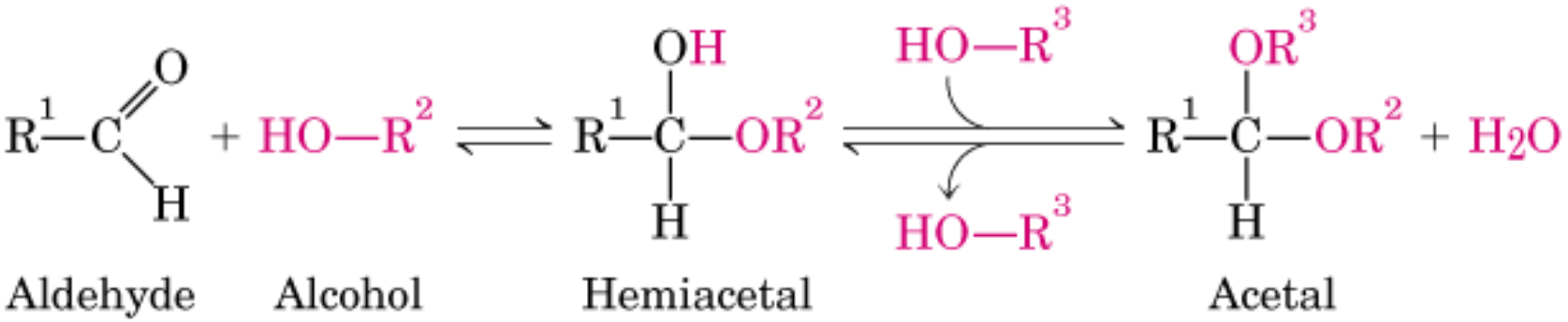
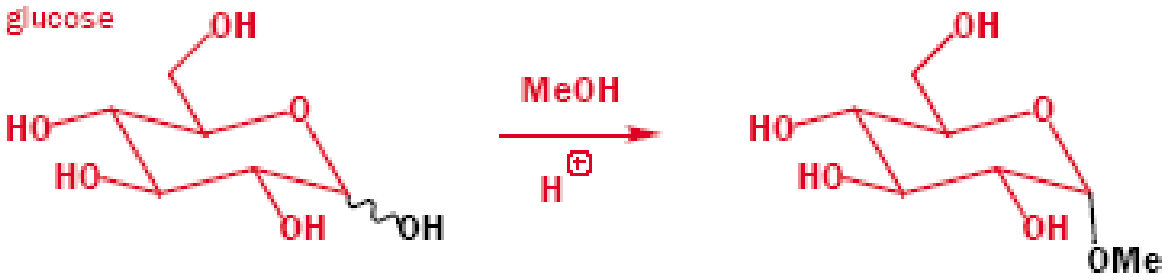
TEMA 3.

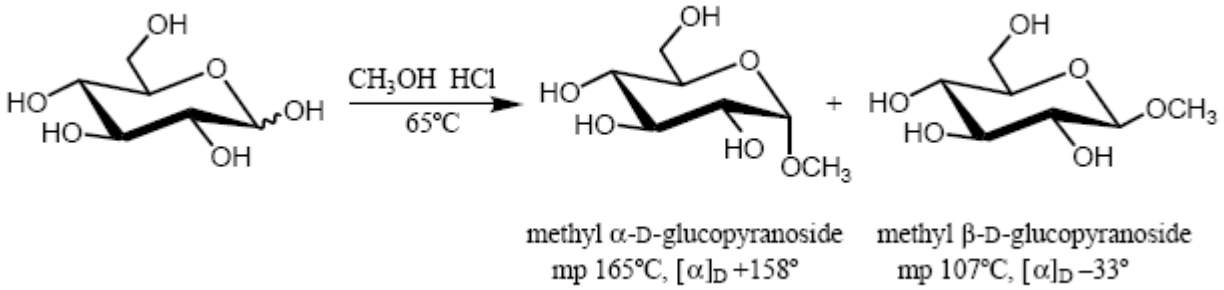
CARBOHIDRATOS: GLICÓSIDOS Y OLIGOSACÁRIDOS.


R1—C(=O)—H
+ HO—R2
R1—C(OH)(H)—OR2
HO—R3
HO—R3
R1—C(OR3)(H)—OR2
+ H2O
Aldehyde
Alcohol
Hemiacetal
Acetal

Las estructuras piranósicas de los azúcares pueden ser ancladas mediante la formación de acetales



Síntesis de Fisher (1893)

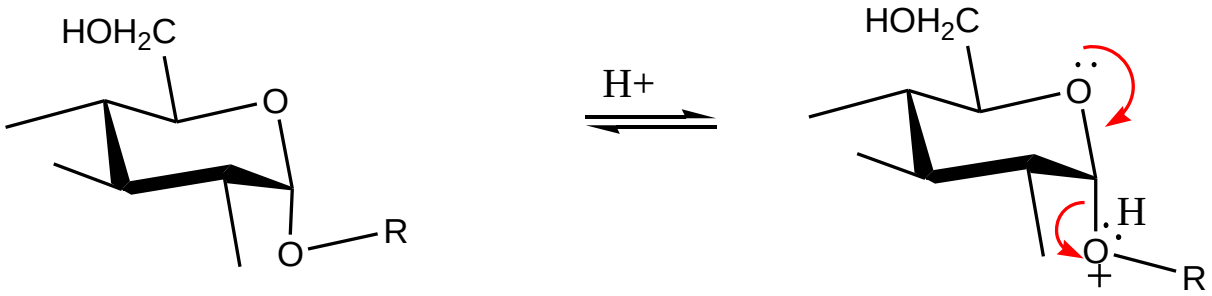


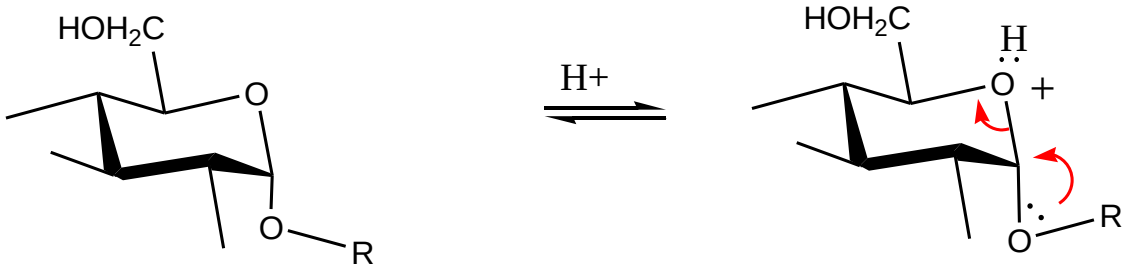
methyl α-D-glucopyranoside
mp 165°C, $[\alpha]_D$ +158°

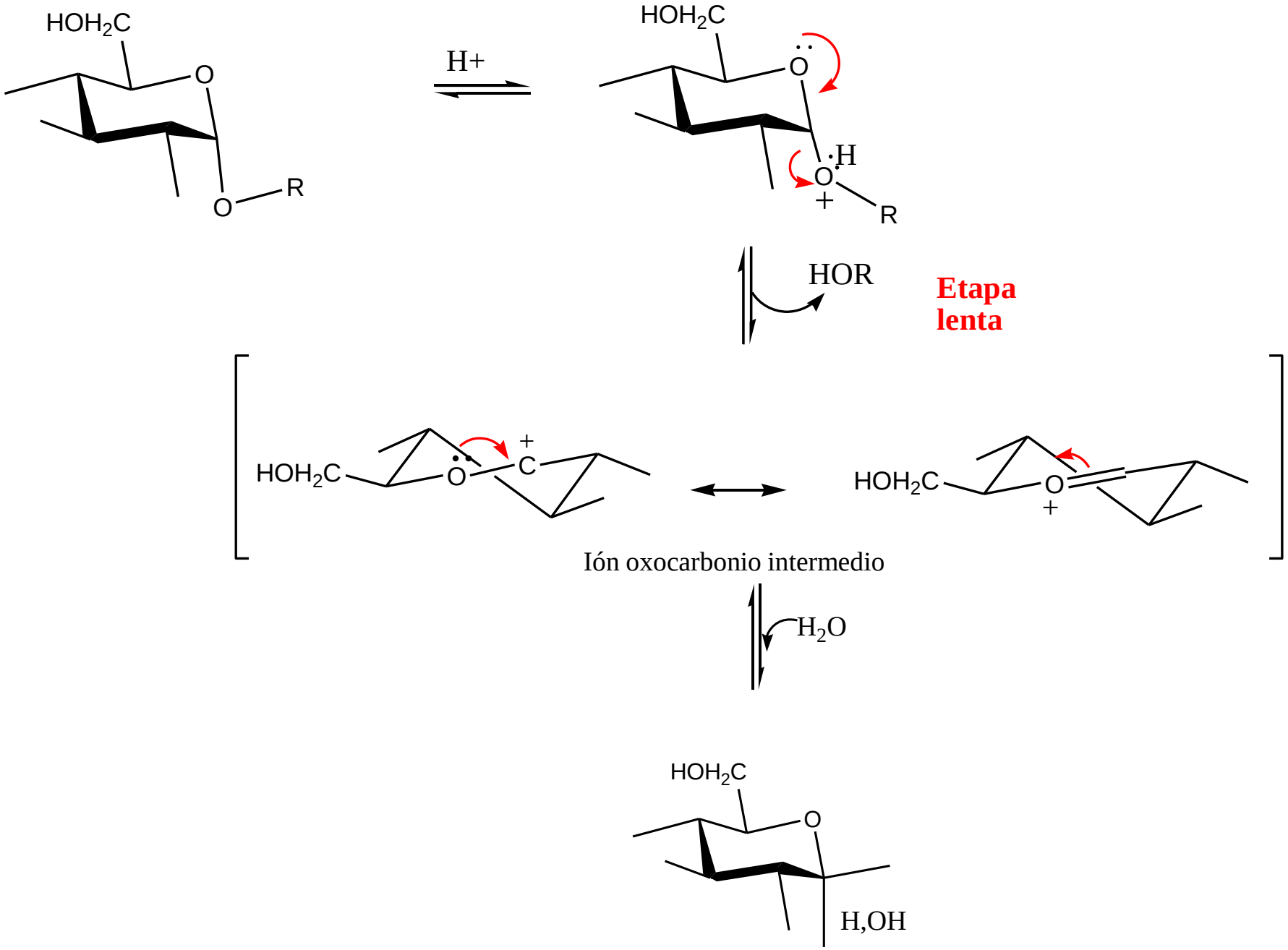
methyl β-D-glucopyranoside
mp 107°C, $[\alpha]_D$ –33°

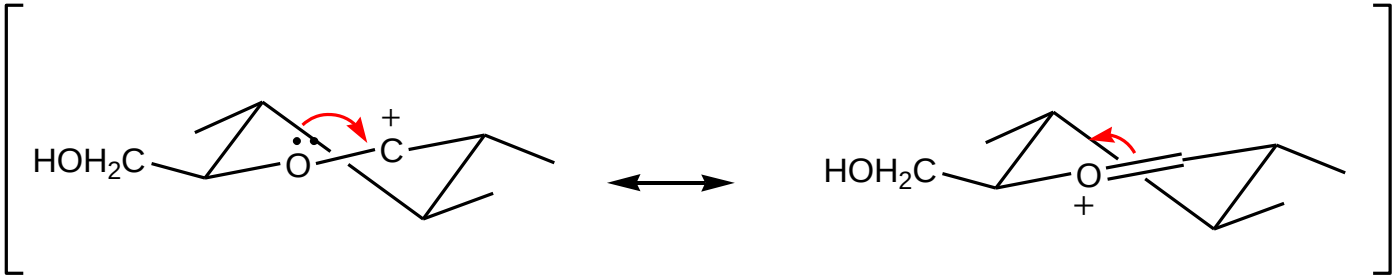
mayoritario

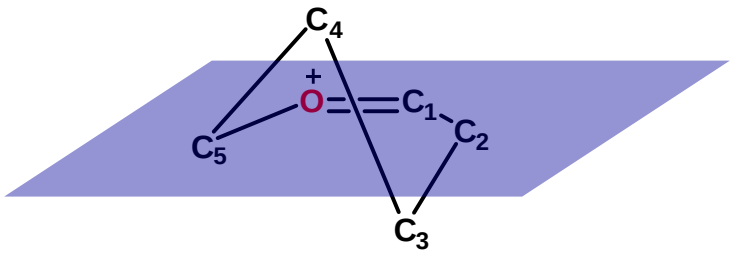
HIDRÓLISIS DE GLICÓSIDOS



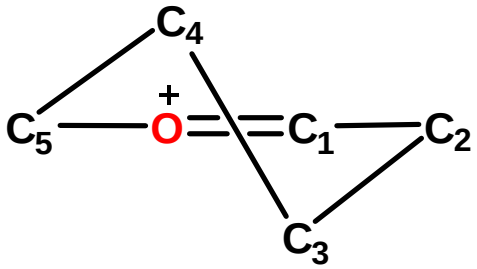


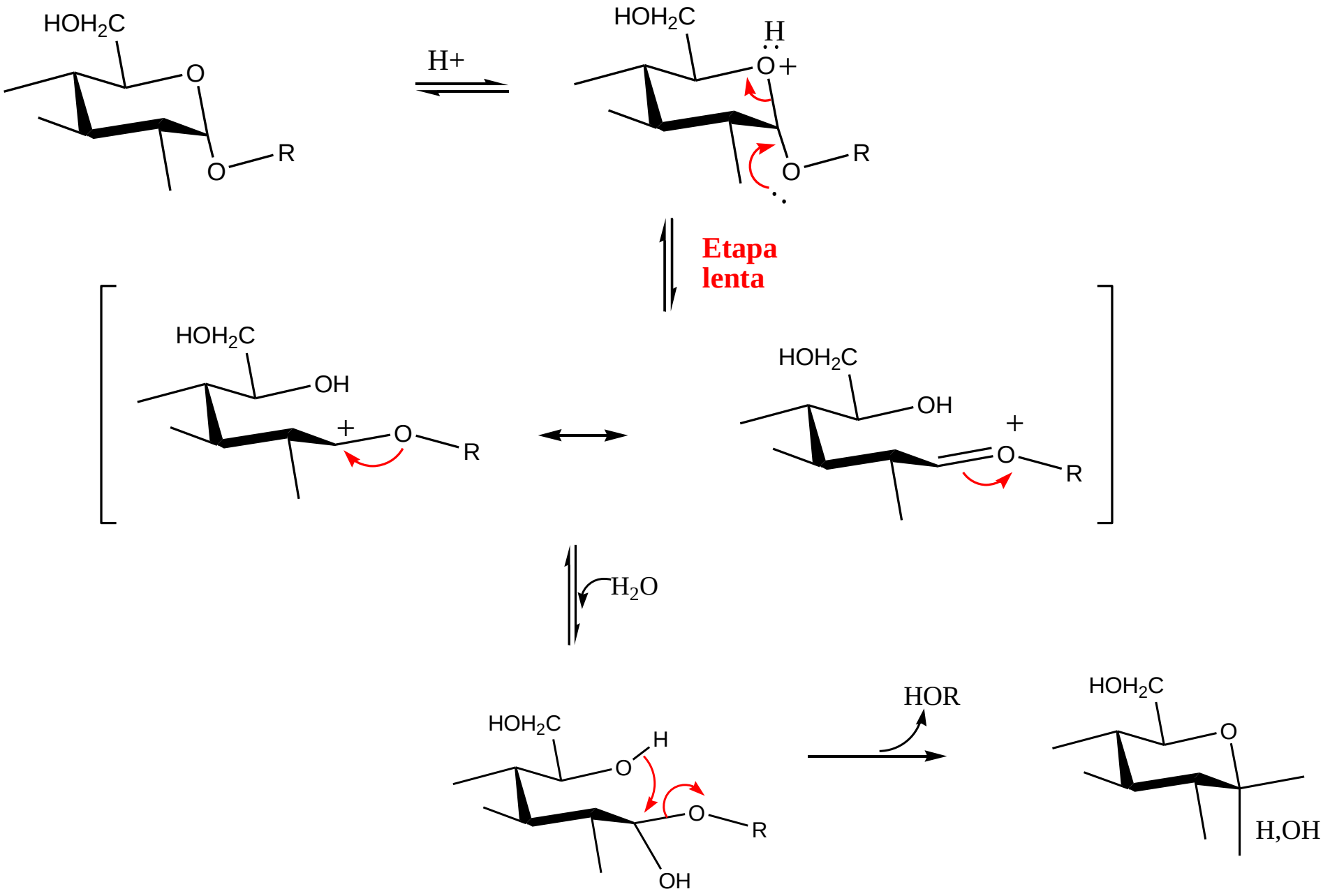

HOH2C
O
O
R
H+
HOH2C
O
O
H
+
R
HOR
Etapa lenta
HOH2C
O
+
C
HOH2C
O
+
Ión oxocarbonio intermedio
H2O
HOH2C
O
H,OH





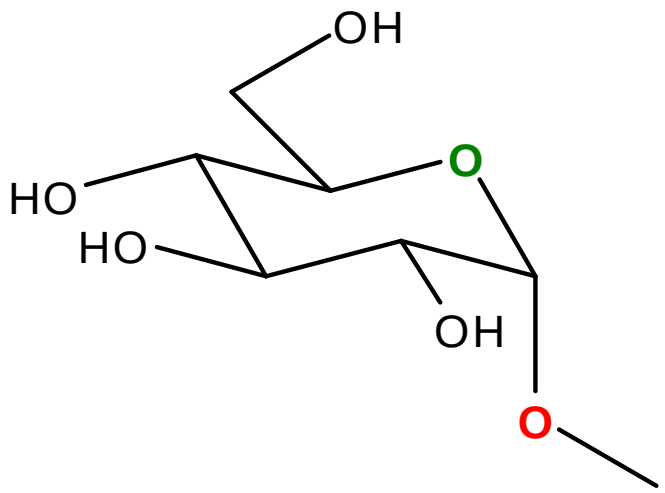
Conformación en hemisilla H_3^4




HOH2C
O
O
R
H+
HOH2C
H
O+
O
R
Etapa
lenta
HOH2C
OH
+
O
R
HOH2C
OH
+
O
R
H2O
HOH2C
H
O
O
R
OH
HOR
HOH2C
O
H,OH

No se observa Efecto isotópico

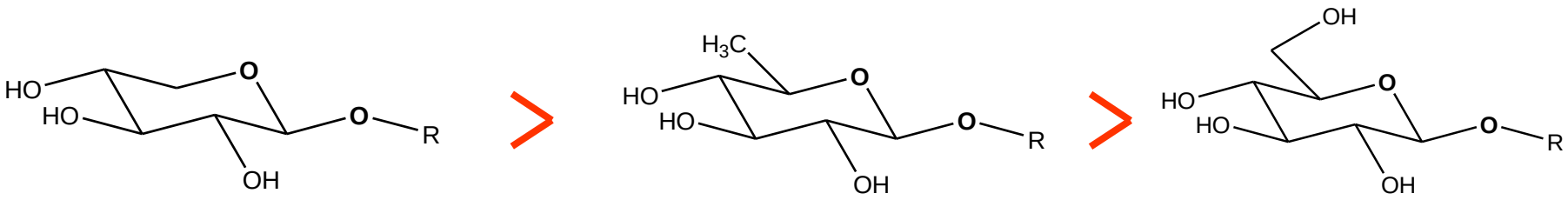
$$\frac{K_{16}}{K_{18}} = 1{,}00$$



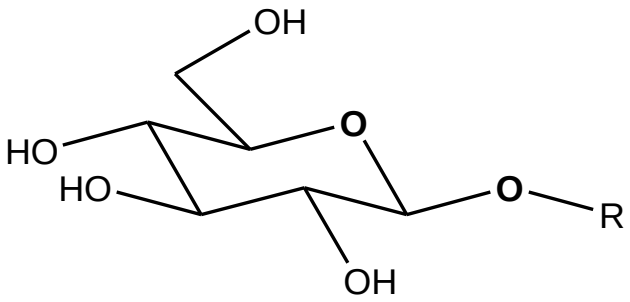
Efecto isotópico

$$\frac{K_{16}}{K_{18}} = 1{,}03$$

Velocidades relativas de Hidrólisis



Velocidades relativas de Hidrólisis



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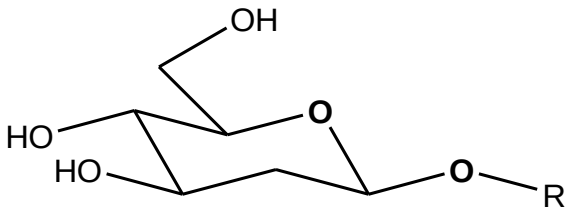
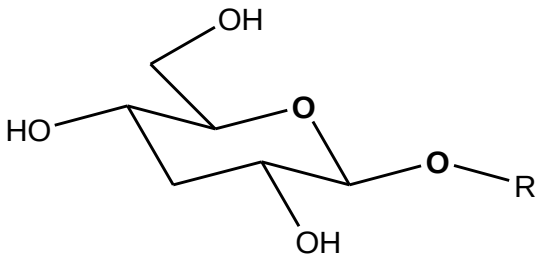


2.090



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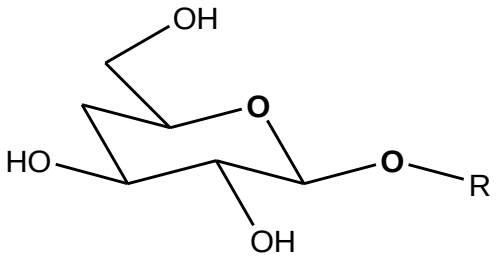

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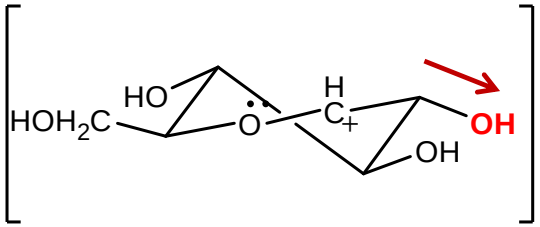
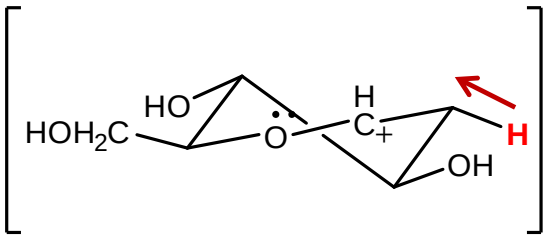
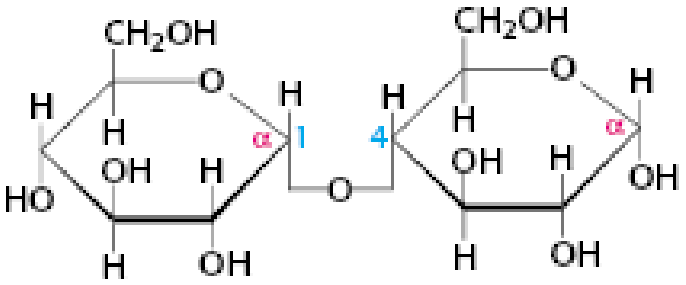
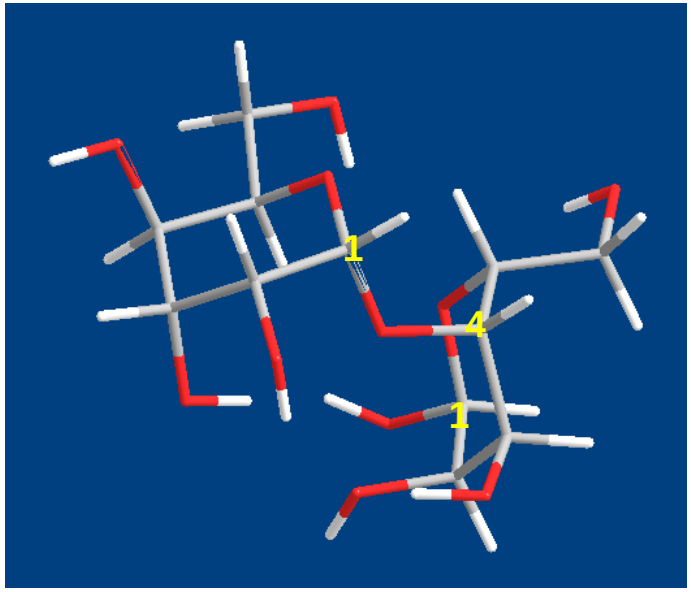
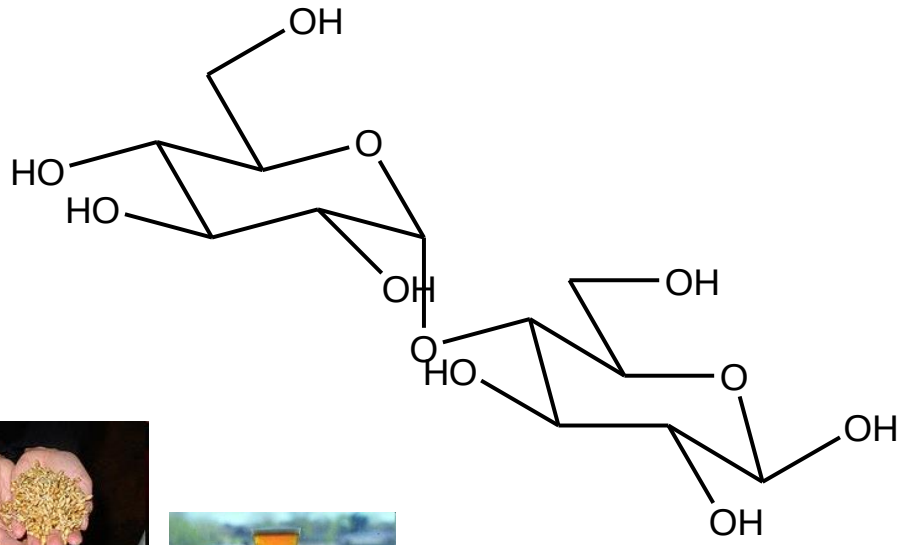


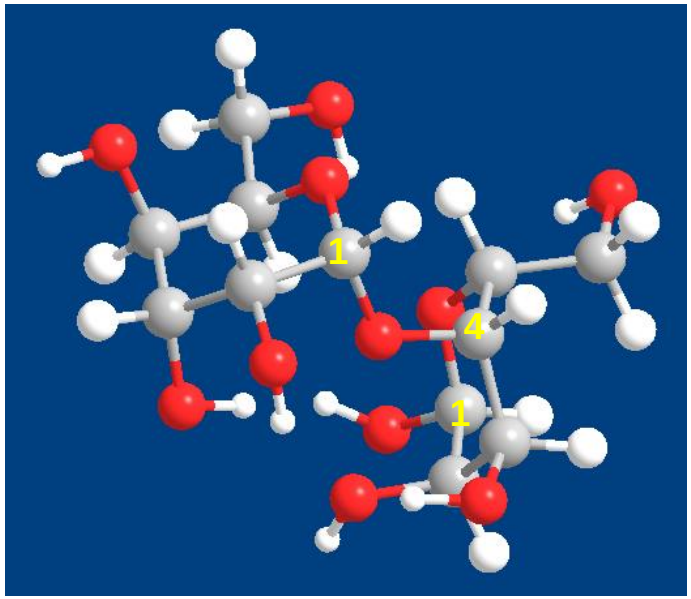


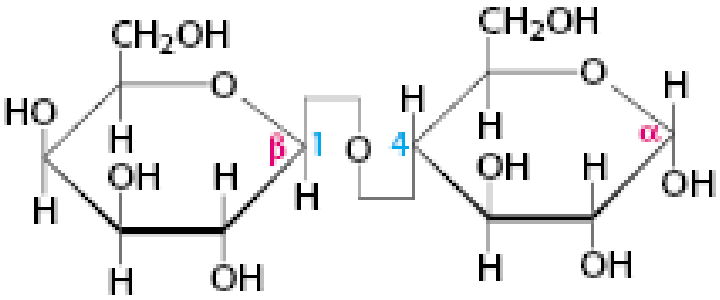


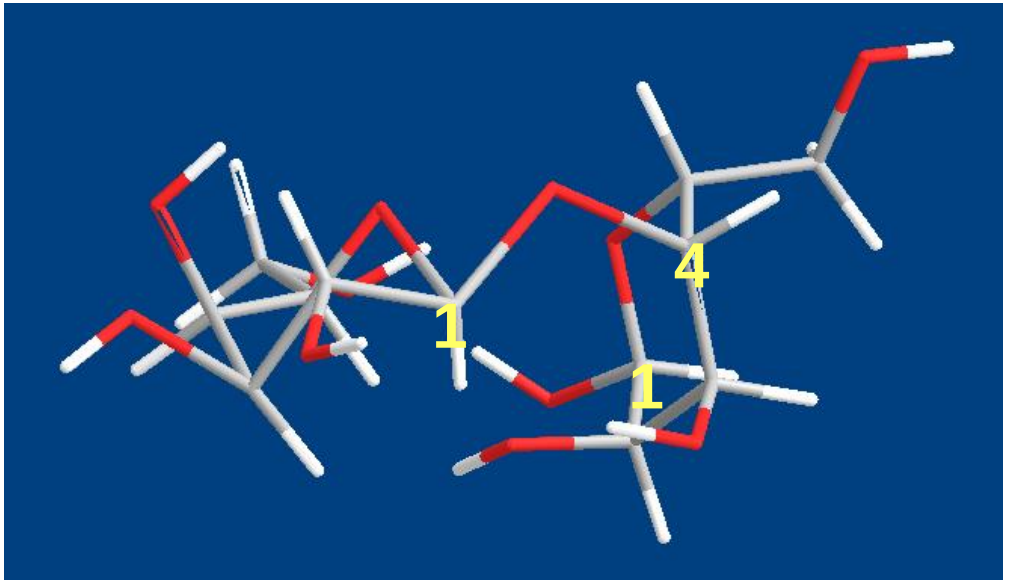
Maltose
(α-D-Glucopyranosyl-(1→4)-α-D-glucopyranose





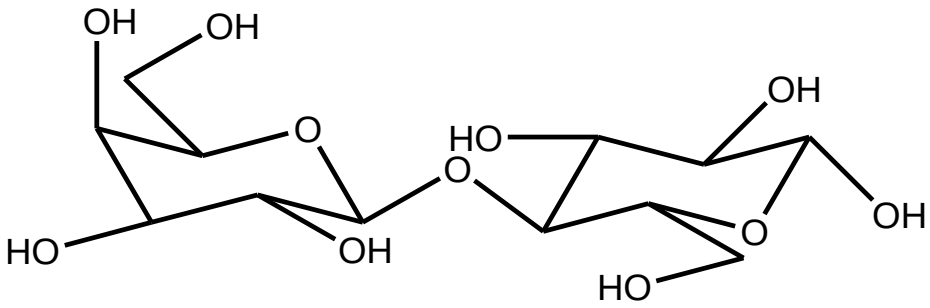


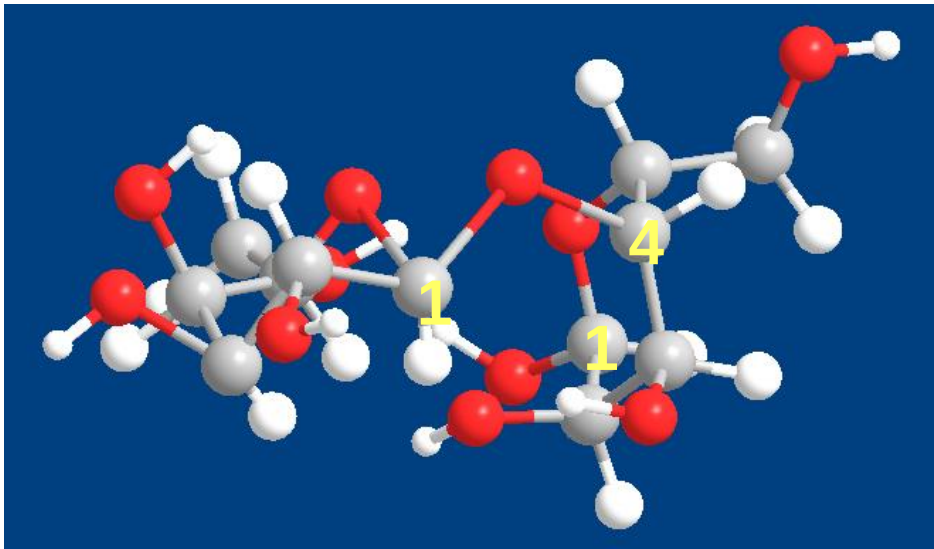


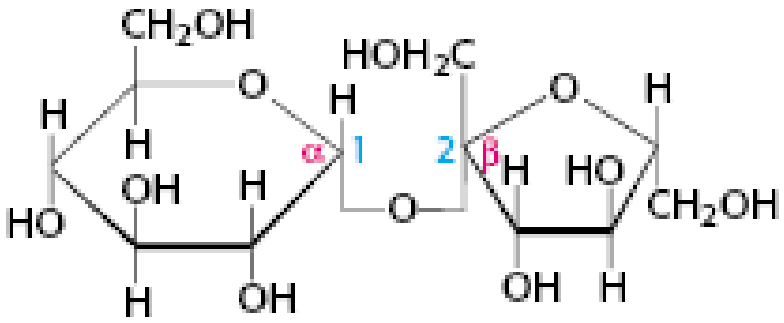


Lactosa

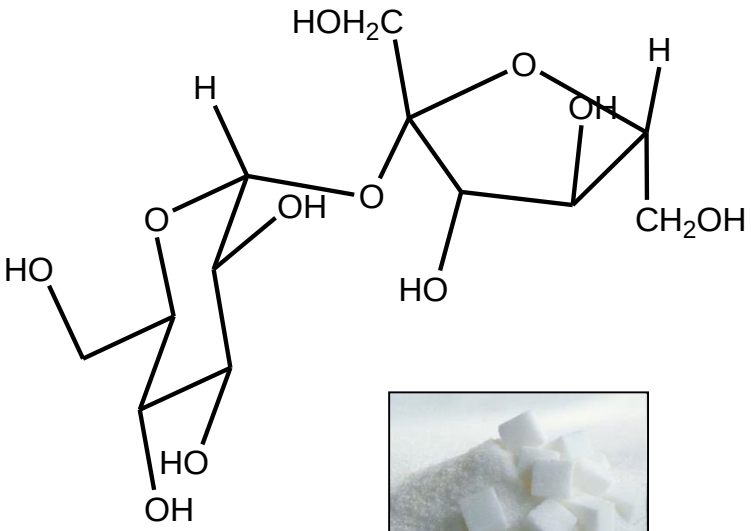
β-D-galactopiranosil-(1-4)-D-glucopiranosa

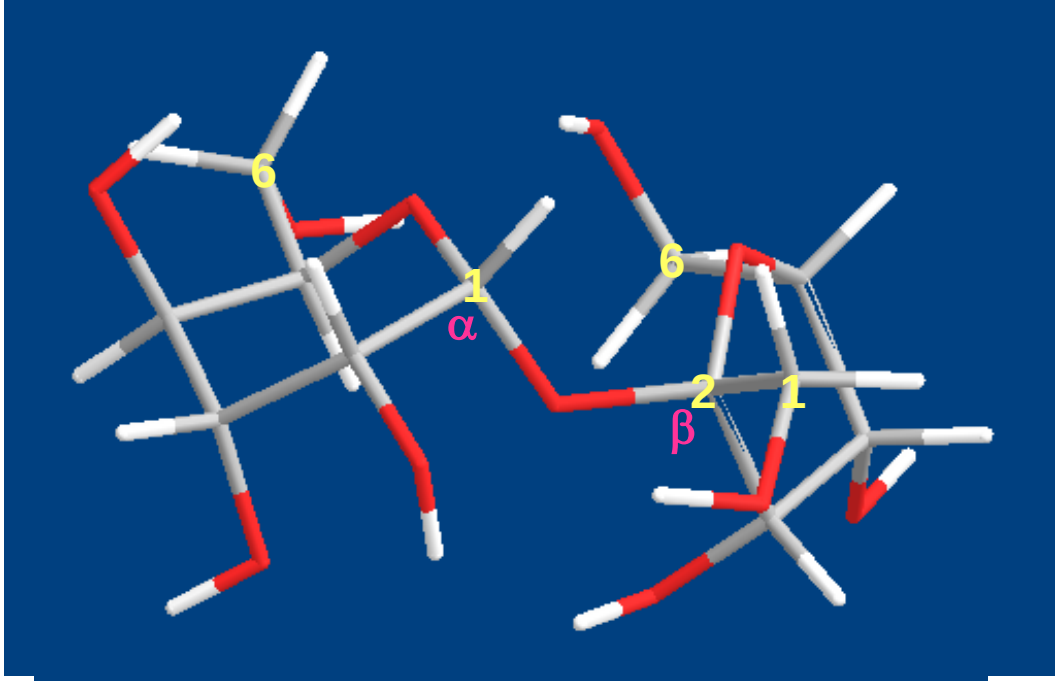


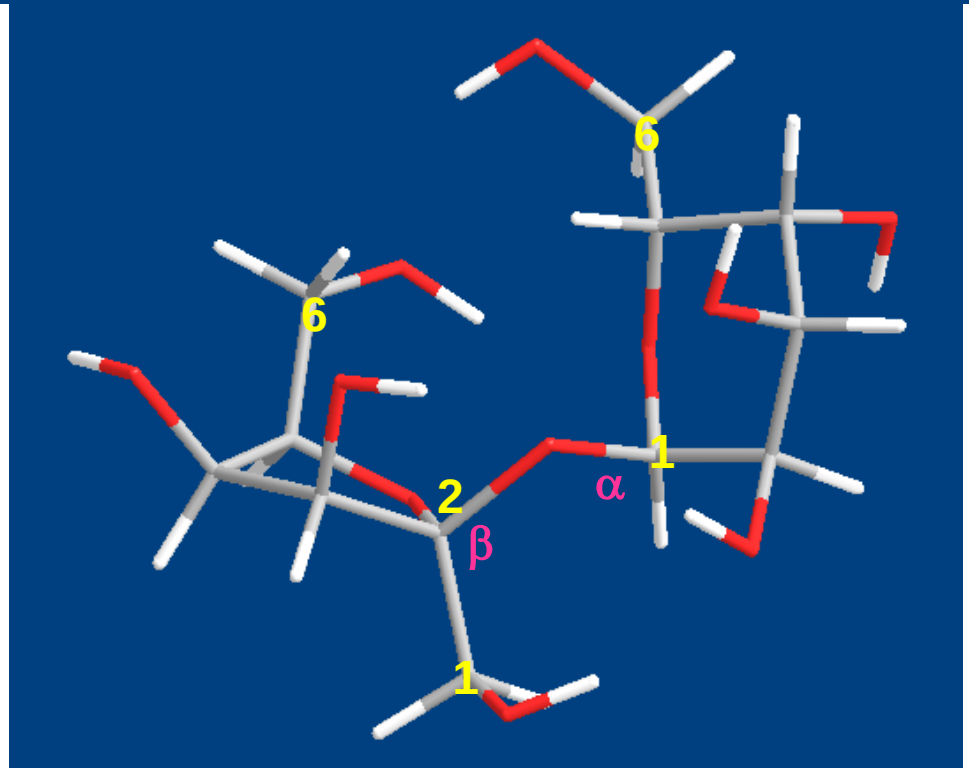


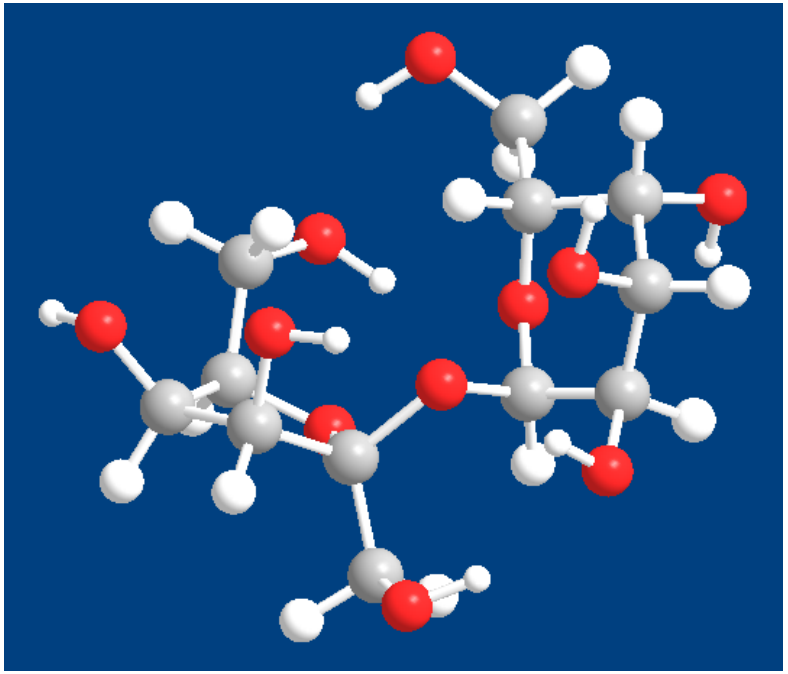


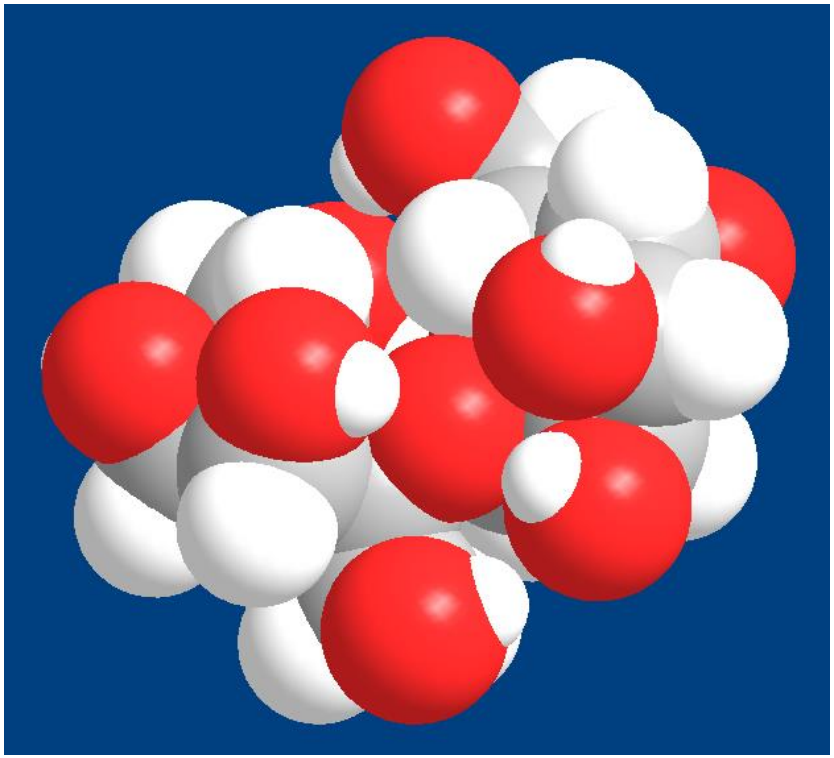
Sucrose
(α-D-Glucopyranosyl-(1 → 2)-β-D-fructofuranose











Características:

No reductor

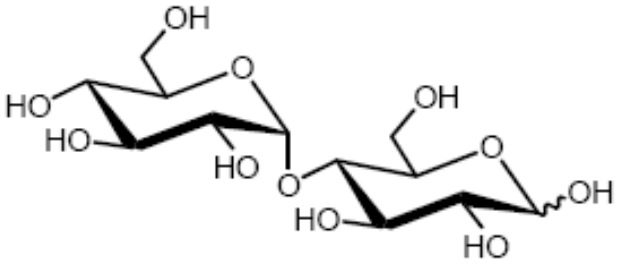
sacarosa $[\alpha]^D$ **+66º**

por hidrólisis se obtiene una mezcla equimolecular de D-glucosa y D-fructosa conocida como azúcar invertido

$[\alpha]^D$ **-22º**

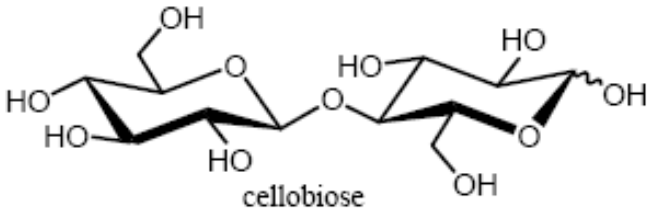
Homodisacáridos naturales de glucosa

Conexión 1-4



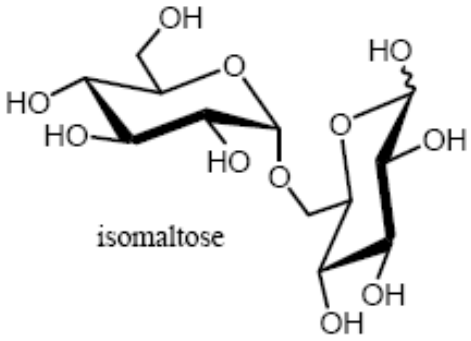
maltose

4-*O*-α-D-glucopyranosyl-D-glucopyranose

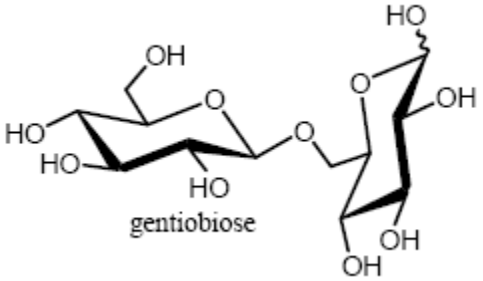


cellobiose

Conexión 1-6

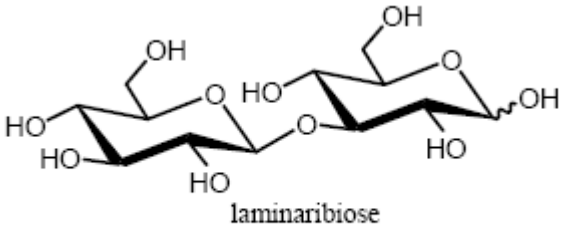


isomaltose



gentiobiose

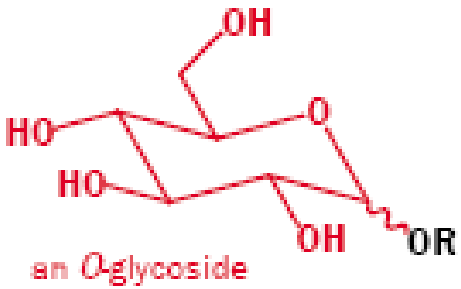
Conexión 1-3



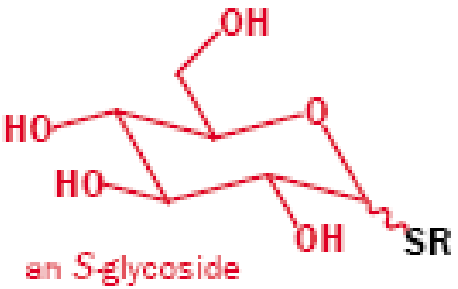
laminaribiose

Son todos reductores

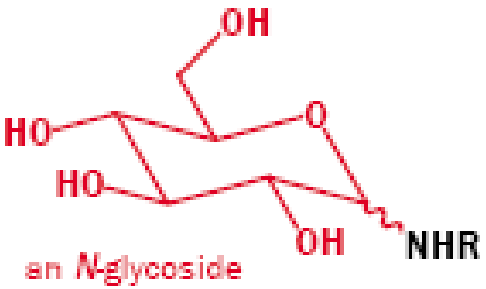
Otros glicósidos naturales



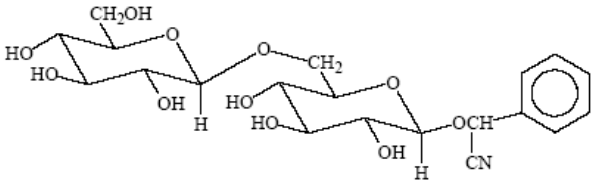
an *O*-glycoside



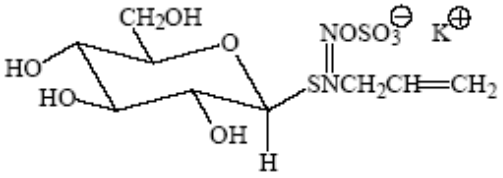
an *S*-glycoside



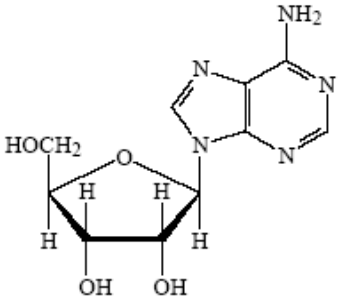
an *N*-glycoside



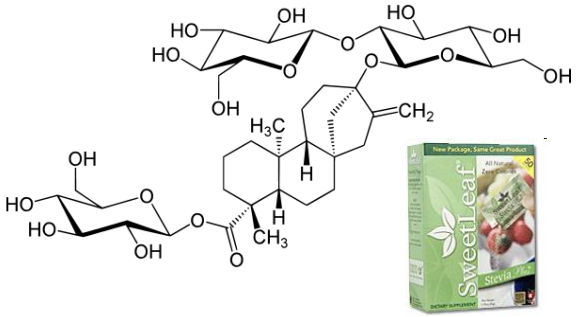
Amygdalen, an *O*-glycoside, is from bitter almonds and the pits of peaches and apricots.



Sinigrin, an *S*-glycoside, provides the characteristic flavor of horseradish and mustard.



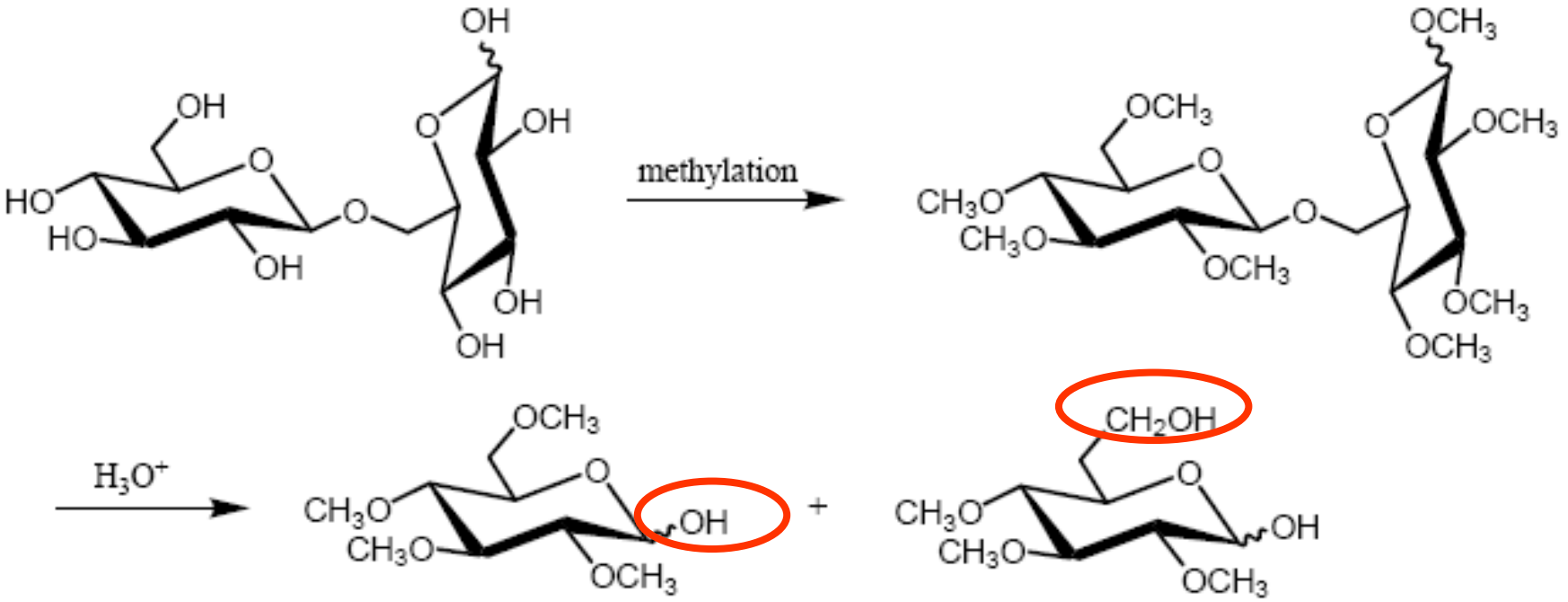
Adenosine, an *N*-glycoside, the "A" part of ATP.



estevióside

Métodos químicos de estudio

1. Determinación cuali-cuantitativa de los monosacáridos
2. Determinación de anoméricos libres
3. Hidrólisis enzimática
4. Permetilación e hidrólisis



5. Oxidación de Malaprade

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