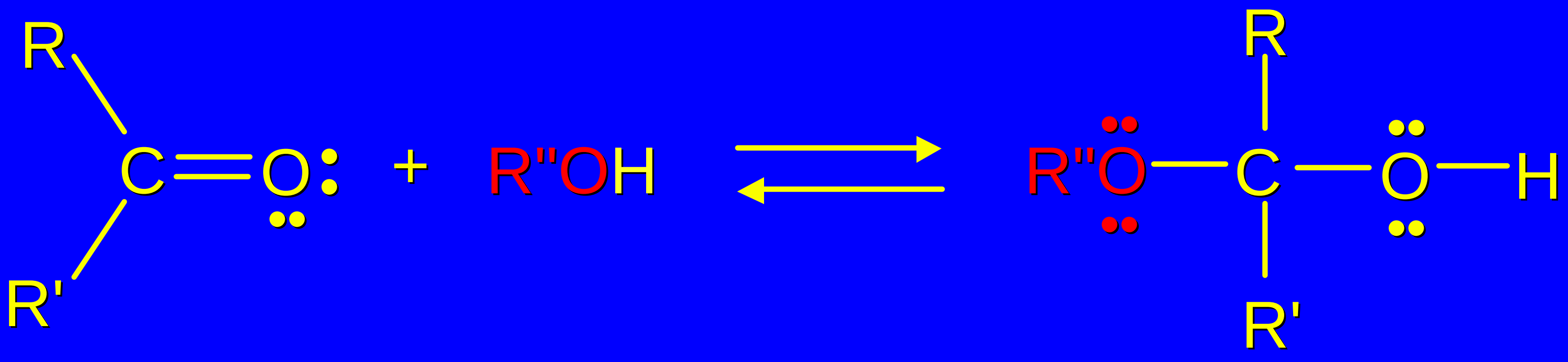
25.6

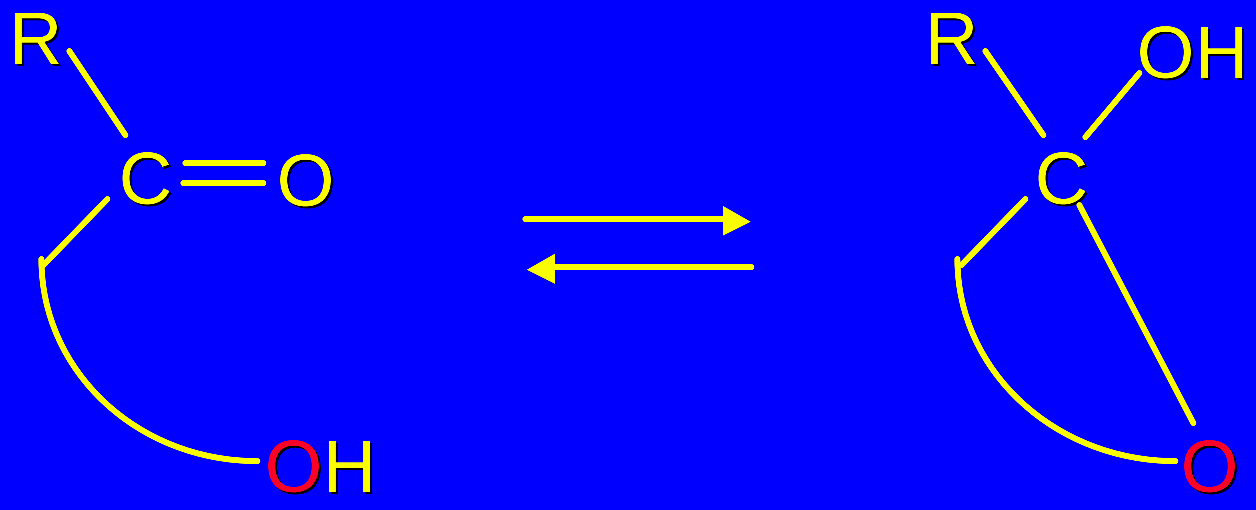
Cyclic Forms of Carbohydrates: Furanose Forms

Recall from Section 17.8



Product is a hemiacetal.

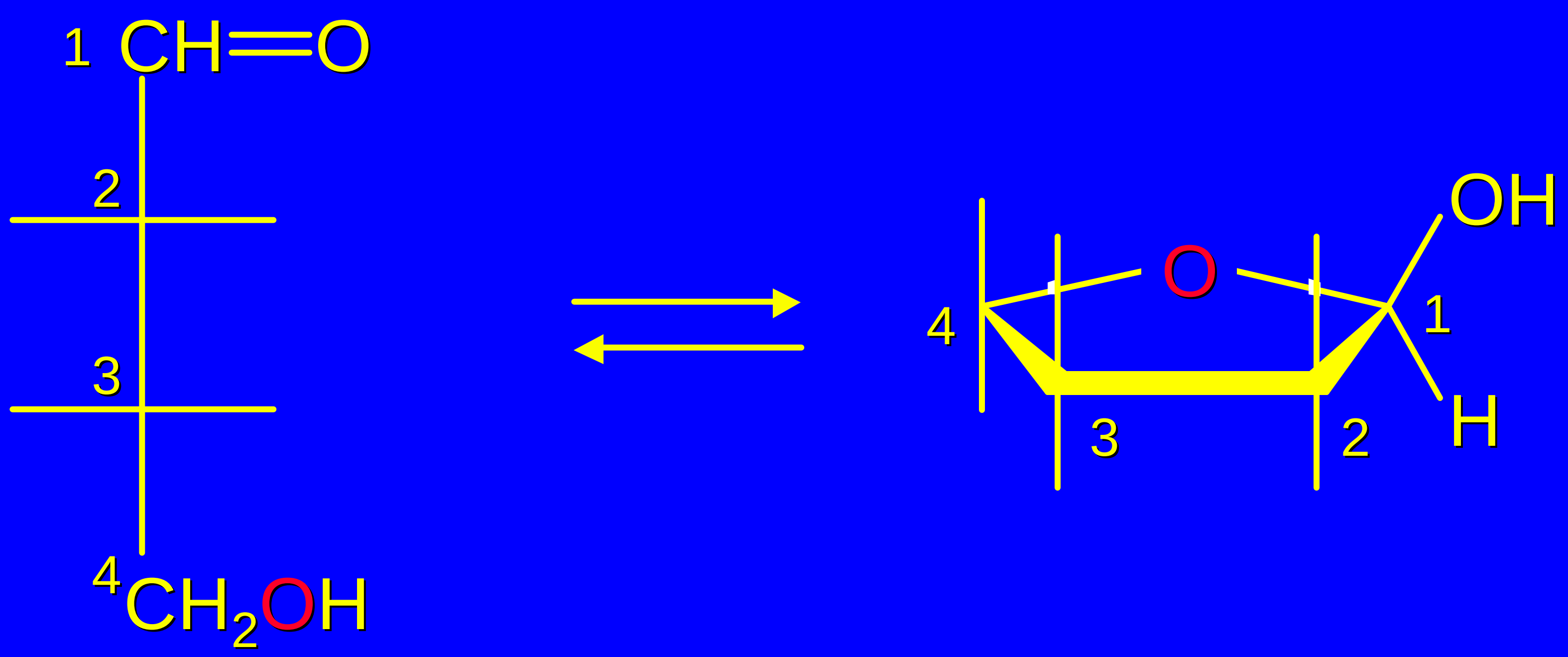
Cyclic Hemiacetals



Aldehydes and ketones that contain an OH group elsewhere in the molecule can undergo intramolecular hemiacetal formation.

The equilibrium favors the cyclic hemiacetal if the ring is 5- or 6-membered.

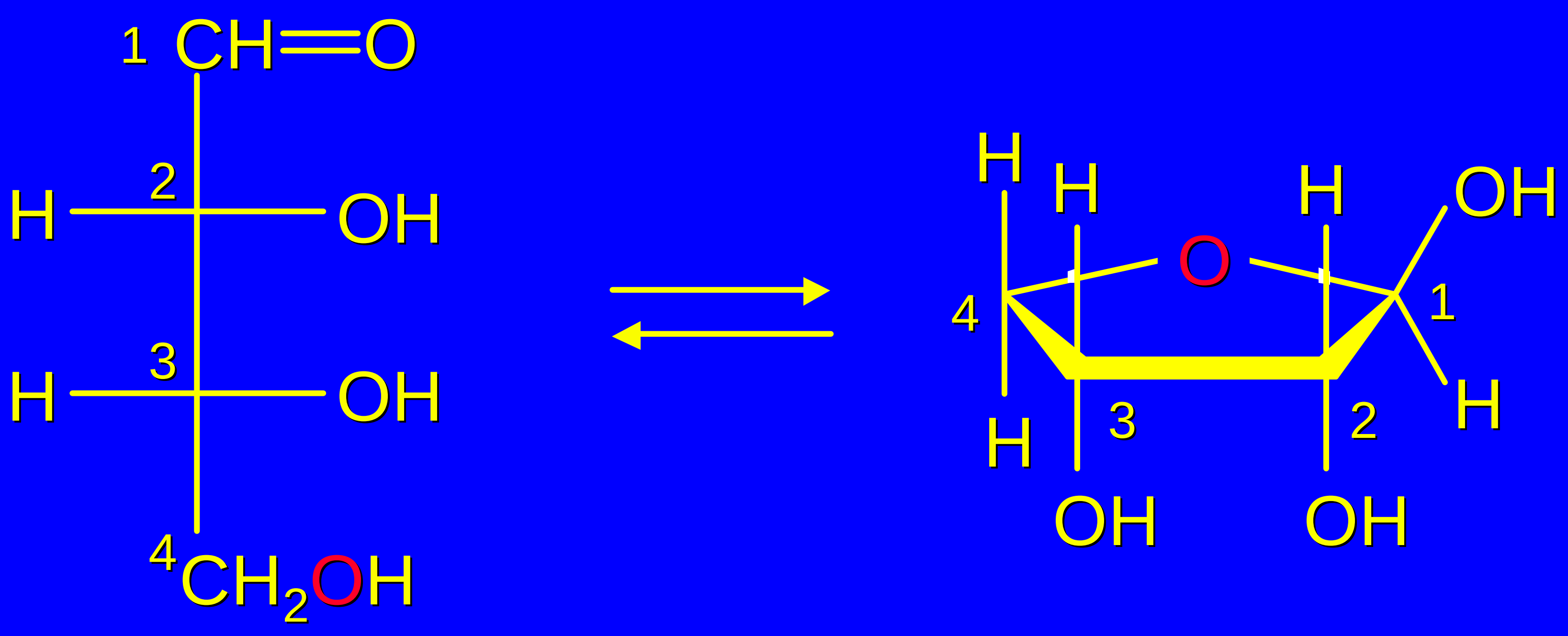
Carbohydrates Form Cyclic Hemiacetals



equilibrium lies far to the right

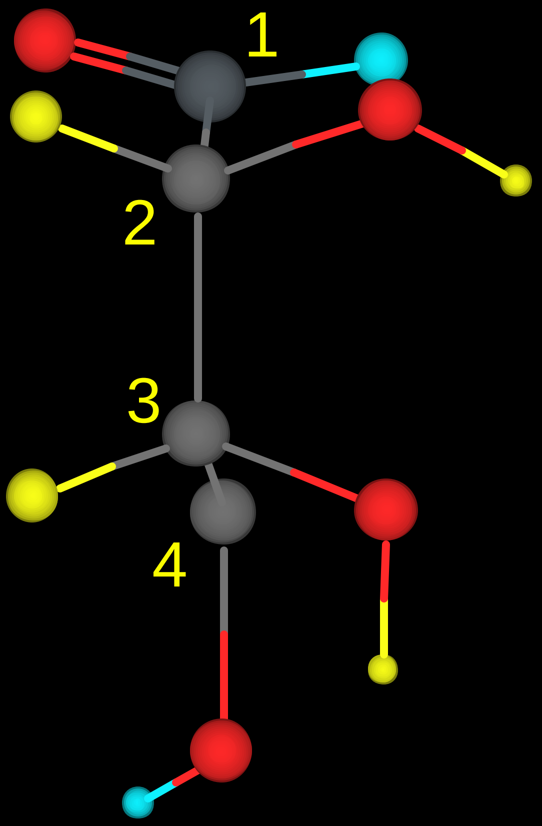
cyclic hemiacetals that have 5-membered rings are called furanose forms

D-Erythrose

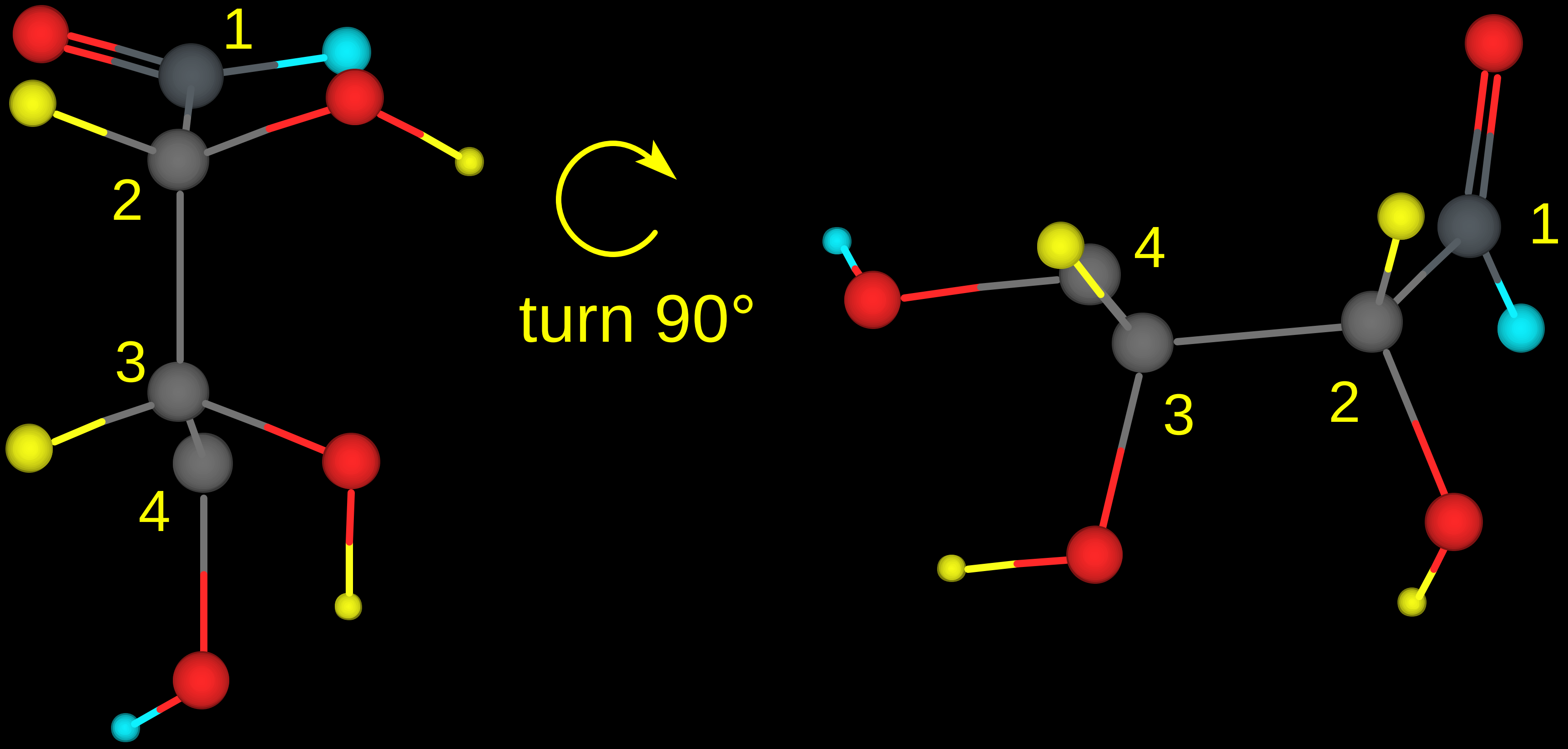


stereochemistry is maintained during cyclic hemiacetal formation

D-Erythrose

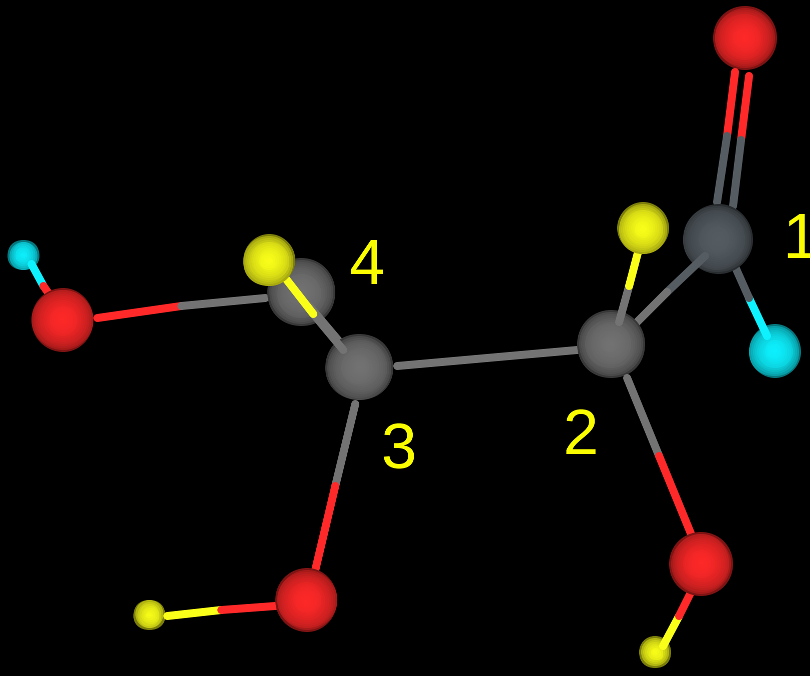


D-Erythrose

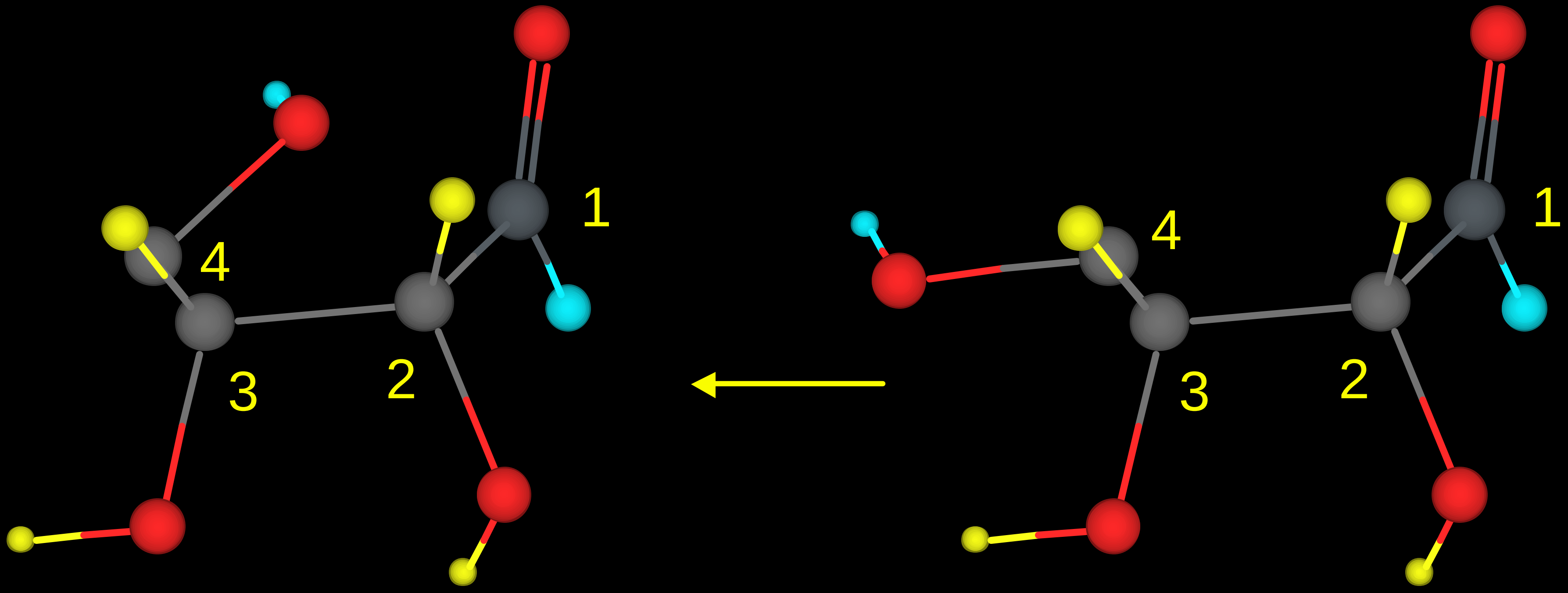


D-Erythrose

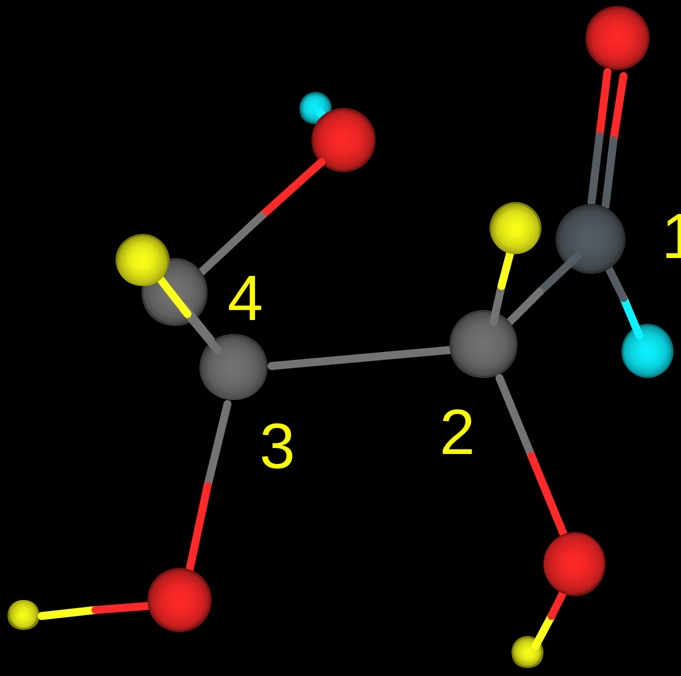
move O into position by rotating about bond between carbon-3 and carbon-4



D-Erythrose

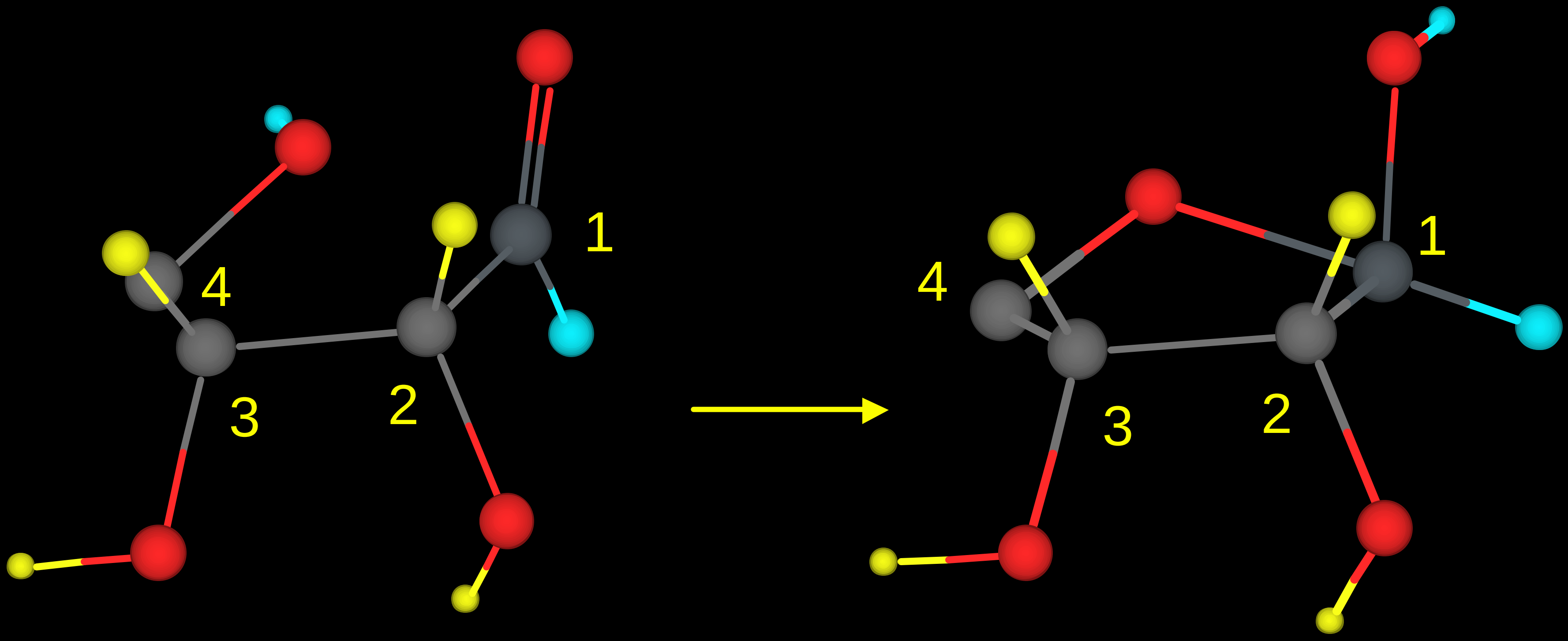


D-Erythrose

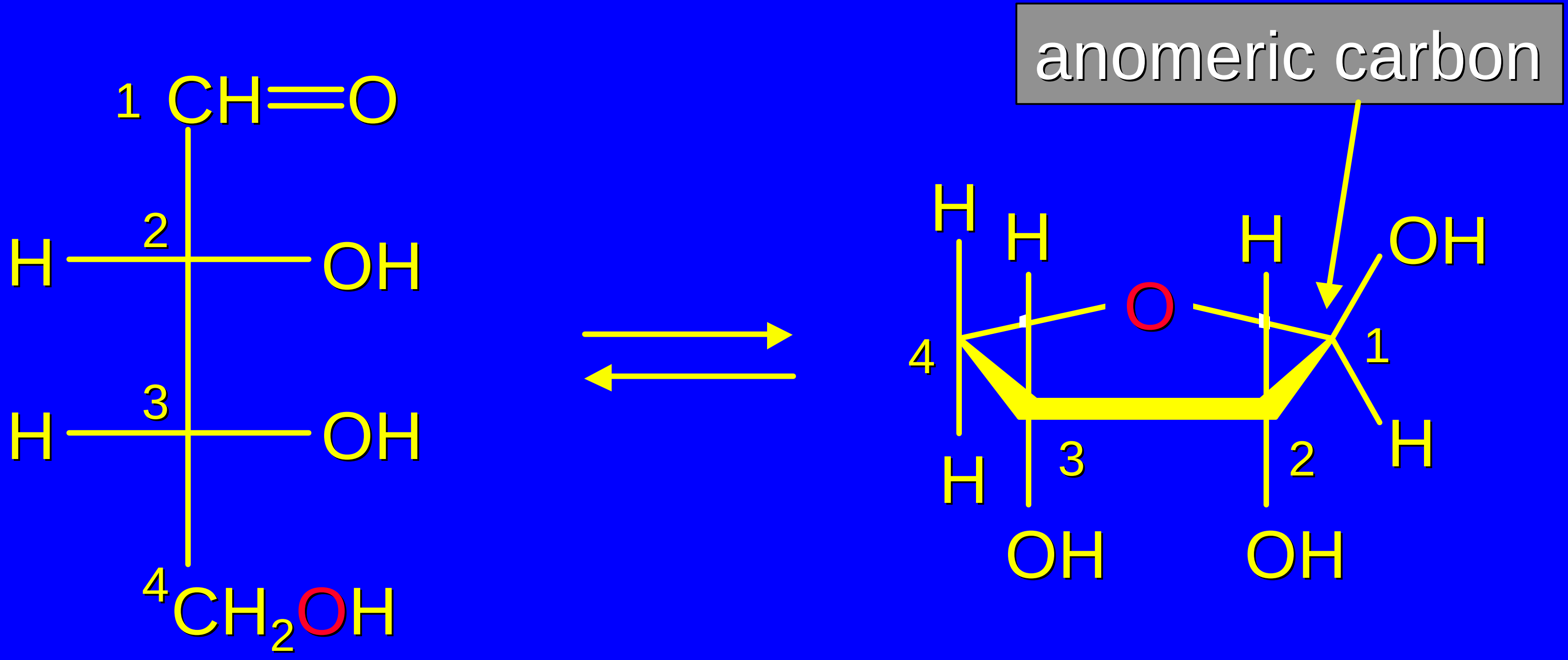


close ring by
hemiacetal formation
between OH at C-4
and carbonyl group

D-Erythrose



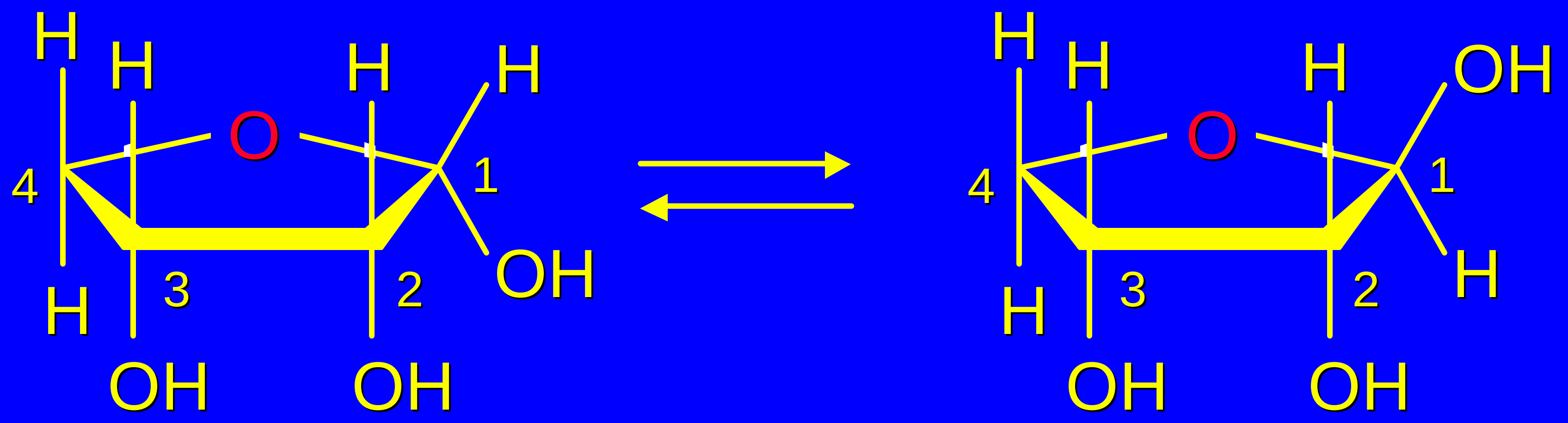
D-Erythrose



anomeric carbon

stereochemistry is variable at anomeric carbon; two diastereomers are formed

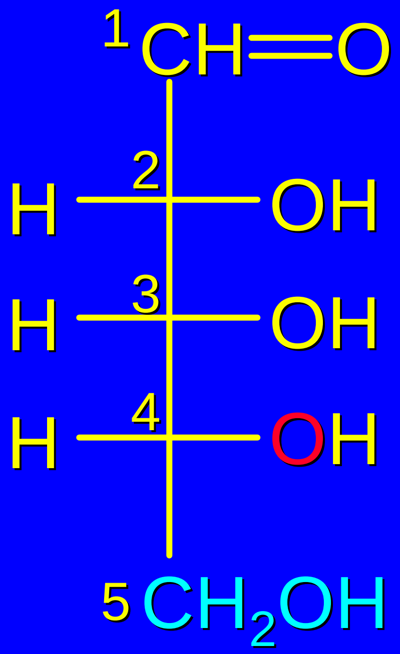
D-Erythrose



α-D-Erythrofuranose

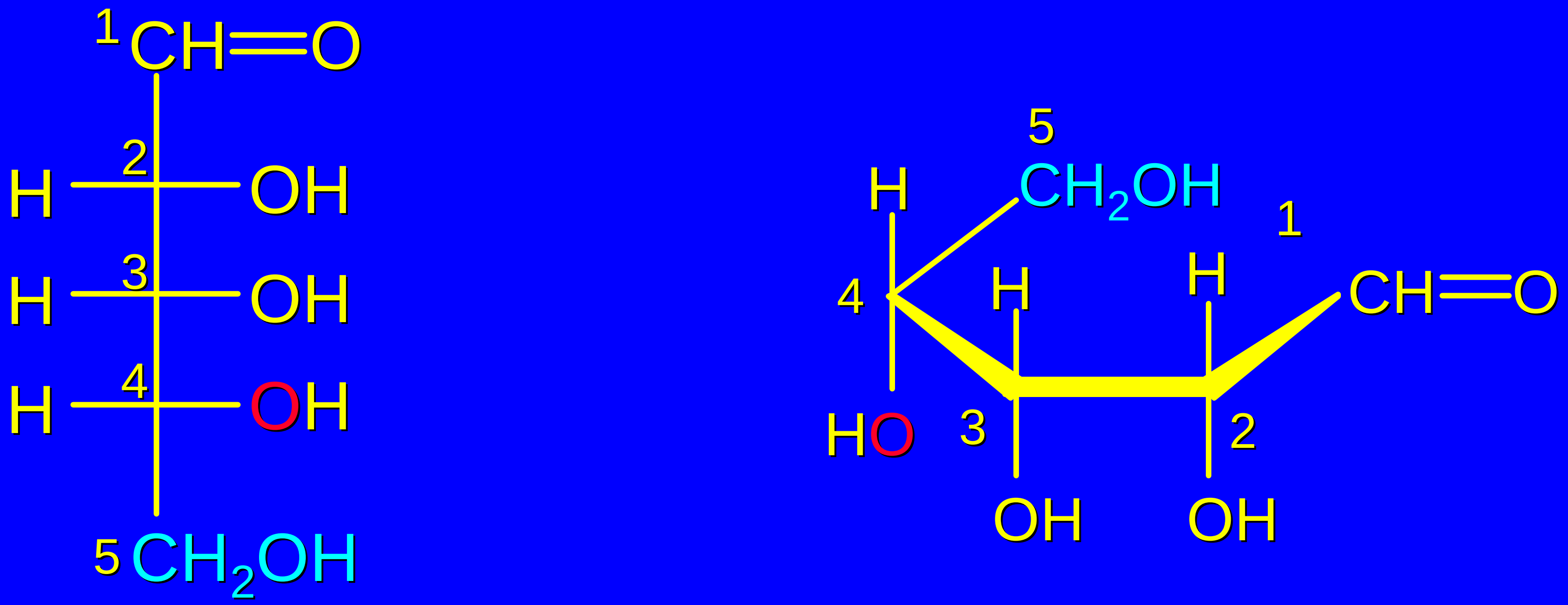
β-D-Erythrofuranose

D-Ribose



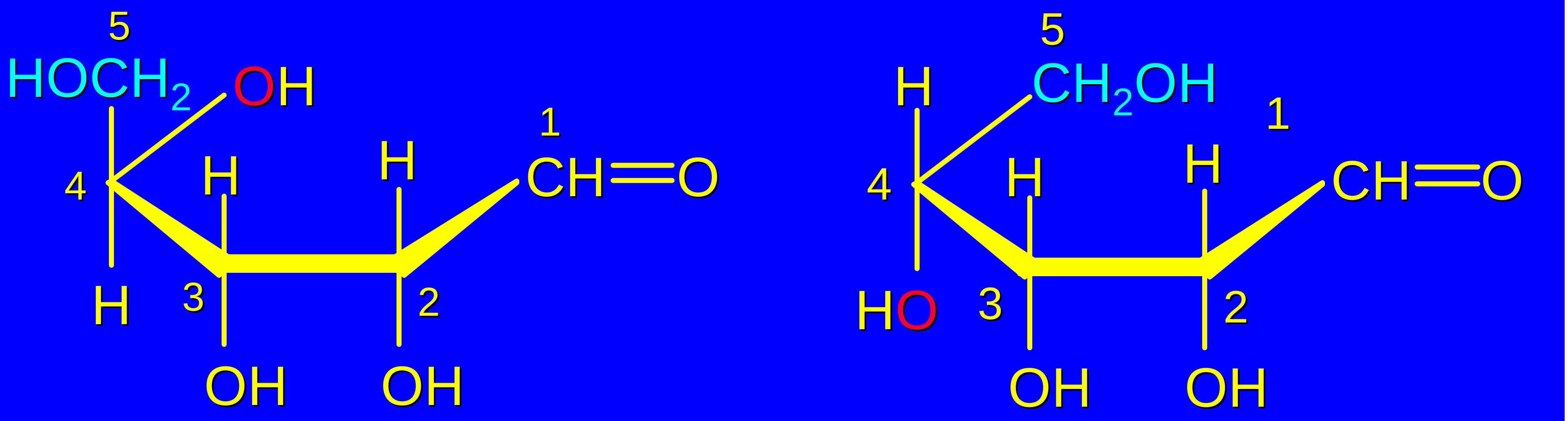
furanose ring formation involves OH group at C-4

D-Ribose

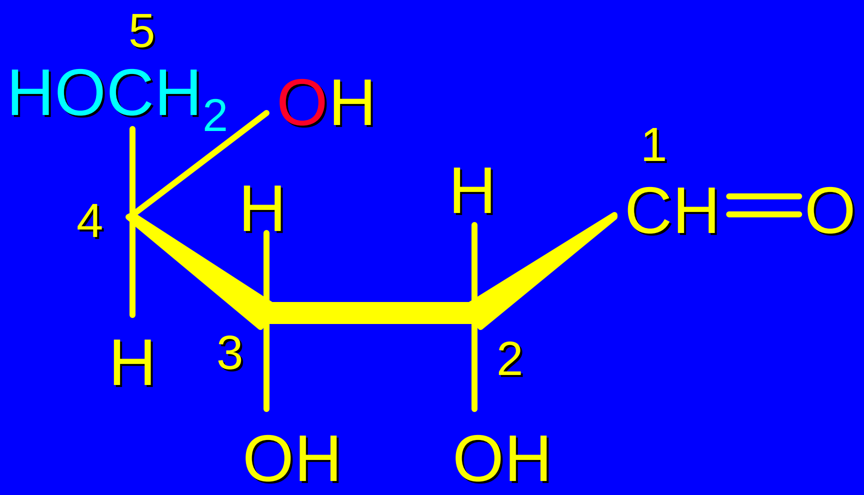


need C(3)-C(4) bond rotation to put OH in proper orientation to close 5-membered ring

D-Ribose

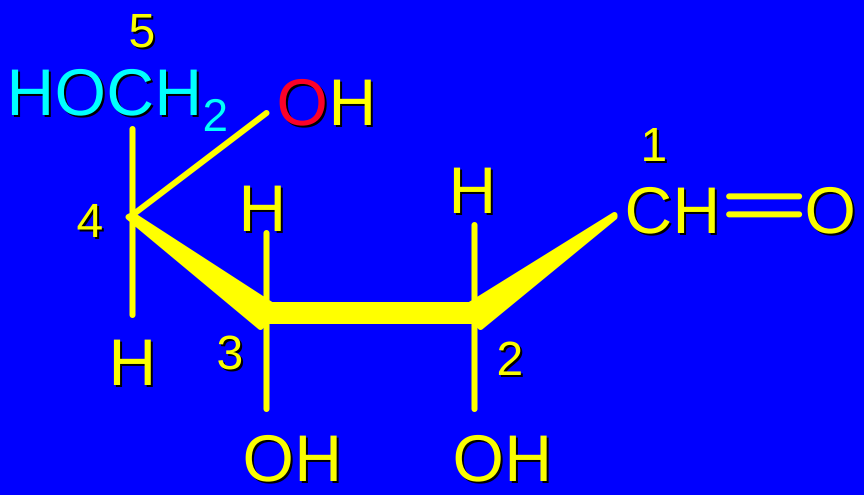


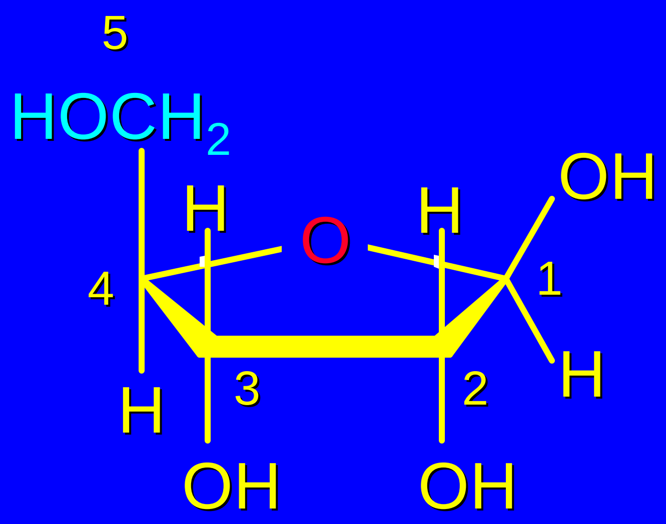
D-Ribose



CH_2OH group becomes a substituent on ring

D-Ribose





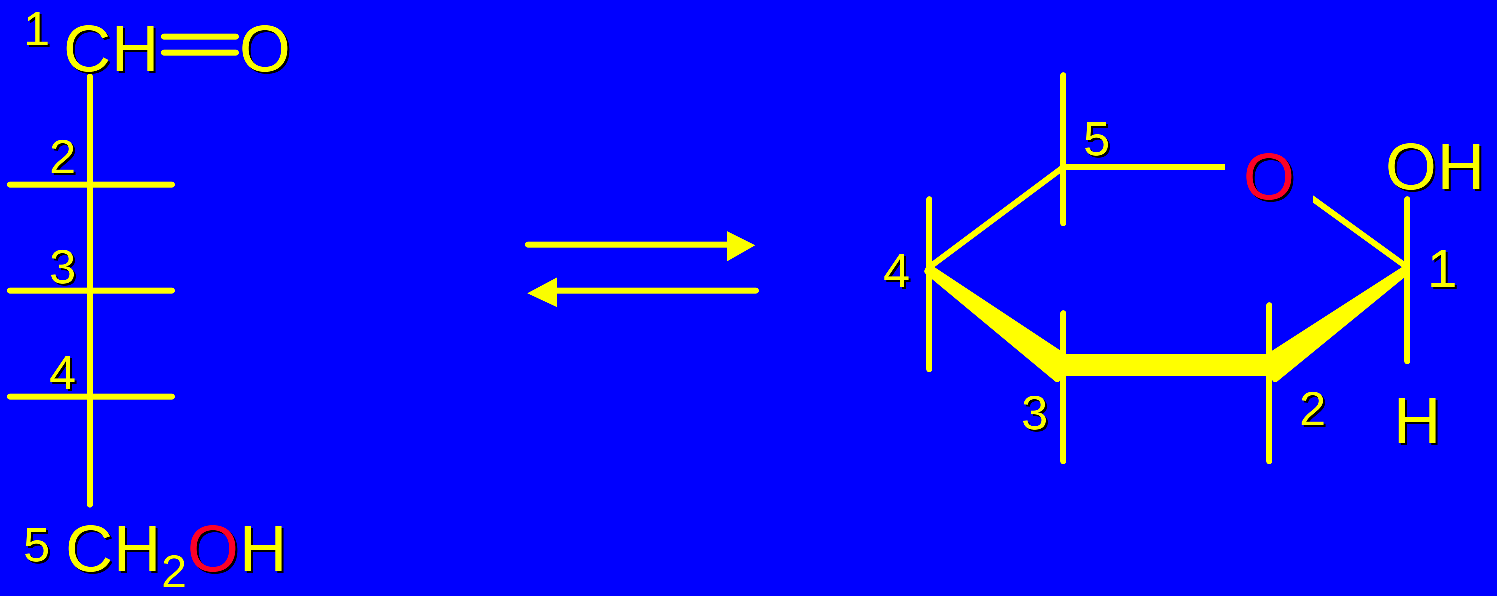
β-D-Ribofuranose

CH_2OH group becomes a substituent on ring

25.7

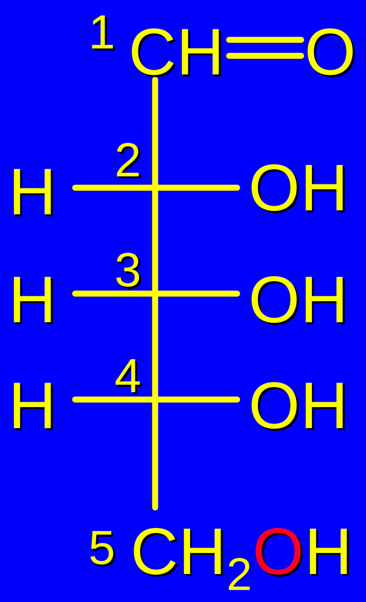
Cyclic Forms of Carbohydrates: Pyranose Forms

Carbohydrates Form Cyclic Hemiacetals



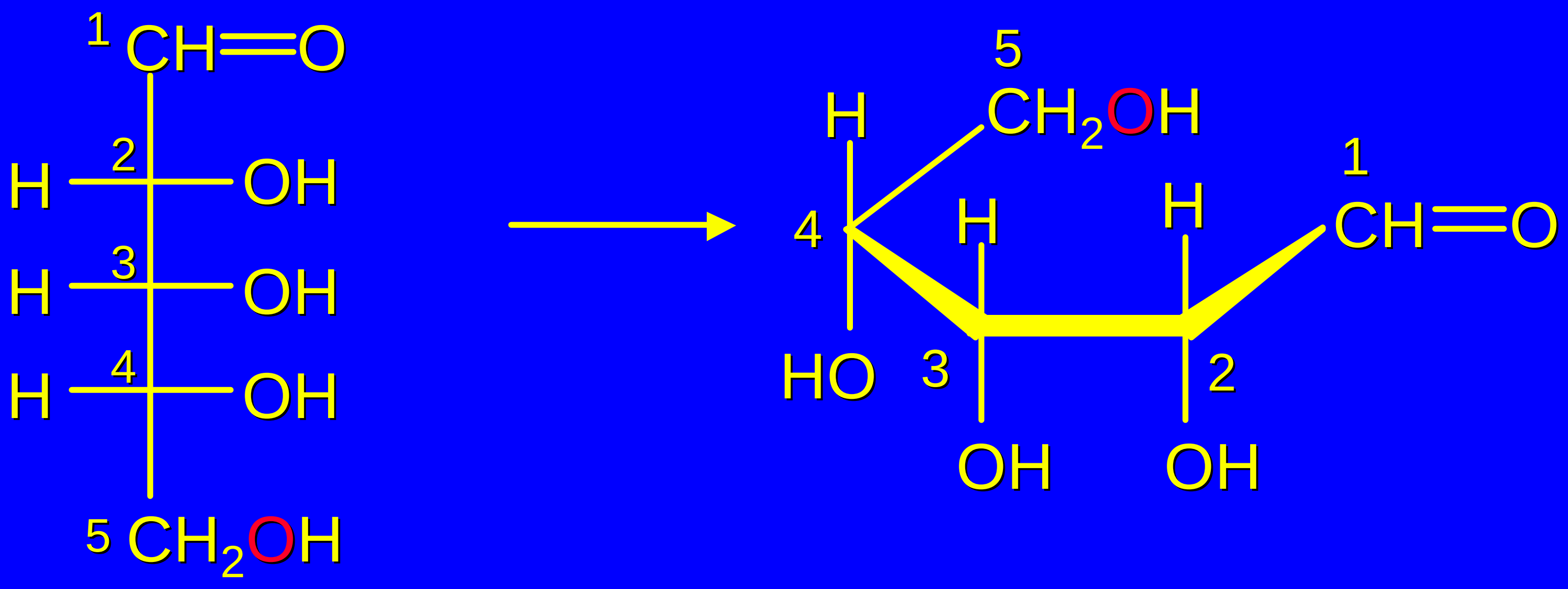
cyclic hemiacetals that have 6-membered rings are called pyranose forms

D-Ribose



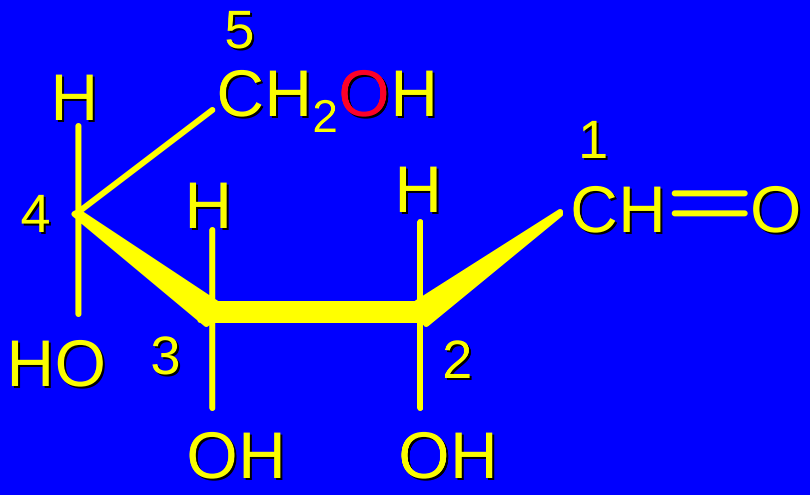
pyranose ring formation involves OH group at C-5

D-Ribose



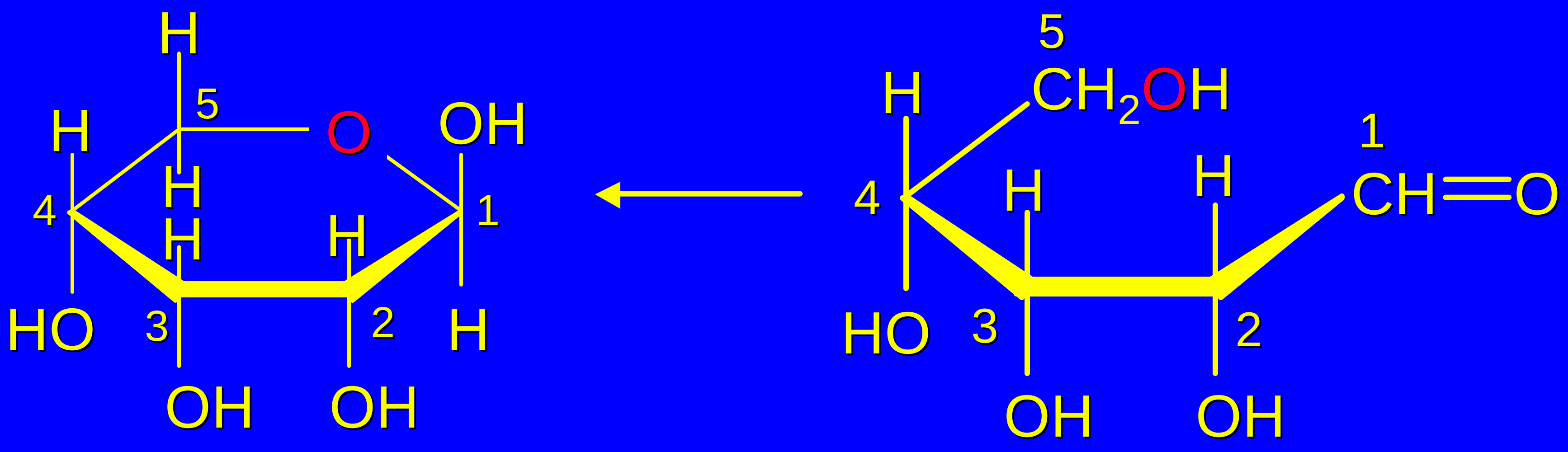
pyranose ring formation involves OH group at C-5

D-Ribose



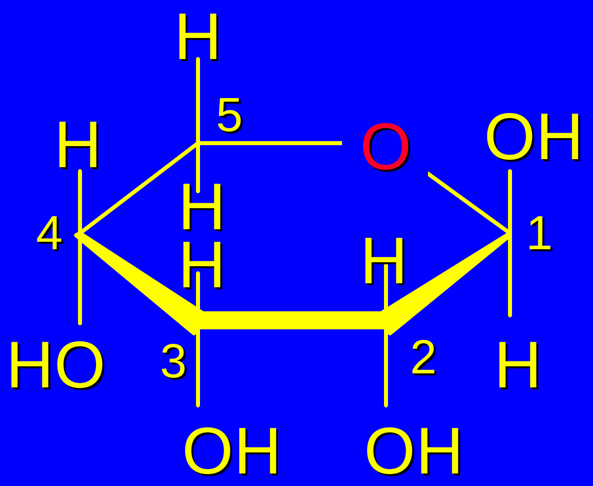
pyranose ring formation involves OH group at C-5

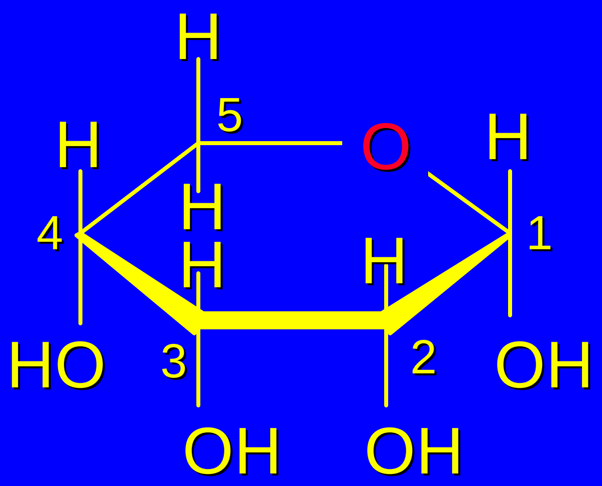
D-Ribose



β-D-Ribopyranose

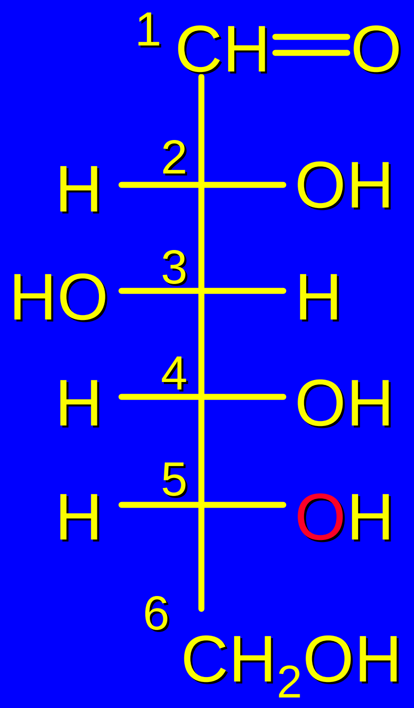
D-Ribose





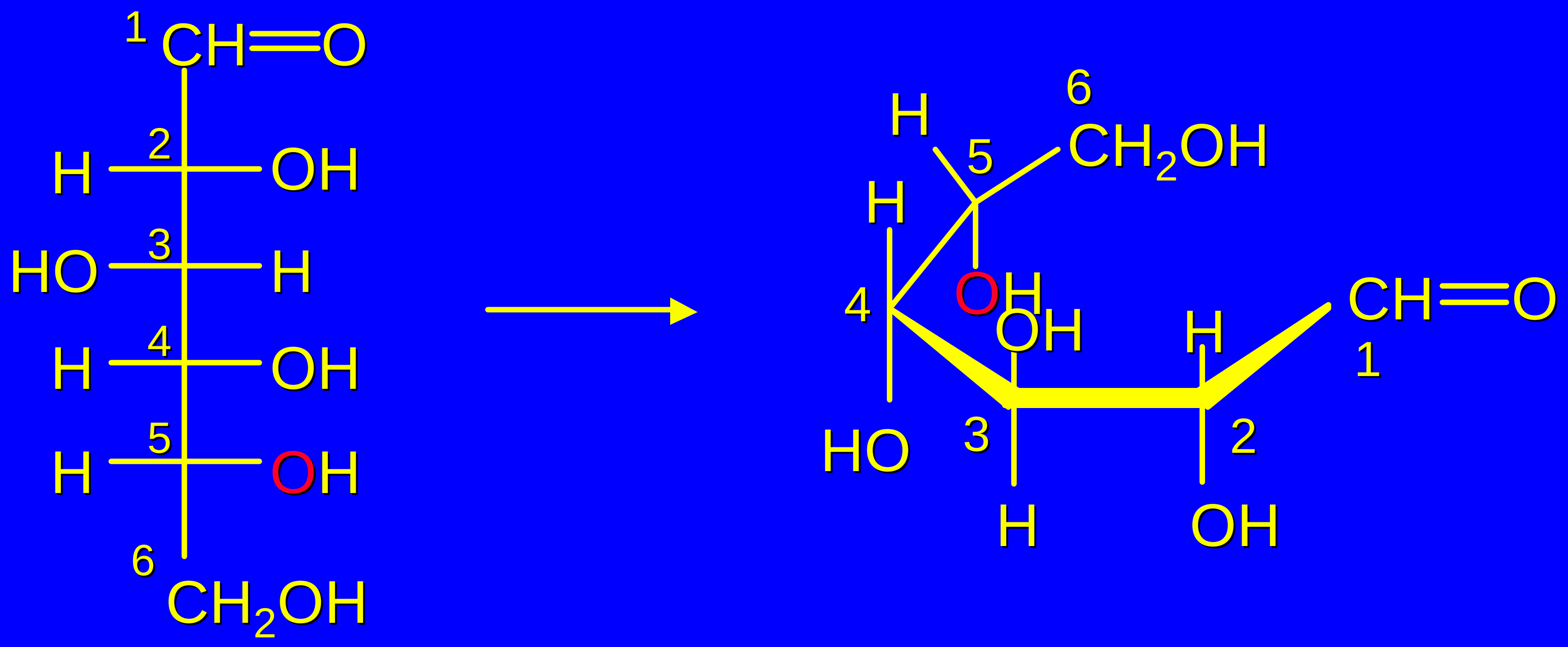
α-D-Ribopyranose

D-Glucose



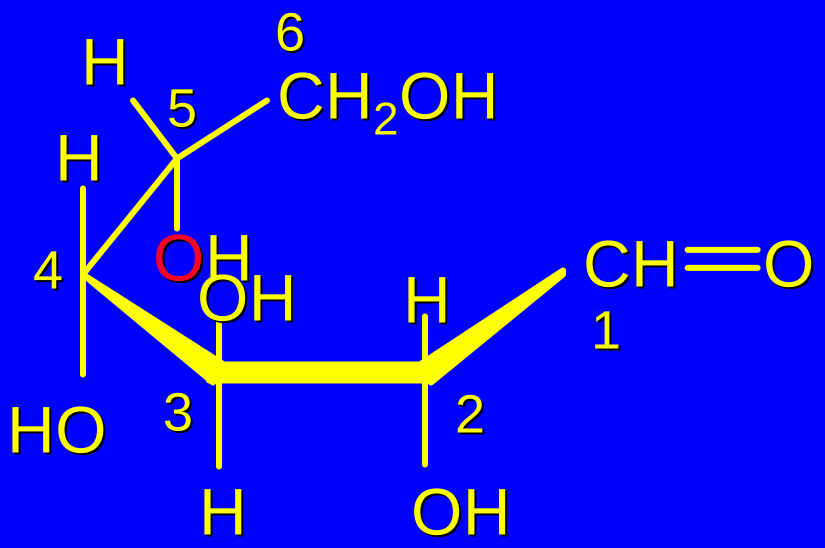
pyranose ring formation involves OH group at C-5

D-Glucose



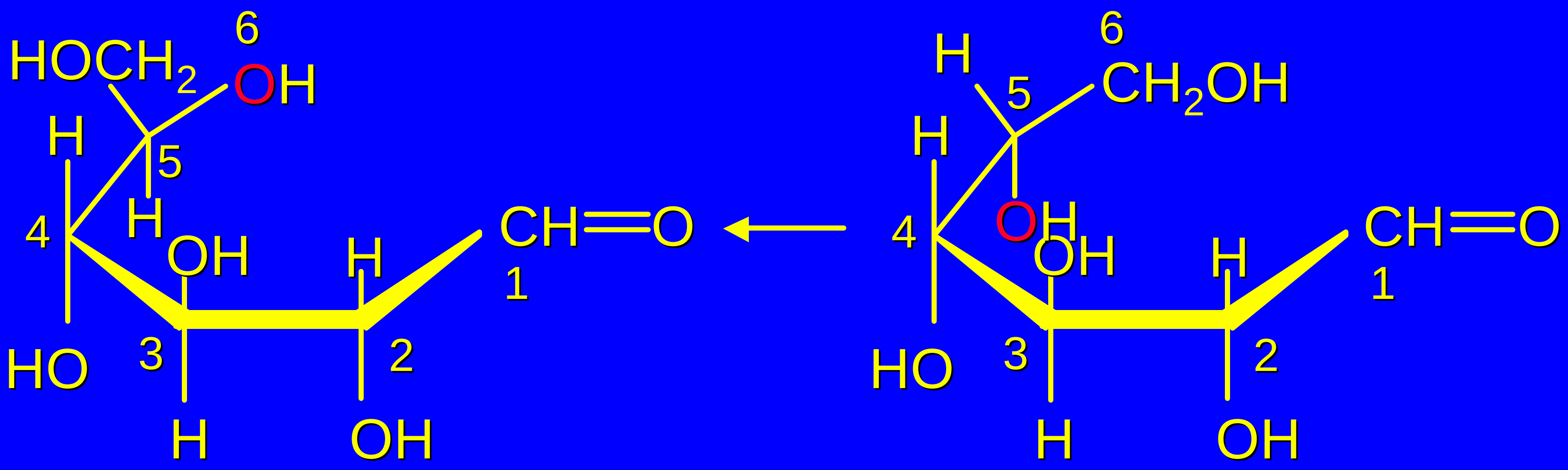
pyranose ring formation involves OH group at C-5

D-Glucose



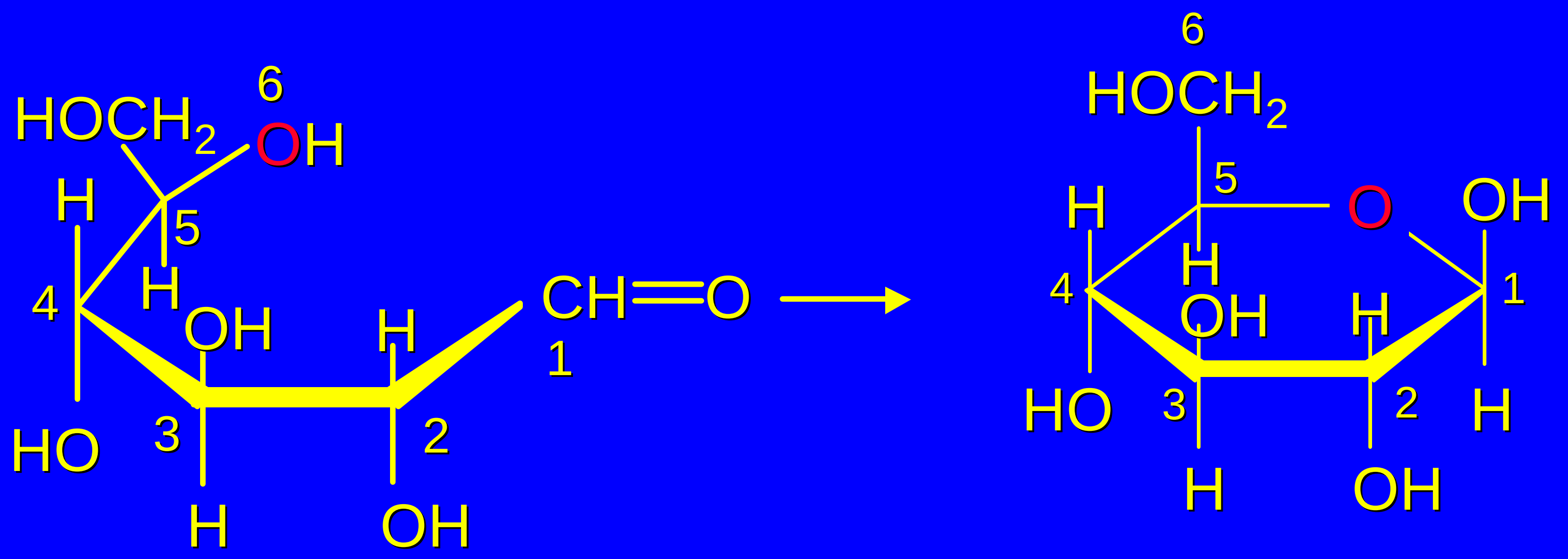
need C(4)-C(5) bond rotation to put OH in proper orientation to close 6-membered ring

D-Glucose



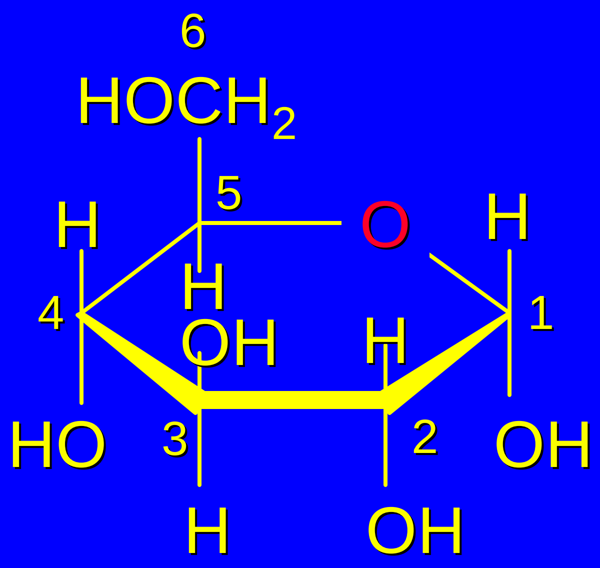
need C(4)-C(5) bond rotation to put OH in proper orientation to close 6-membered ring

D-Glucose

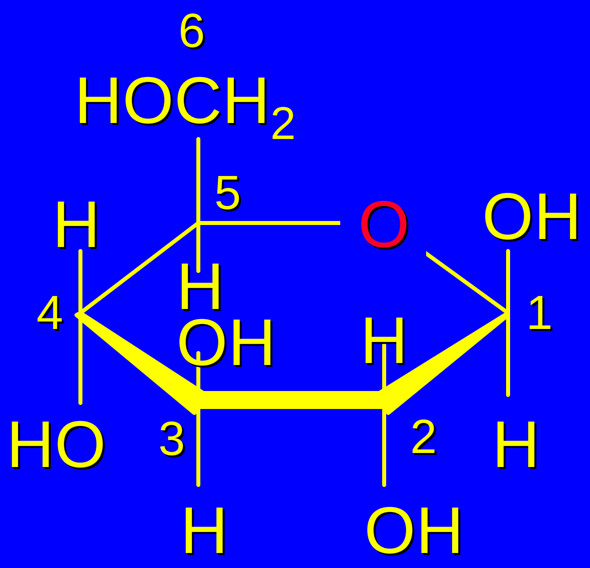


β-D-Glucopyranose

D-Glucose

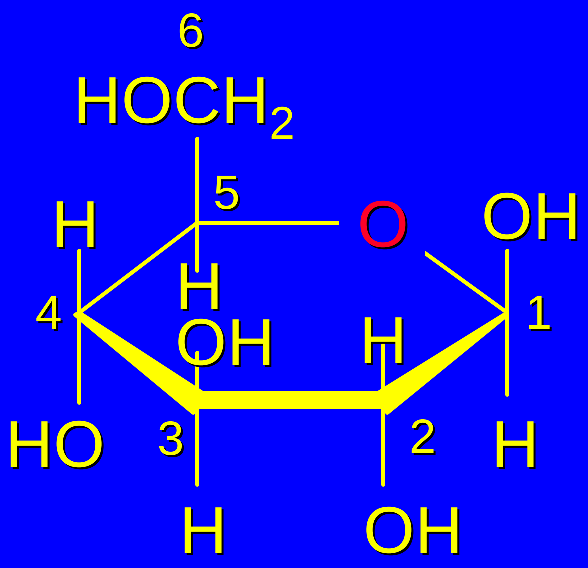


α-D-Glucopyranose



β-D-Glucopyranose

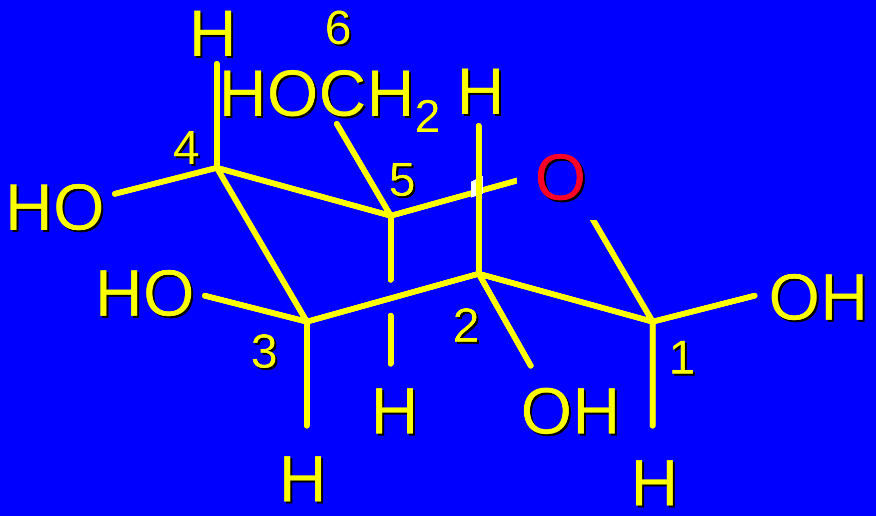
D-Glucose

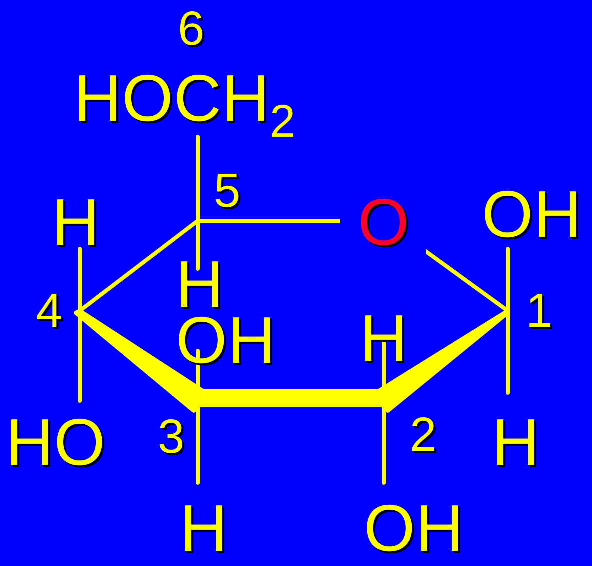


β-D-Glucopyranose

pyranose forms of carbohydrates adopt chair conformations

D-Glucose

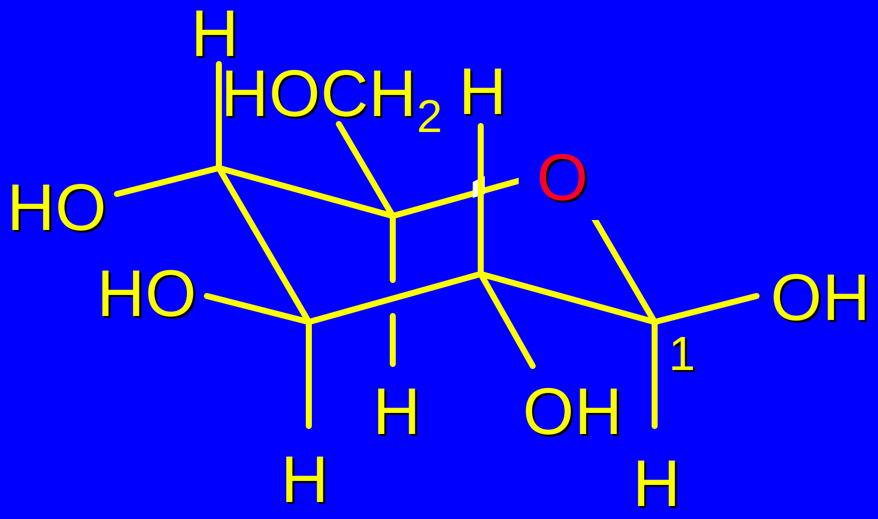




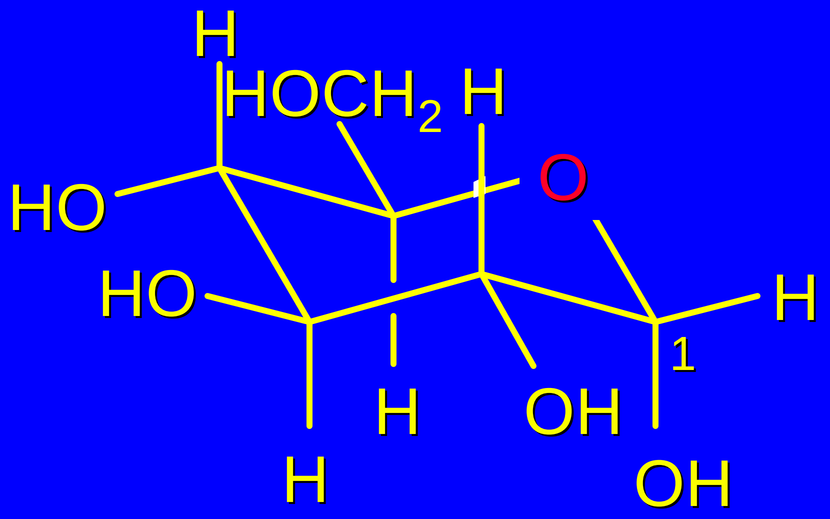
β-D-Glucopyranose

all substituents are equatorial in β-D-glucopyranose

D-Glucose



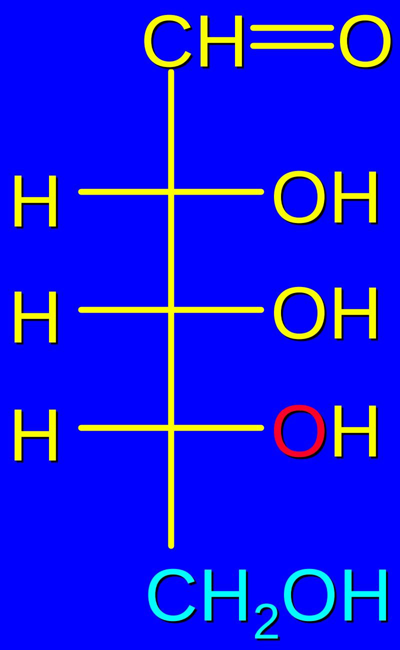
β-D-Glucopyranose



α-D-Glucopyranose

OH group at anomeric carbon is axial
in α-D-glucopyranose

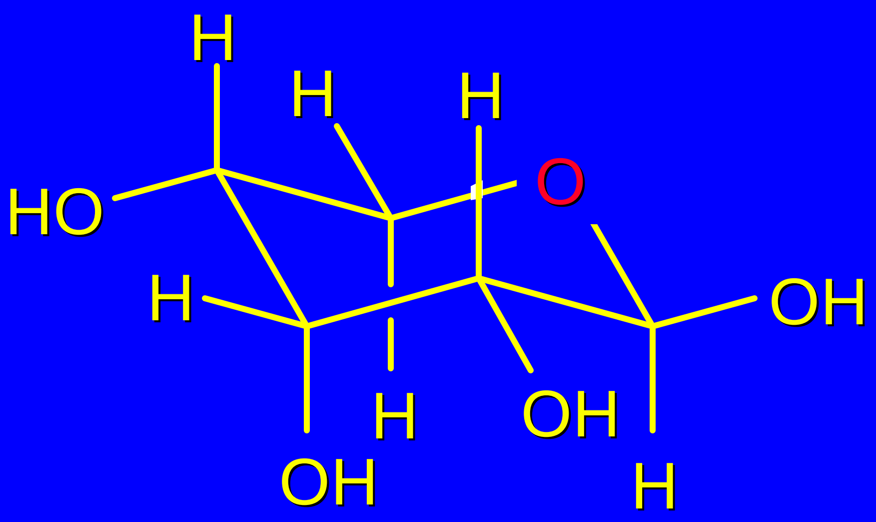
Figure 25.5



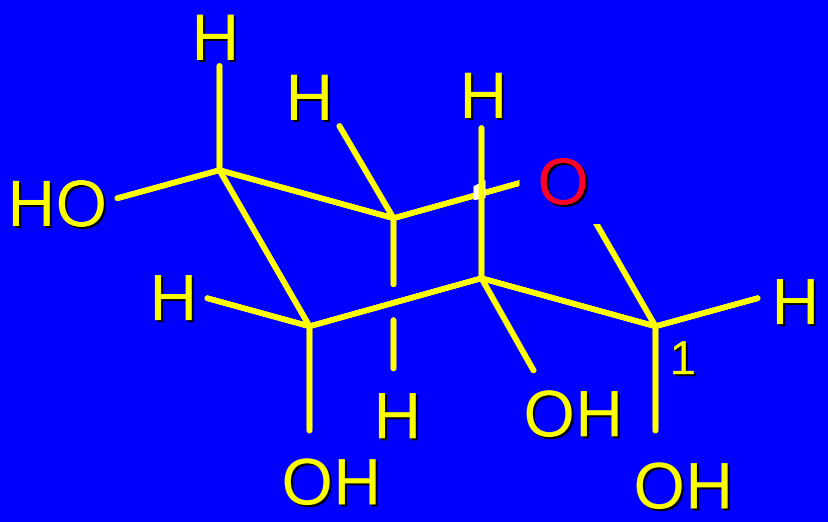
Less than 1% of the open-chain form of D-ribose is present at equilibrium in aqueous solution.

Figure 25.5

76% of the D-ribose is a mixture of the α and β-pyranose forms, with the β-form predominating



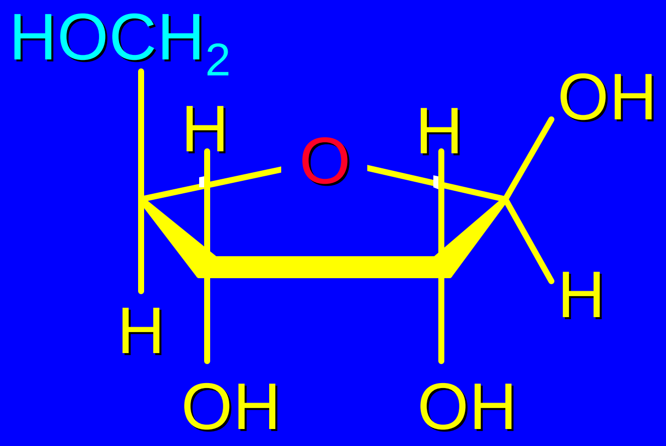
β-D-Ribopyranose (56%)



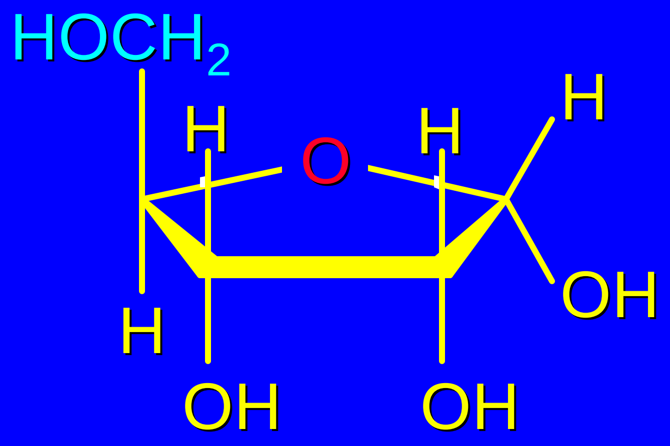
α-D-Ribopyranose (20%)

Figure 25.5

The α and β-furanose forms comprise 24% of the mixture.



β-D-Ribofuranose (18%)



α-D-Ribofuranose (6%)

25.8

Mutarotation

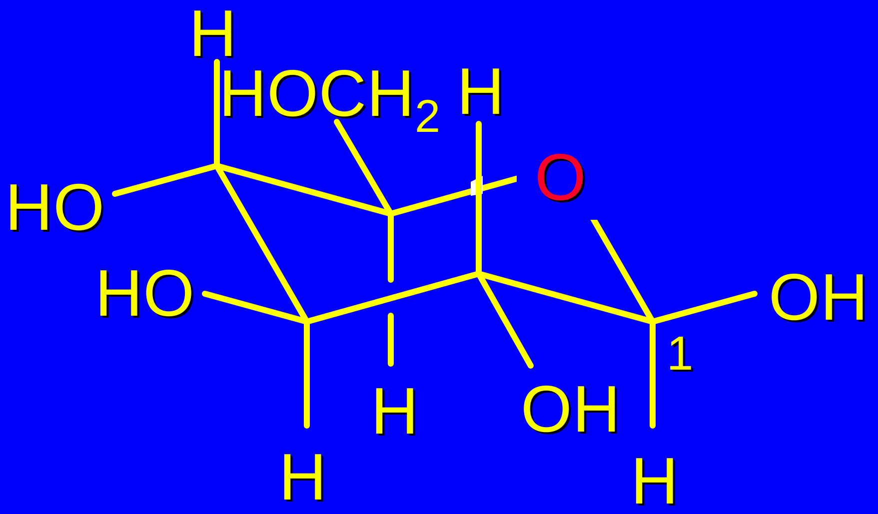
Mutarotation

Mutarotation is a term given to the change in the observed optical rotation of a substance with time.

Glucose, for example, can be obtained in either its α or β-pyranose form. The two forms have different physical properties such as melting point and optical rotation.

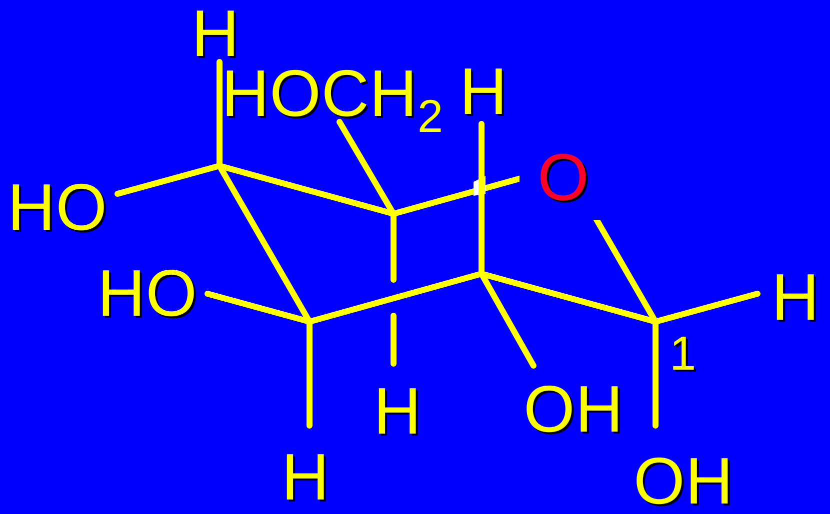
When either form is dissolved in water, its initial rotation changes with time. Eventually both solutions have the same rotation.

Mutarotation of D-Glucose



β-D-Glucopyranose

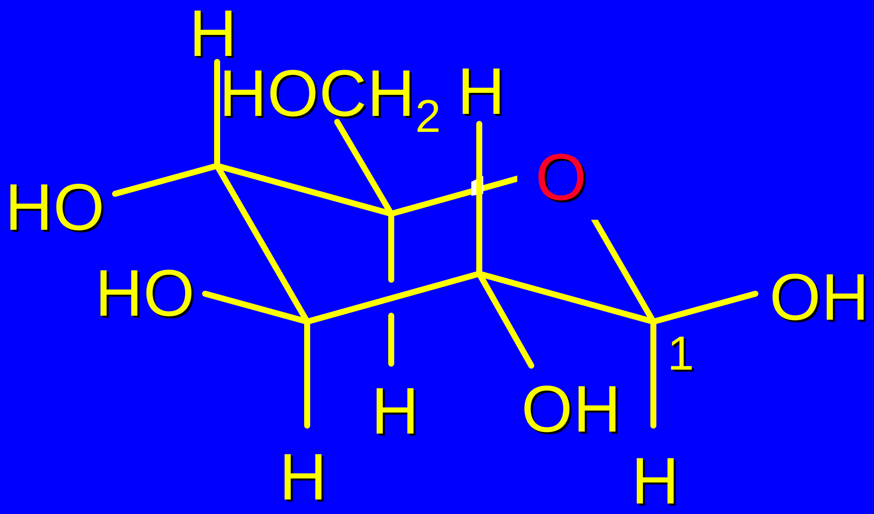
Initial: $[\alpha]_D$ +18.7°



α-D-Glucopyranose

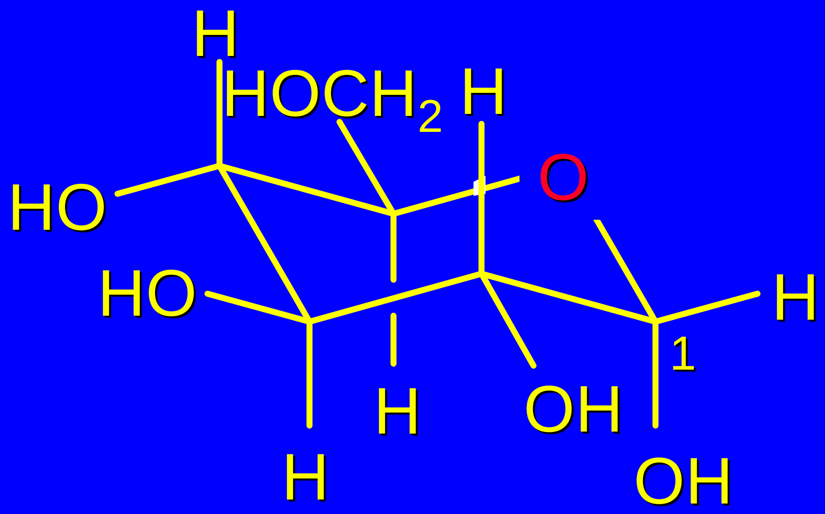
Initial: $[\alpha]_D$ +112.2°

Mutarotation of D-Glucose



β-D-Glucopyranose

Initial: $[\alpha]_D$ +18.7°

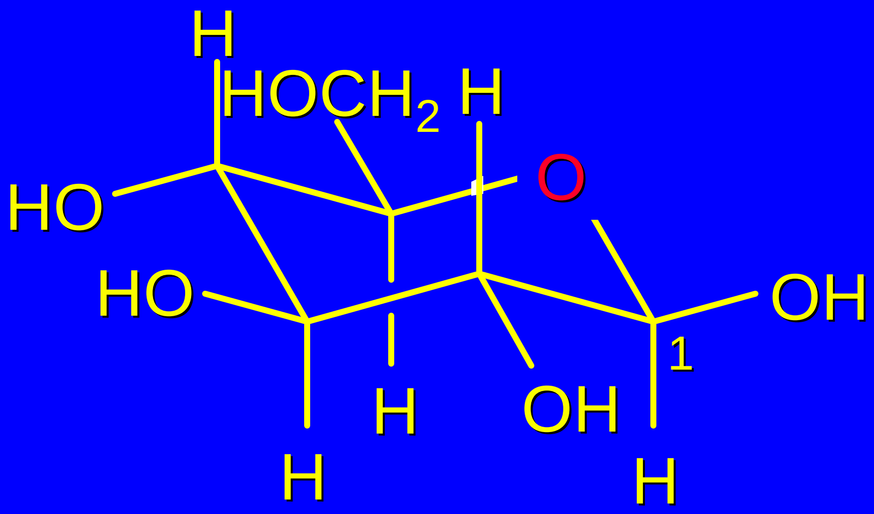


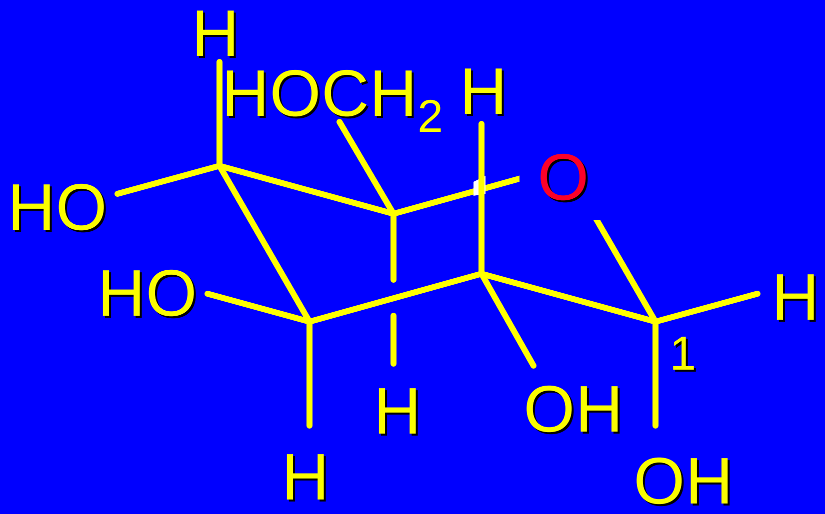
α-D-Glucopyranose

Initial: $[\alpha]_D$ +112.2°

Final: $[\alpha]_D$ +52.5°

Mutarotation of D-Glucose





β-D-Glucopyranose

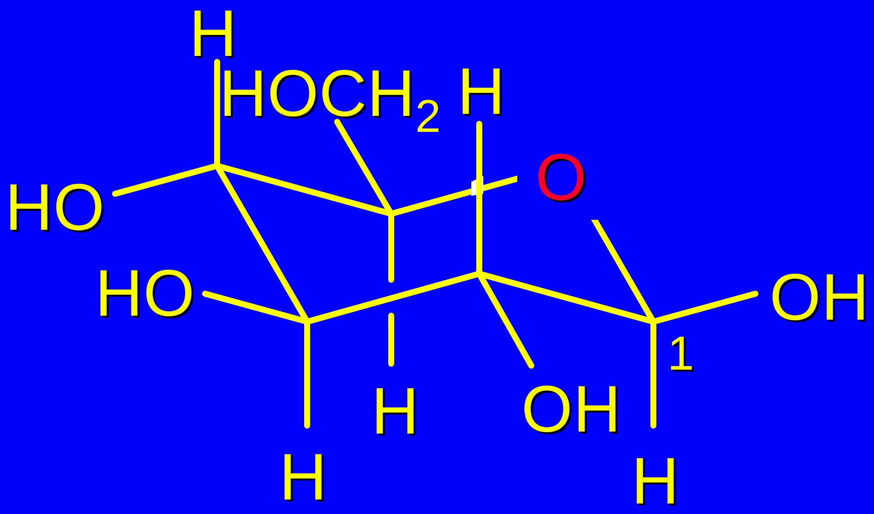
Initial: $[\alpha]_D$ +18.7°

α-D-Glucopyranose

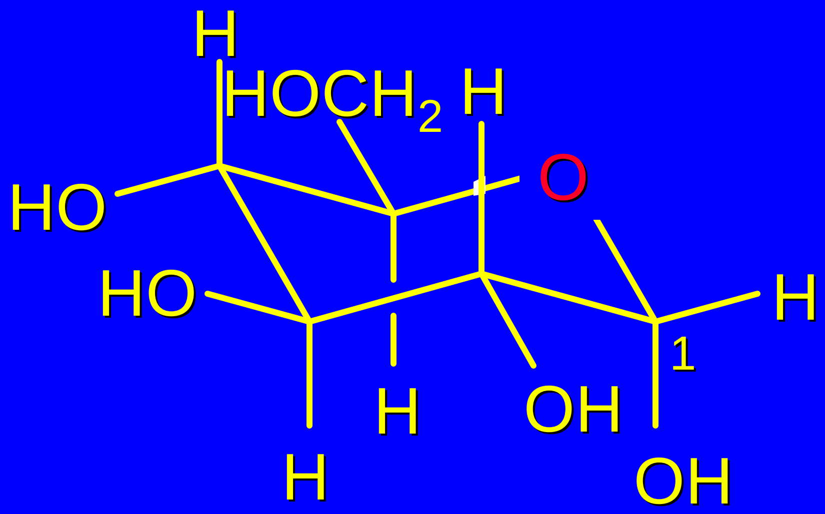
Initial: $[\alpha]_D$ +112.2°

→ Final: $[\alpha]_D$ +52.5° ←

Mutarotation of D-Glucose



β-D-Glucopyranose



α-D-Glucopyranose

Explanation: After being dissolved in water, the α and β forms slowly interconvert via the open-chain form. An equilibrium state is reached that contains 64% β and 36% α.