: Cyclic structure of Glucose :

$CH=O$

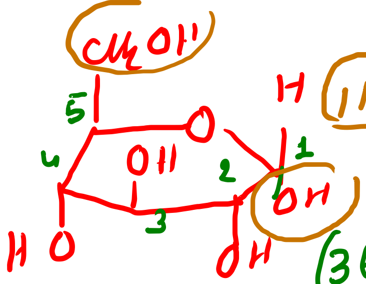
It is observed glucose does not react with 2, 4. D. N. P; $NaHSO_3$, NH_3

~~G~~. Give -ve test with $NaHSO_3$ & NH_3 which indicates such str of glucose exists where $-CH=O$ grp is absent. Also it is observed when a sample of glucose with optical rotation 112° is dissolved in water for a long time. It's optical rotation changes & value becomes 52.5°. So change in optical rotation with time is called Mutarotation. May be glucose exists more than 1 form in equilibrium.

Mutarotation exists & -ve test for all the reagents indicates such str (may be more than one) exists where $-CH=O$ is not present. Then cyclic structure is proposed. Tollens suggest 5 membered ring str for glucose fixer.

After that Haworth suggest that Glucose exists in 6 membered ring structure.

CYCLIC



112°

(36%)

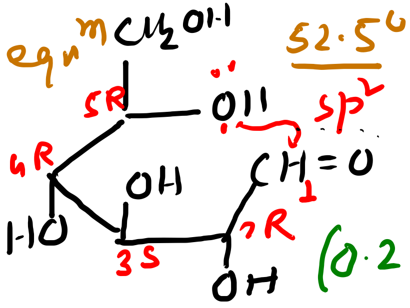
D-Glucose.

α-D-glucopyranose.

(free $-CH=O$ is missing)

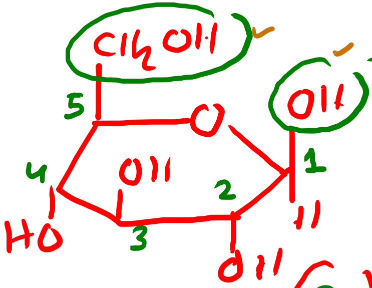
$\longleftarrow$ eqm $\rightleftharpoons$

52.5°



(0.2%)

Pyran $\longrightarrow$ $\rightleftharpoons$



→ same side

19°

63.8%

β-D-glucopyranose

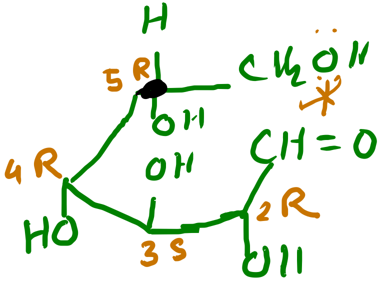
D-gluco

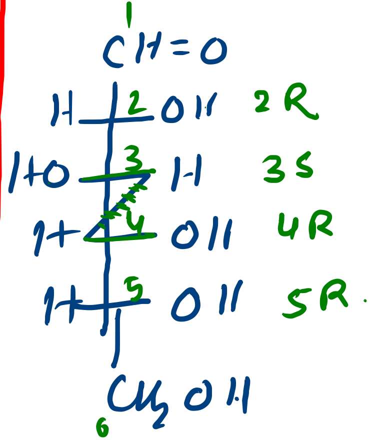
CYCLIC

free $-CH=O$ is missing

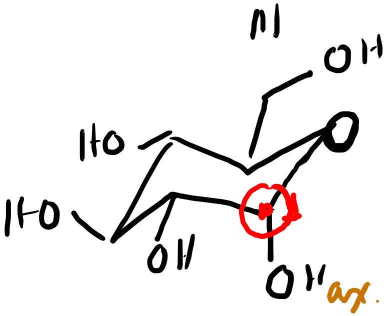
OPEN STRUCTURE

Open chain (very less) so it can not give +ve test for 2,4-D.N.P., $NaHSO_3$, NH_3.



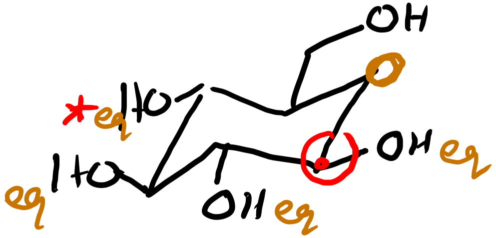


openchain (D-glucose)



Anomeric carbon of glucose is at carbon (1).

α-form is less stable.



all -OH groups are at equatorial position. So β-form is more stable.

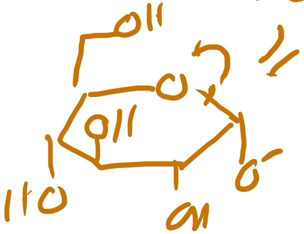
3 form exists for D-glucose

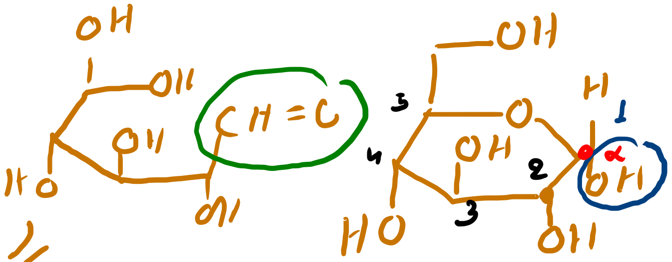
α form ⇌ open chain ⇌ β-form.

36% 0.2% 63.8%

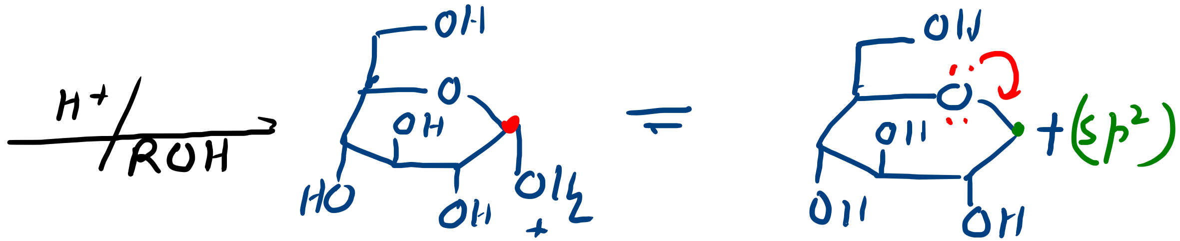
ANOMERS.

Two cyclic str. of Glucose which are in eqm are called anomers.

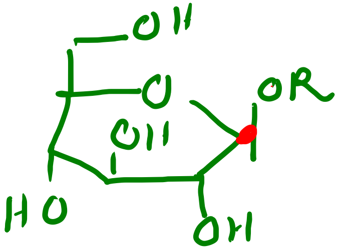




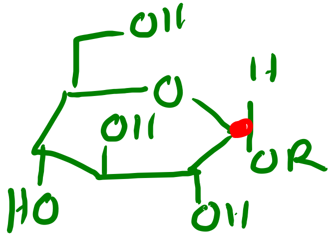
α-D-glucopyranose
(α-hydroxy ether)
hemiacetal
(+ve Tollens test)



$\downarrow$ ROH



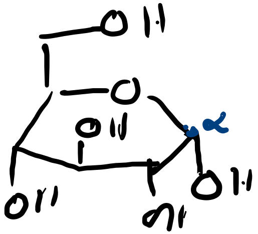
+



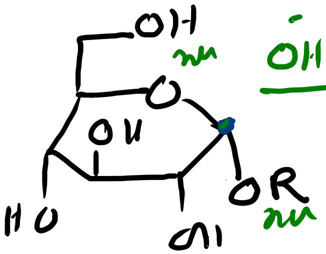
β-form D-gluco pyranoside
gemdiether
(acetal)

α-form D-gluco (pyranoside)
gemdiether
(acetal)

$\uparrow \overline{OH}/AgNO_3$



Pyranose
α-hydroxy ether
(Hemiacetal)



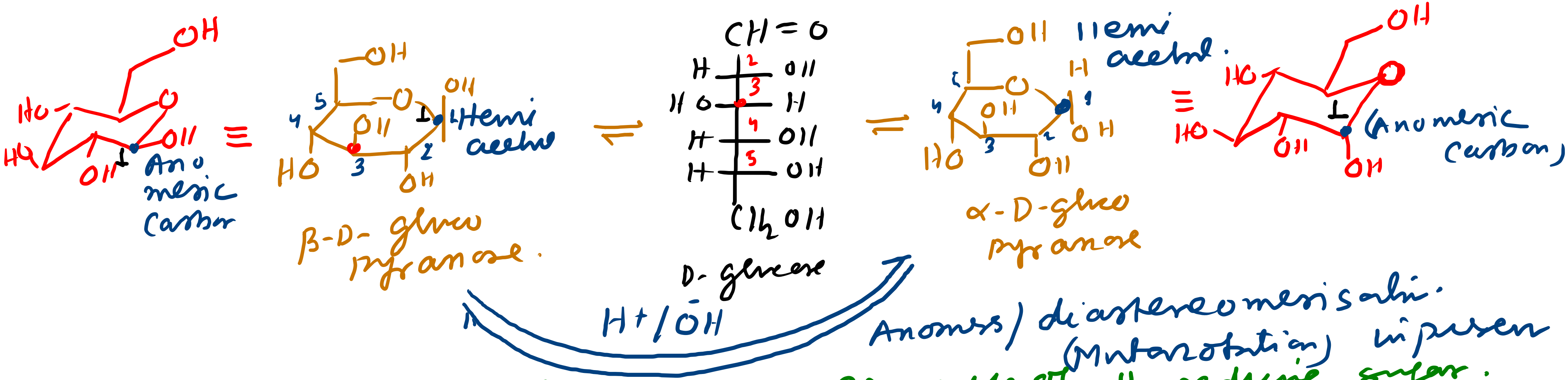
$\overline{OH}$ no reaction.

Pyranoside
gemdiether
(Acetal) (Nonreducing sugar)

⇒ Reducing sugar
(α-hydroxy ether)(Hemiacetal) linkage present

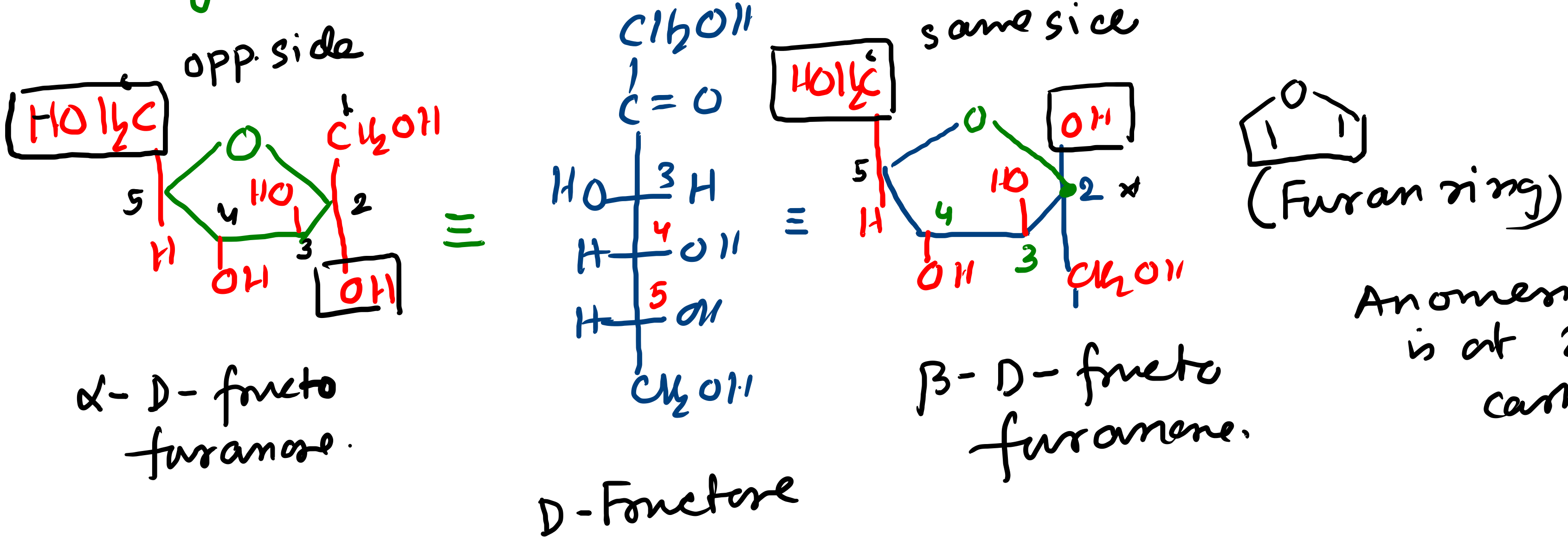
Reducing sugar. (Hemiacetal linkage)

⇒ Nonreducing sugar. (Acetal)



Anomers / diastereomerisation. (Mutarotation) is present.

Cpds showing mutarotation are example of the reducing sugar.



Anomeric carbon is at 2nd carbon.

Disaccharide

=> Maltose $\xrightarrow{H_3O^+}$

2eq. α-D-glucopyranose.

=> Lactose $\xrightarrow{H_3O^+}$

1eq β-D-glucopyranose

+ 1eq

β-D-galactopyranose.

4th chiral carbon changed.

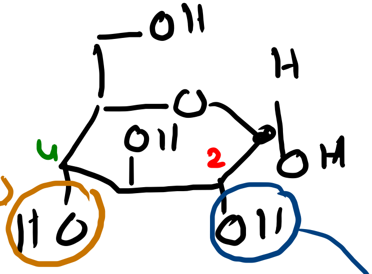
=> Sucrose $\xrightarrow{H_3O^+}$

α-D-glucopyranose

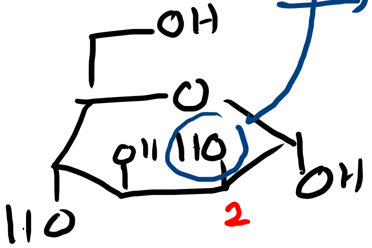
+ β-D-fructofuranose.

[Aldose + ketose]

α-form β-form.

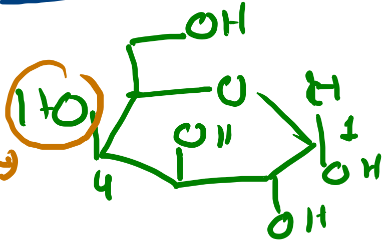


α-D-glucopyranose

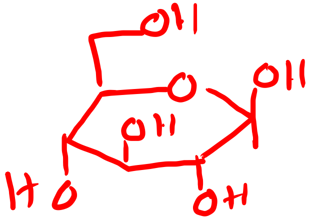


2nd chiral carbon change.

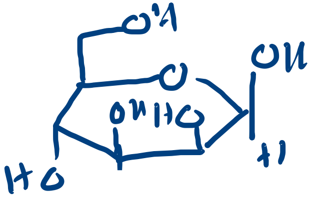
α-D-Mannopyranose



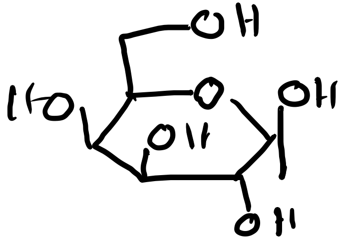
α-D-galactopyranose.



β-D-glucopyranose.



β-D-Mannopyranose.



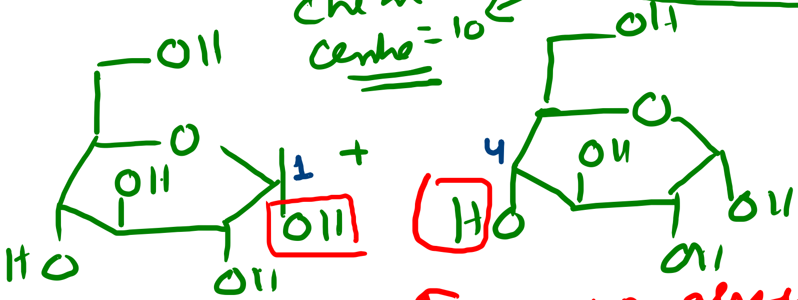
β-D-galactopyranose.

=) Maltose

α form + α form
(C1 + C4)

D-glucopyranose

chiral centre = 10



α-D-glucopyranose

α-D-glucopyranose

H_2O

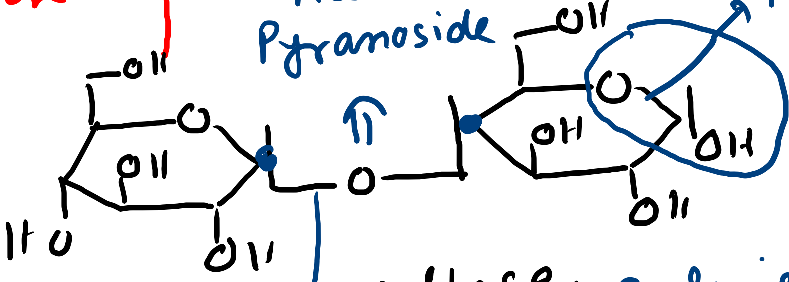
Acetal linkage present in both Maltose & Lactose structure.

Hemiacetal linkage is also present

Both are reducing sugar.

Acetal Pyranoside

Reducing



=) Hemiacetal Linkage

Non reducing.

Maltose.
[C1 + C4]

Reducing sugar.

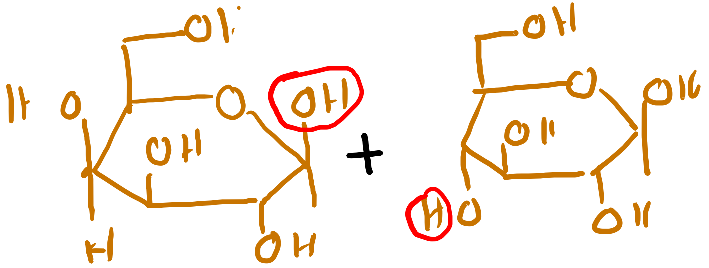
+ve Tollens
+ve Fehling.

=) water soluble.

=) Lactose.

galact(C1) + glucose(C4)

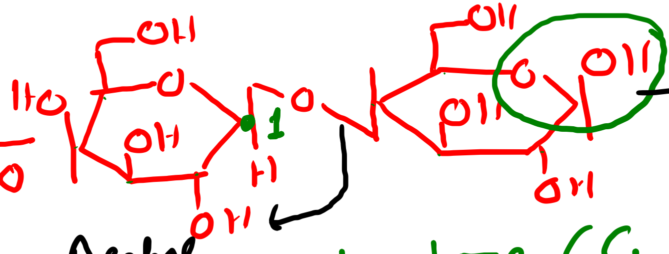
β form + β form.



β-form of galactopyranose

β-form of glucopyranose

H_2O



Acetal

Hemiacetal
Reducing sugar.

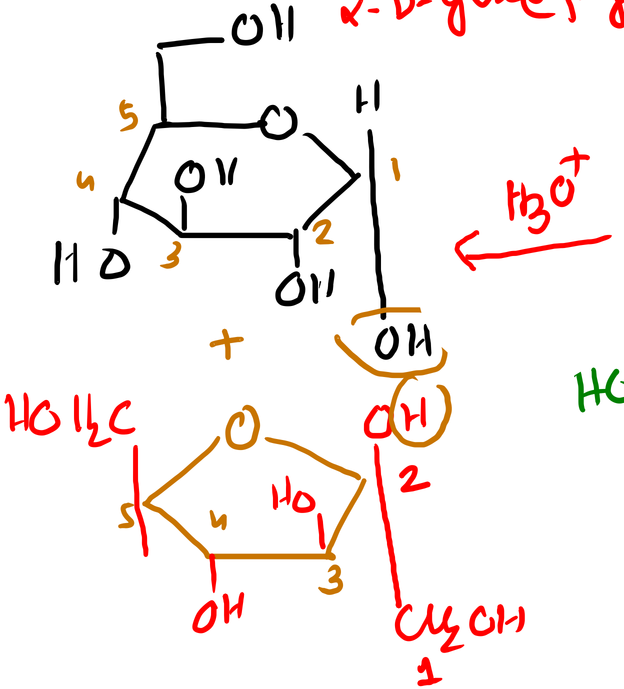
water soluble.

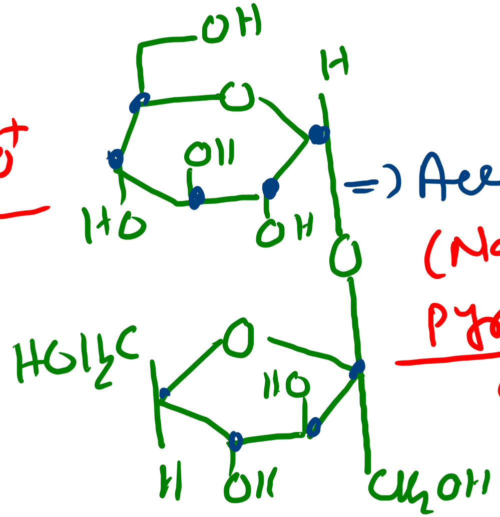
Lactose (C1 => galactopyranose
+
C4 => glucopyranose)

Sucrose: (α-D-glucopyranose + β-D-fructofuranose) (C_1 + C_2)

No hemiacetal
Nonreducing sugar. linkage.

α-D-glucopyranose





=) Acetal linkage
(Nonreducing)
pyranoside.
α-β

β-D fructofuranose.

Sucrose.

Total chiral centre = 9.
(no hemiacetal linkage)
Nonreducing sugar.
–ve Tollens test.
–ve Fehling test

Starch $\xrightarrow{H_3O^+}$ α-D-glucopyranose.

Cellulose $\xrightarrow{H_3O^+}$ β-D-glucopyranose.

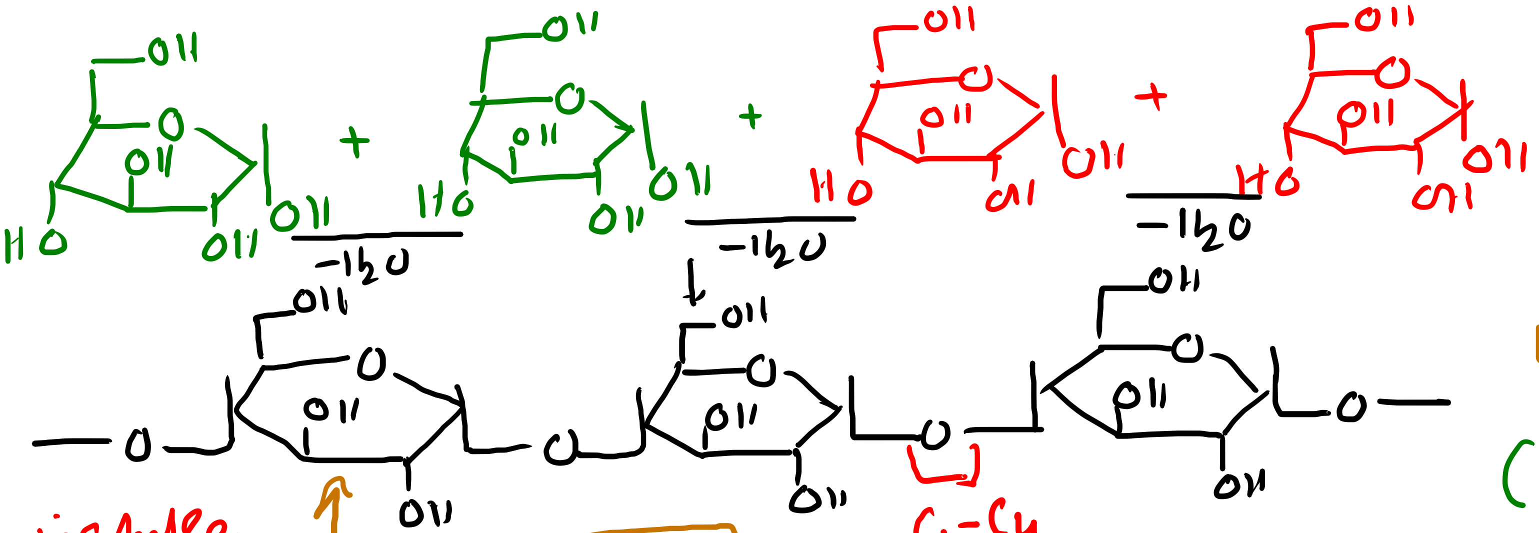
Polysaccharide

=) Starch * → Amylose
→ Amylopectin

* =) Cellulose
(Plant kingdom)
most abundant.

* =) glycogen
(animal tissue)

* Polymers
(natural)

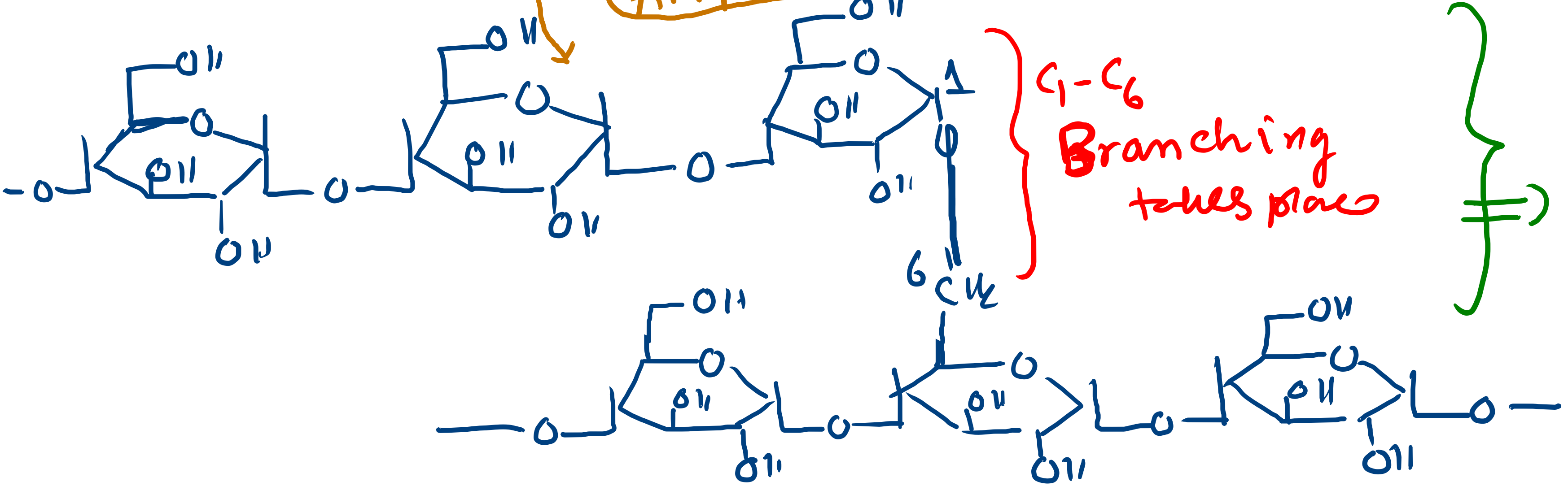


water insoluble.

$\boxed{\text{STARCH}}$ ⇒ $\boxed{\text{AMYLOSE}}$, $\boxed{\text{AMYLOPECTIN}}$

$C_1 - C_4$ Polymerisation takes place.

No branching
Linear polymer
(Amylose)
(10-15% in starch)
water soluble.



$C_1 - C_6$ Branching takes place

water insoluble due to branching ⇒ Amylopectin
(80-85% starch)

Cellulose:

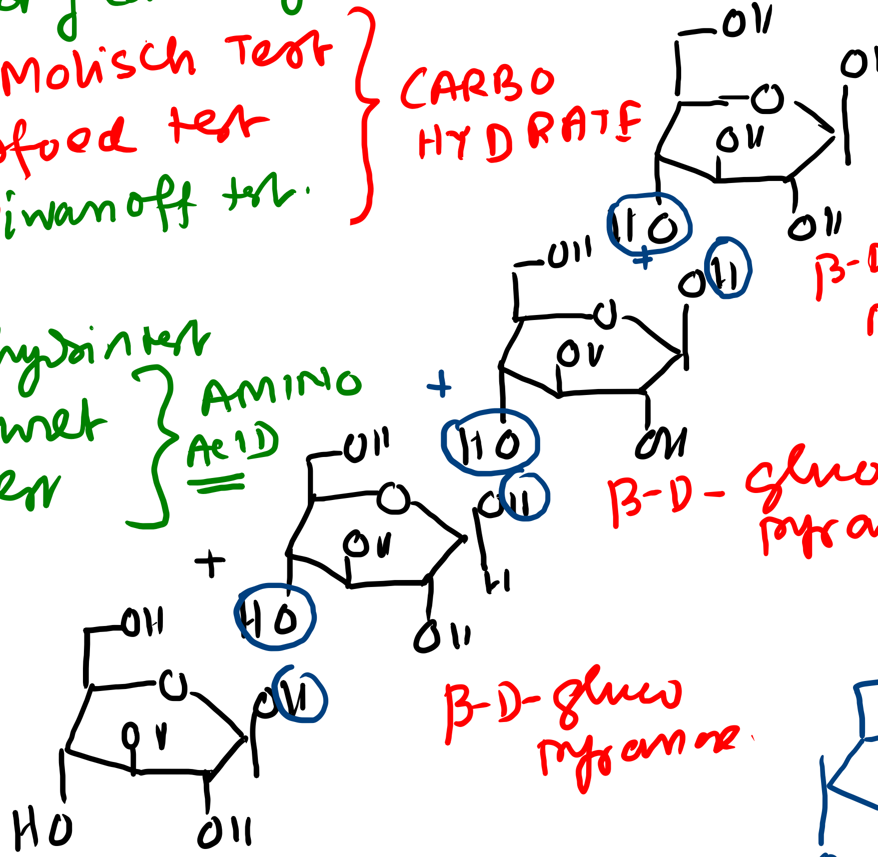
Test of Carbohydrate & Amino Acid

- ⇒ Molisch Test
- ⇒ Barfoed test
- ⇒ Seliwanoff test

} CARBOHYDRATE

- ⇒ Ninhydrin test
- ⇒ Biuret test

} AMINO ACID



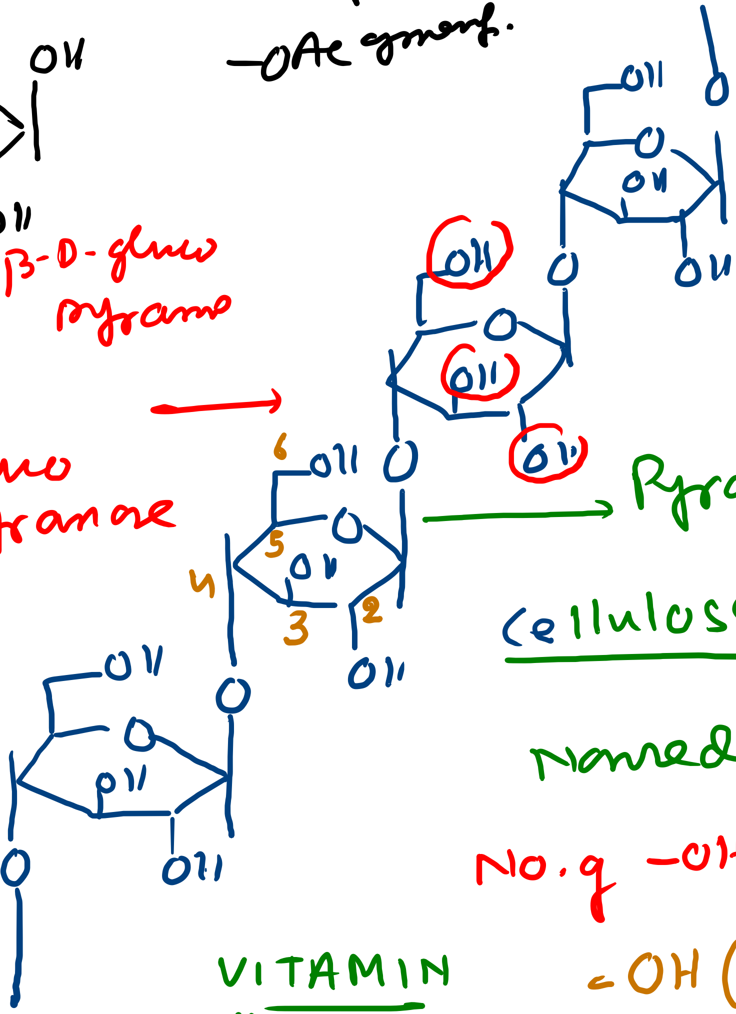
β-D-gluco pyranose

β-D-gluco pyranose

β-D-gluco pyranose

β-D-gluco pyranose

In product all an acylation all –OH groups are substituted by –OAc group.



$\xrightarrow[(XS)]{Ac_2O}$ Cellulose triacetate

RAYON

semisynthetic polymer.

β-β-form.

→ Pyranoside / Acetal

cellulose (no hemiacetal linkage)

Nonreducing sugar.

No. of –OH group in each unit = 3.

–OH (C_2; C_3; C_6)

it form triacetate.

VITAMIN

Next class: DNA & RNA; "POLYMER QS"