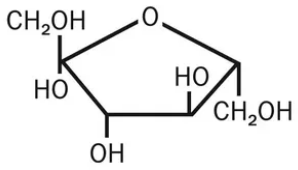
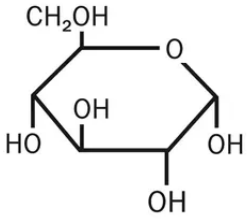
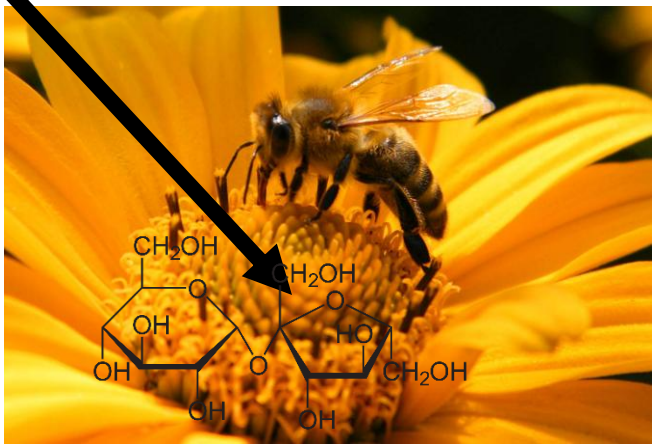
Honey is produced by honey bees from the ***nectar*** of flowers. Honey is a mixture of simple sugars: fructose and glucose



fructose



glucose



Chapter 25

Biomolecules: **Carbohydrates**

Outline

Administrative

Background

Classification of Carbohydrates

Representing Carbohydrate Stereochemistry: Fischer Projections

D, L Sugars

Configurations of the Aldoses

Cyclic Structures of Monosaccharides: Anomers

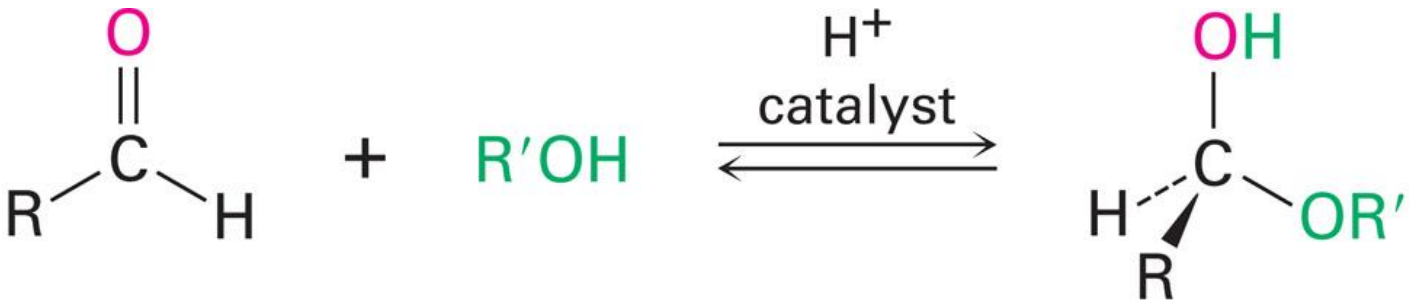
The Eight Essential Monosaccharides

Disaccharides

Polysaccharides and their Synthesis

Other important carbohydrates

Recall: Sect 19.10



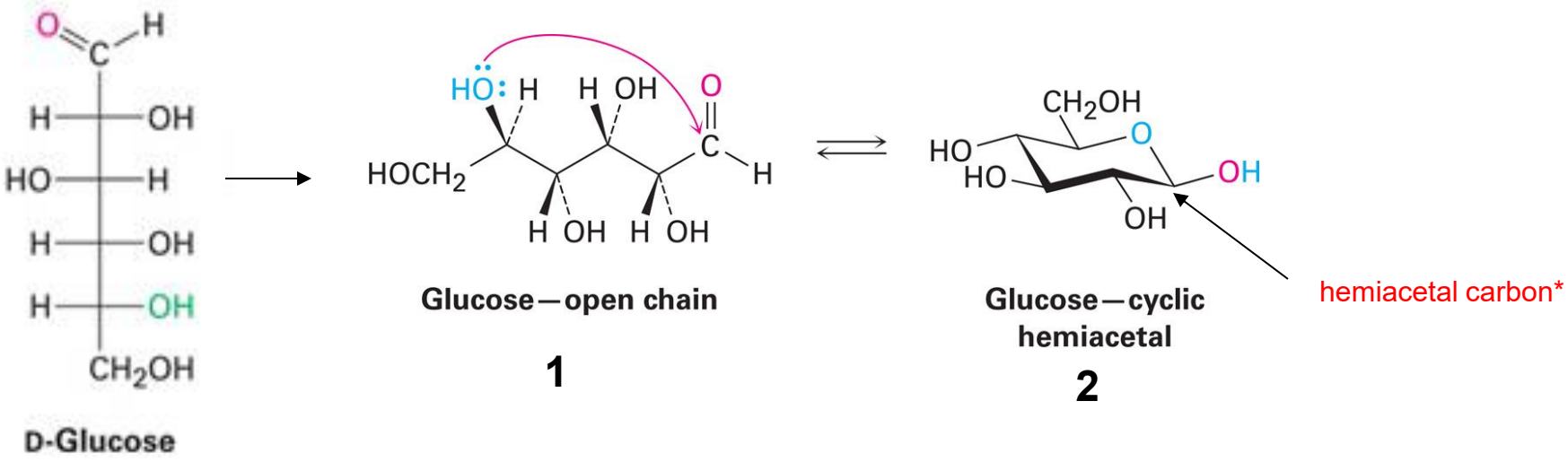
An aldehyde

A hemiacetal

or ketone

Note: They can be chains or rings

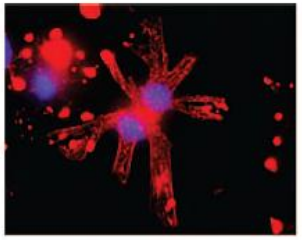
Cyclic Structures of Monosaccharides: Anomers



1) Glucose (open chain**)** undergoes an internal nucleophilic addition reaction

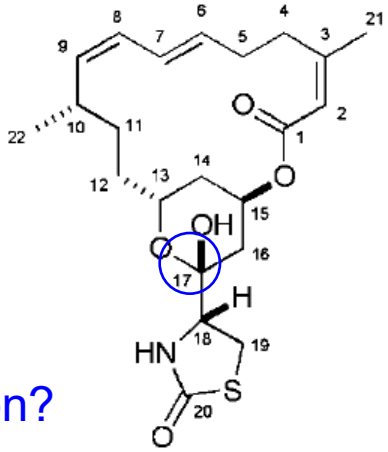
and

exists primarily as a cyclic hemiacetal (**2**)



latrunculin A (**1**)

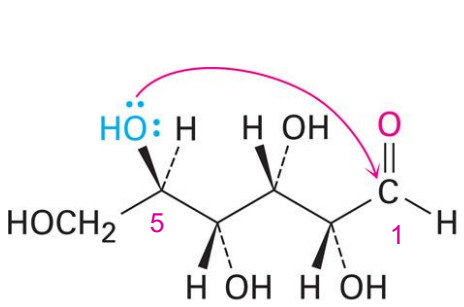
actin inhibitor (cytotoxin)



Recall: Where is the hemiacetal carbon?

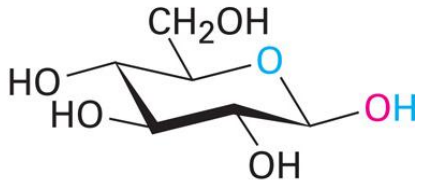
Cyclic Structures of Monosaccharides: Anomers

Mechanism



Glucose—open chain

H_2O
OH-
H_3O^+



Glucose—cyclic hemiacetal

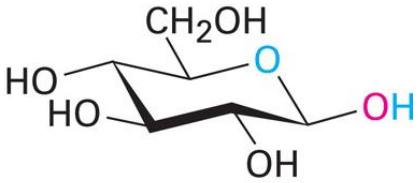
(in class ~ next slide)
Draw intermediate steps…

Notes:
Many carbohydrates exist in equilibrium b/w chain and ring forms

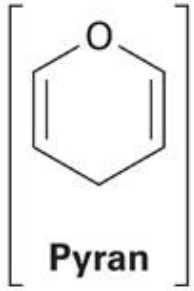
5 & 6 membered ***cyclic*** hemiacetals are ~ strain free & stable ~ thus form easy ☺

Glucose in ***aqueous solution*** exists mainly in **pyranose** (6 membered ring) form

pyranose form

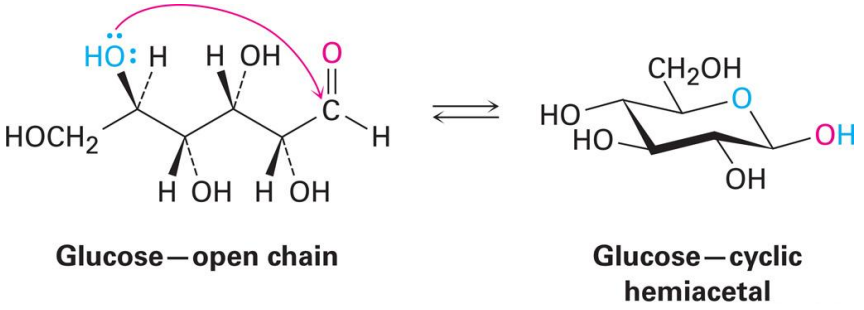


(based on ~ pyran)

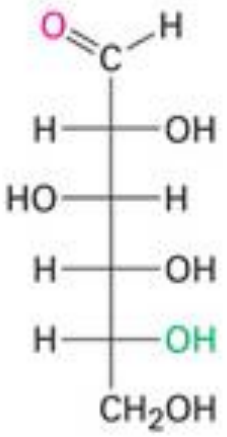


Recall

Mechanism to form pyranose (ringed sugar)

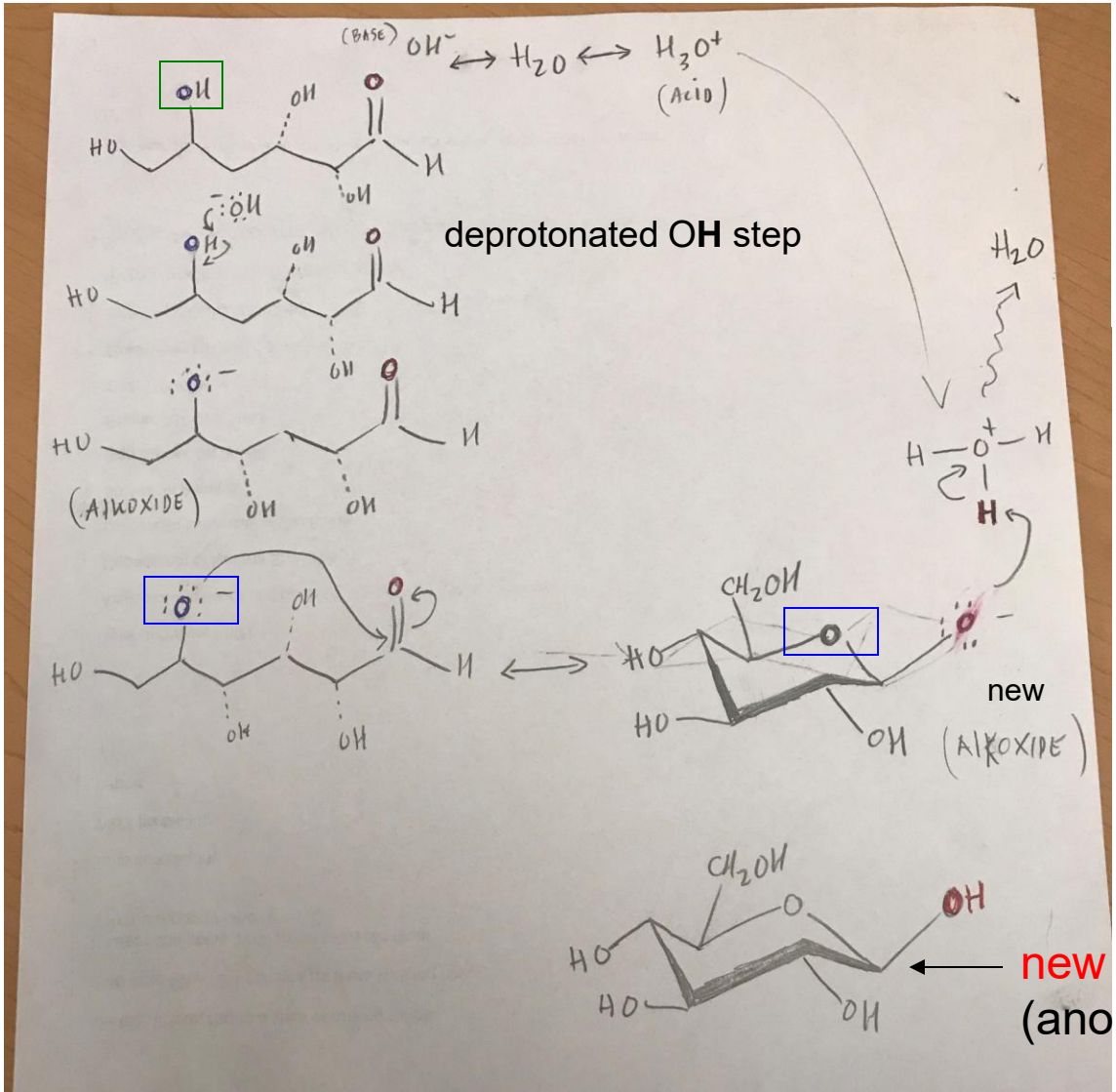


Glucose—open chain ⇌ **Glucose—cyclic hemiacetal**



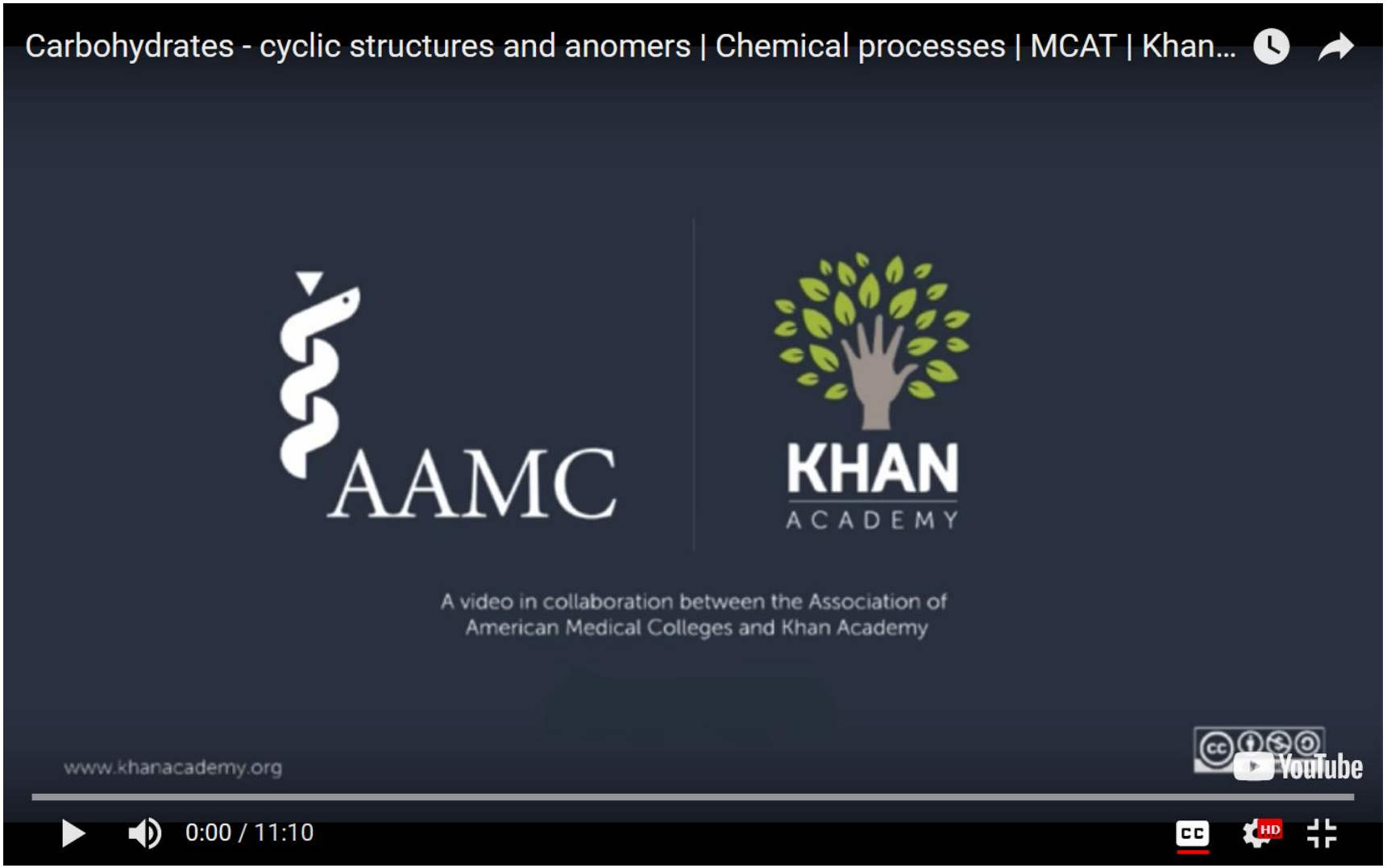
D-Glucose

in ***aqueous solution***



new chiral center*
(anomeric carbon)

Animated example - for your review - **MCAT**



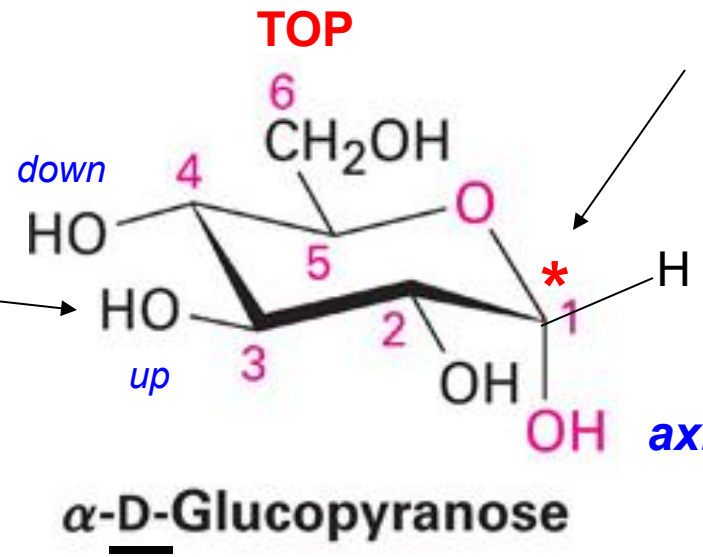
https://www.khanacademy.org/test-prep/mcat/chemical-processes/carbohydrates-5d/v/carbohydrates-cyclic-structures-and-anomers

Recall: *equatorial* and *axial* positions & STERICS

Summing up the video

Standard drawing position: Oxygen (**O**) in **top right**

Lets draw…



equatorial (OH semi *down* or *up*)

axial (OH straight up or down)

NOTES: for **D sugars** the terminal CH_2OH group (6) is on the **TOP (UP)**

For **L** sugars (NOT shown) the CH_2OH group is on the bottom (**down**)

HW 25.13-15

Cyclic Structures of Monosaccharides: *anomers*

Middle "chain structure **1**" can go two ways as: α or β *anomer*

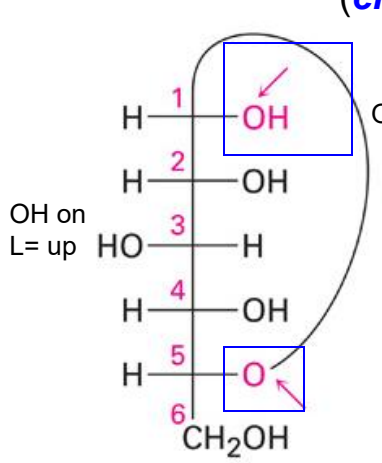
Lets draw…

(***cis*** – OH on C1 & ***C5*** same side)

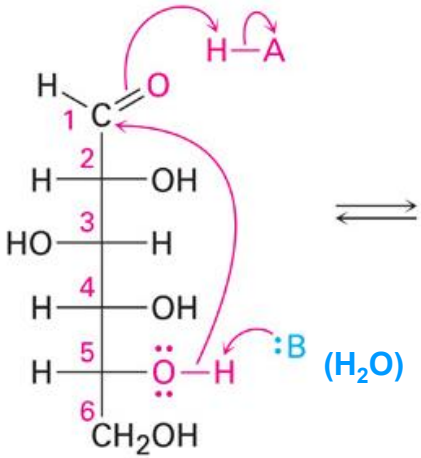
OH on Right side = down

OH on L= up

cis oxygens (α anomer)



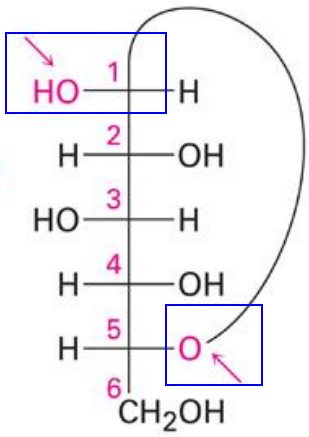
2a



1

trans oxygens (β anomer)

(***trans*** – OH on C1 & C5 opposite side)



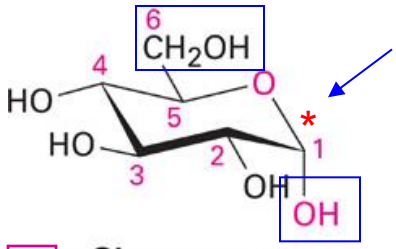
2b

NOTES: cis (**α**) / trans (**β**) designation changes based on if looking at the:
A) chain form (C1 & C5) TOP
B) ring form (C1 & C6) BELOW

Updated 4/20/22
T. Simpson

Comparing different carbons:

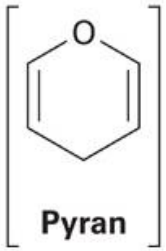
(***trans*** – OH on C1 & ***C6*** opposite side)



anomeric carbon

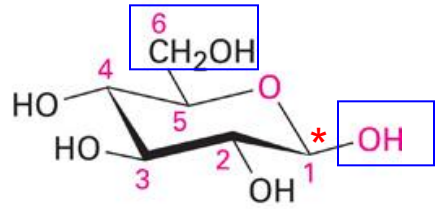
α-D-Glucopyranose (37.3%)

(0.002%)



Pyran

(***cis*** – OH on C1 & C6 same ~ side)

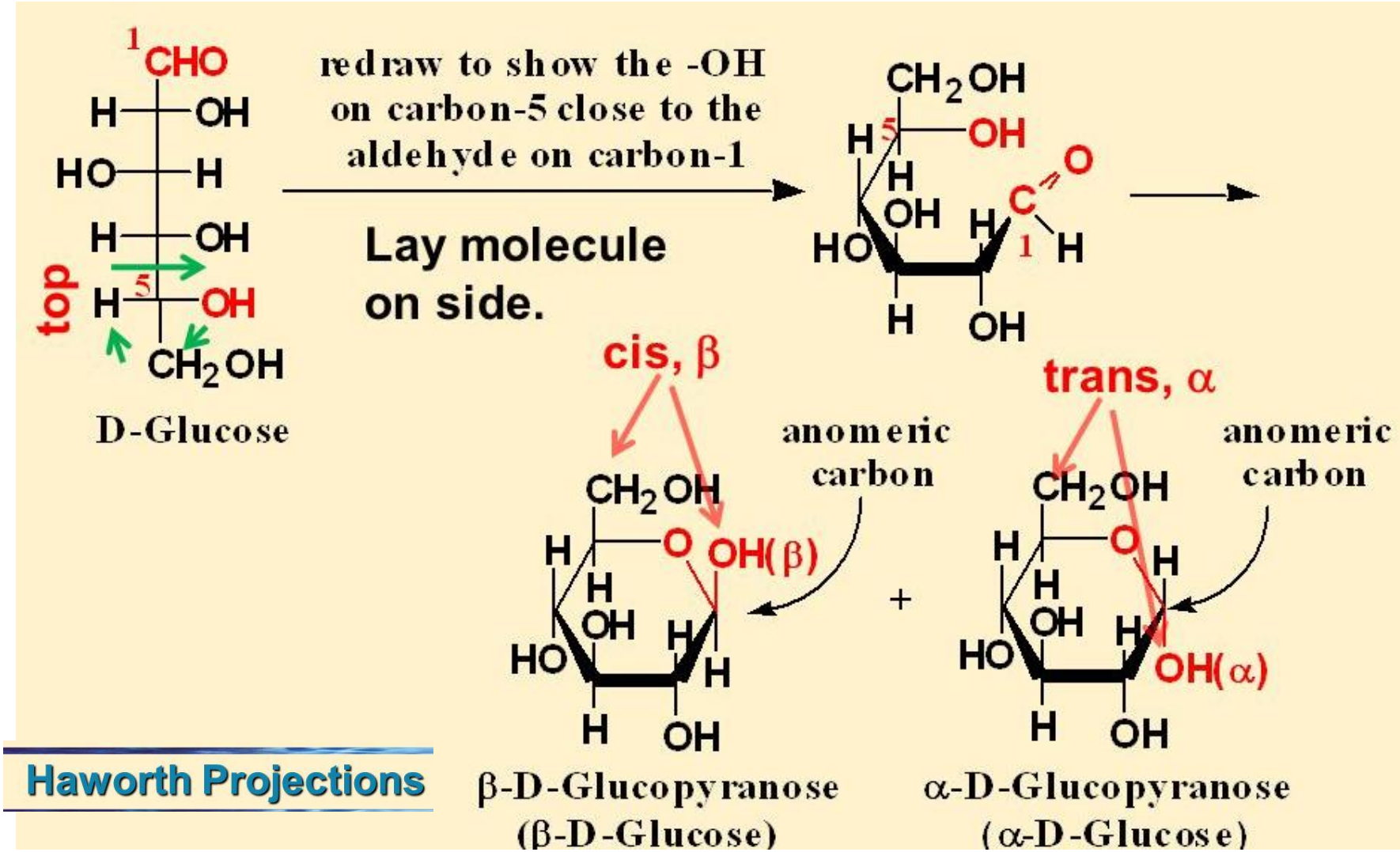


β-D-Glucopyranose (62.6%)

HW 25.13-15

Fisher project

Lets review visually

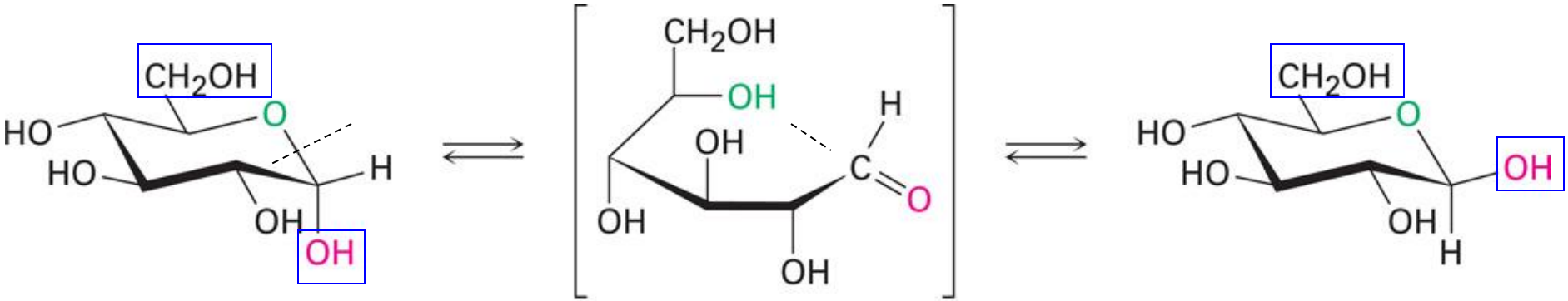


Haworth Projections

HW 25.13-15

Optical rotation: optically active ***sugar*** molecules under go…

Mutorotation



α-D-Glucopyranose
$[\alpha]_D = +112.2$

(trans, 37%)

β-D-Glucopyranose
$[\alpha]_D = +18.7$

(cis, 63%)

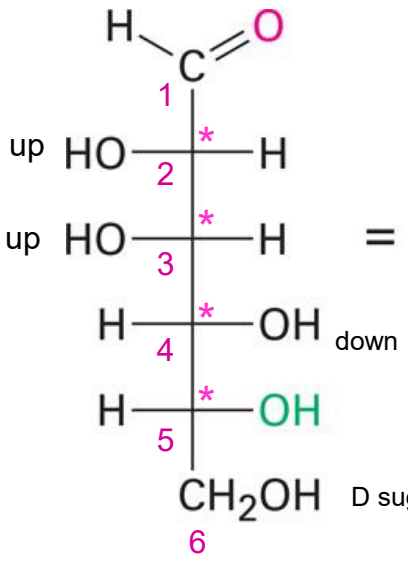
more stable
(less stericaly hindered)

Notes: slow interconversion of **α** and **β anomers**

HW 25.13-15

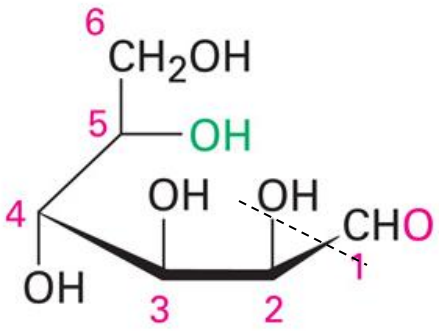
Confirming Your Knowledge

D- mannose differs from D-glucose in one if it's stereocenters. Draw Mannose in its:

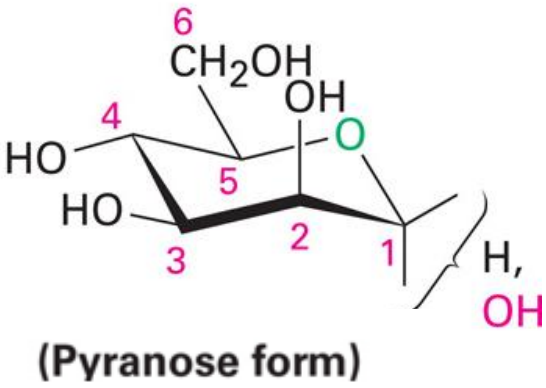


D-Mannose

=

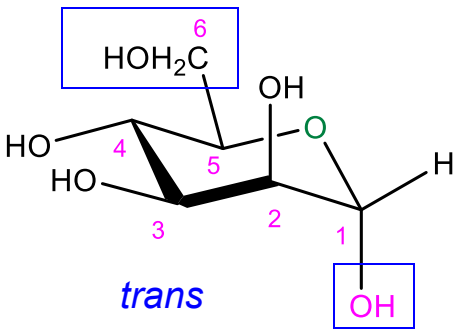


⇌

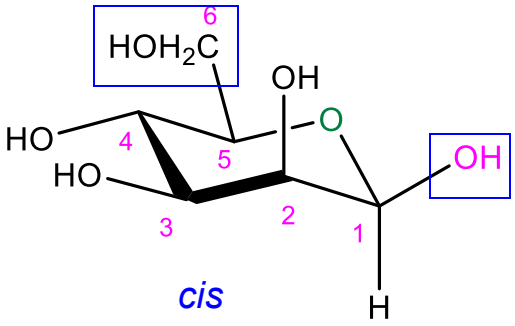


(Pyranose form)

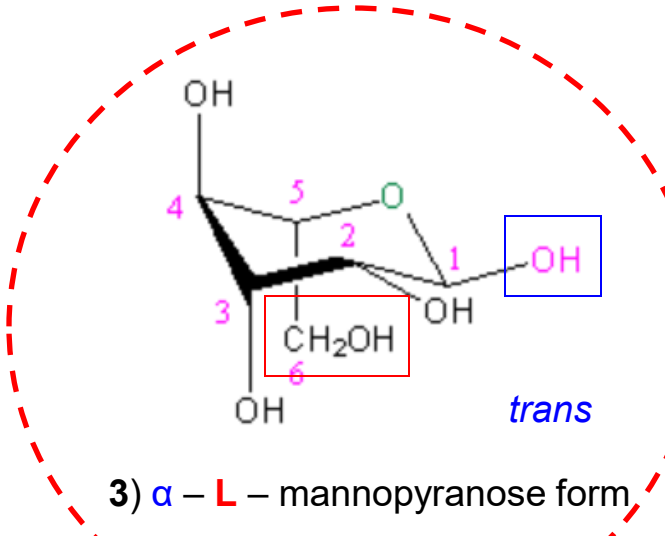
Note: Compound **3** structure revised below (not shown in video).
Every OH on the chiral centers* (2-5) needs to swap sides for the **L** designation. The most stable form of compound **3** is shown below after a ring flip… (Ref. Lect. 18 – slide 9 for more details) - Y. Lee. & J. Lee.



1) α – D – mannopyranose form

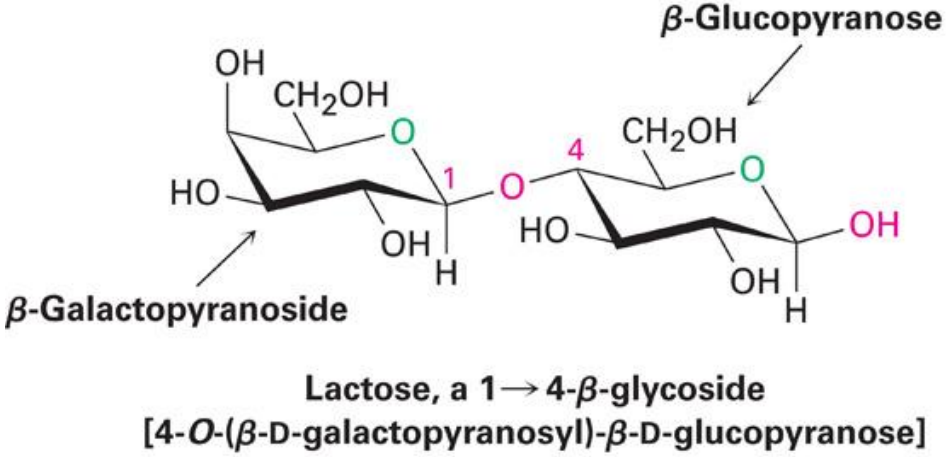


2) β – D – mannopyranose form

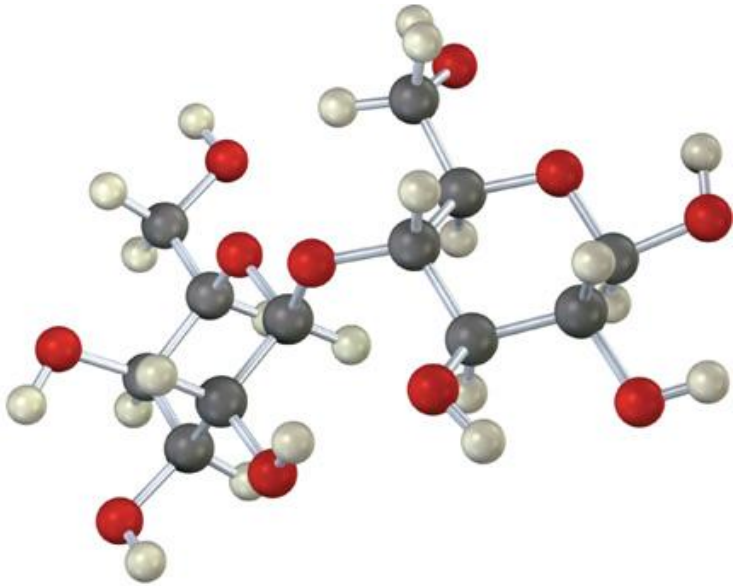


3) α – **L** – mannopyranose form

Lactose



Lactose, a 1→4-β-glycoside
[4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranose]



Notes:

Occurs naturally in humans and in cow's milk.

It exhibits *motorotation*

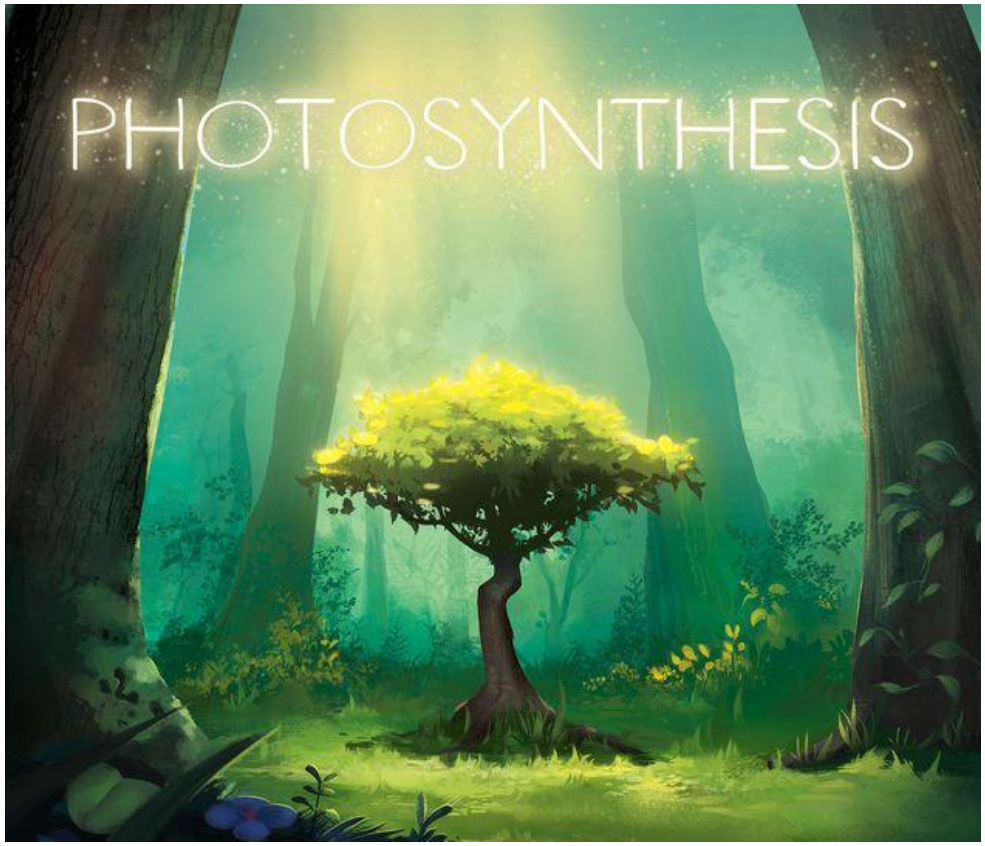
Lactose intolerance originates from a lack of the enzyme in our stomach to digest lactose

Lactobaccilus rudii

***"Lactaid ®"** can assist in the enzymatic breakdown of* **lactose**

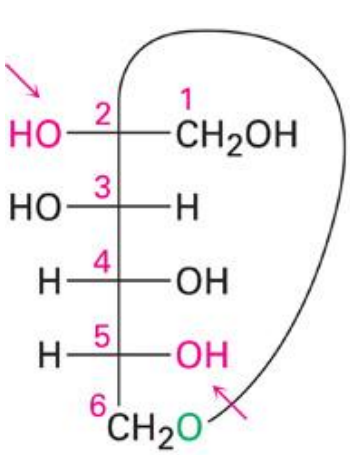
to allow people to enjoy more dairy products ☺

HW Chap 25 –
2, 3, 4, 6, 7, 8, 9, 13-15

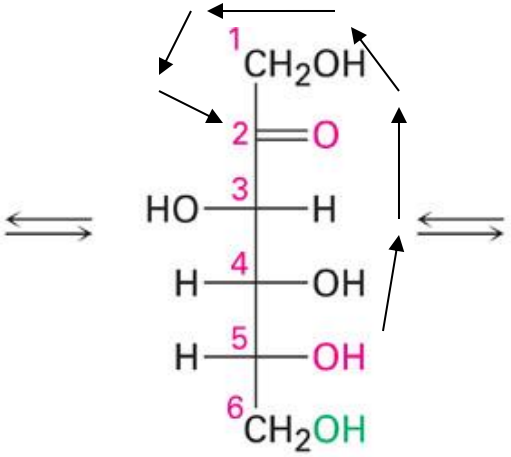


Have a green week ☺

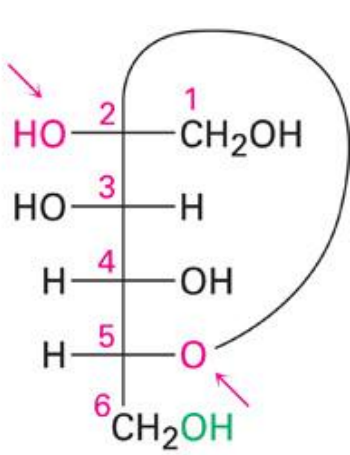
Cyclic Structures of Monosaccharides: **Anomers**



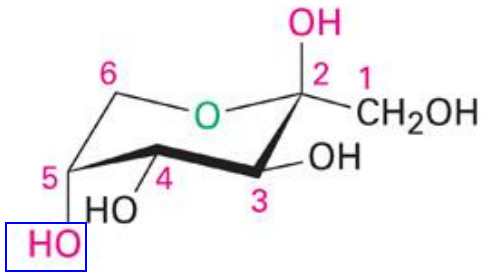
trans oxygens
(β anomer)



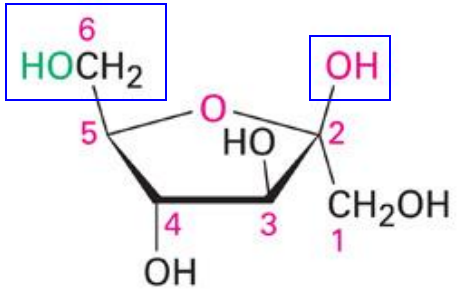
trans oxygens
(β anomer)



a) **(0.5%)** **b)**



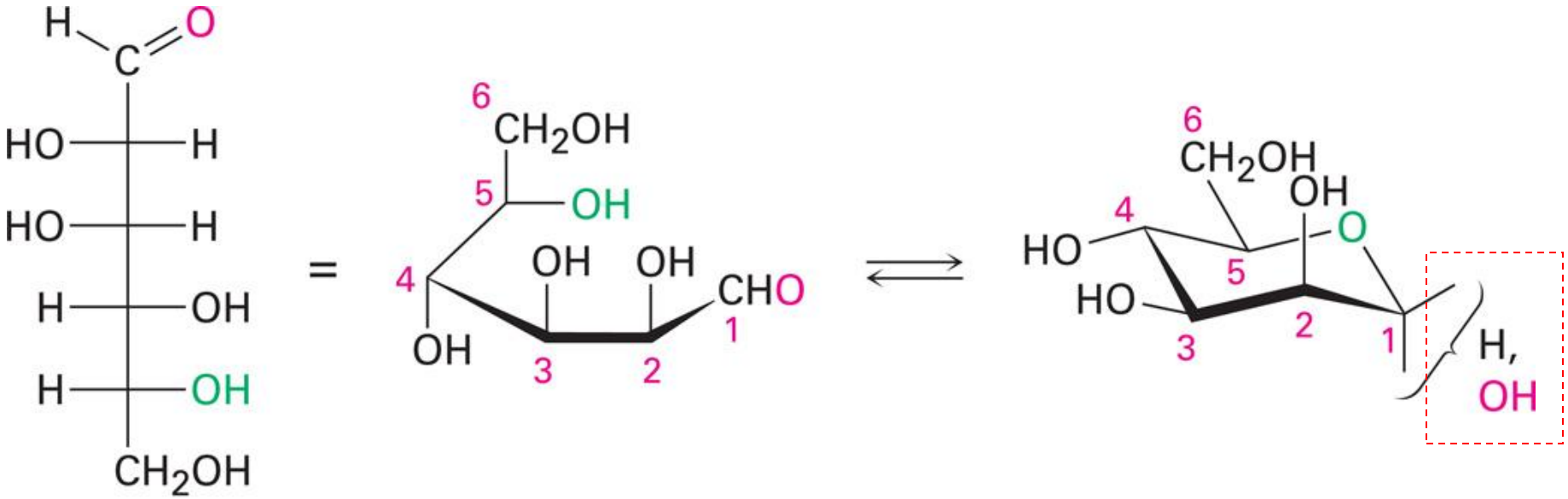
β-D-Fructopyranose (68.2%)
(+2.7% α anomer)



β-D-Fructofuranose (22.4%)
(+6.2% α anomer)
cis

NOTES: some monosacharides also exist in 5-membered form (furanose)
a) pyranose form results from addition of the –OH at C6 to carbonyl while…
b) furanose form results from addition of the –OH at C5 to carbonyl group

Mutorotation _ Summing it up



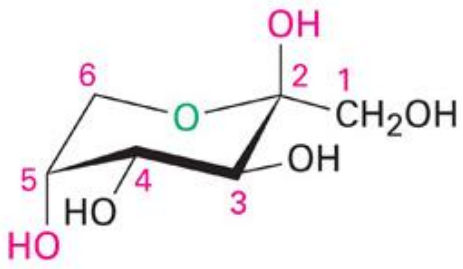
D-Mannose **(Pyranose form)**

Fisher projection Haworth projection Chair form

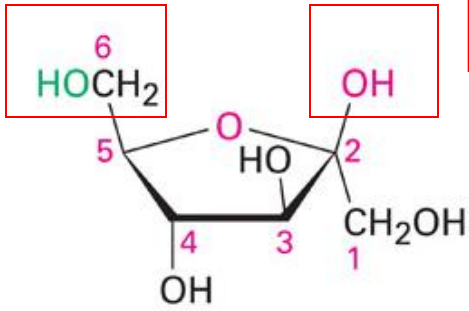
@ position 1 ~ can form either the:
a) **α anomer** (OH down)
b) **β anomer** (OH up)

Challenge Question - skip

Please draw the α-pyranose and α-furanose *anomers* of D-fructose?

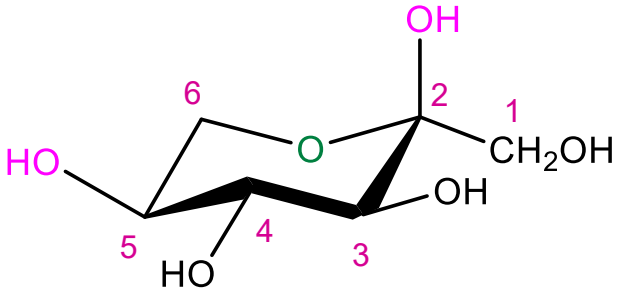


β-D-Fructopyranose (68.2%)
(+2.7% α anomer)

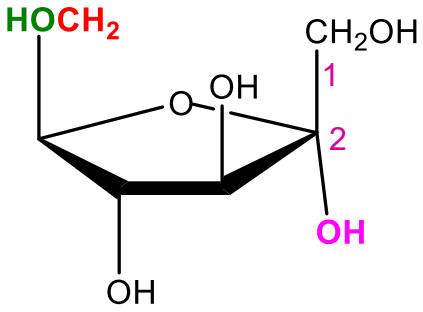


cis

β-D-Fructofuranose (22.4%)
(+6.2% α anomer)



α-D- Fructopyranose



α-D- Fructofuranose