

Isomería y estructura de Carbohidratos



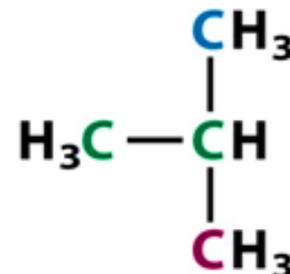
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DOBC / Facultad de Medicina,
Universidad de Chile

Isómeros: compuestos que poseen la misma fórmula molecular pero diferente estructura.

| | | |
|-------------|----------------|--|
| <u>Ejs:</u> | C_2H_6O | etanol o dimetiléter |
| | C_3H_6O | acetona o propanal |
| | C_4H_{10} | butano o isobutano |
| | $C_4H_{11}N$ | dietilamina, butilamina, metil-propilamina |
| | C_5H_{10} | ciclopentano o 2-penteno |
| | $C_7H_6O_2$ | o-, m-, p-hidroxibenzaldehido o ác. benzoico |
| | $C_6H_{12}O_6$ | glucosa, manosa, galactosa, fructosa |

Isómeros estructurales

de esqueleto
o cadena

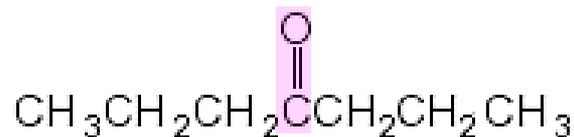
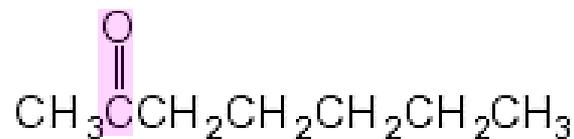
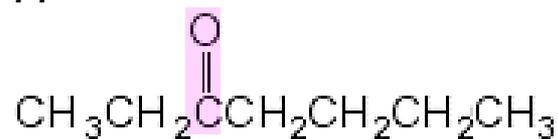
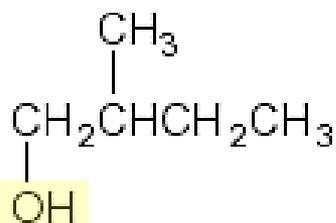
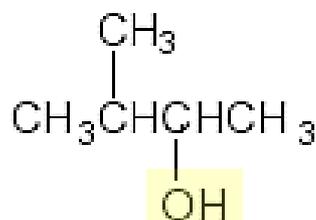
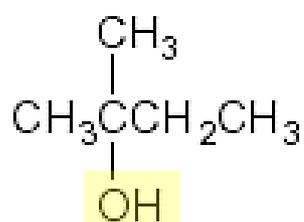
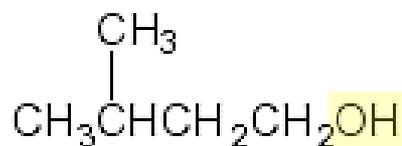
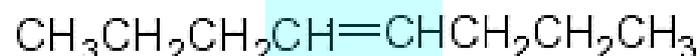


de posición

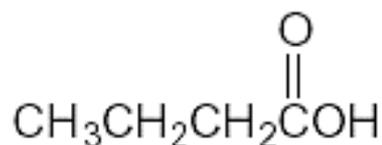


de función

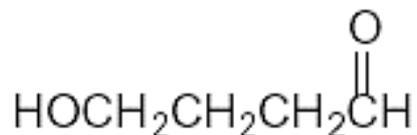




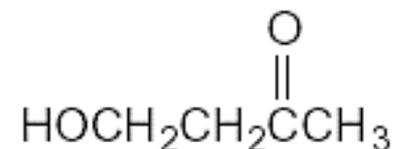
Isómeros de función



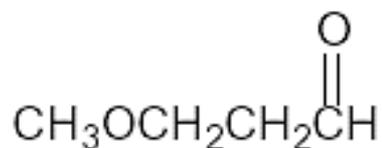
carboxylic acid



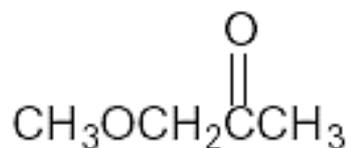
alcohol-aldehyde



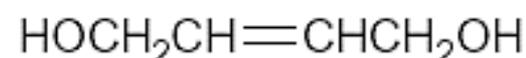
alcohol-ketone



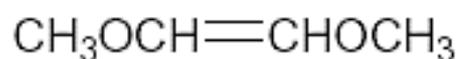
ether-aldehyde



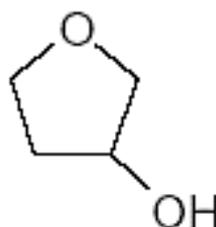
ether-ketone



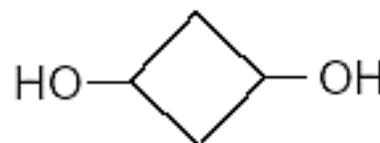
alkene-dialcohol



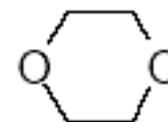
alkene-diether



alcohol-ether



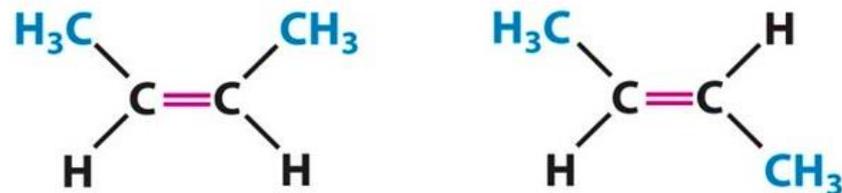
dialcohol



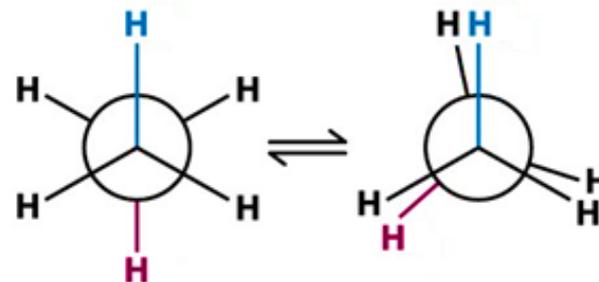
diether

Estereoisómeros

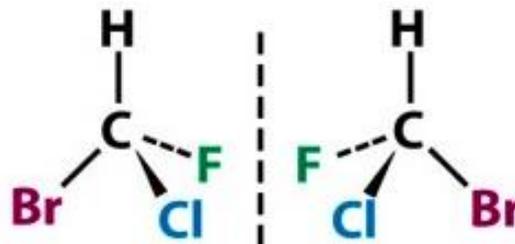
geométricos



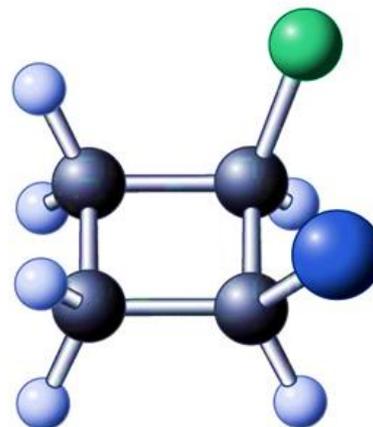
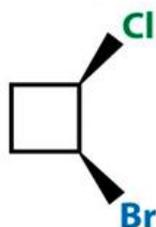
de conformación



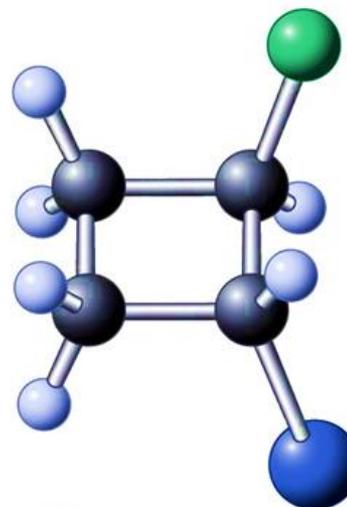
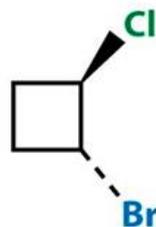
ópticos



**Cicloalcanos
disustituidos
cis/trans**



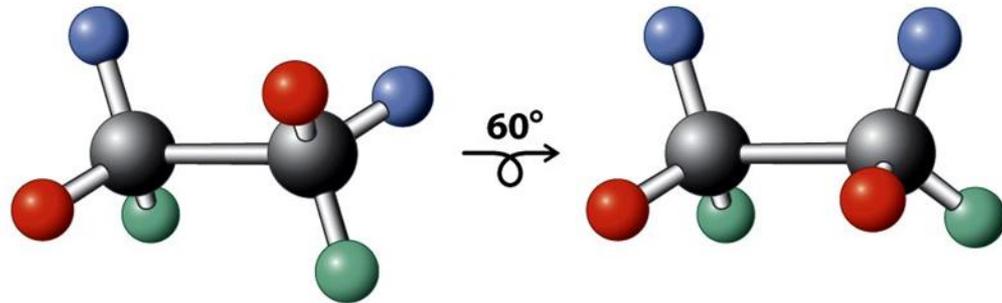
cis-1-Bromo-2-clorociclobutano



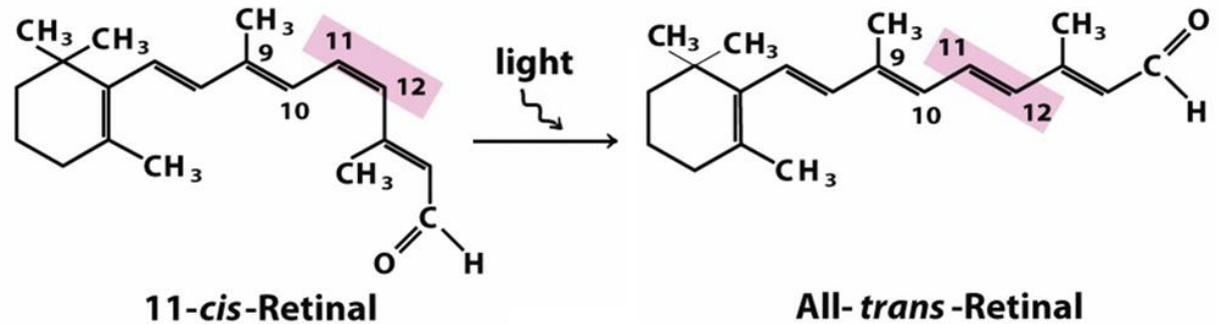
trans-1-Bromo-2-clorociclobutano

Conformación vs configuración

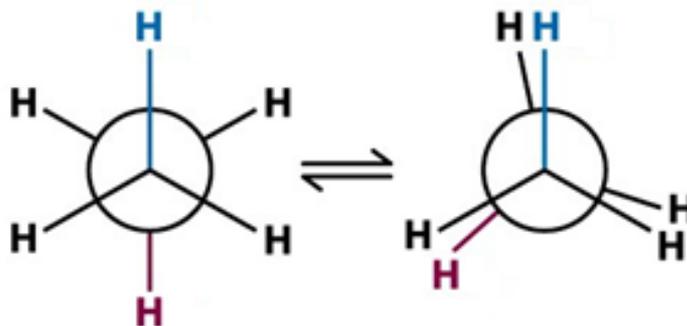
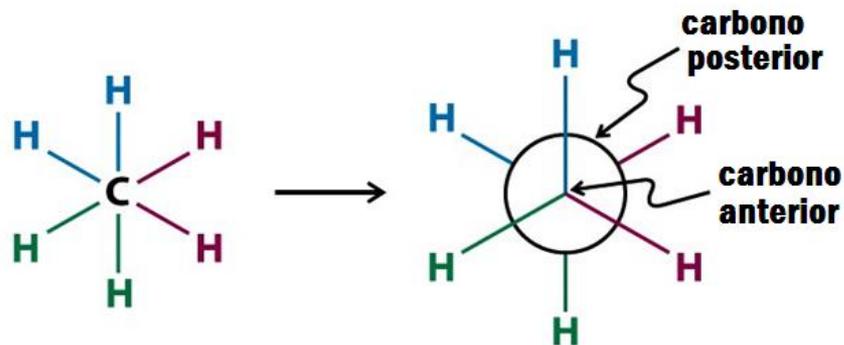
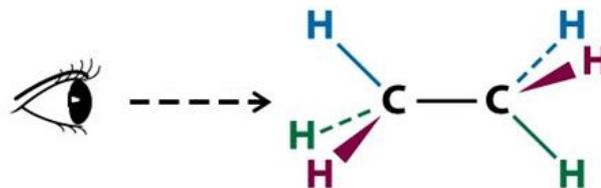
Conformación:
los grupos de una molécula cambian de posición sin que ocurra ruptura de enlaces



Configuración:
la distribución de los grupos cambia sólo si ocurre ruptura y formación de enlaces.



Etano – proyección de Newman



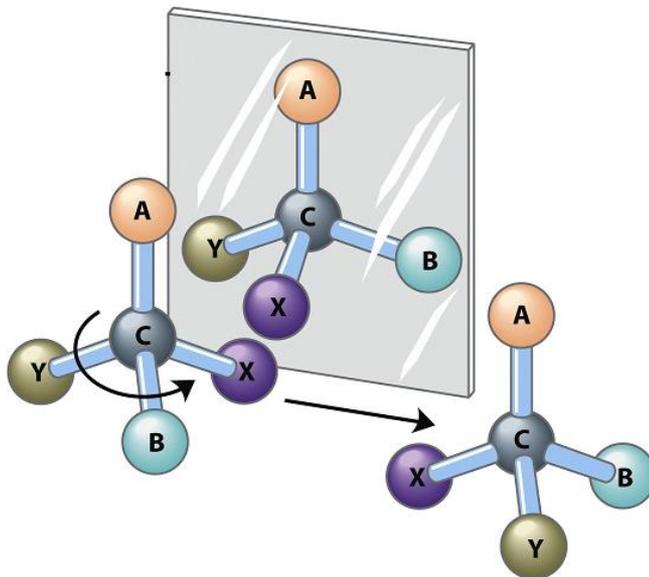
conformaciones

alternada

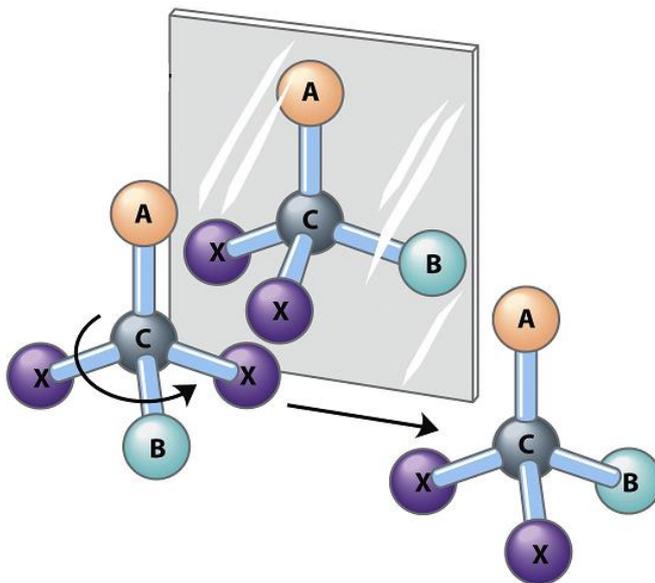
eclipsada

Simetría
molecular

Quiral
(asimétrico)



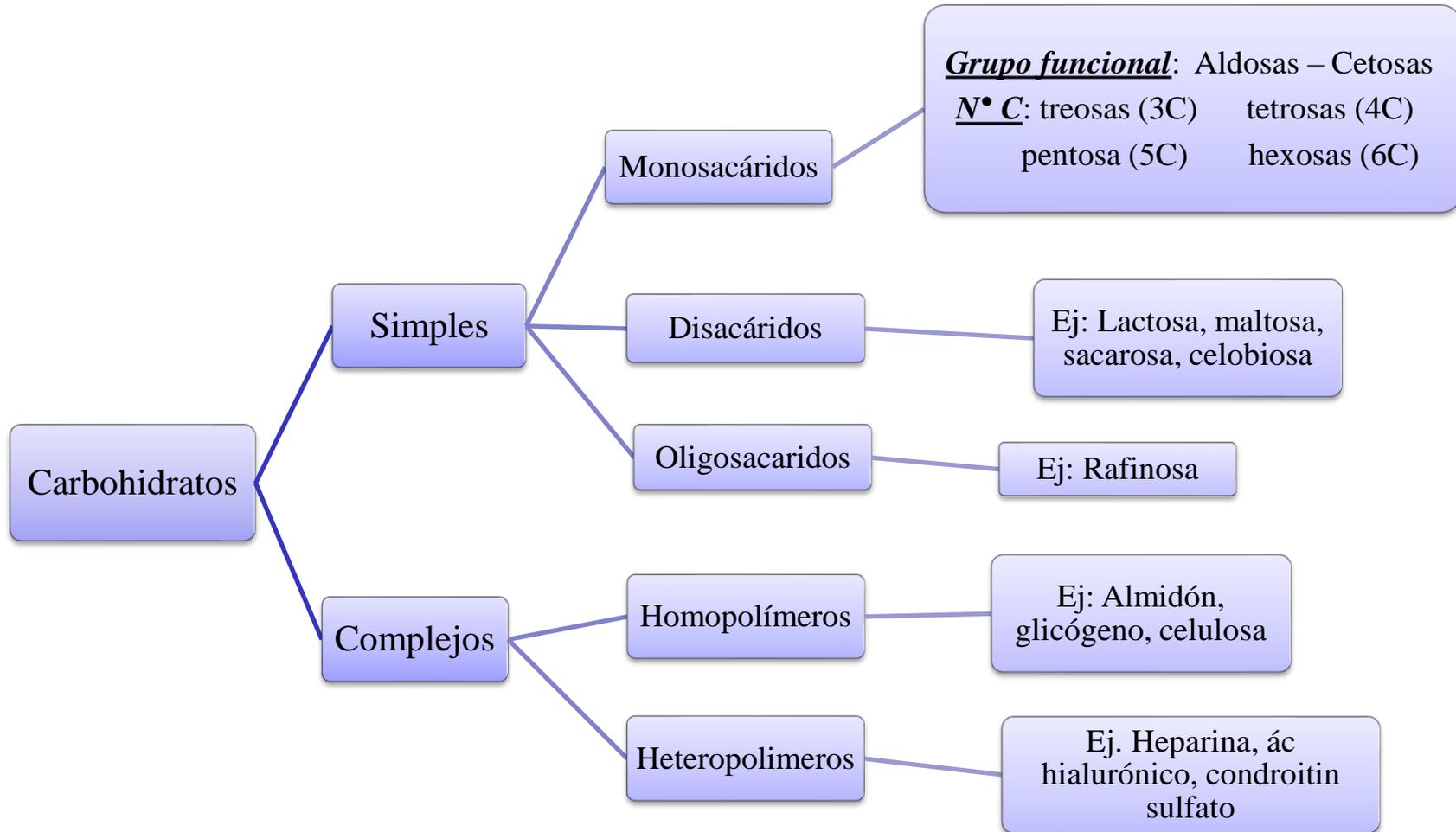
Aquiral
(simétrico)



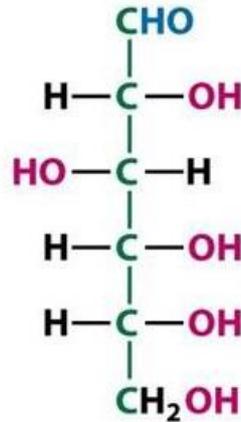
ENANTIOMEROS

*Poseen idénticas
propiedades
físicoquímicas*

Carbohidratos: aldehídos y cetonas polihidroxiladas

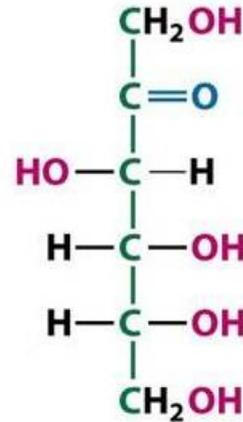


Los monosacáridos contienen uno o más carbonos asimétricos.



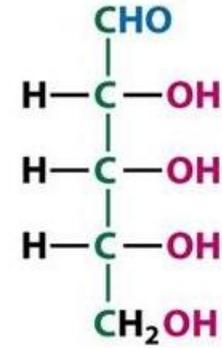
Glucosa

una aldohexosa



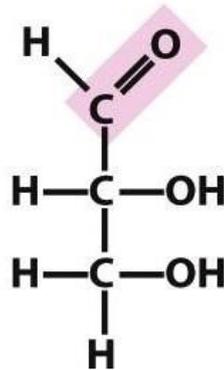
Fructosa

una cetohehexosa

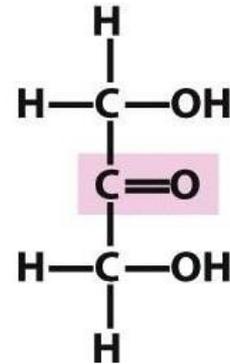


Ribosa

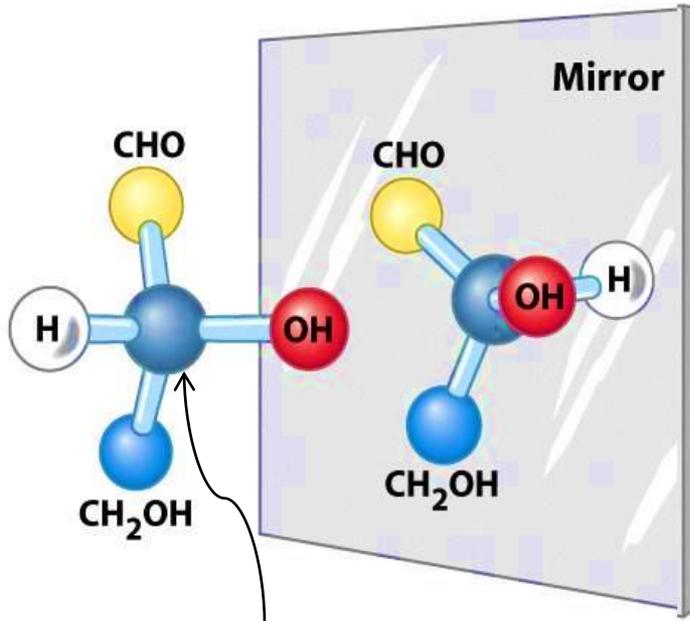
una aldopentosa



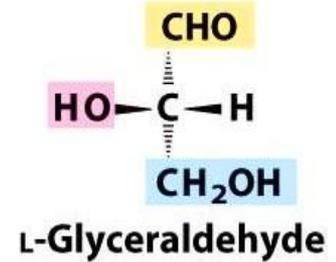
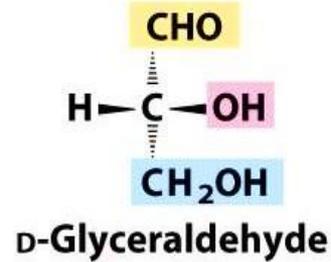
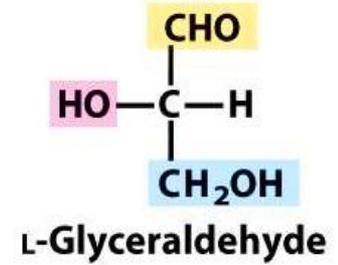
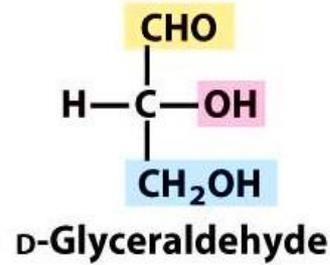
Gliceraldehido

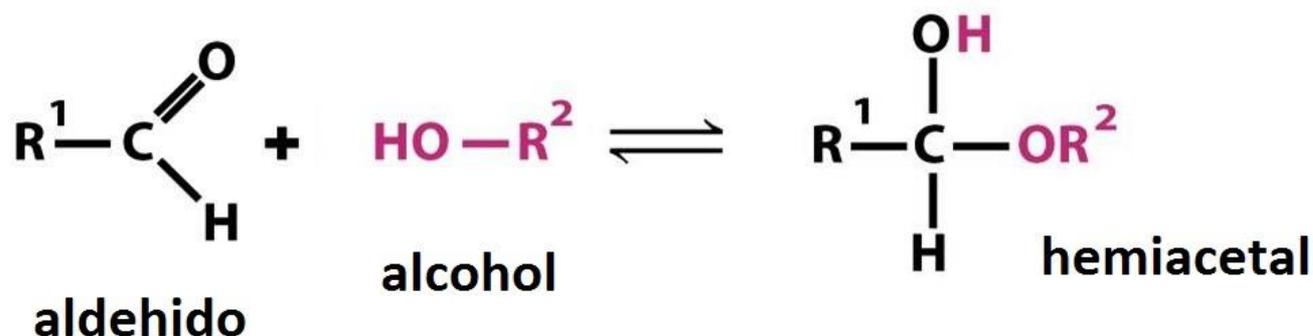


Dihidroxiacetona

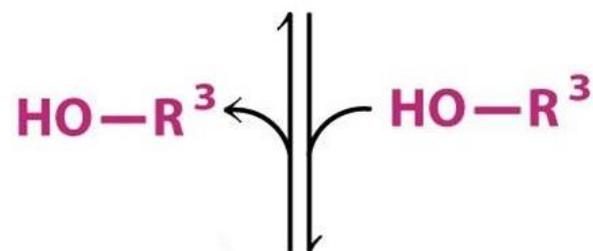


*Carbóno
asimétrico*

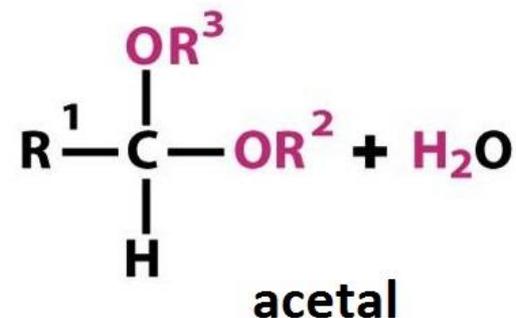




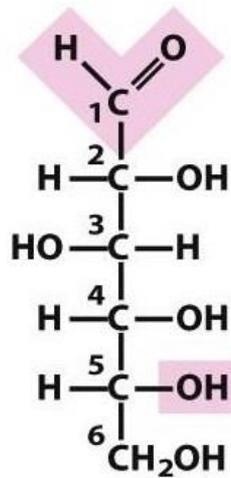
- **Paso 1:** Se produce una adición nucleofílica en medio ácido. El alcohol $\text{OH}-\text{R}^2$ actúa como nucleófilo.



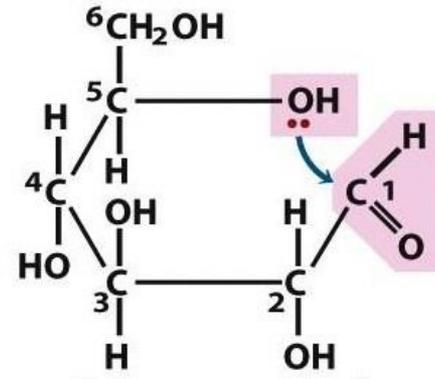
- **Paso 2:** Se produce un segundo ataque nucleofílico por otra molécula de alcohol ($\text{OH}-\text{R}^3$).



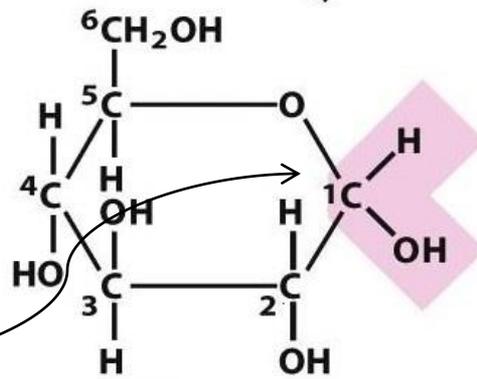
Glucosa- anómeros alfa y beta



D-Glucosa

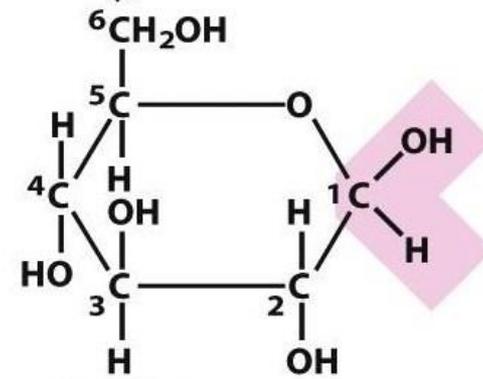


~ 0,1 %



α -D-Glucopiranososa

~ 36%



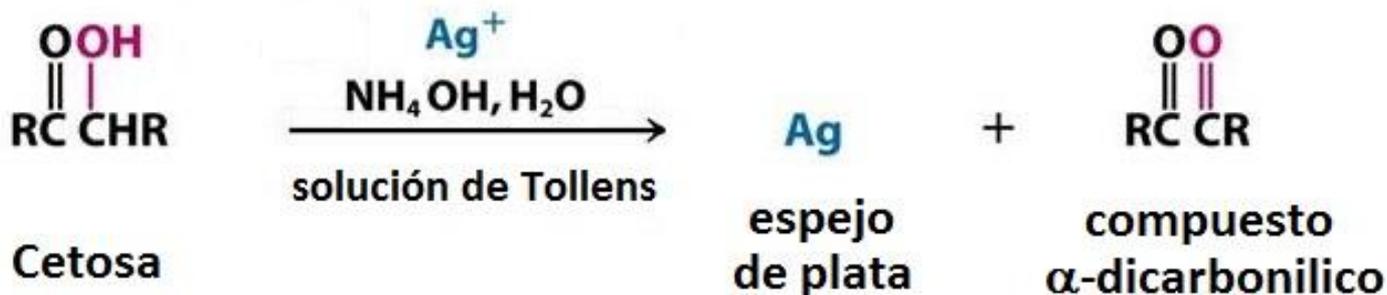
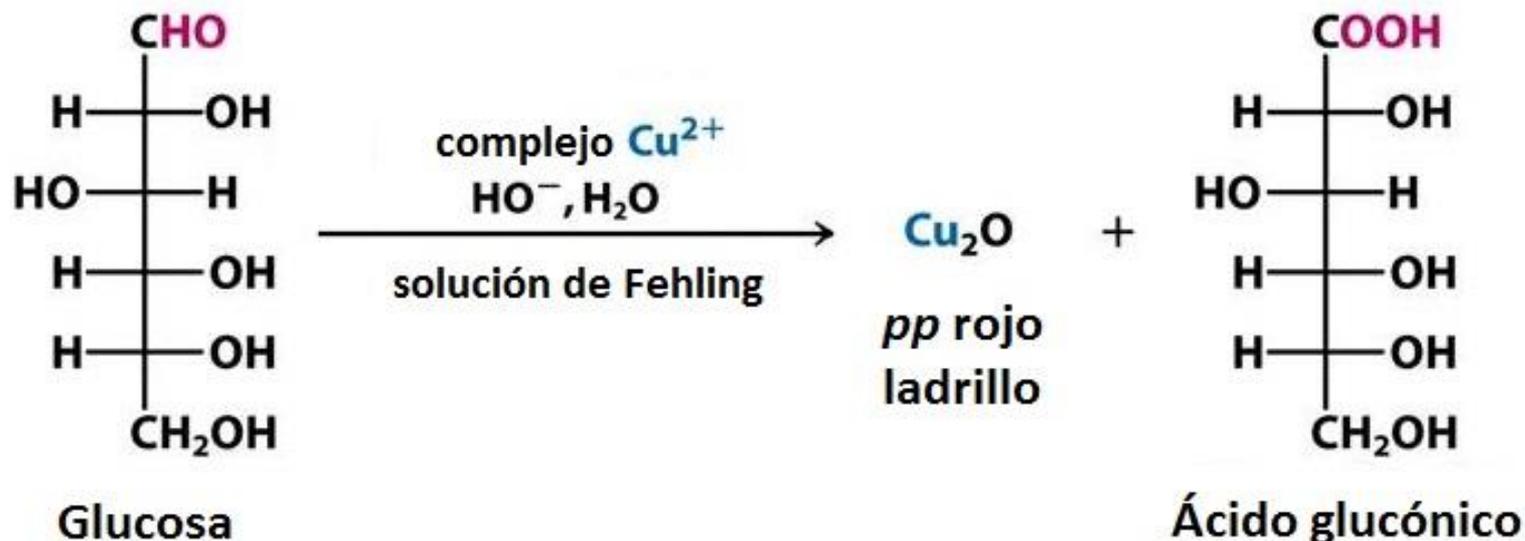
β -D-Glucopiranososa

~ 64%

C1 es el carbono anomérico

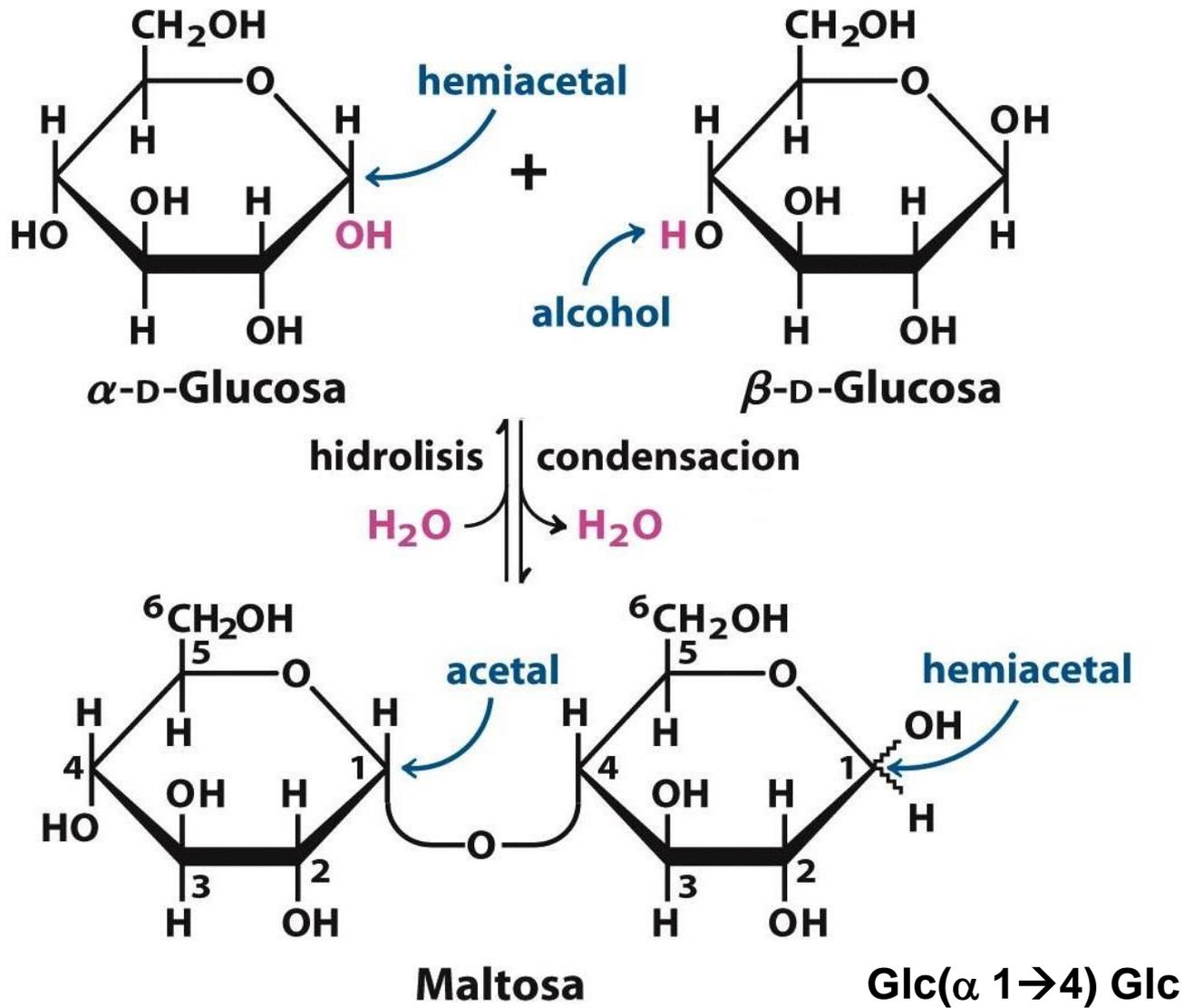
Mutarrotación

Oxidación de Glucosa – azúcares reductores

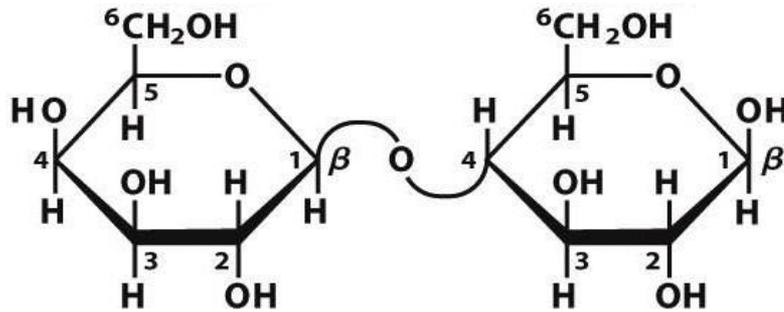


Cuando el carbono anomérico (C1) de la forma cíclica tiene libertad para *abrirse* y *generar la forma lineal*, puede ser oxidado. En este caso se trata de un **azúcar reductor**.

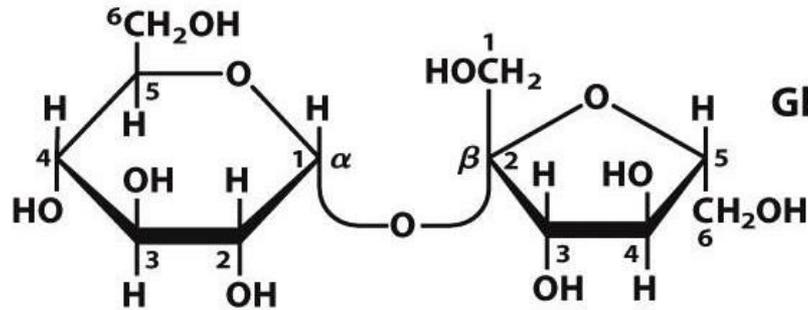
Formación de disacáridos – maltosa



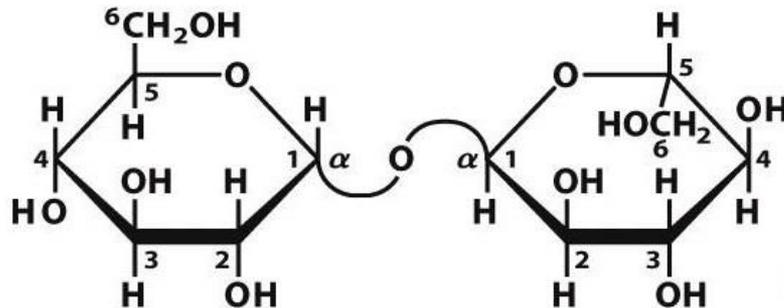
Otros disacáridos



Lactosa
Gal(β1→4)Glc

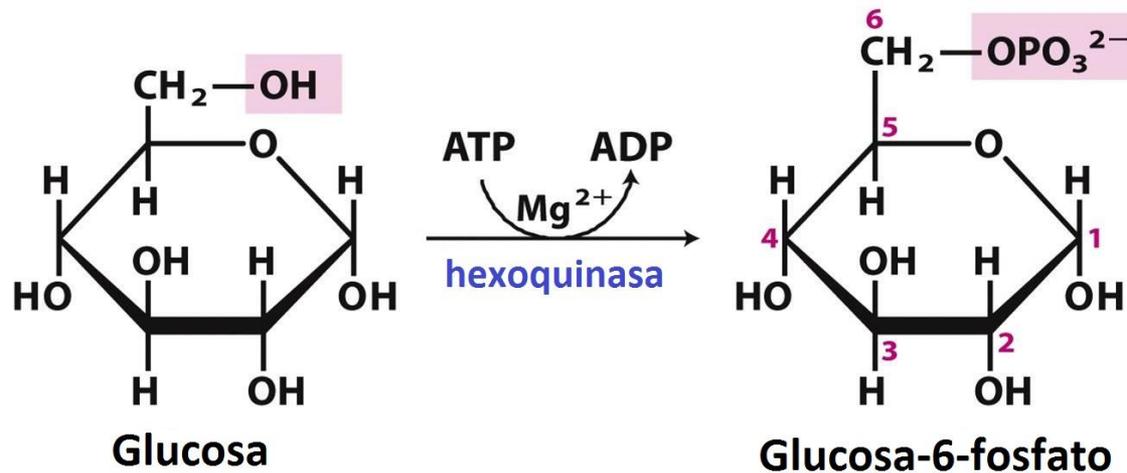
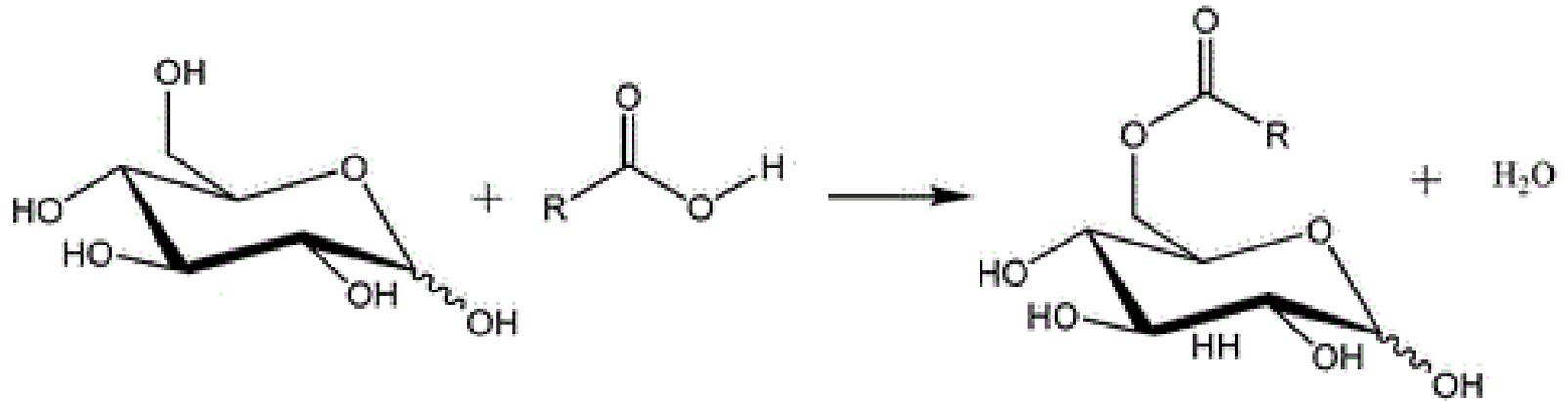


Sacarosa
Glc(α1↔2β)Fru



Trehalosa
Glc(α1↔1α)Glc

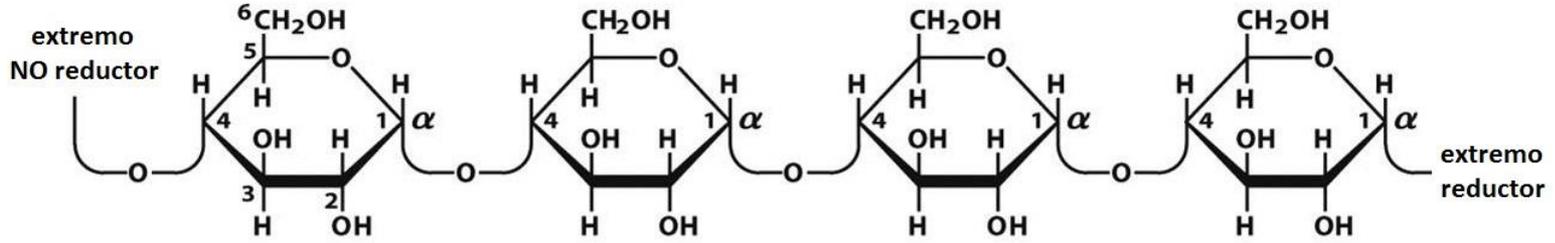
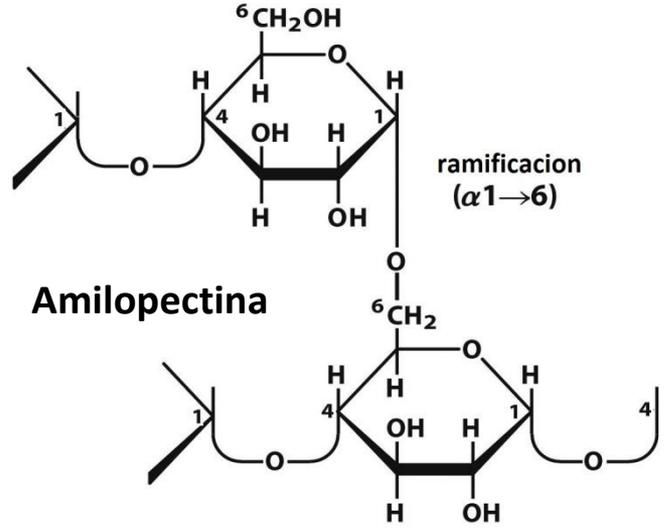
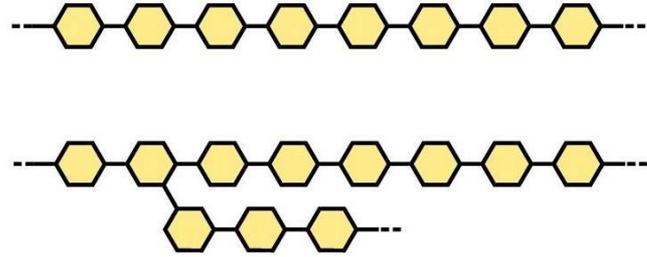
Esterificación de glucosa – glucosa-6-P



$$\Delta G'^{\circ} = -16.7 \text{ kJ/mol}$$

Homopolisacáridos lineales y ramificados:

- Glicógeno $\alpha 1 \rightarrow 4, \alpha 1 \rightarrow 6$
- Almidón $\alpha 1 \rightarrow 4, \alpha 1 \rightarrow 6$
- Celulosa $\beta 1 \rightarrow 4$



Amilosa

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Bibliografía

- Lehninger 5ed, 2008
- Stryer 7ed, 2012