



BIOCHEMISTRY

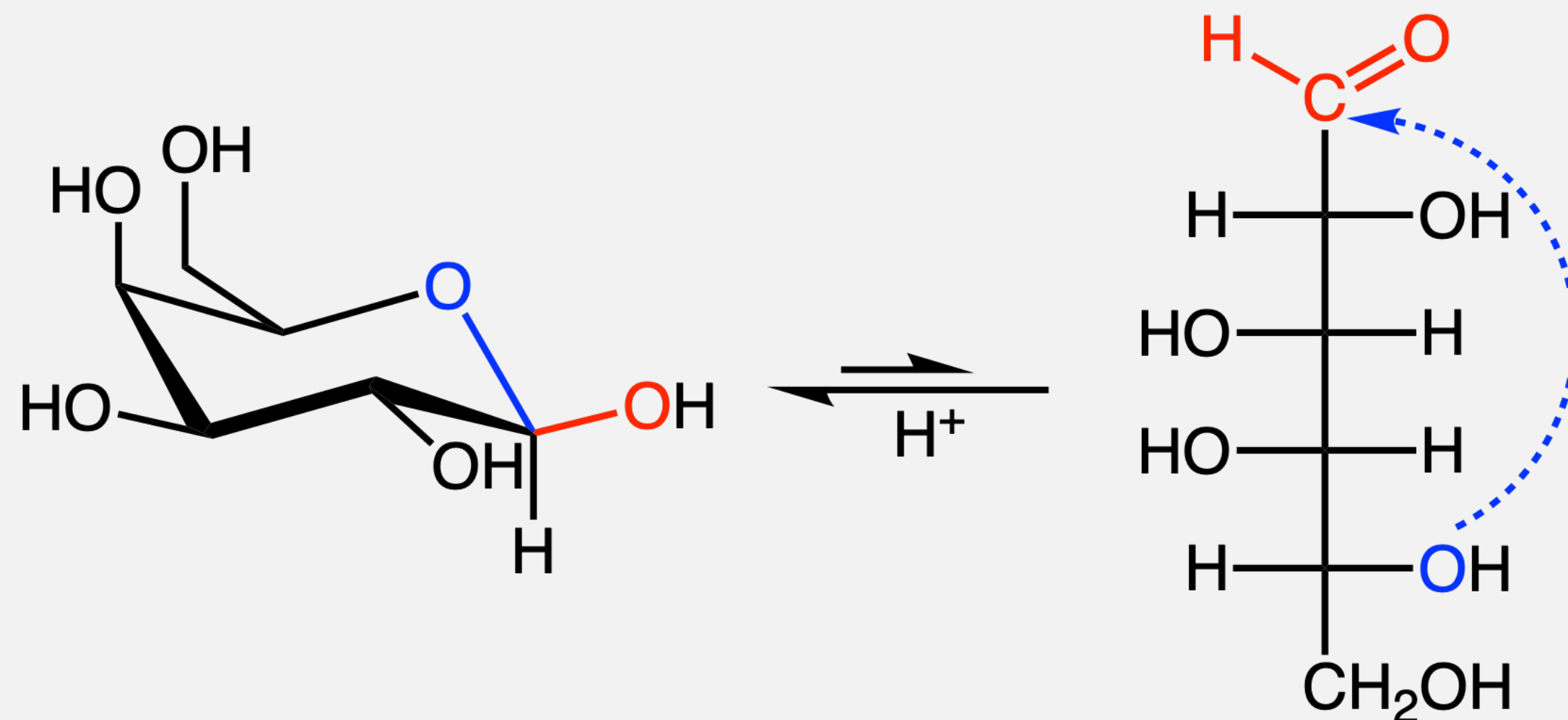
GLYCOSIDES & REDUCING SUGARS

CHEMISTRY 165 // SPRING 2020

Sugars: open-chain \rightleftharpoons cyclic

Recall that in acidic (H^+) media, sugars exist predominantly in their cyclized form: furanoses and pyranoses. This means that the cyclic form is in equilibrium with the open-chain/linear form (aldoses and ketoses).

Consider the equilibrium between D-galactose and β -D-galactopyranose – note the unequal equilibrium arrows (\rightleftharpoons) indicate that the pyranose form is favored.



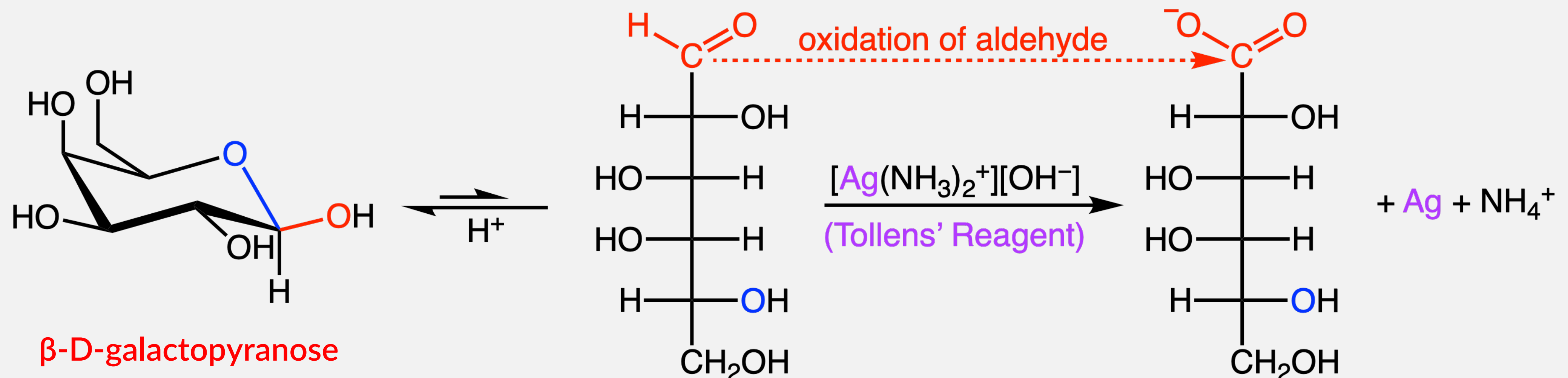
β -D-galactopyranose

D-galactose
(aldohexose)

Tollens' reagent: Test for reducing sugars

Recall that in acidic (H^+) medium sugars exist predominantly in their cyclized form: furanoses and pyranoses. but they are in equilibrium with their open-chain/linear form (aldoses and ketoses).

Consider the equilibrium between D-galactose and β -D-galactopyranose – note the unequal equilibrium arrows (\rightleftharpoons) indicate that the pyranose form is favored.

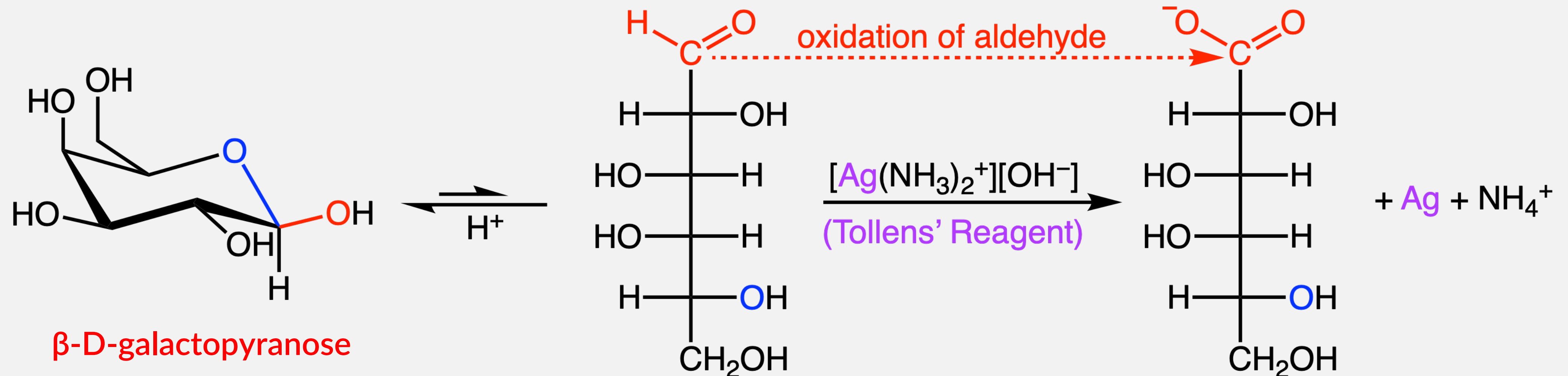


D-galactose is called a reducing sugar because:

If we add the Tollens' reagent $[Ag(NH_3)_2^+][OH^-]$ to the equilibrium solution, the **sugar's aldehyde group is oxidized to a carboxylic acid group** (deprotonated) and the Ag^+ reduced to Ag (s).

Tollens' reagent: What won't react?

Consider the equilibrium between D-galactose and β -D-galactopyranose – note the unequal equilibrium arrows (\rightleftharpoons) indicate that the pyranose form is favored.



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If we add the Tollens' reagent $[Ag(NH_3)_2^+][OH^-]$ to the equilibrium solution, the **sugar's aldehyde group is oxidized to a carboxylic acid group** (deprotonated) and the Ag^+ reduced to Ag (s).

The Tollens' reagent will only act on the open-chain form (D-galactose) and not the β -D-galactopyranose.

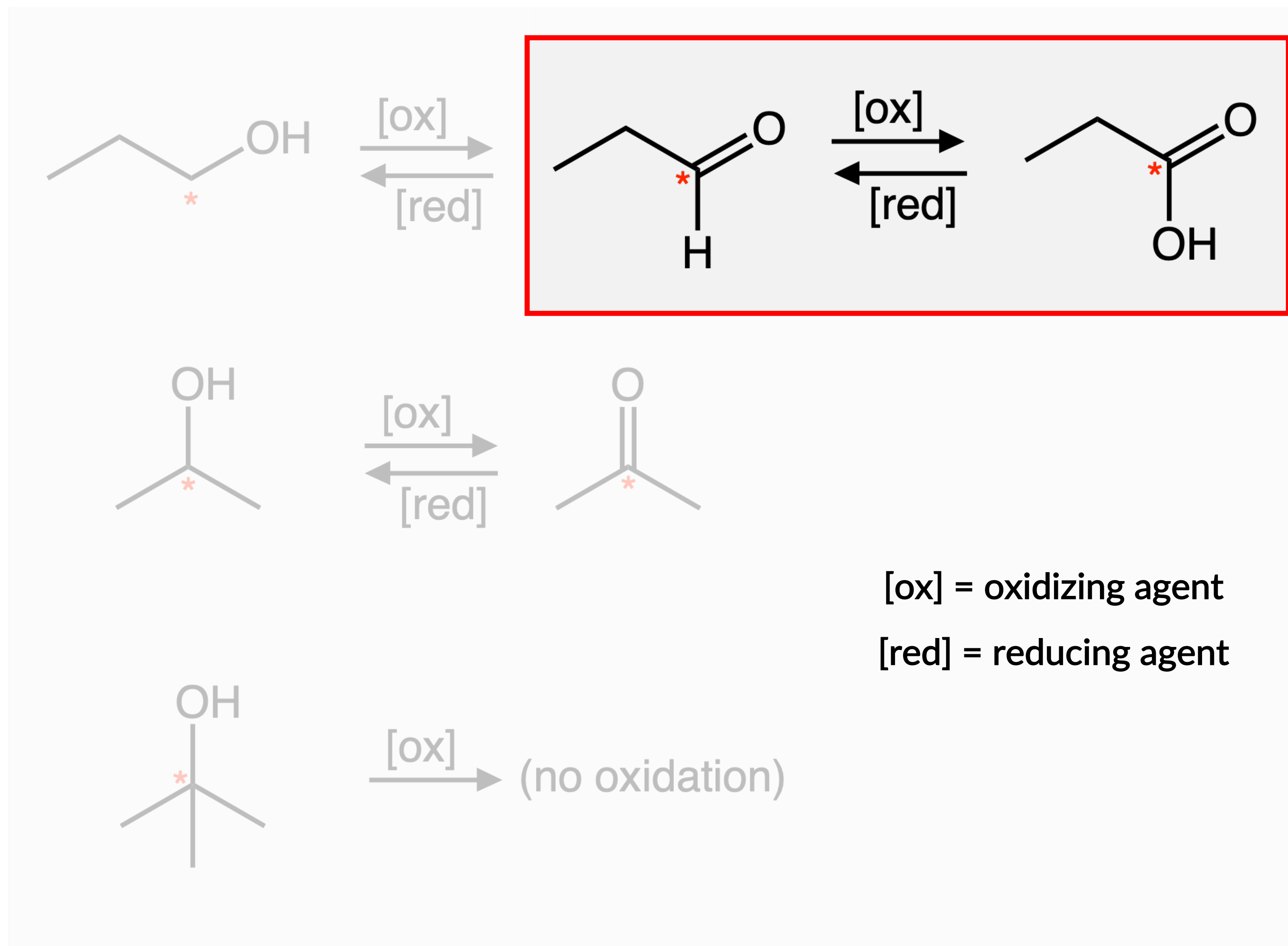
The Tollens' reagent will only act on aldoses, which contain the aldehyde group, and not ketoses.

Recall: Oxidation of aldehydes

We have a slightly different mechanism by which reductions and oxidations (redox) occur in organic chemistry. Electrons are still being gained or lost.

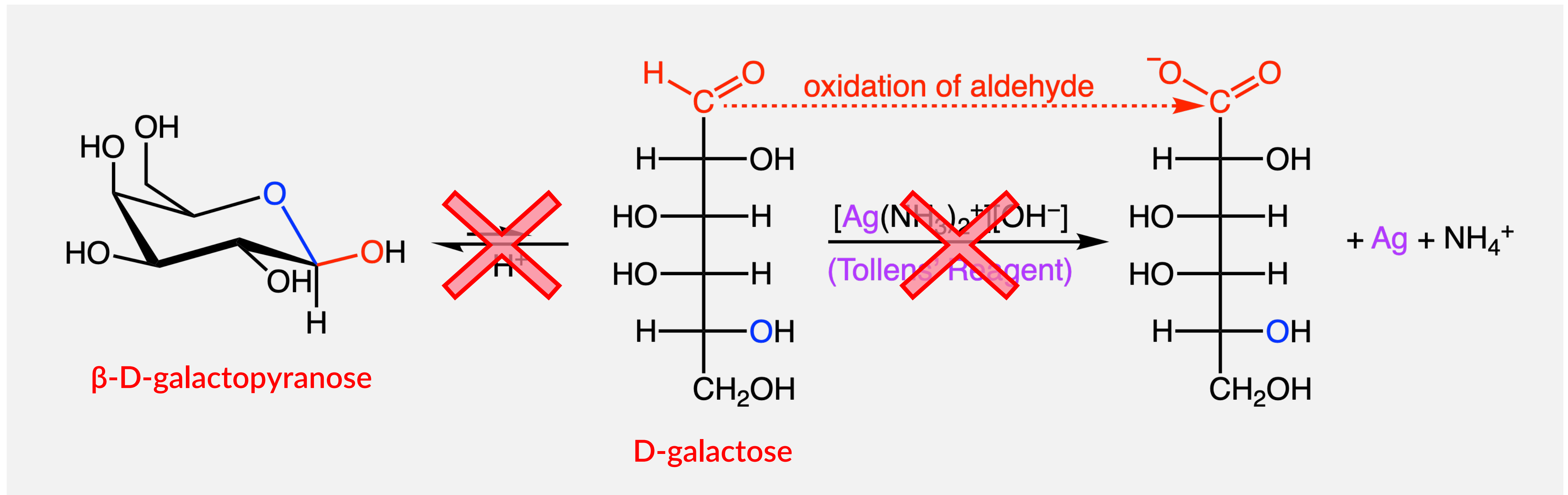
Oxidation: Carbon atom (*) loses electrons by losing C-H bonds and gains a C-O bond.

Because the O atom is more electronegative, it pulls the electrons away from the carbon atom, effectively oxidizing the C atom.



A query to consider

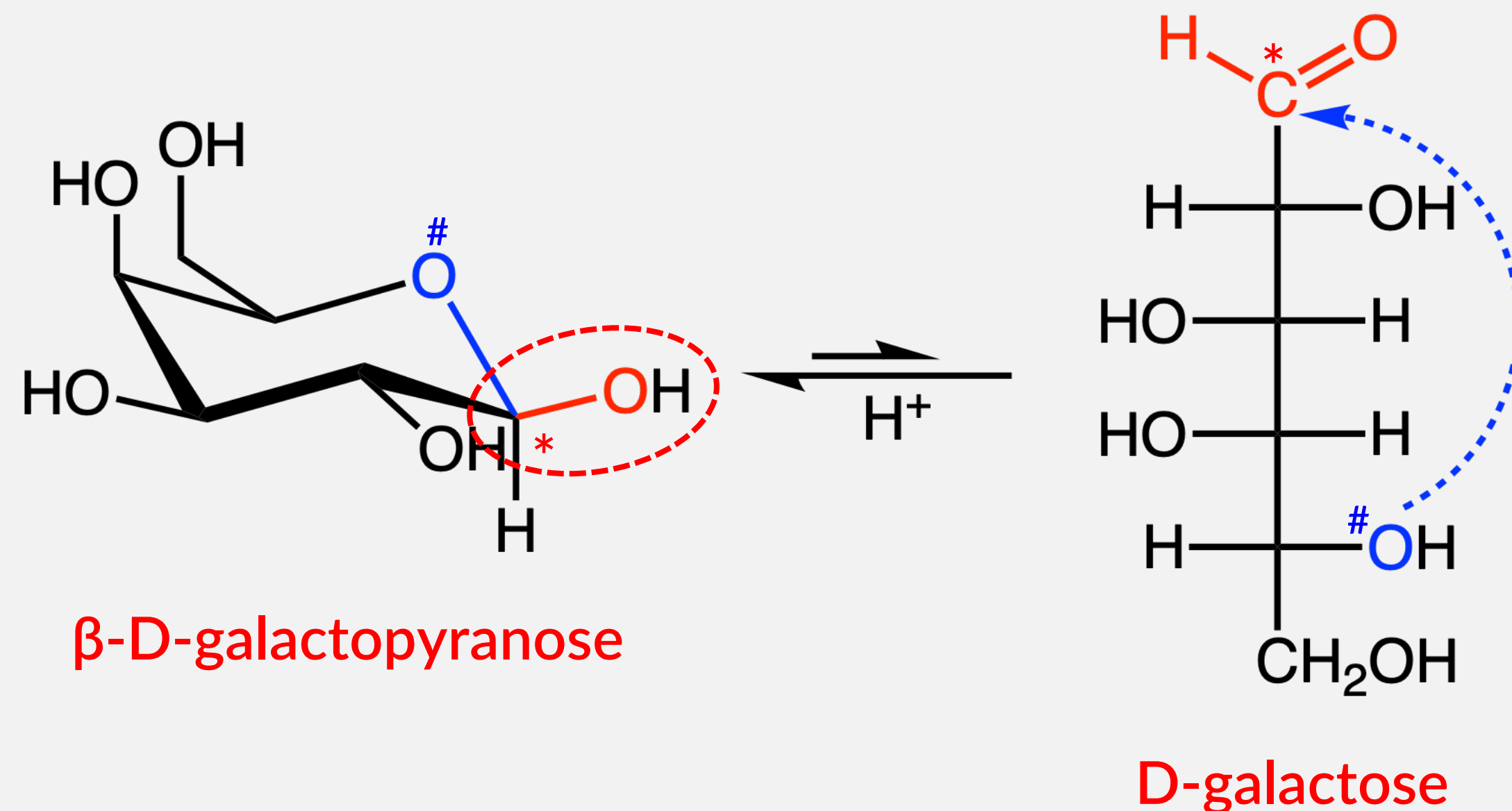
Because the Tollens' reagent only acts on the aldehyde group of aldoses in their open-chain form, we can prevent oxidation of the sugar from occurring if we stop the ring from opening into the open-chain form.



But how do we prevent the ring from opening?

What causes ring-opening anyway?

Because the Tollens' reagent only acts on the aldehyde group of aldoses in their open-chain form, we can prevent oxidation of the sugar from occurring if we stop the ring from opening into the open-chain form.

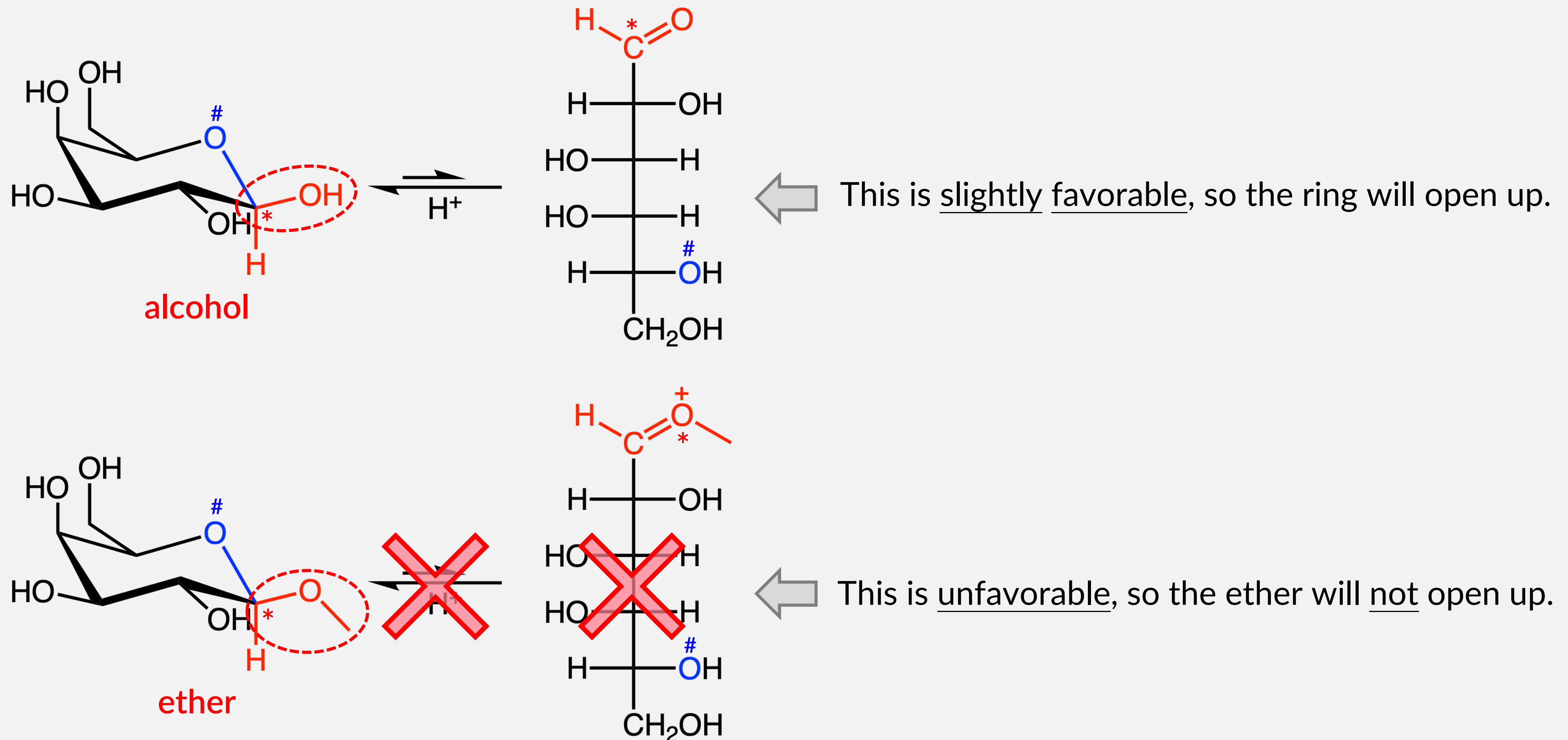


What allows this ring-opening and ring-closing equilibrium to occur in a sugar solution is the free **C-OH group** on the anomeric carbon (marked with *****) that forms a new bond to the **-OH group** on the bottom-most chiral center (marked with a **#**).

So we need to remove the C-OH group!

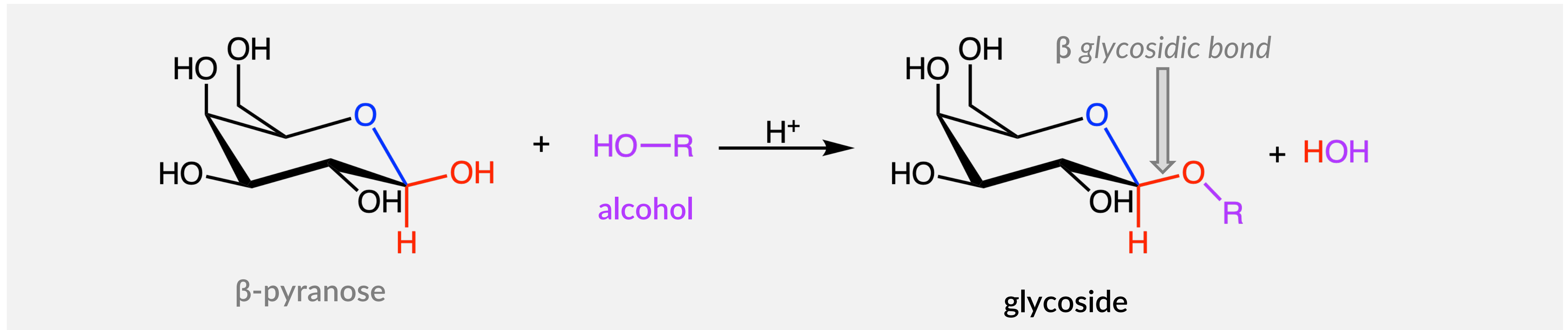
Ethers don't ring-open

We can stop the ring-opening by changing the alcohol group (C-OH) into an ether group (C-O-C), which will not allow the ring to open up.



Glycosidic bonds protect sugars from oxidation

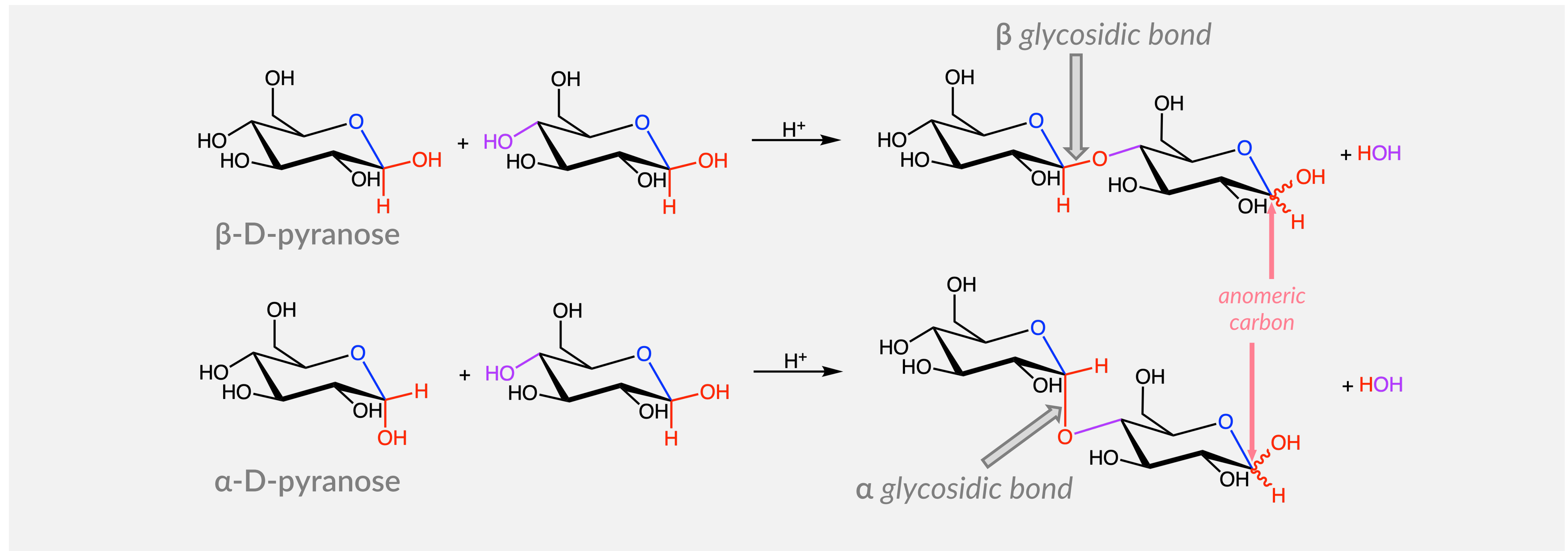
We can use a condensation reaction to change the alcohol group to an ether group.



In such a condensation reaction, we convert the pyranose (or could have been a furanose) into an ether-containing compound called a glycoside and the $\text{C}-\text{OR}$ bond is called a glycosidic bond.

Polysaccharides as glycosides

More often, glycosides are formed between multiple sugar molecules (polysaccharides).



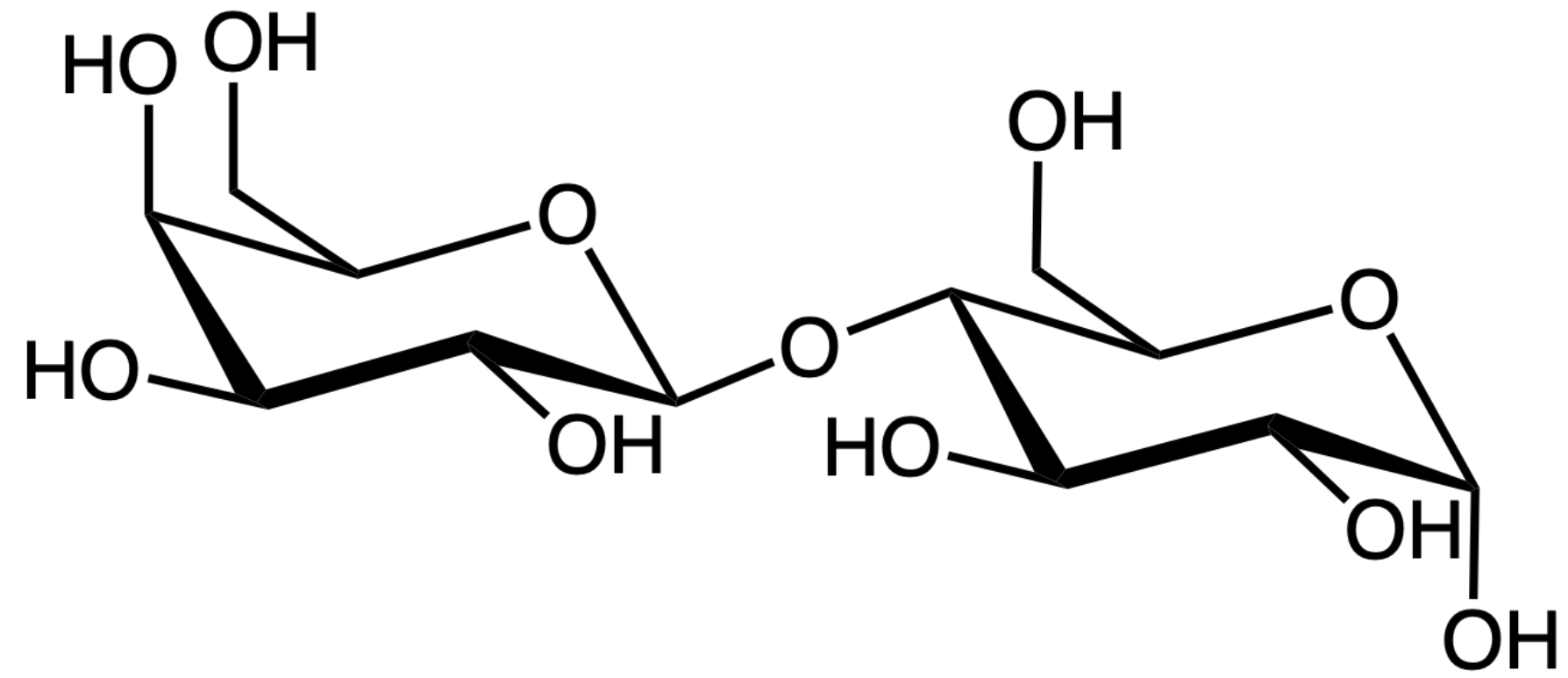
Depending on the anomeric carbon of the left-most sugar, you can form either an α or β glycosidic bond. Obviously, you can connect the second sugar using a different -OH than the one I chose (shown in purple), and those would be different types of glycosides.

PRACTICE PROBLEM 1

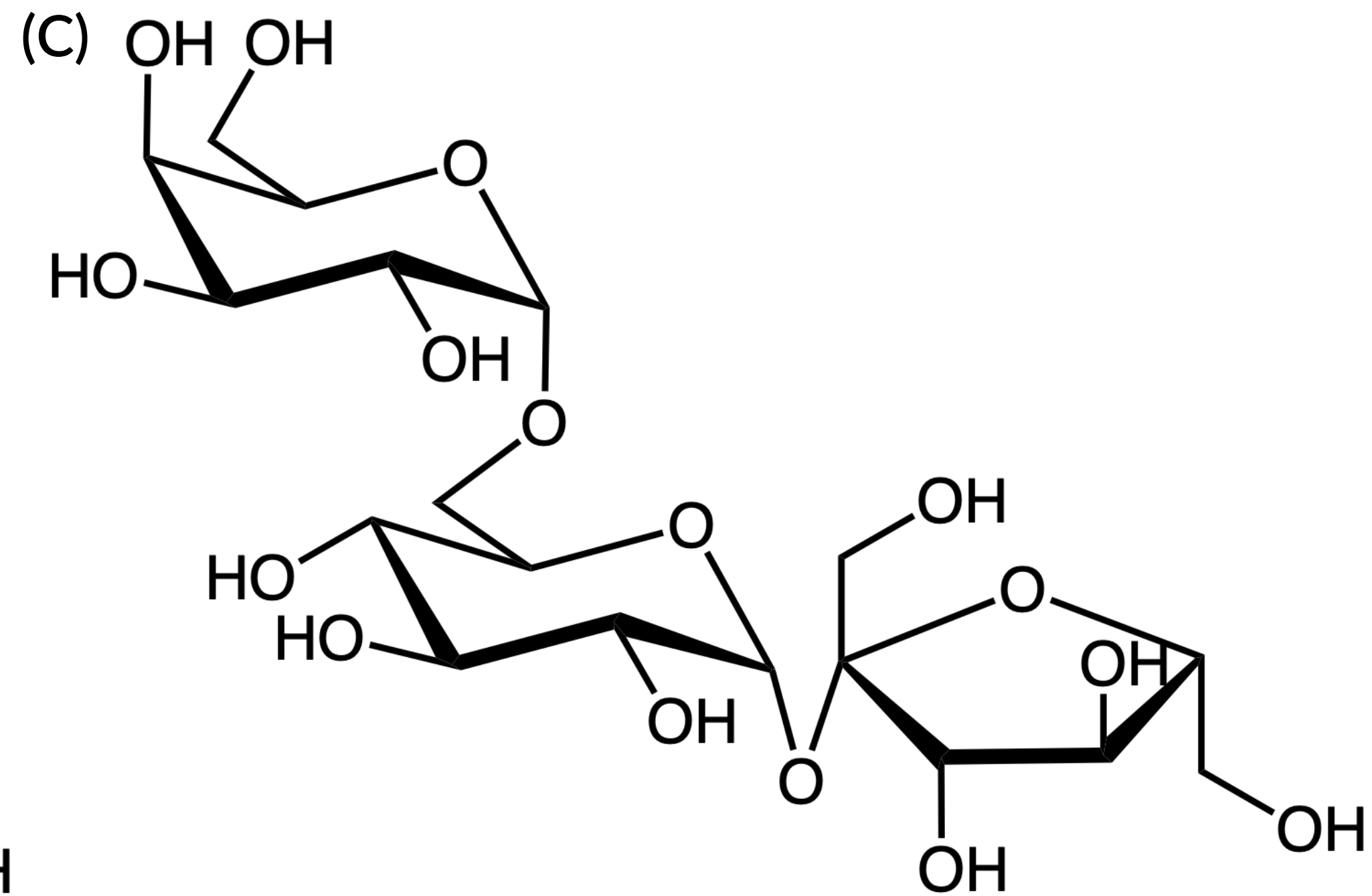
Which of the following polysaccharides are reducing sugars?

— answer —

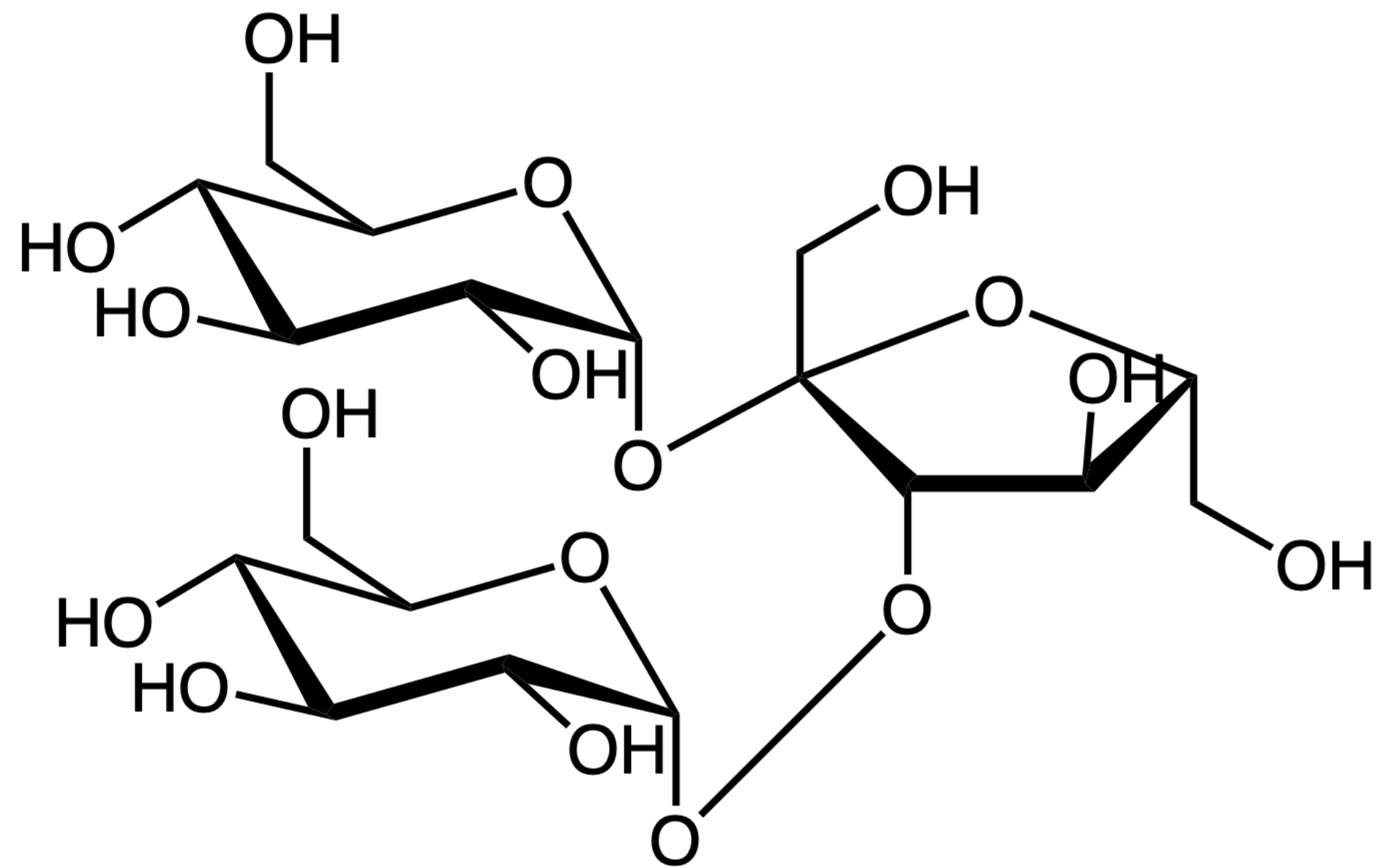
(A)



(C)



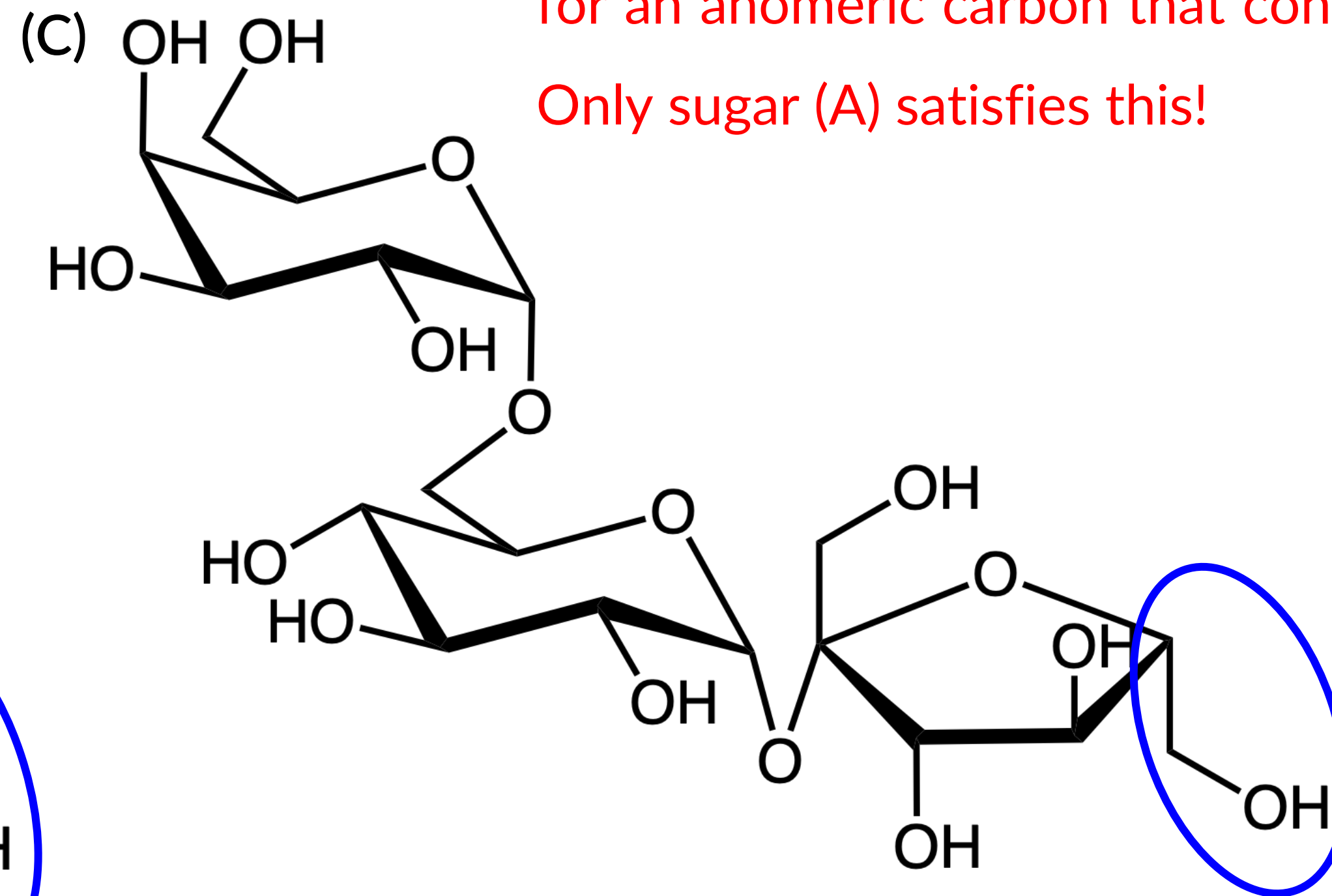
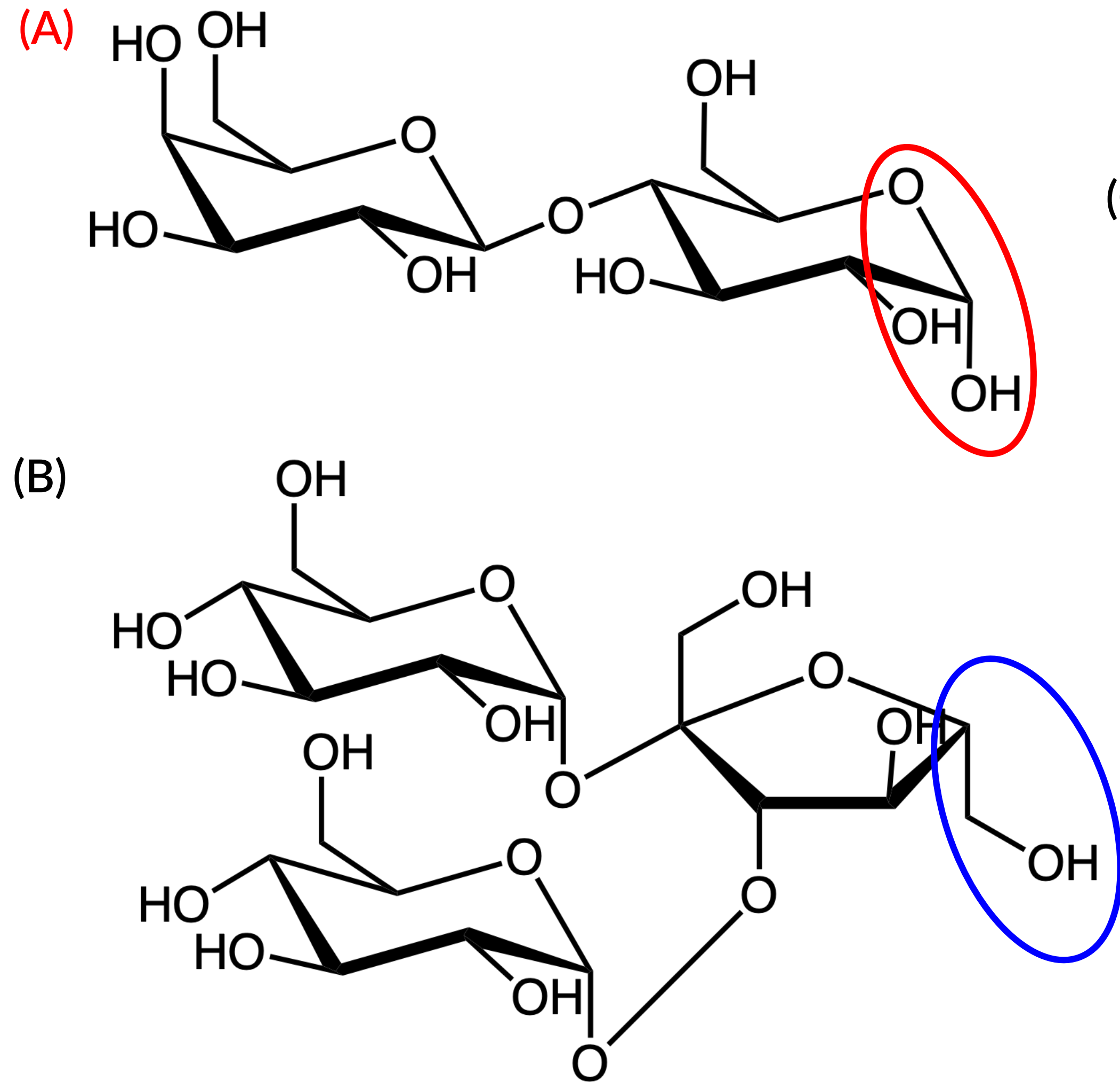
(B)



PRACTICE PROBLEM 1

Which of the following polysaccharides are reducing sugars?

— answer —



In order for a polysaccharide to be a reducing sugar, the ring must be able to open into the open-chain form with an aldehyde. To identify ring-opening potential, look for an anomeric carbon that contains a O-C-OH group. Only sugar (A) satisfies this!

The other sugars contain O-C-CH₂OH groups at the anomeric carbons that will not ring-open into aldehydes; thus, sugars (B) and (C) are not reducing sugars.