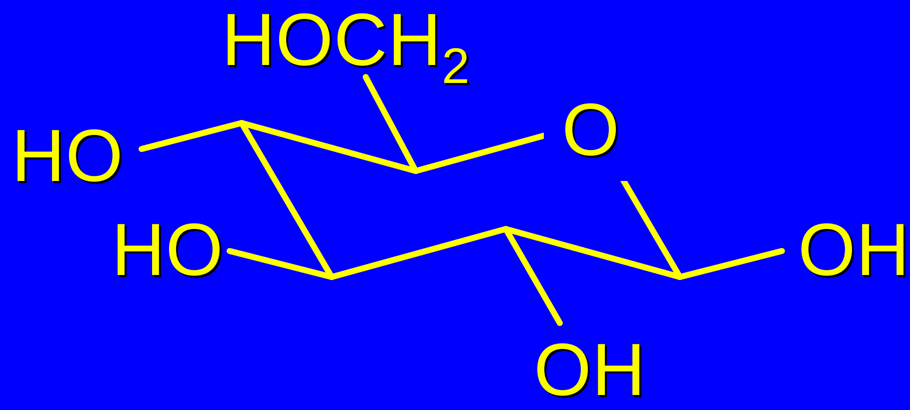
25.13
Glycosides

Glycosides

Glycosides have a substituent other than OH at the anomeric carbon.

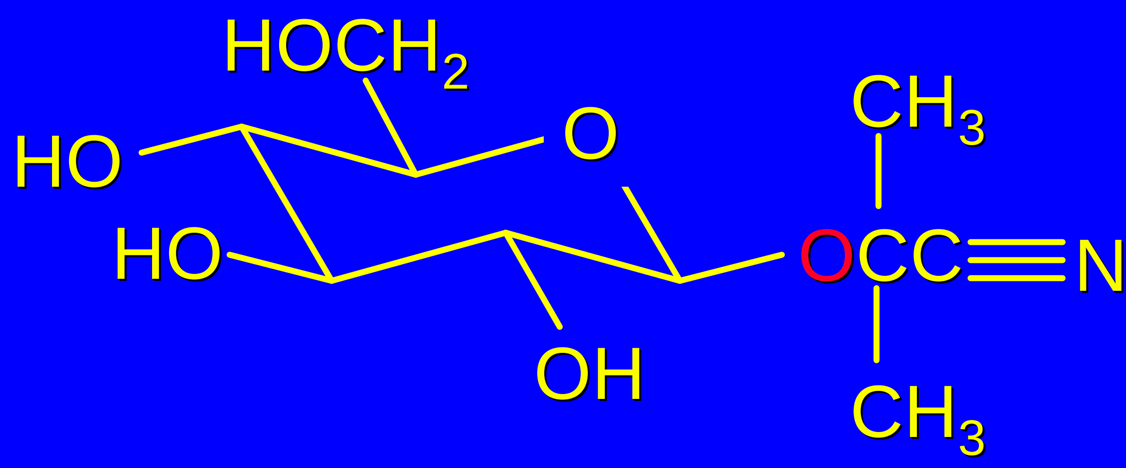
Usually the atom connected to the anomeric carbon is oxygen.

Example



D-Glucose

Linamarin is an *O*-glycoside derived from D-glucose.



Glycosides

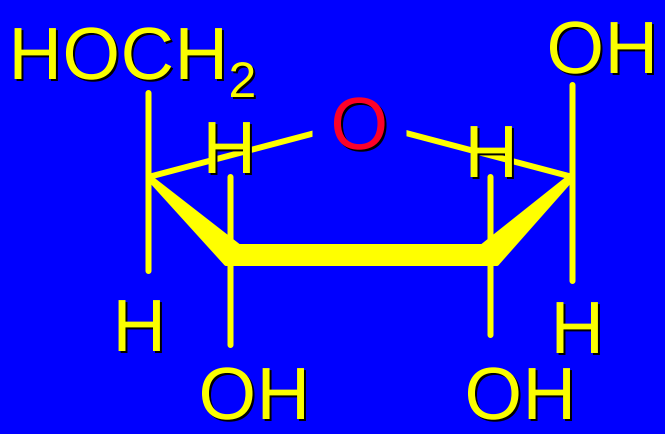
Glycosides have a substituent other than OH at the anomeric carbon.

Usually the atom connected to the anomeric carbon is oxygen.

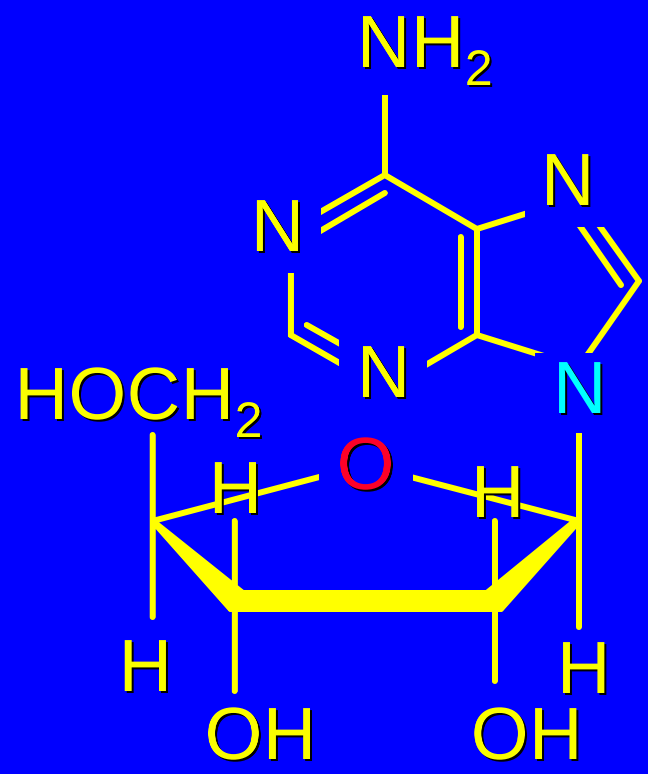
Examples of glycosides in which the atom connected to the anomeric carbon is something other than oxygen include *S*-glycosides and *N*-glycosides.

Example

Adenosine is an *N*-glycoside derived from D-ribose

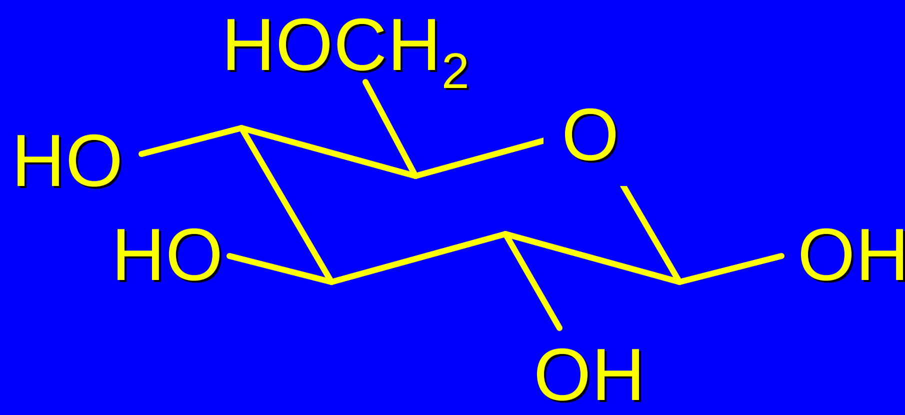


D-Ribose

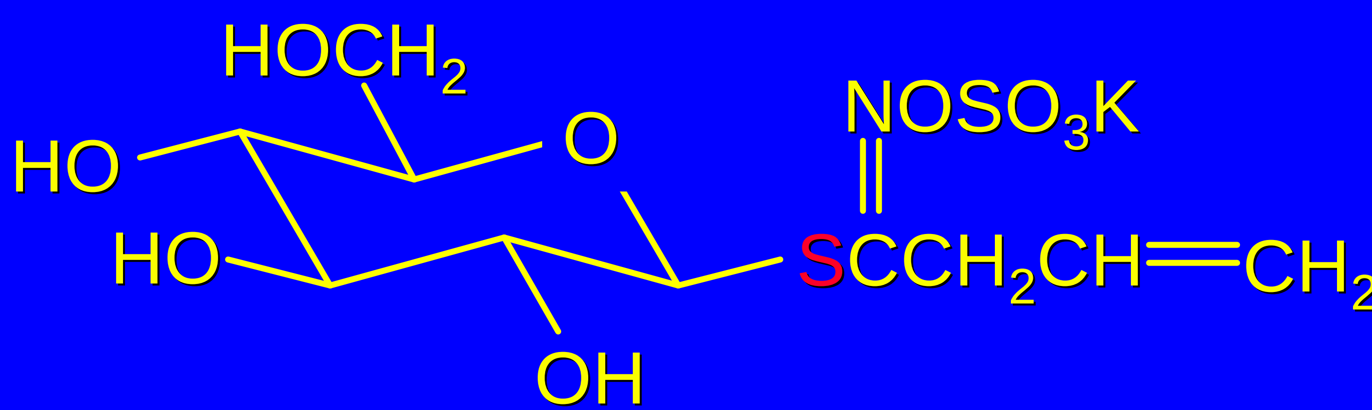


Adenosine

Example



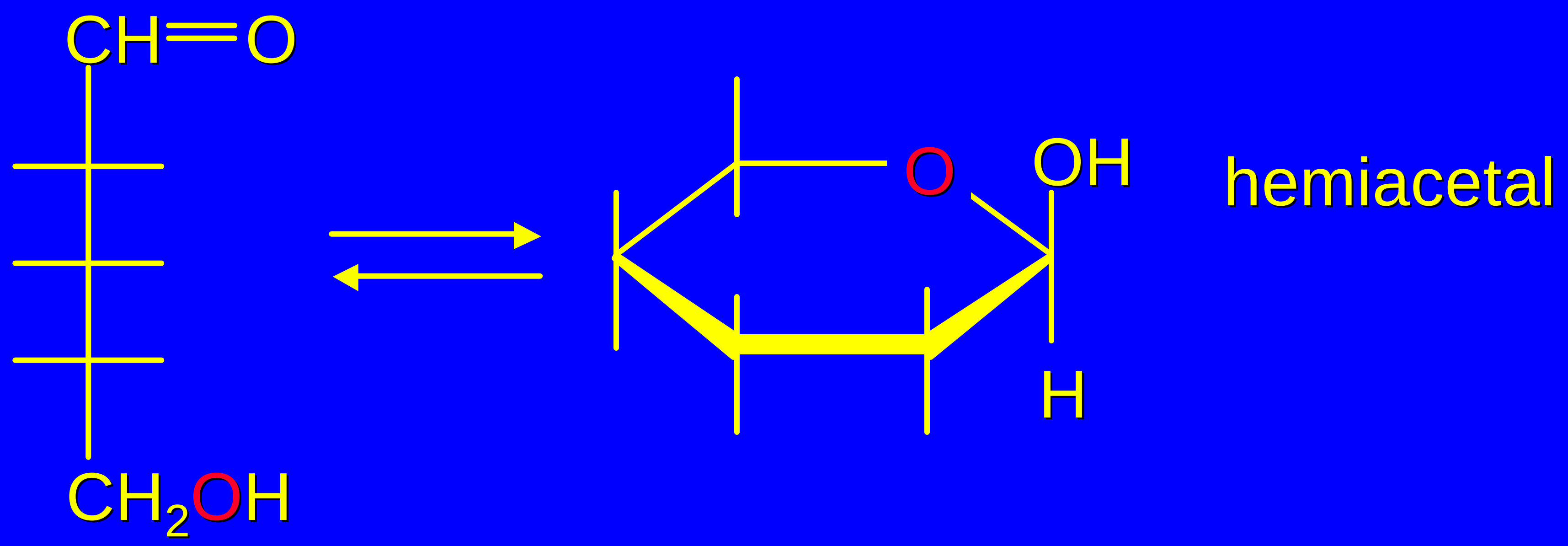
Sinigrin is an *S*-glycoside derived from D-glucose.



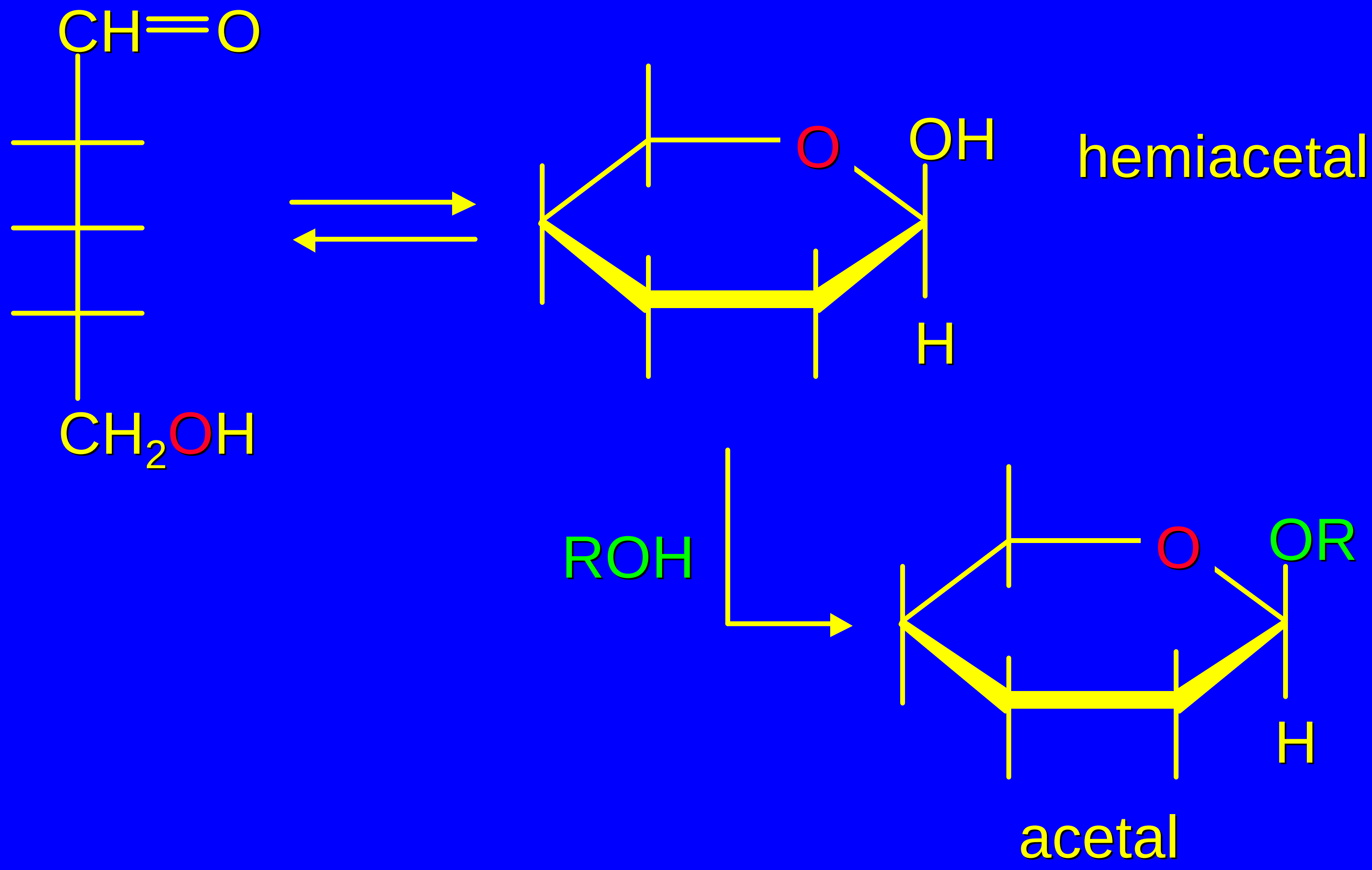
Glycosides

O-Glycosides are mixed acetals.

O-Glycosides are mixed acetals



O-Glycosides are mixed acetals



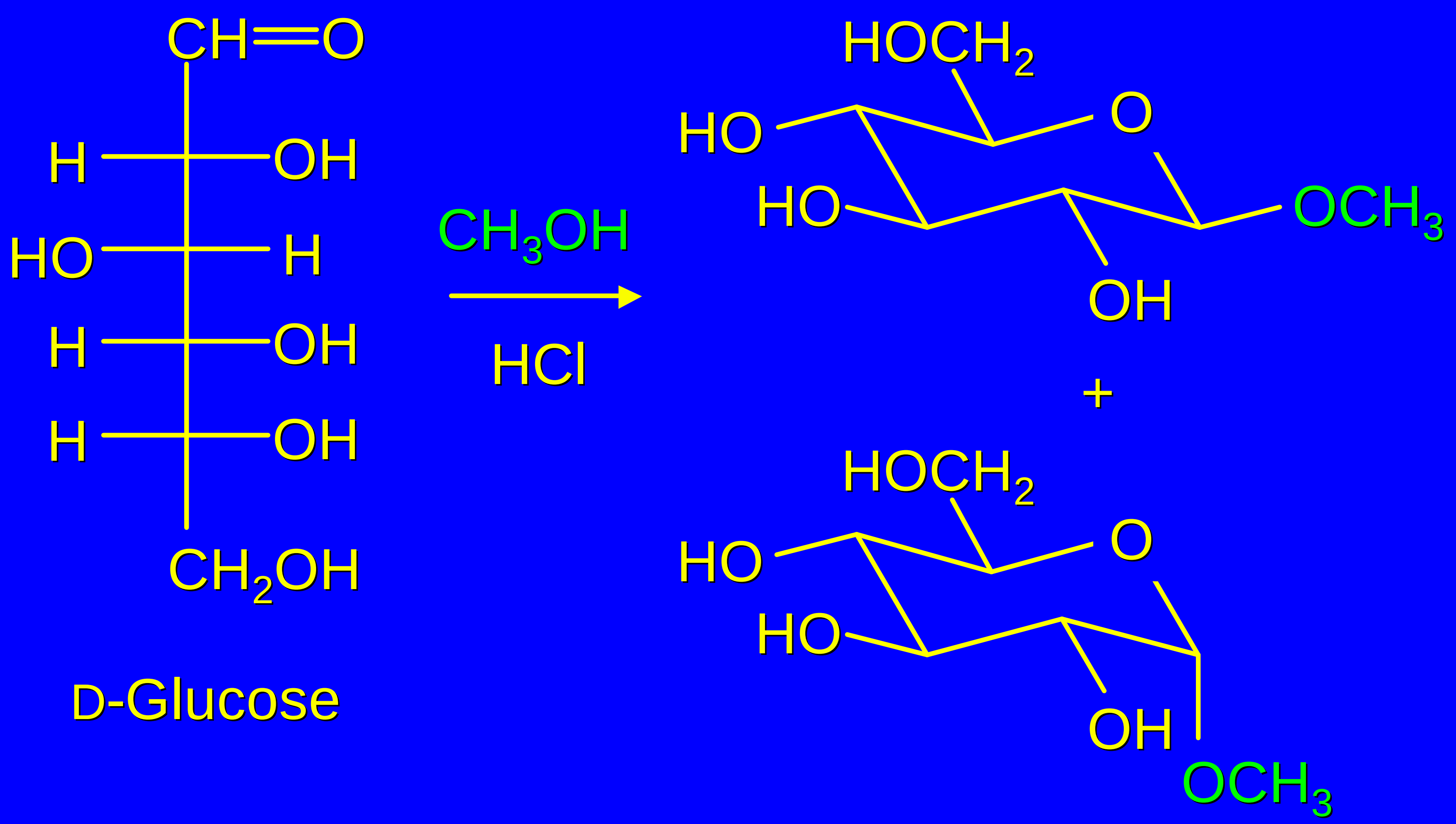
Preparation of Glycosides

Glycosides of simple alcohols (such as methanol) are prepared by adding an acid catalyst (usually gaseous HCl) to a solution of a carbohydrate in the appropriate alcohol.

Only the anomeric OH group is replaced.

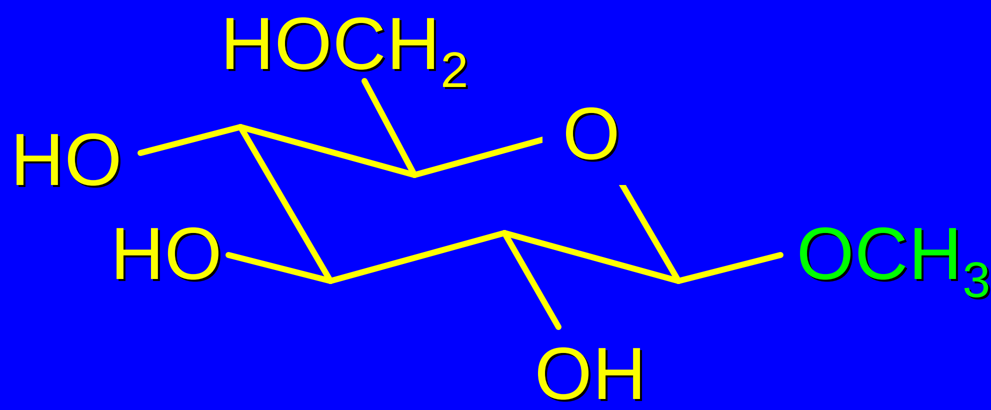
An equilibrium is established between the α and β-glycosides (thermodynamic control). The more stable stereoisomer predominates.

Preparation of Glycosides



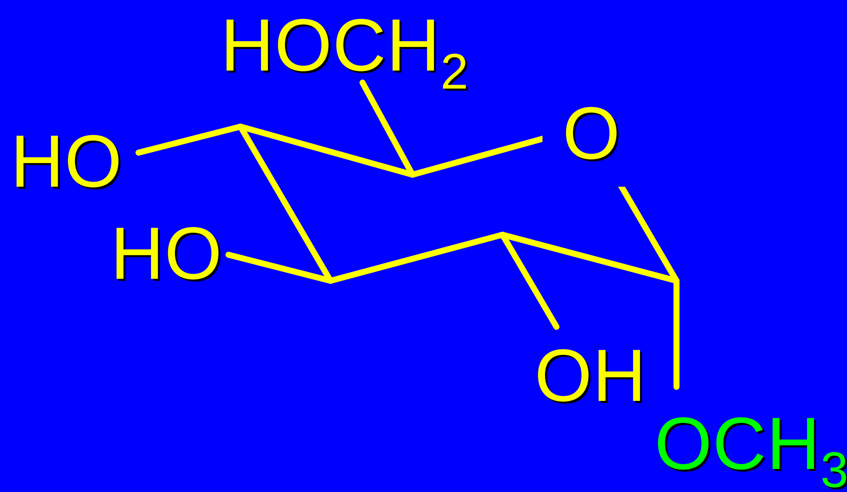
Preparation of Glycosides

Methyl
β-D-glucopyranoside

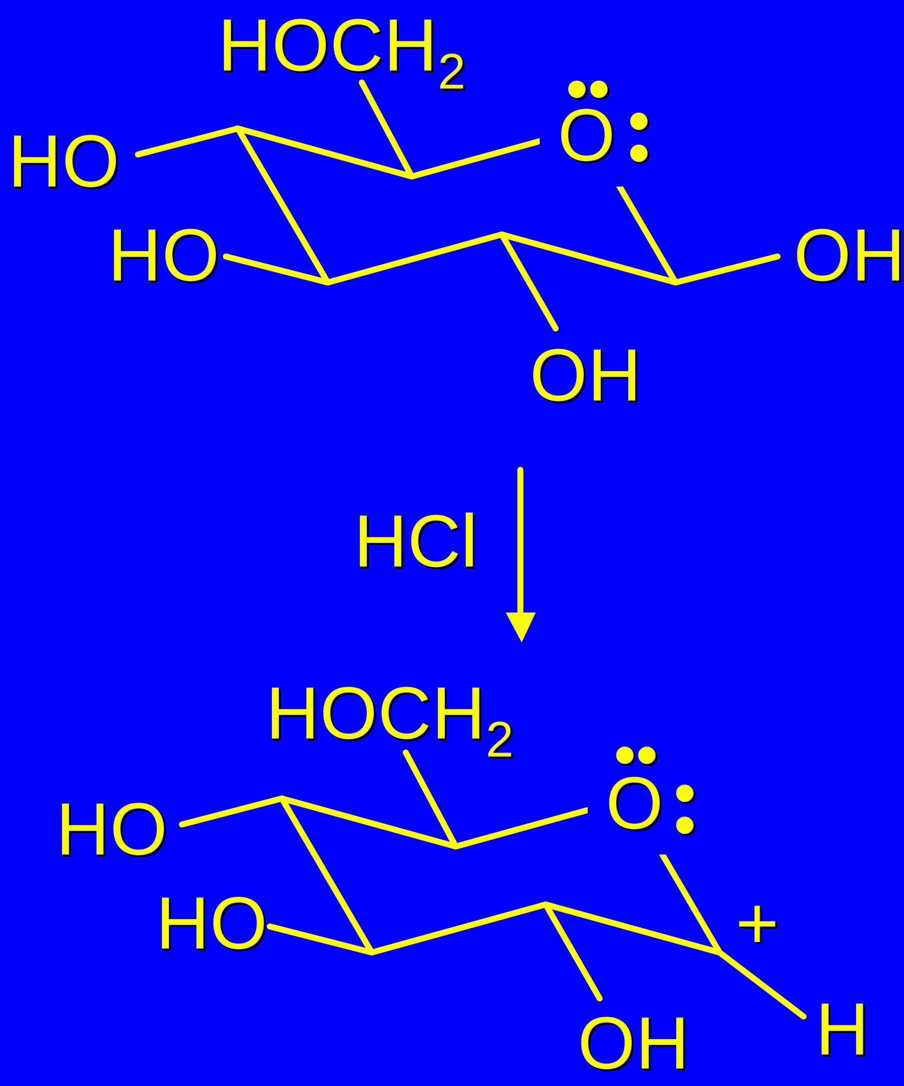


+

Methyl
α-D-glucopyranoside
(major product)

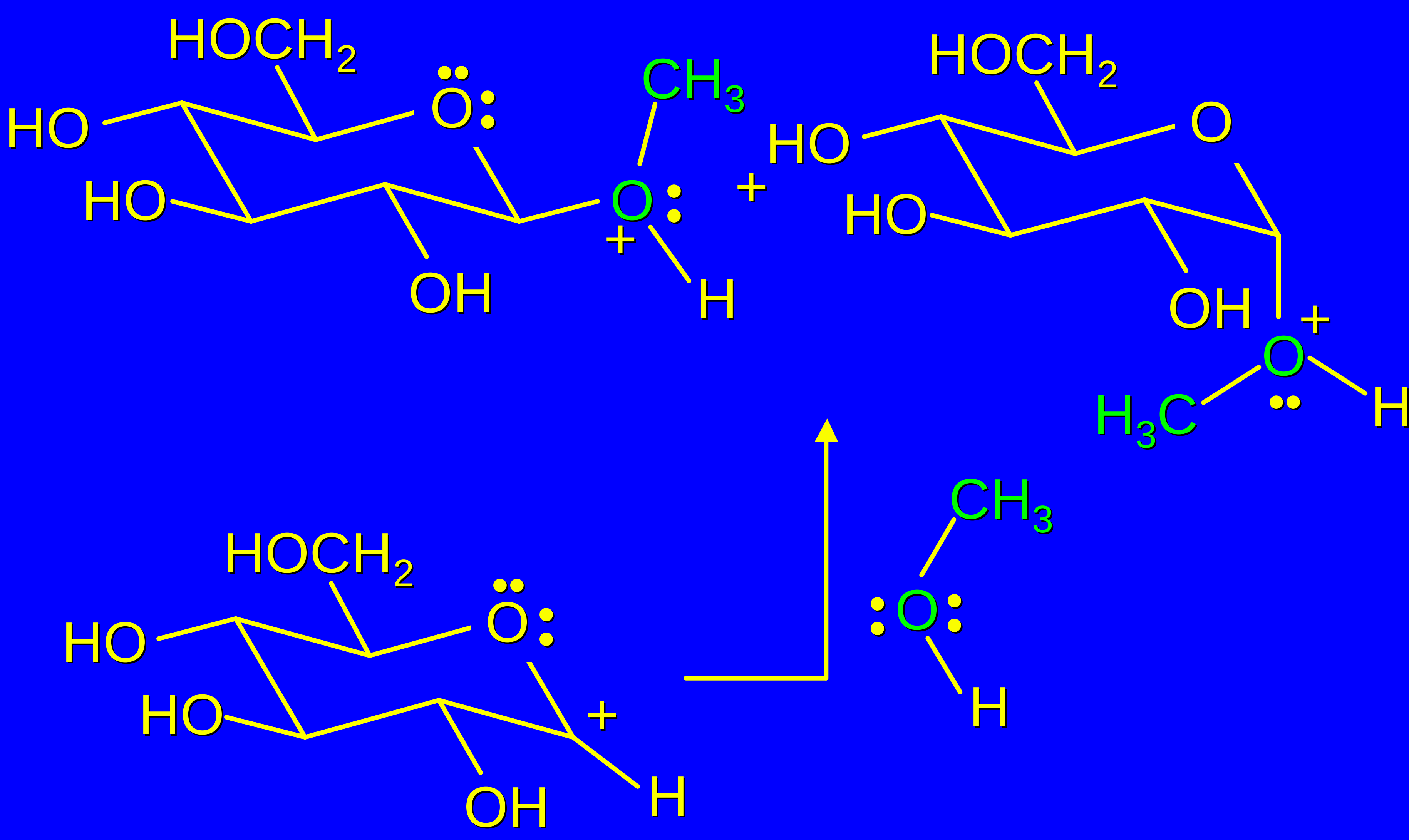


Mechanism of Glycoside Formation

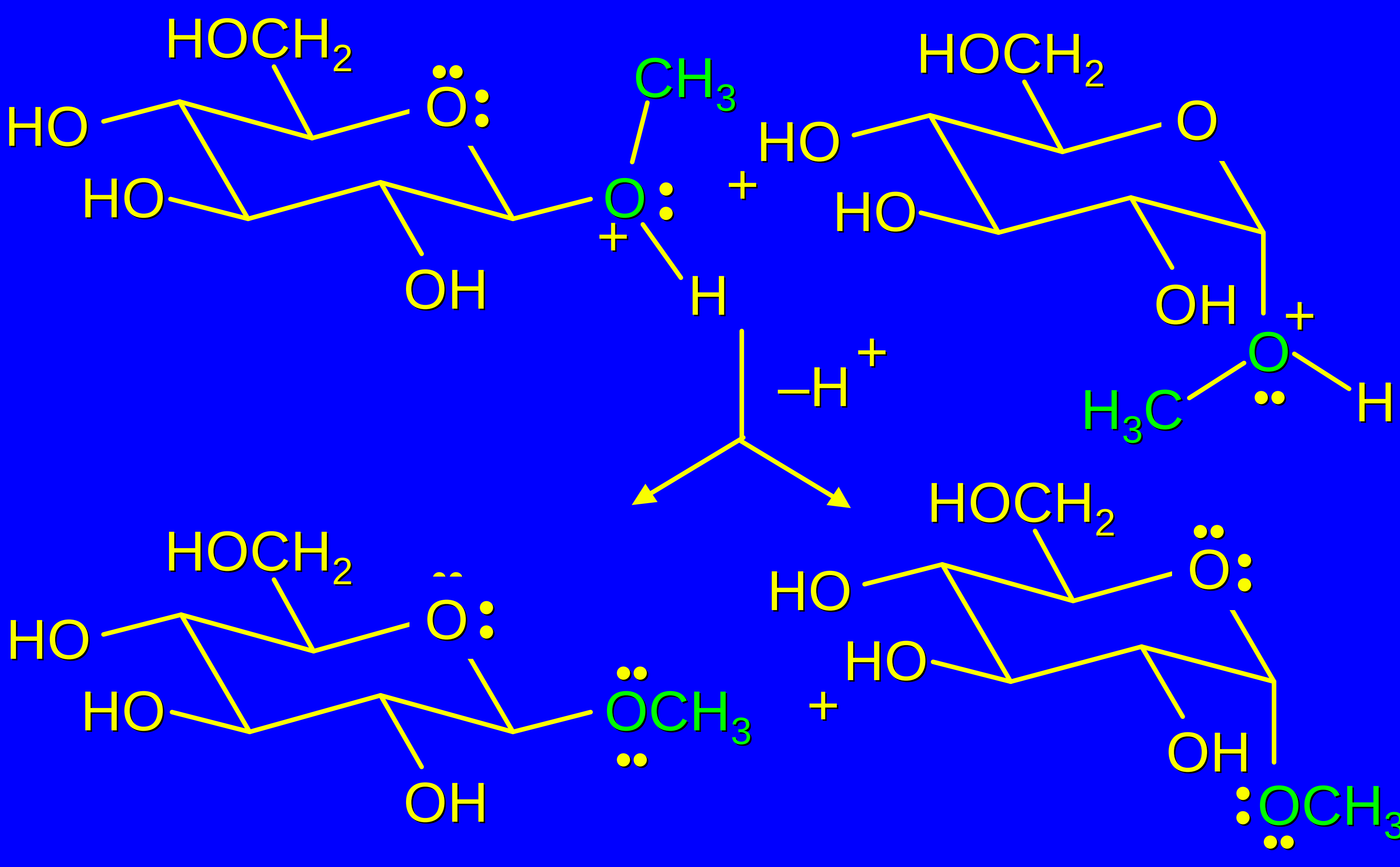


carbocation is stabilized by lone-pair donation from oxygen of the ring

Mechanism of Glycoside Formation



Mechanism of Glycoside Formation



25.14
Disaccharides

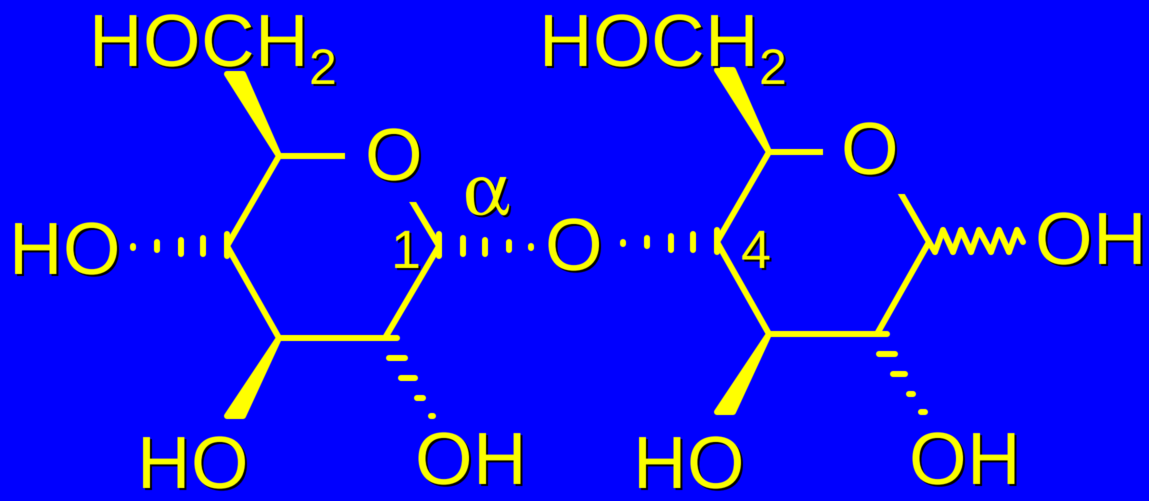
Disaccharides

Disaccharides are glycosides.

The glycosidic linkage connects two monosaccharides.

Two structurally related disaccharides are cellobiose and maltose. Both are derived from glucose.

Maltose and Cellobiose



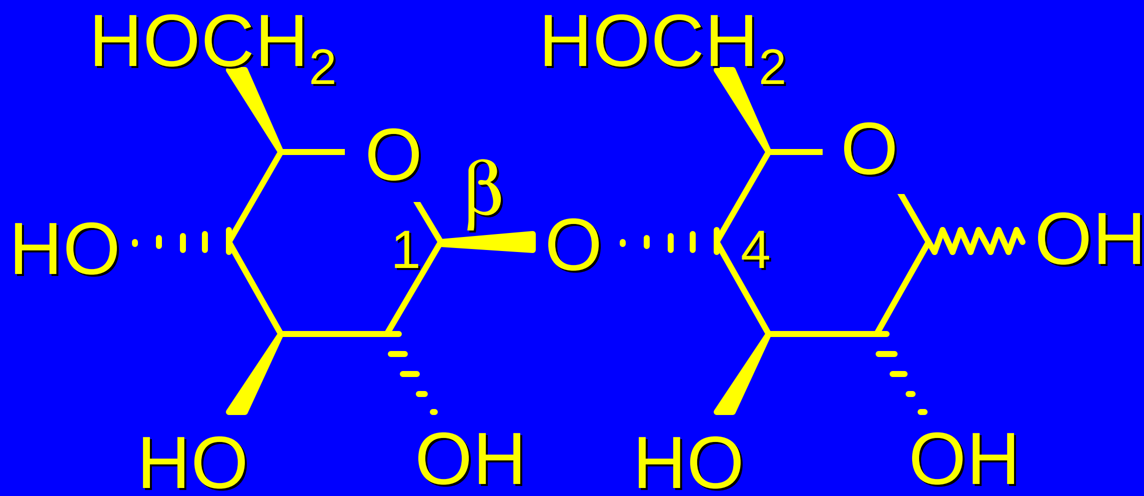
Maltose

Maltose is composed of two glucose units linked together by a glycosidic bond between C-1 of one glucose and C-4 of the other.

The stereochemistry at the anomeric carbon of the glycosidic linkage is α.

The glycosidic linkage is described as α(1,4)

Maltose and Cellobiose

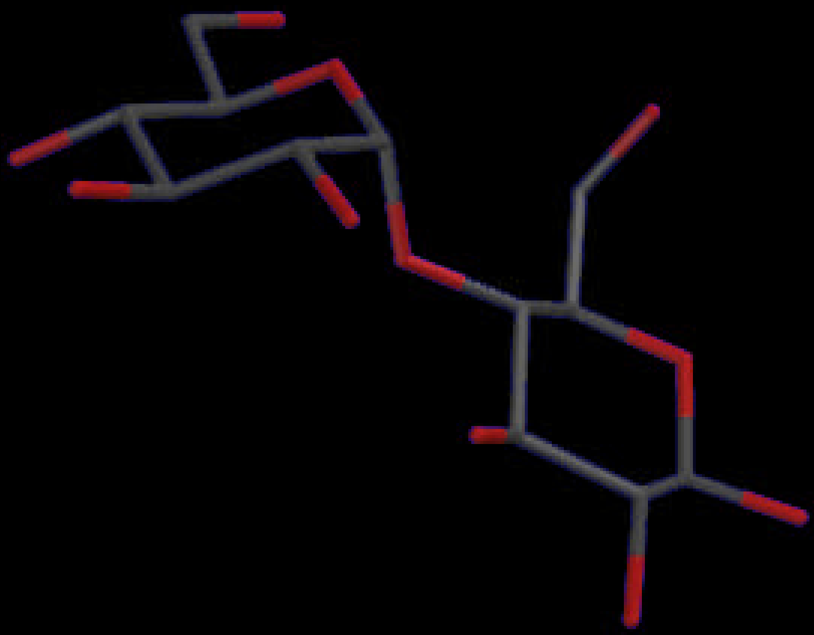


Cellobiose

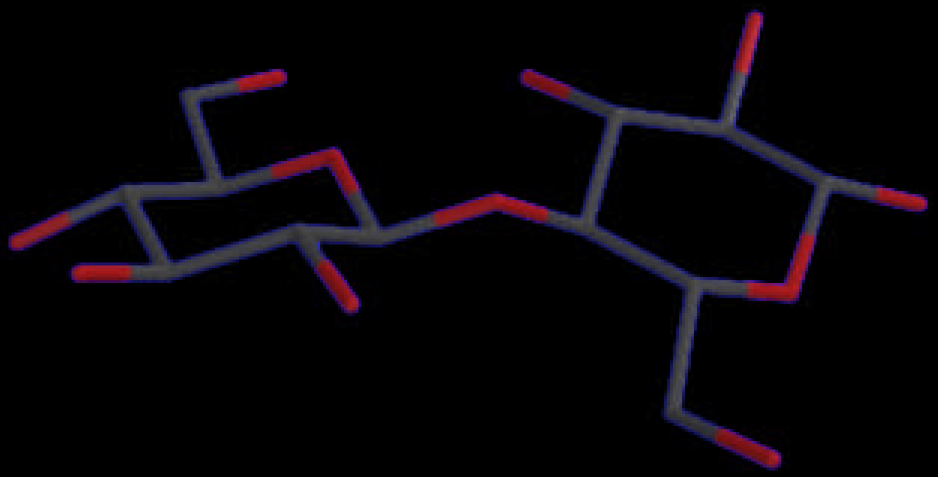
Cellobiose is a stereoisomer of maltose.

The only difference between the two is that cellobiose has a β(1,4) glycosidic bond while that of maltose is α(1,4).

Maltose and Cellobiose

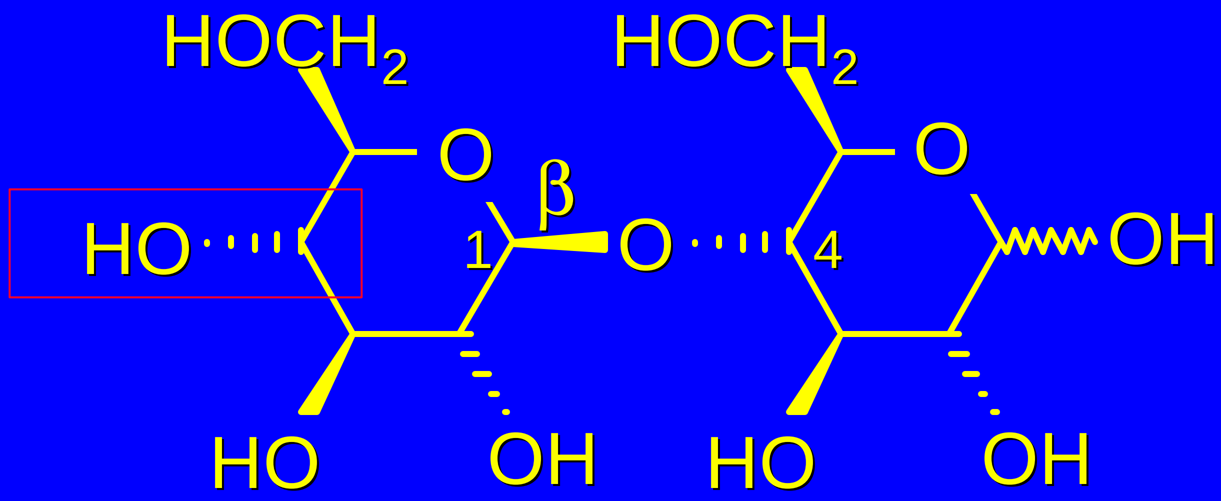


Maltose



Cellobios
e

Cellobiose and Lactose



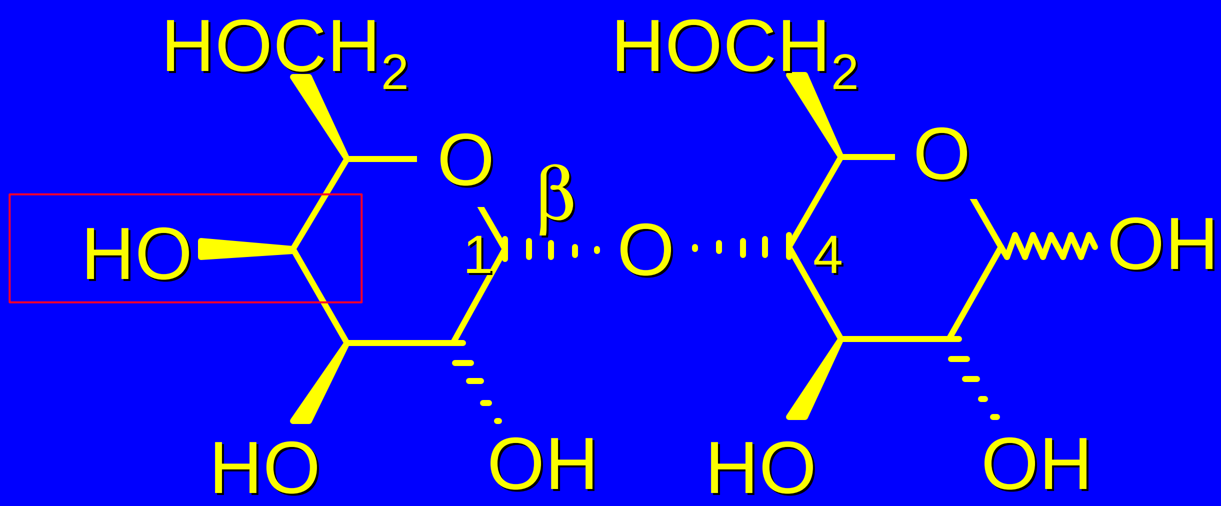
Cellobiose

Cellobiose and lactose are stereoisomeric disaccharides.

Both have β(1,4) glycosidic bonds.

The glycosidic bond unites two glucose units in cellobiose. It unites galactose and glucose in lactose.

Cellobiose and Lactose



Lactose

Cellobiose and lactose are stereoisomeric disaccharides.

Both have β(1,4) glycosidic bonds.

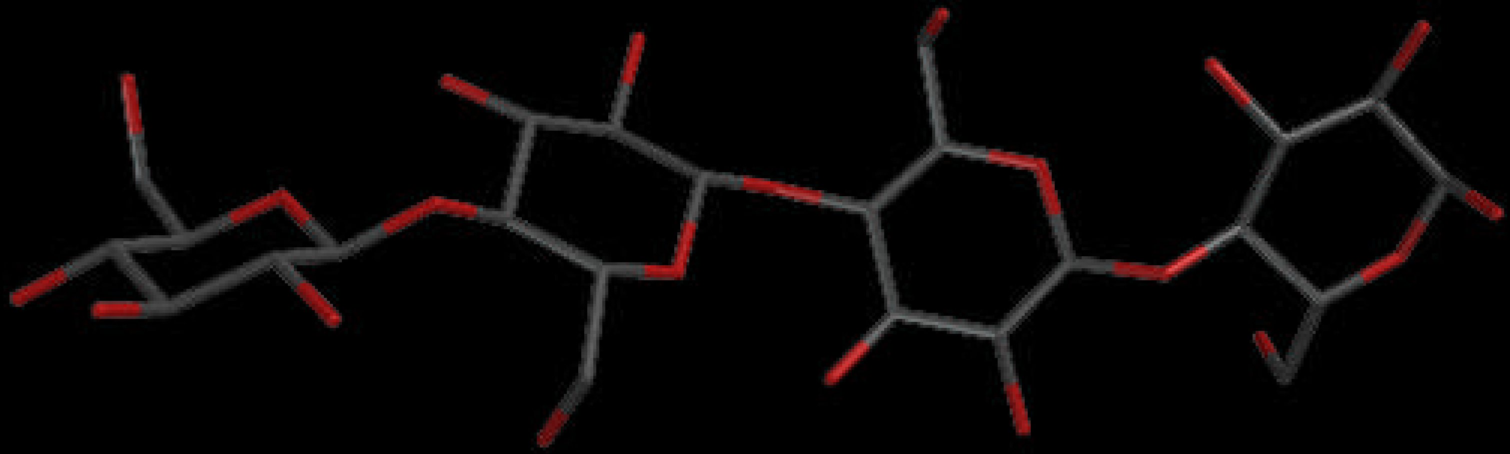
The glycosidic bond unites two glucose units in cellobiose. It unites galactose and glucose in lactose.

25.15
Polysaccharides

Cellulose

Cellulose is a polysaccharide composed of several thousand D-glucose units joined by β(1,4)-glycosidic linkages. Thus, it can also be viewed as a repeating collection of cellobiose units.

Cellulose



Four glucose units of a cellulose chain.

Starch

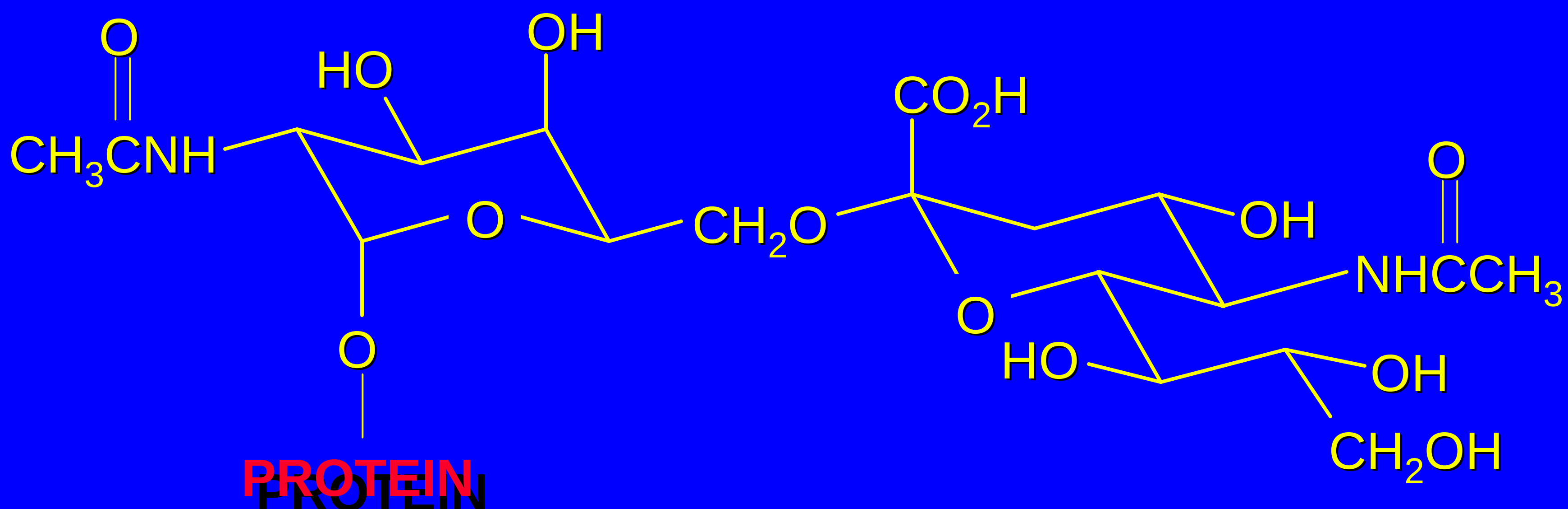
Starch is a mixture of amylose and amylopectin.

Amylose is a polysaccharide composed of 100 to several thousand D-glucose units joined by α(1,4)-glycosidic linkages.

25.16
Cell-Surface Glycoproteins

Glycoproteins

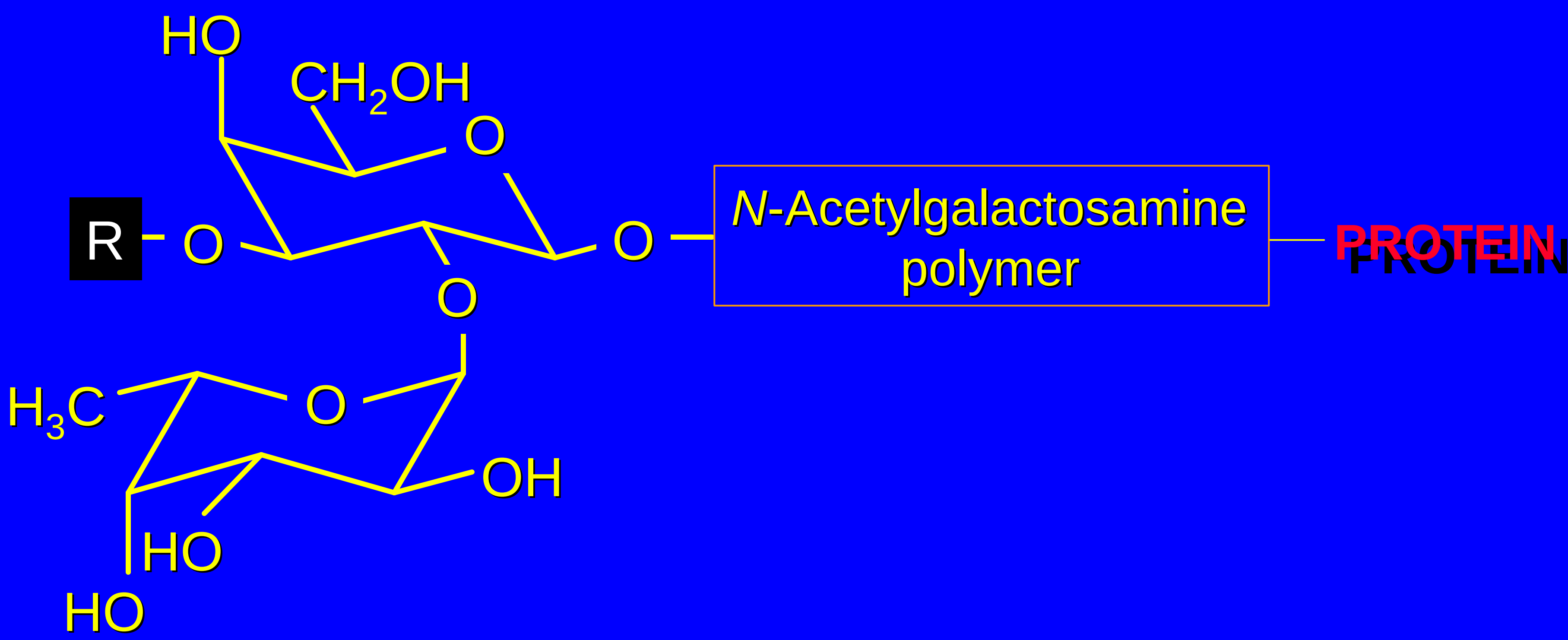
Glycoproteins have a protein backbone to which carbohydrates are attached. One example is the cell-surface glycoprotein that is recognized by the influenza virus.



Glycoproteins

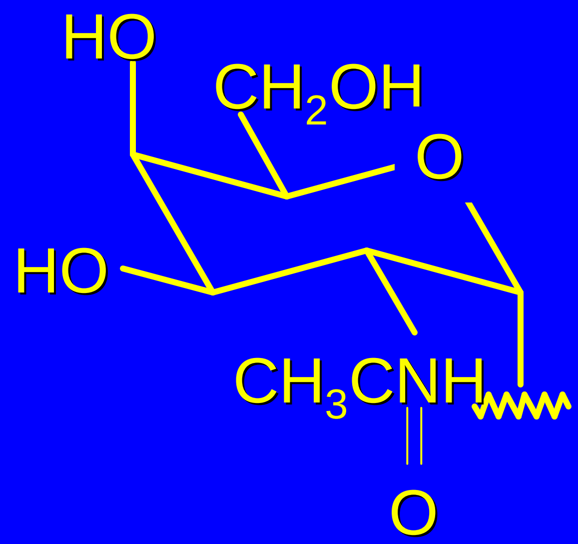
A second example is the group of glycoproteins that define the various human blood groups.

Human-Blood-Group Glycoproteins



Type O: R = H

Type A: R =



Type B: R =