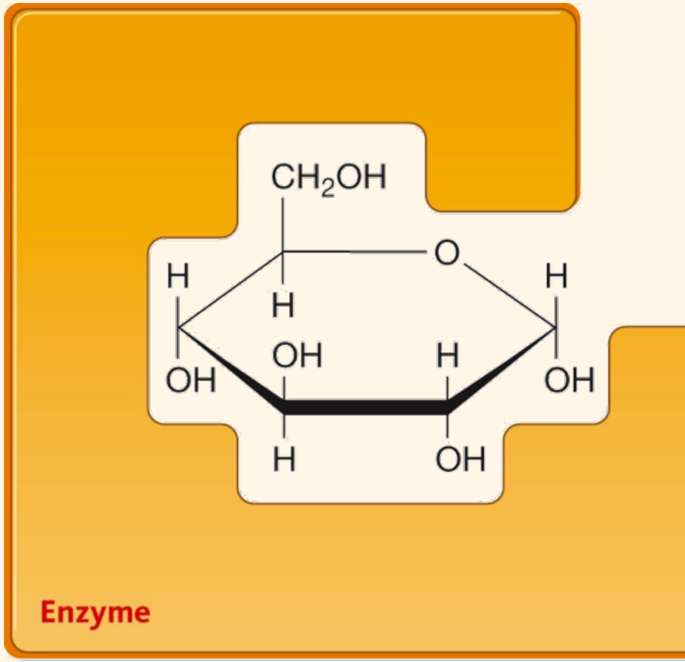
Enantiomers

- D-glucose has several chiral atoms, so it has an enantiomer (a non-superimposable mirror image) known as L-glucose.



L-Glucose vs D-Glucose

- While L- and D-glucose have nearly identical physical and chemical properties, enzymes (which are chiral themselves) can distinguish the difference.

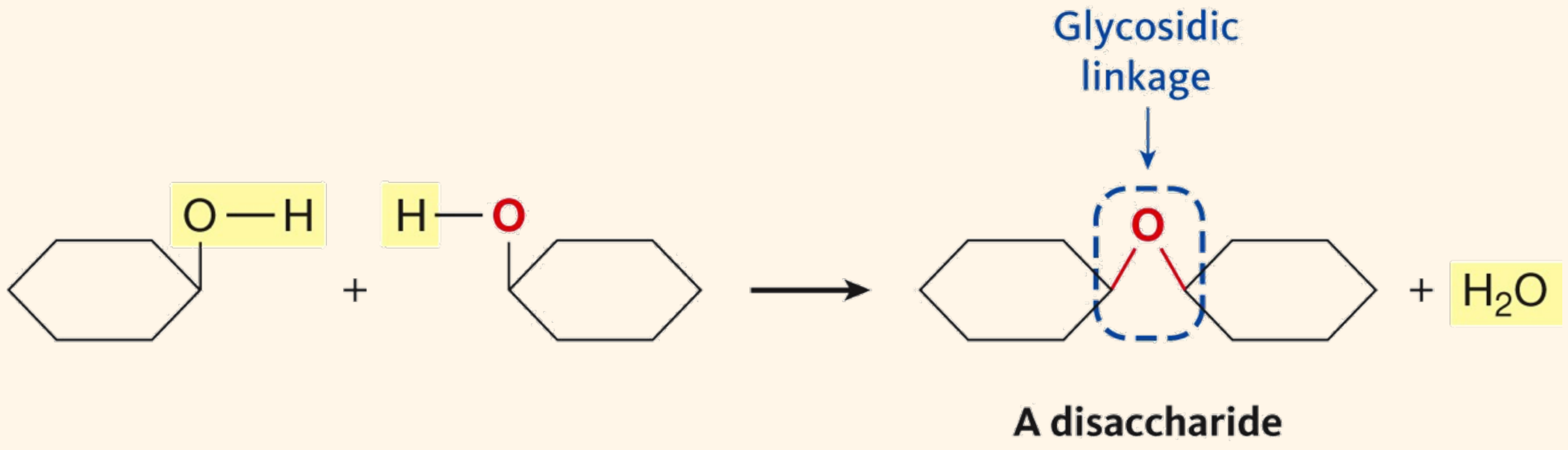


α-D-Glucose fits into the active site of the enzyme.

α-L-Glucose does not fit into the active site.

15.3 Disaccharides and the Glycosidic Linkage

- Most monosaccharides are found bonded to other compounds or to other monosaccharides.
- Two monosaccharides form a disaccharide in a condensation reaction.



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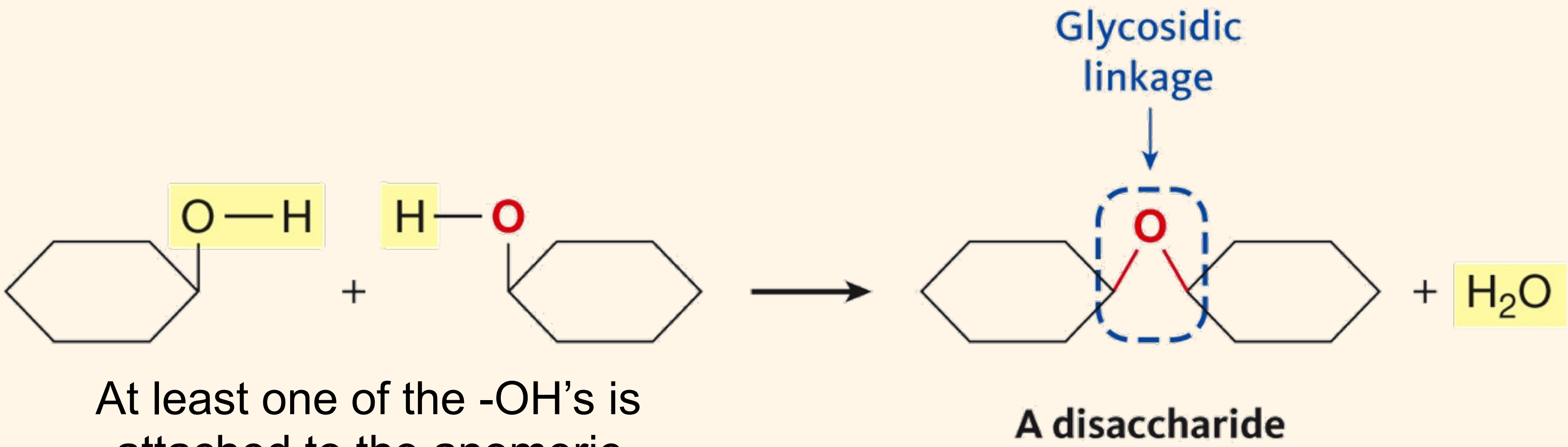
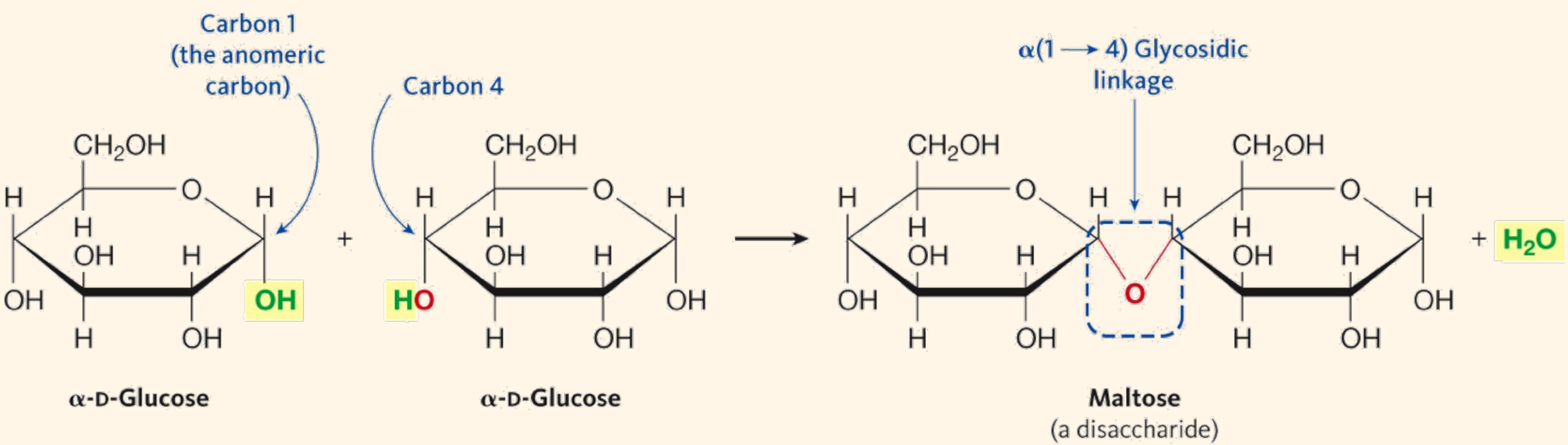


At least one of the -OH's is attached to the anomeric (hemiacetal) carbon

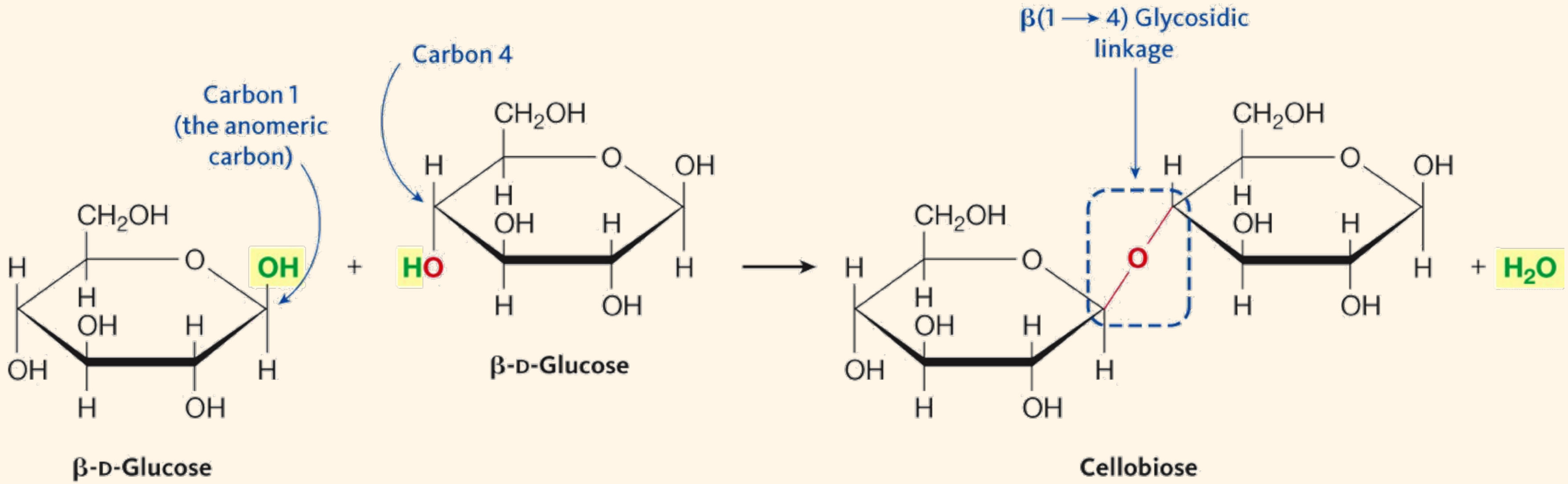
Glycosidic Linkages

- Glycosidic linkages are identified by the carbons that compose them.
- Maltose is a disaccharide with an α(1→4) glycosidic linkage. The link is between the OH on carbon 1 (originally α) of a glucose and carbon 4 of another glucose.



β (1→4) Glycosidic Linkage

- Cellobiose is a disaccharide with a β(1→4) glycosidic linkage. The link is between the OH on carbon 1 (originally β) of a glucose and carbon 4 of another glucose.

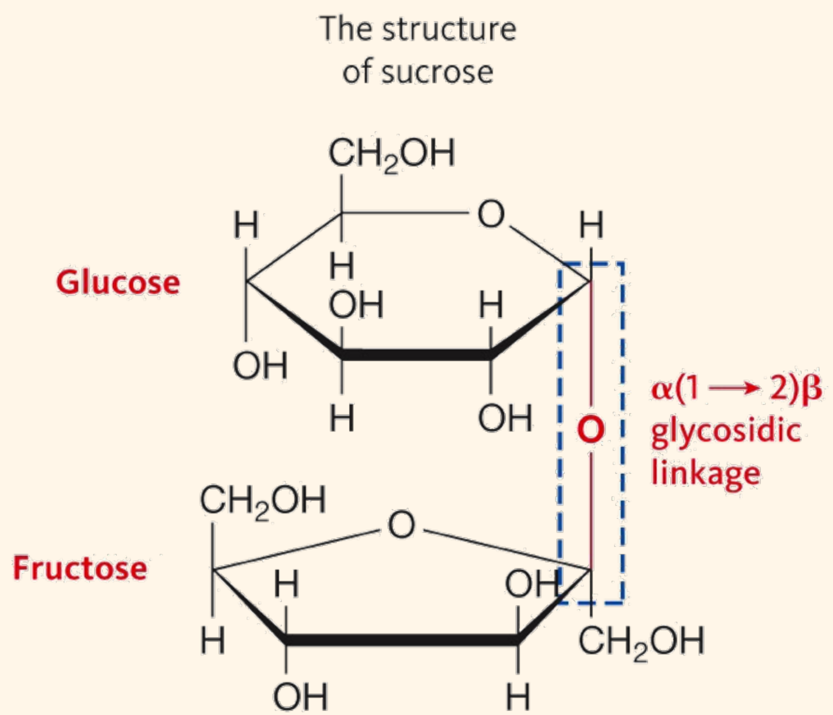


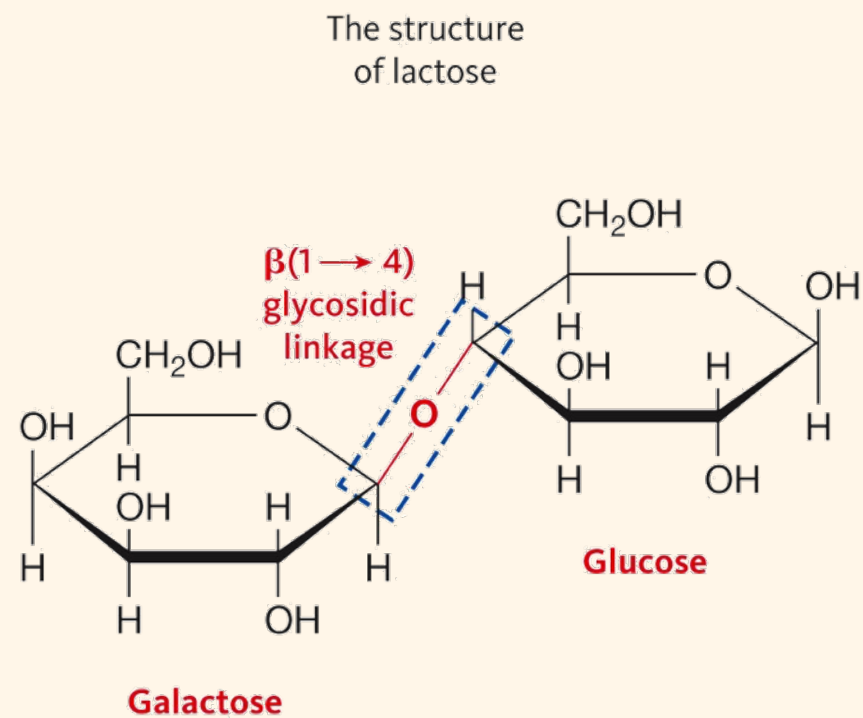
Nutritive Value

- Enzymes in the human digestive system can hydrolyze $\alpha(1\rightarrow4)$ glycosidic linkage but not $\beta(1\rightarrow4)$ glycosidic linkage.
- Therefore maltose, which is derived from start, can be broken down into glucose and used for energy by humans, while cellobiose, which is derived from cellulose, cannot.

15.4 Common Disaccharides and Polysaccharides

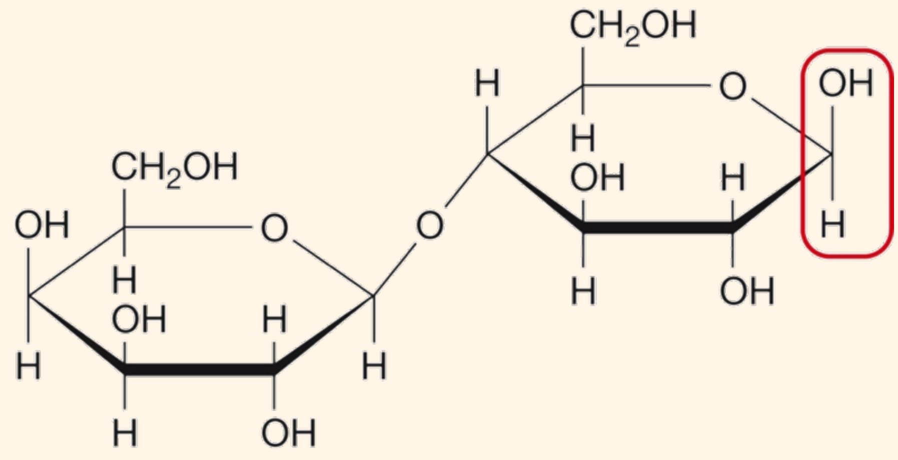
- Table sugar (sucrose) and milk sugar (lactose) are disaccharides.



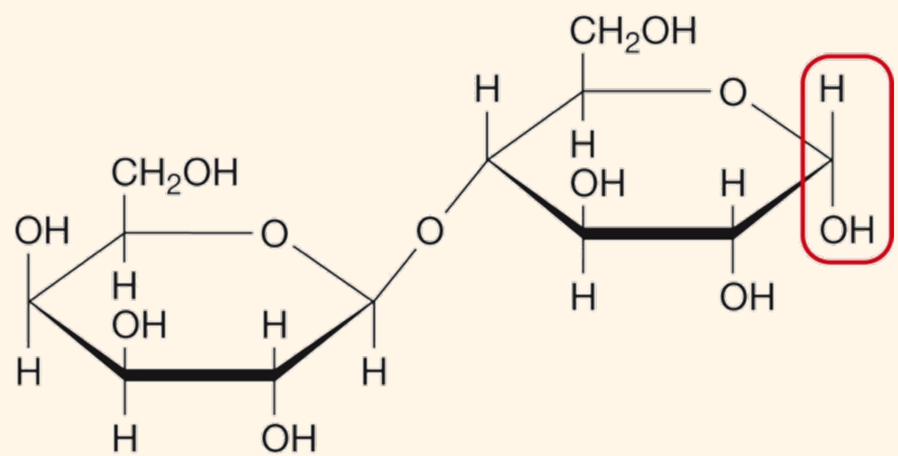


Lactose

- Lactose is a reducing sugar because it contains an hemiacetal group.
- The right had ring in lactose can undergo **mutarotation** so both α- and β-anomers of lactose exist in solution



β-Lactose



α-Lactose

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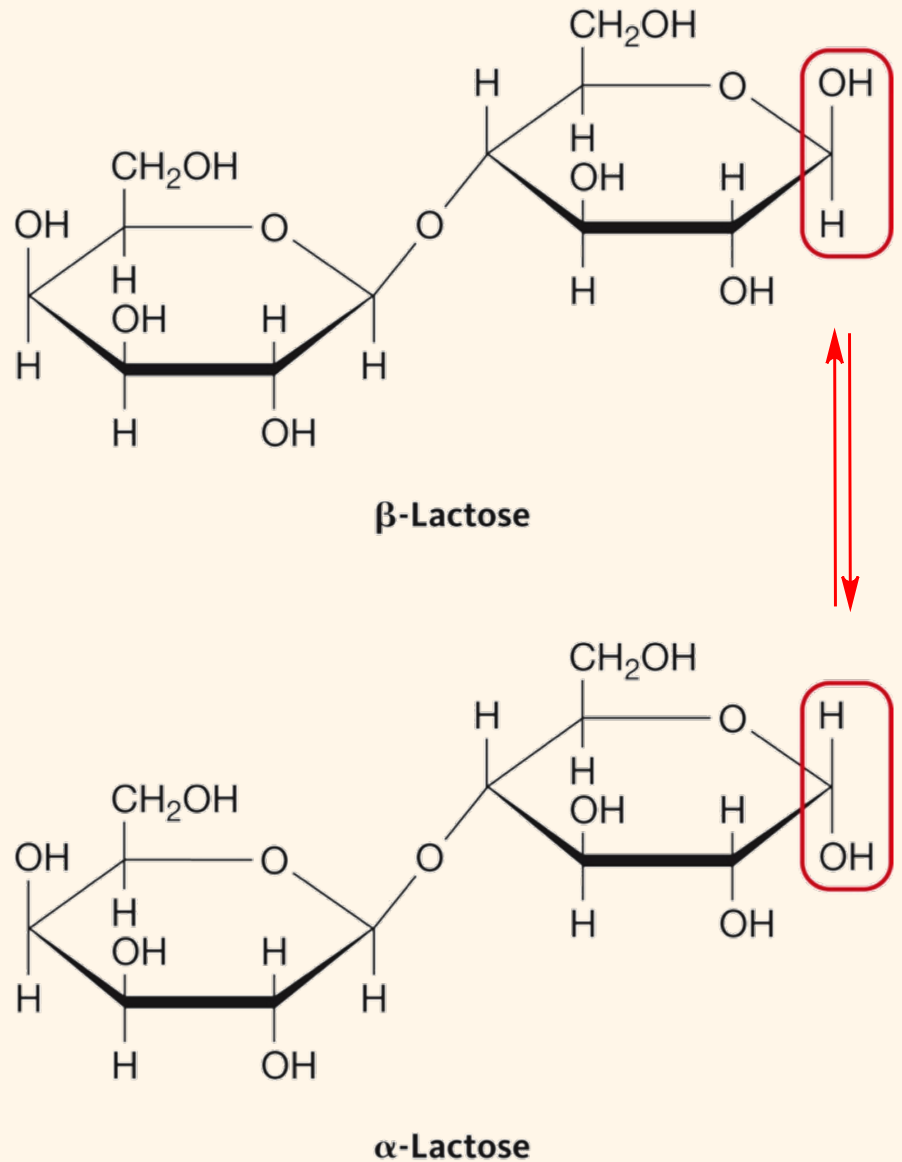
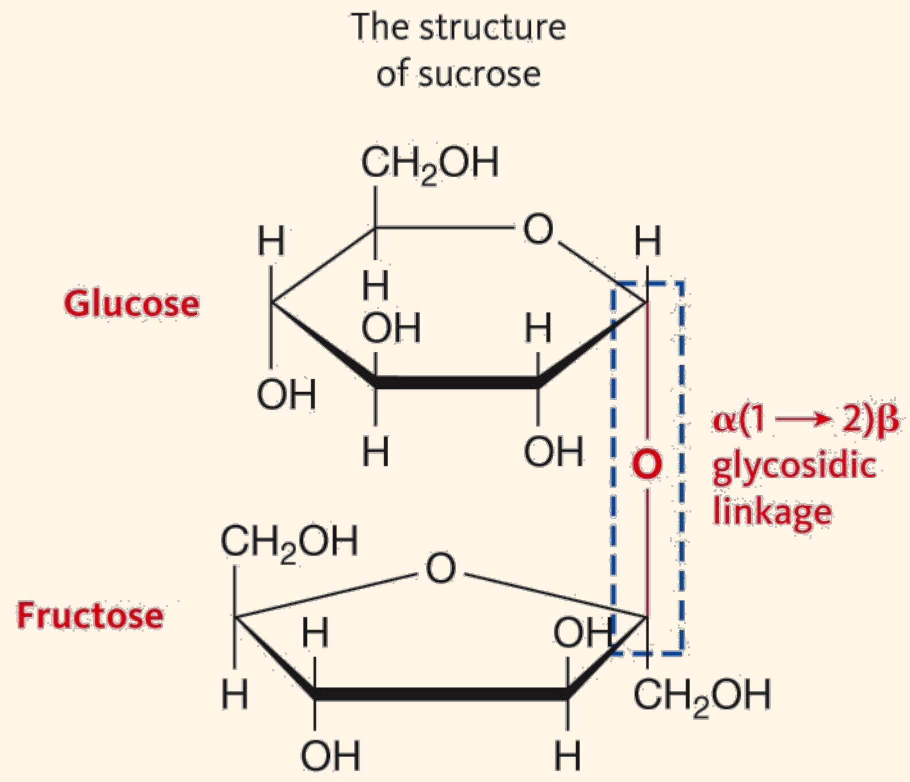


Sucrose

- Sucrose does not contain an hemiacetal and therefore is not a reducing sugar.
- As such, it can not undergo mutarotation and there is only one form of sucrose.

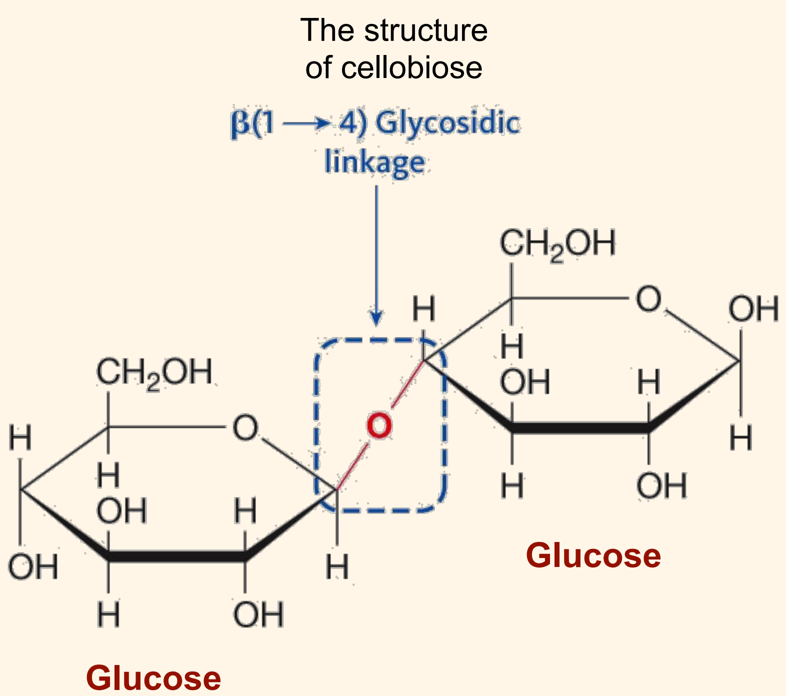


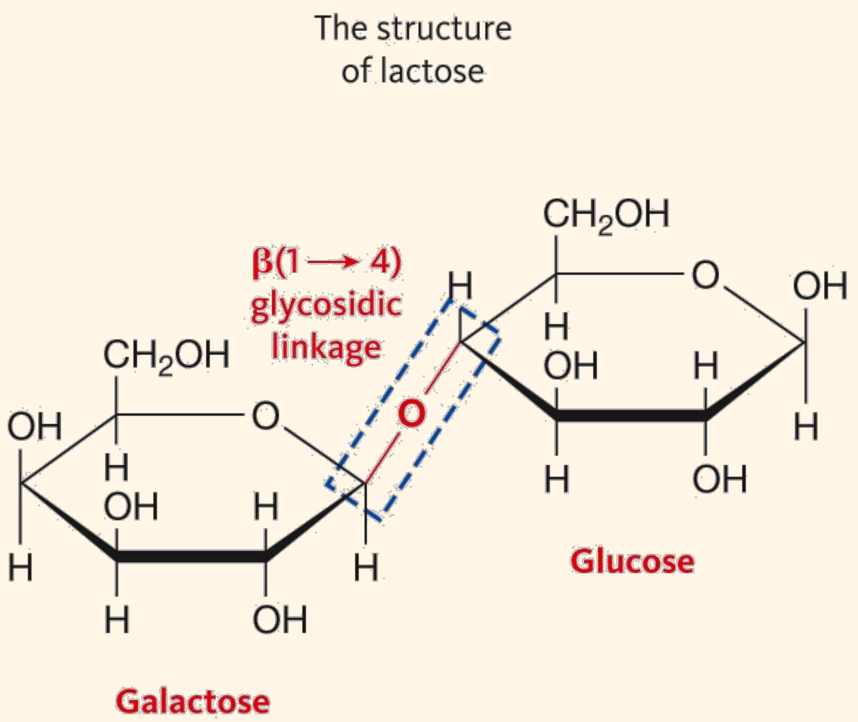
Enzymes

- Sucrase is the enzyme that breaks down sucrose, and the human digestive tract makes ample amounts of sucrase.
- Lactase is the enzyme that breaks down lactose. Infants have sufficient lactase, but after 1-2 years of age humans and most mammals make less lactase, leading to lactose intolerance in some adults.
  - A genetic mutation in some groups of humans (northern Europeans and certain African groups) allow them to continue to make lactase into adulthood.

15.4 Common Disaccharides and Polysaccharides

- Unlike the β(1→4) glycosidic bond in cellobiose, many people have the enzyme lactase, which allows them to hydrolyze the β(1→4) glycosidic bond in lactose.





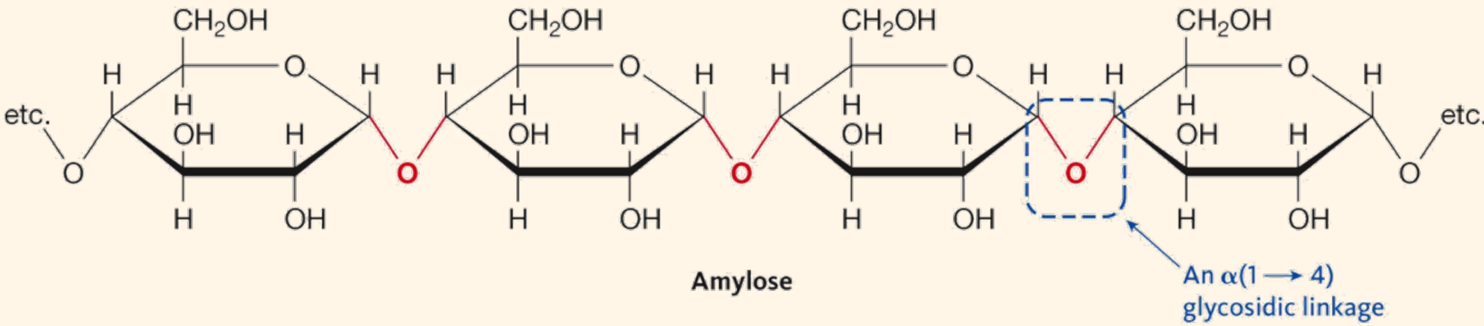
Polysaccharides

- Polysaccharides (complex carbohydrates), are long chains of monosaccharide units.
  - Storage polysaccharides are energy sources for animals and plants.
    - Examples: Starch and Glycogen
  - Structural polysaccharides are used to build structural components such as plant fibers and the shells of many animals.
    - Examples: Cellulose and Chitin

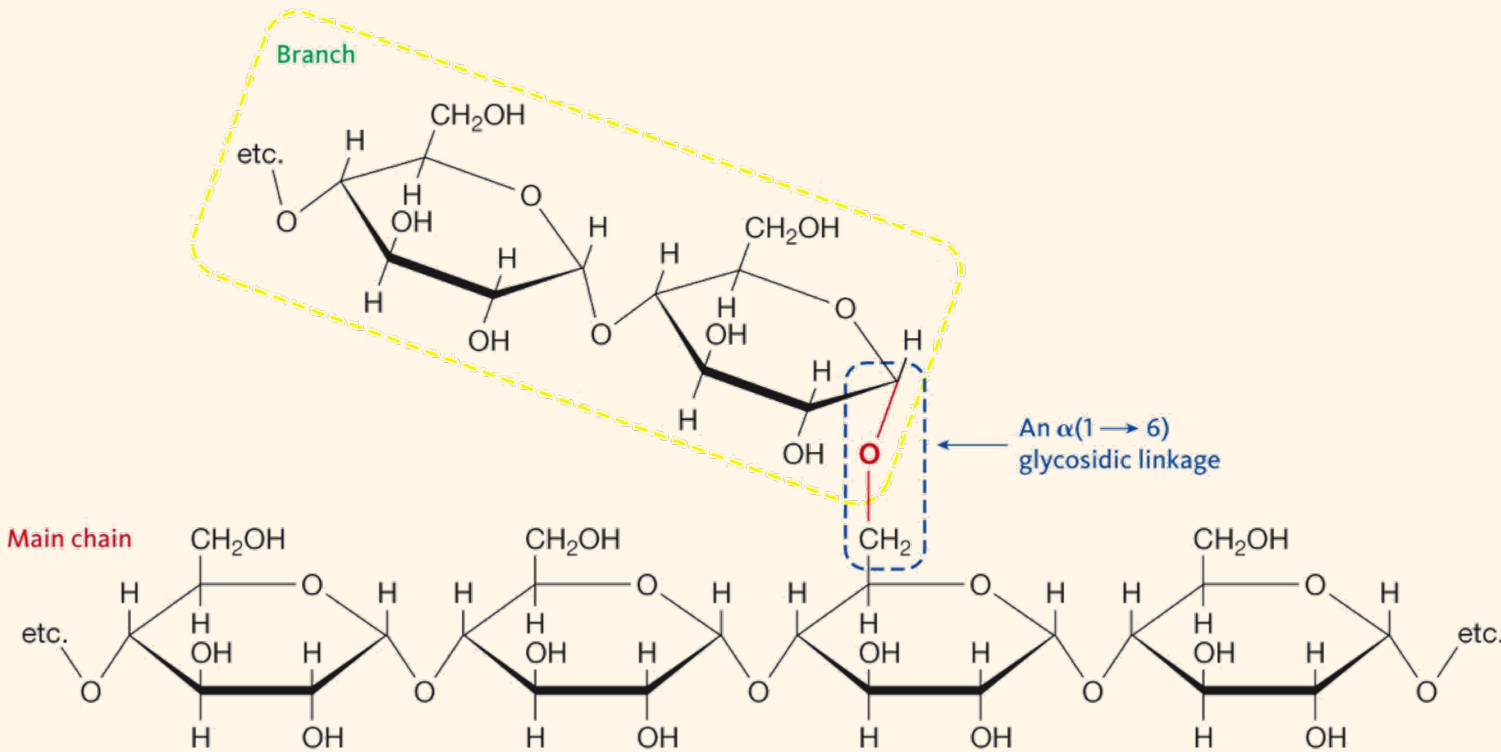
Starch

- There are two types of starch, amylose and amylopectin.
- **Amylose** comprises glucose units connected by an $\alpha(1\rightarrow4)$ glycosidic linkages.
- **Amylopectin** also comprises glucose units connected by $\alpha(1\rightarrow4)$ glycosidic linkages but it also has some $\alpha(1\rightarrow6)$ glycosidic linkages, which creates branchs every 25 to 30 units.
  - Many plants, such as rice, potatoes, and bananas, contain starch. Dried starches are often used for energy storage in plants and are difficult to digest, but cooking restores the water and makes them digestible.

Amylose and Amylopectin



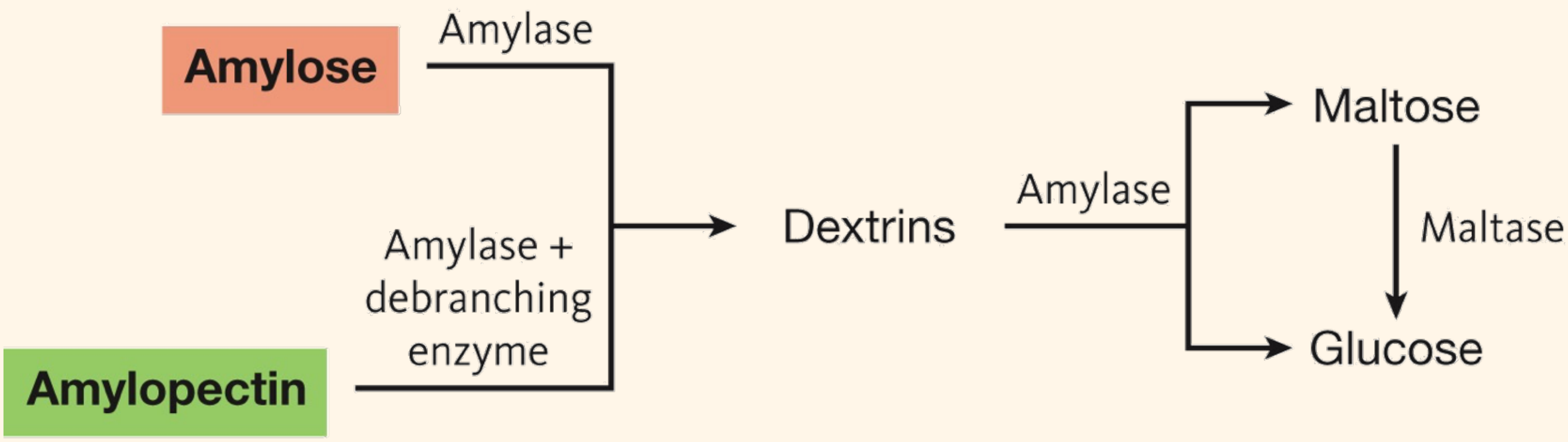
Amylose



Amylopectin

Digestion of Amylose and Amylopectin

- Amylose is digested using the enzyme amylase.
- Amylopectin requires amylase and an additional debranching enzyme to break the α(1→6) glycosidic linkage

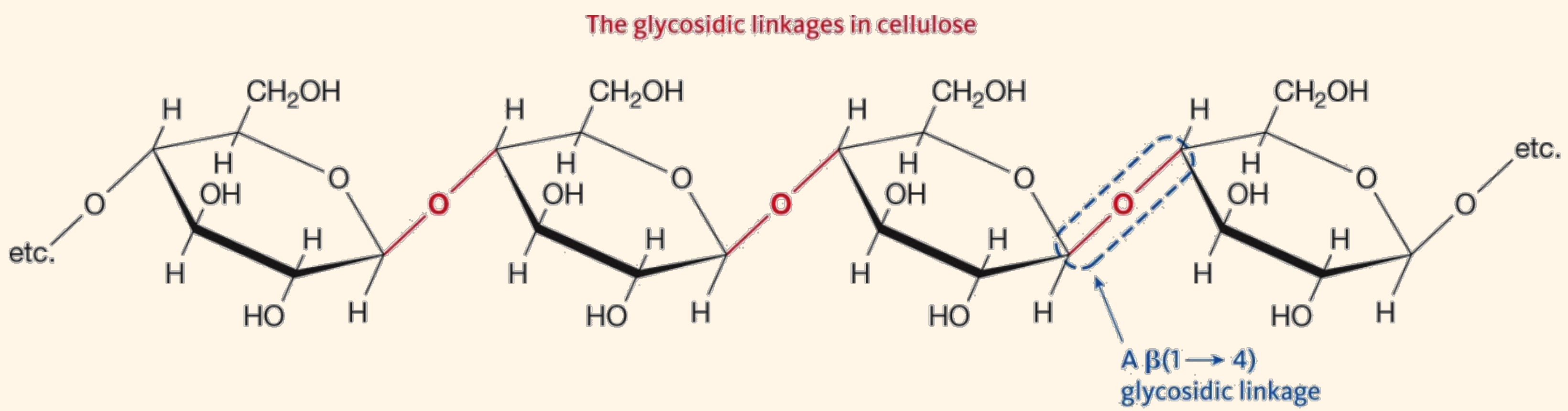


Glycogen

- Glycogen, used in animals as glucose storage, is similar to amylopectin, except glycogen is much larger and has branches occurring every 8-12 glucose units.
- Glycogen is made and stored in the liver and in the muscles.
  - Between meals, the liver breaks down glycogen and releases glucose into the blood to maintain a steady blood glucose level.
  - The muscles store glycogen for future energy needs.

Cellulose

- Cellulose is composed of glucose units with β(1→4) glycosidic linkages.
- Cellulose chains lie side by side and form a huge number of hydrogen bonds, making strong fibers.



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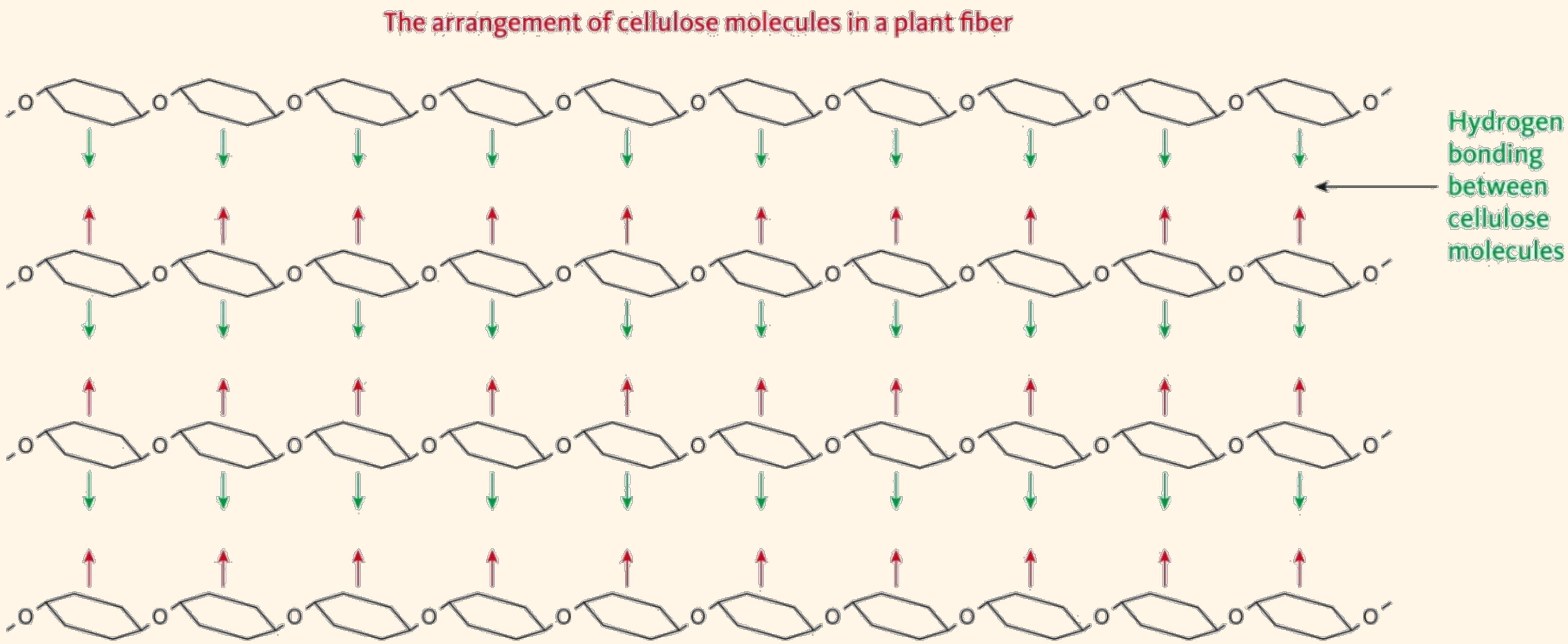
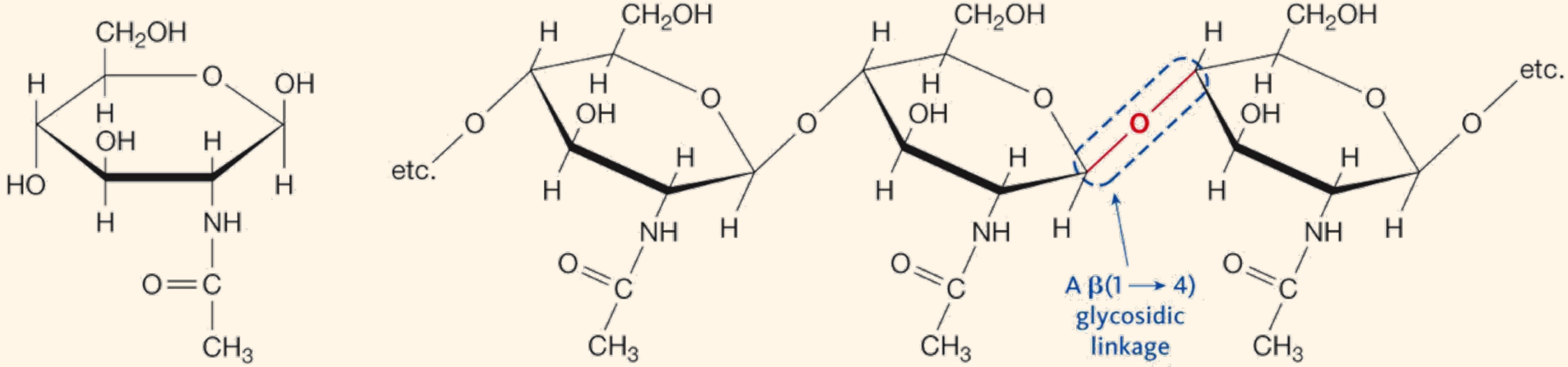


Chitin

- The shells of insects and crustaceans is made of **chitin.**
  - Chitin is similar to cellulose except that it comprises a modified glucose (N-acetylglucosamine).



N-Acetylglucosamine
(β anomer)

Chitin

- Like cellulose, humans are unable to hydrolyze the β(1→4) glycosidic linkages in chitin, so like cellulose, chitin is not digestible by humans.

Summary

TABLE 15.3 The Common Disaccharides and Polysaccharides

Compound	Made from	Types of Glycosidic Linkages	Function	Digestible by Humans
Lactose	Galactose + glucose	$\beta(1\rightarrow4)$	Primary carbohydrate in milk	Yes, but many people lose the ability as adults (requires **lactase**)
Sucrose	Glucose + fructose	$\alpha(1\rightarrow2)\beta$	Primary sugar in plants (fruits, nectar, etc.)	Yes (requires **sucrase**)
Amylose	Glucose	$\alpha(1\rightarrow4)$	Fuel storage in plants (one of the forms of starch)	Yes (requires **amylase**)
Amylopectin	Glucose	$\alpha(1\rightarrow4)$ $\alpha(1\rightarrow6)$ at branch points	Fuel storage in plants (one of the forms of starch)	Yes (requires **amylase** and a **debranching enzyme**)
Glycogen	Glucose	$\alpha(1\rightarrow4)$ $\alpha(1\rightarrow6)$ at branch points	Fuel storage in animals (sometimes called "animal starch")	Yes (requires **amylase** and a **debranching enzyme**)
Cellulose	Glucose	$\beta(1\rightarrow4)$	Structural material in plants	No (requires **cellulase**)
Chitin	*N*-acetylglucosamine	$\beta(1\rightarrow4)$	Structural material in insects, crabs, etc.	No (requires several enzymes)

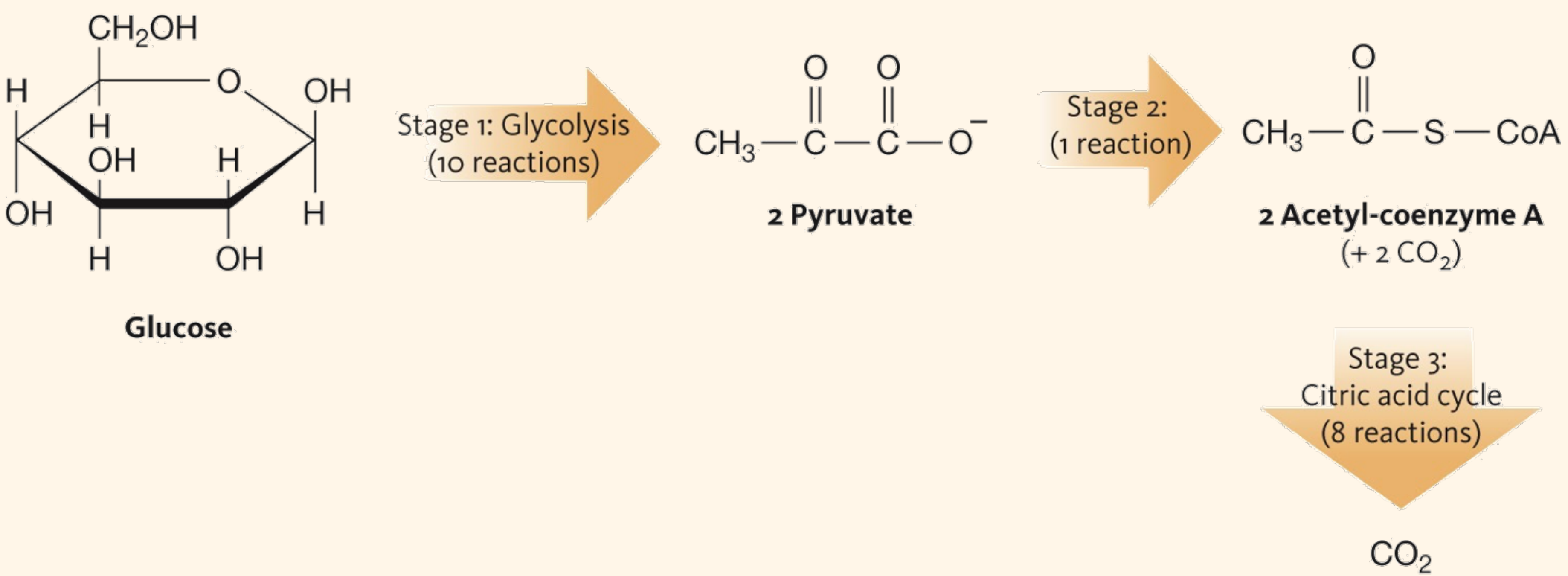
15.5 Carbohydrate Catabolism

- Carbohydrates are the primary energy source for our bodies, with glucose being the most important monosaccharide that can be used as energy by every cell.
- Glucose is broken down in three steps, but is sometimes written as one simple combustion reaction: $C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$
- This complete process involves 19 reactions

Glucose Catabolism in Three stages

- Stage 1 Glycolysis: Glucose is broken down into 2 pyruvate ions in 10 reactions. These can be used to build other molecules and can also be converted back to glucose.
- Stage 2: Pyruvate ions are converted to acetyl-coenzyme A. This cannot be converted back to glucose and this reaction commits the cell to break down the glucose
- Stage 3 Citric Acid Cycle (Krebs Cycle): Acetyl-coenzyme A is broken down into CO_2 in a series of 8 reactions.

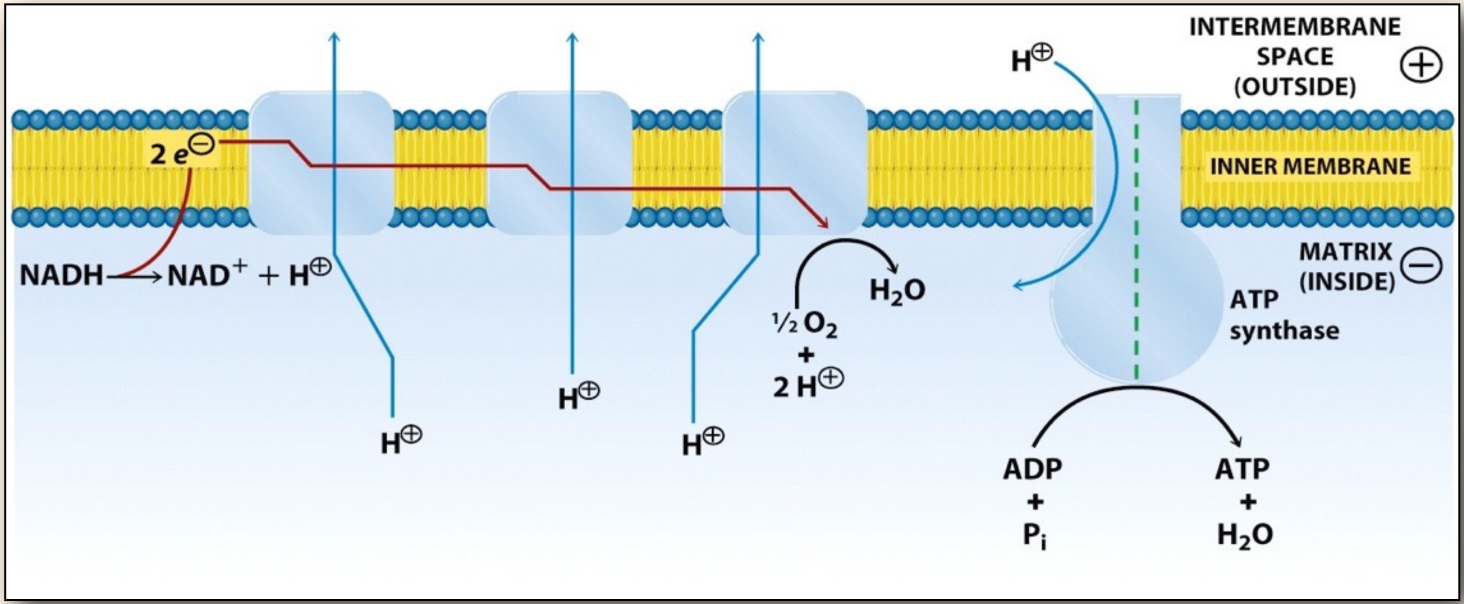
Catabolism of Glucose



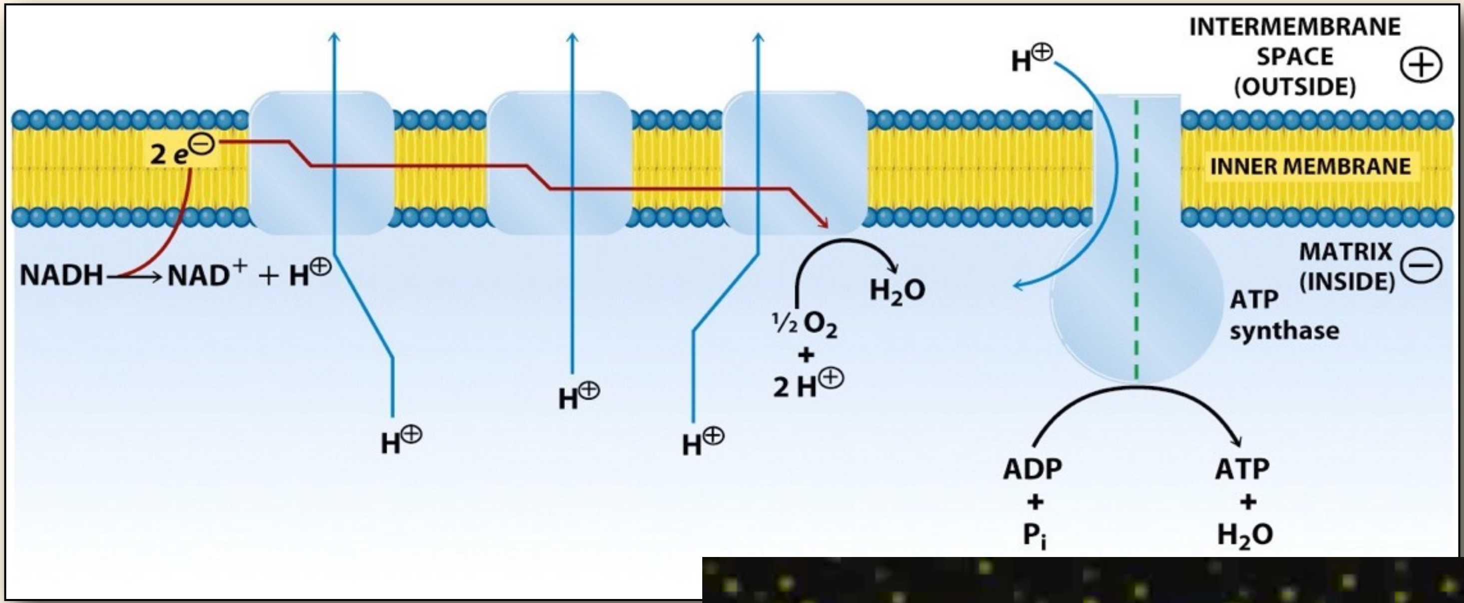
Energy Stored in High Energy Molecules

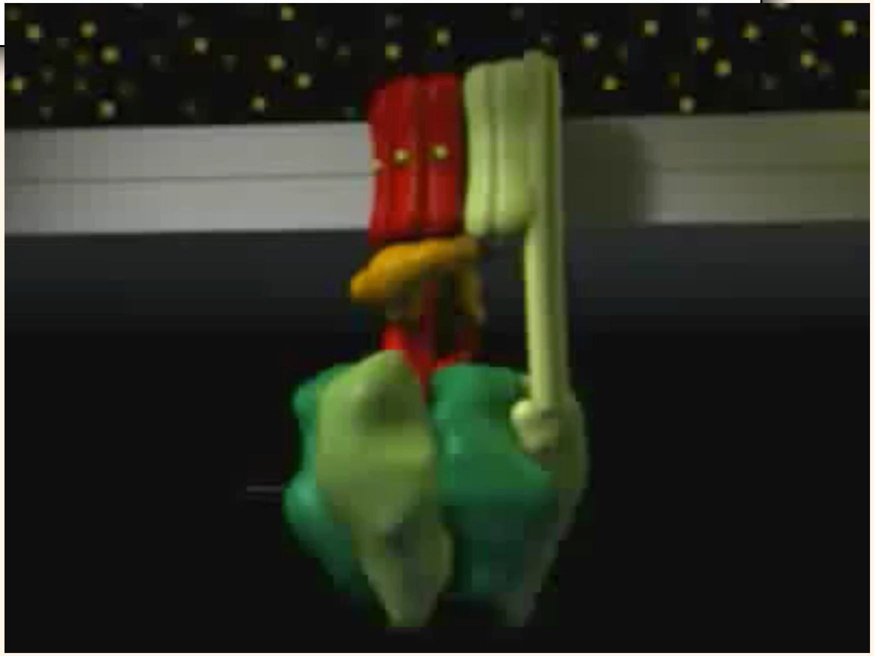
- Each stage of glucose oxidation produces molecules that store energy for our bodies to use
  - ATP, reduced NADH and reduced $FADH_{2.}$ Our bodies can produce ATP by the oxidizing NADH and $FADH_2$
  - One molecule of NADH = 2.5 molecules of ATP
  - One molecule of $FADH_2$ = 1.5 molecules of ATP

Electron Transport Chain and ATP Synthase

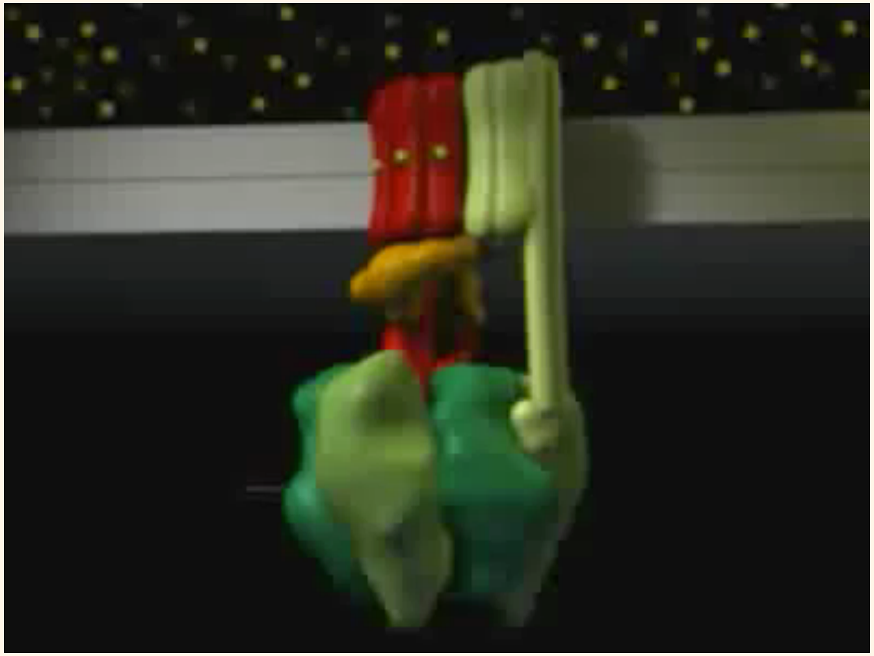


Electron Transport Chain and ATP Synthase





Electron Transport Chain and ATP Synthase



High energy molecules produced during glucose catbolism

TABLE 15.4 High-energy Molecules Produced During Glucose Catabolism

Stage	Number of High-energy Molecules Produced	Total Number of High-Energy Molecules per Molecule of Glucose	Total ATP Yield
1 (glycolysis)	2 ATP 2 NADH	2 ATP 2 NADH	7
2	1 NADH per pyruvate ion	2 NADH	5
3 (citric acid cycle)	1 ATP 3 NADH 1 $FADH_2$ per acetyl-CoA	2 ATP 6 NADH 2 $FADH_2$	20
TOTAL		4 ATP 10 NADH 2 $FADH_2$	32

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O_2 is used to reoxidize the NADH and $FADH_2$ to NAD^+ and FAD

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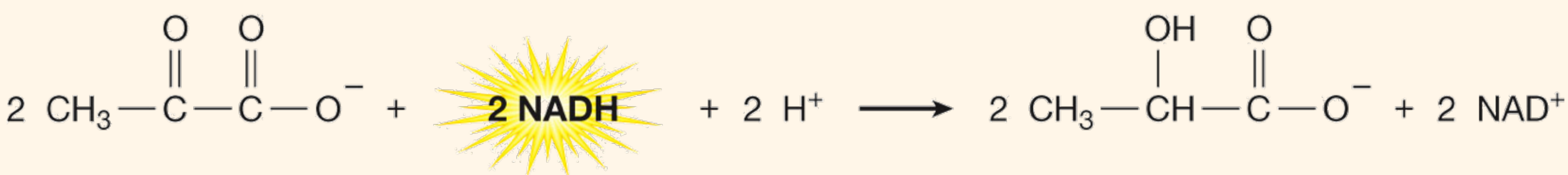
Without O_2, the pyruvate formed from glycolysis does not go on to enter Stages 2 and 3.

O_2 is used to reoxidize the NADH and $FADH_2$ to NAD^+ and FAD

Lactic Acid Fermentation

- Fermentations are anaerobic, meaning they do not require oxygen. When we need an immediate source for ATP for a brief exertion, our bodies can use lactic acid fermentation.
- Muscles use this pathway for energy, and lactate build-up in muscles is responsible for soreness.
- The pathway picks up with pyruvate after the 10 reactions of glycolysis



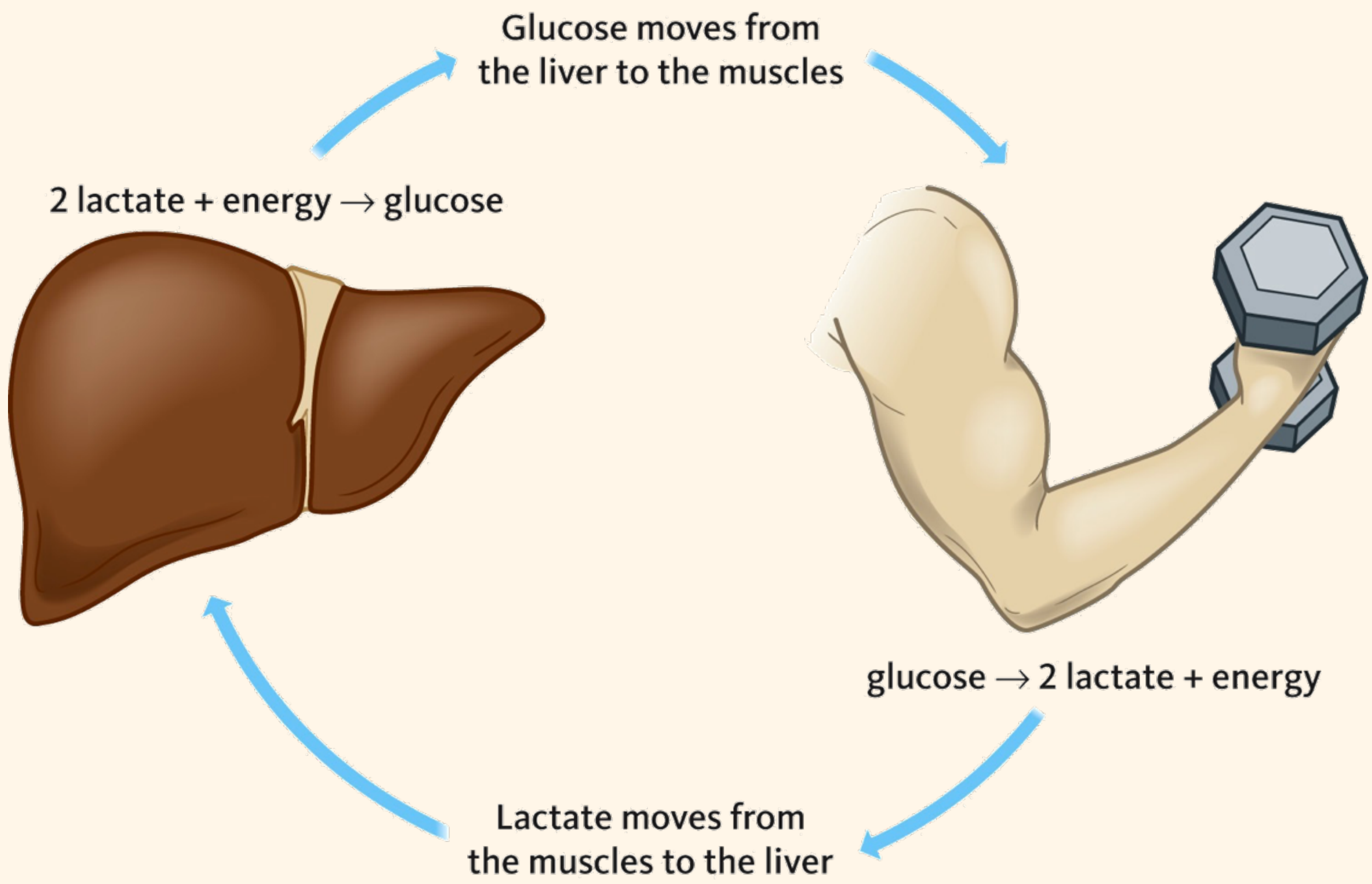
Pyruvate **Lactate**

Lactic Acid Fermentation

- The 2 NADH that were produced in glycolysis are consumed in lactic acid fermentation, so the only high energy products that are formed from pyruvate in lactic acid fermentation are 2 molecules of ATP.
- Therefore, it is not very efficient at getting energy from glucose, but is a fast process ideal for intense muscle effort.

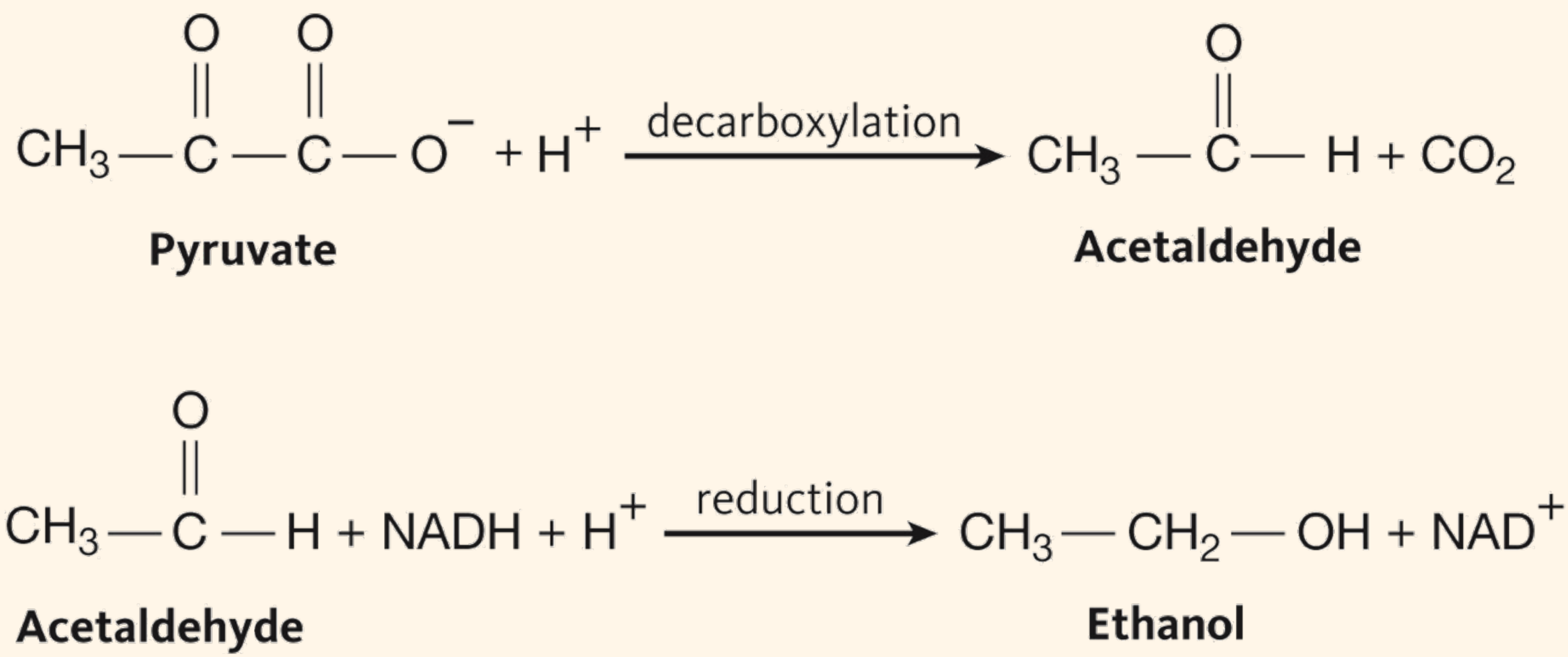
Cori Cycle

- The liver converts lactate from the muscles back to glucose



Alcoholic Fermentation

- Yeast and some bacteria convert glucose into ethanol and carbon dioxide, a two step process which also consumes the NADH produced in glycolysis.



Next Up

- Unit 12 - Lipids and Membranes
- Exam III - Units 9-11