CARBOHYDRATES 1.

19-05-2020 Lecture-4 Deg-II (H&S)

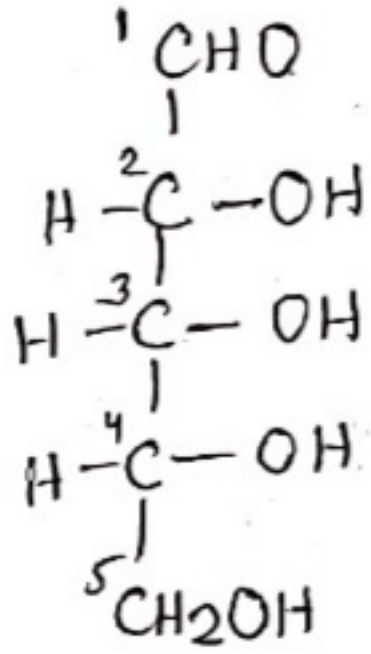
Topic -Configuration Of D-Glucose (Fischer's proof)

By-Dr.Rinky
Dept. of Chemistry

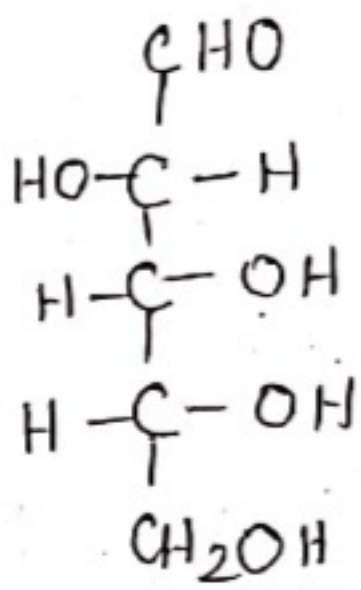
The structure which was discussed in the lecture number three (3) does not give us any idea about the spatial arrangement of the hydroxyl groups and the hydrogen atom around the four asymmetric carbon.

The procedure given below is the one which was used by the great Emil Fischer.

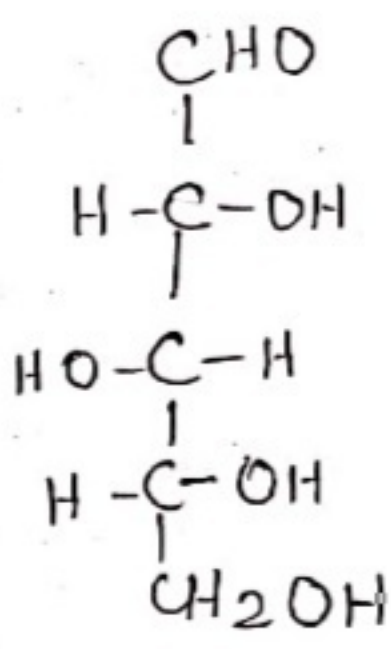
A key compound in this determination is D-arabinose ~~and~~ an aldopentose, which must have one of the following structure (I-IV)



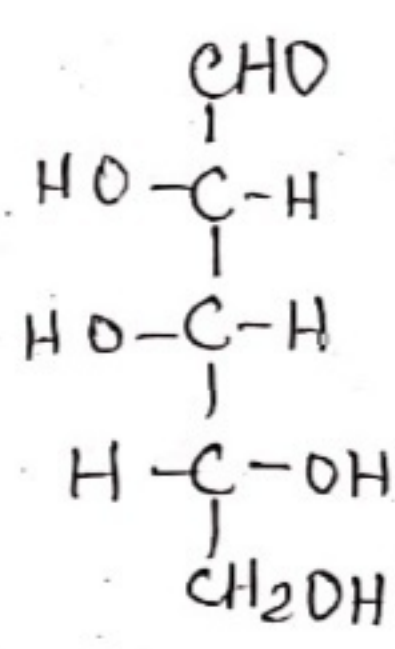
I



II

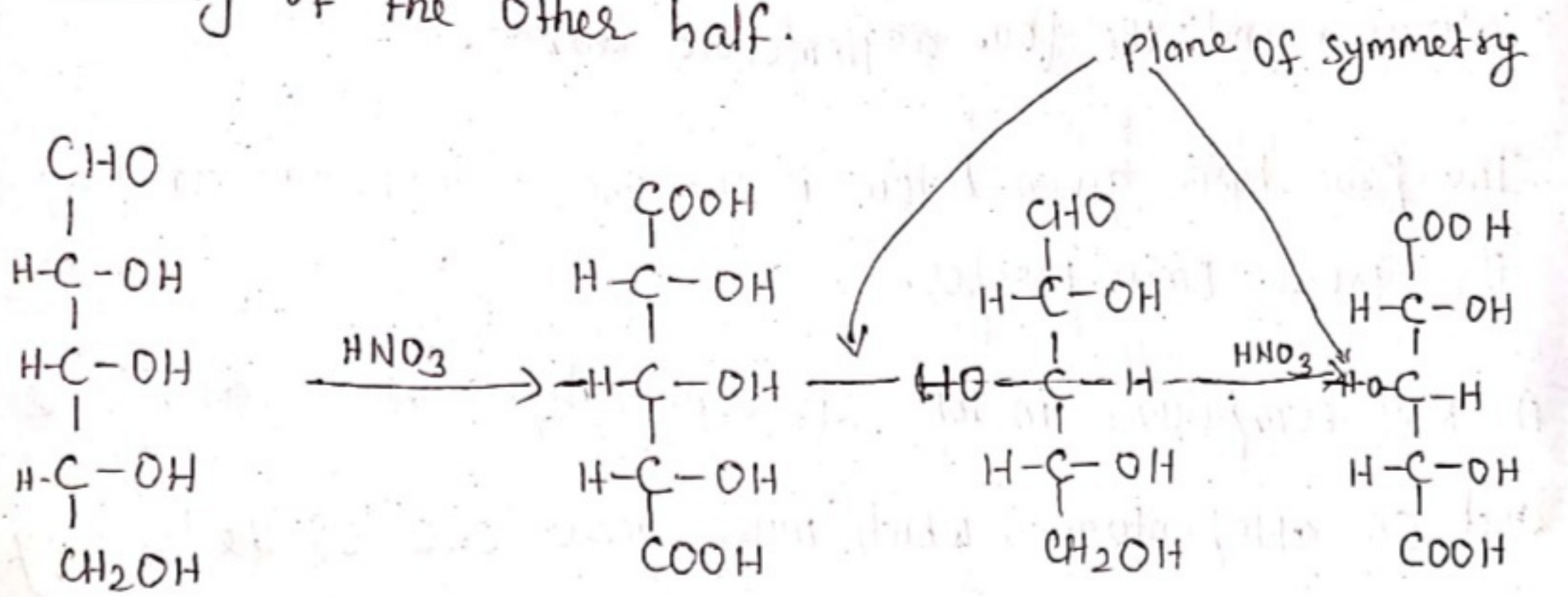


III



IV

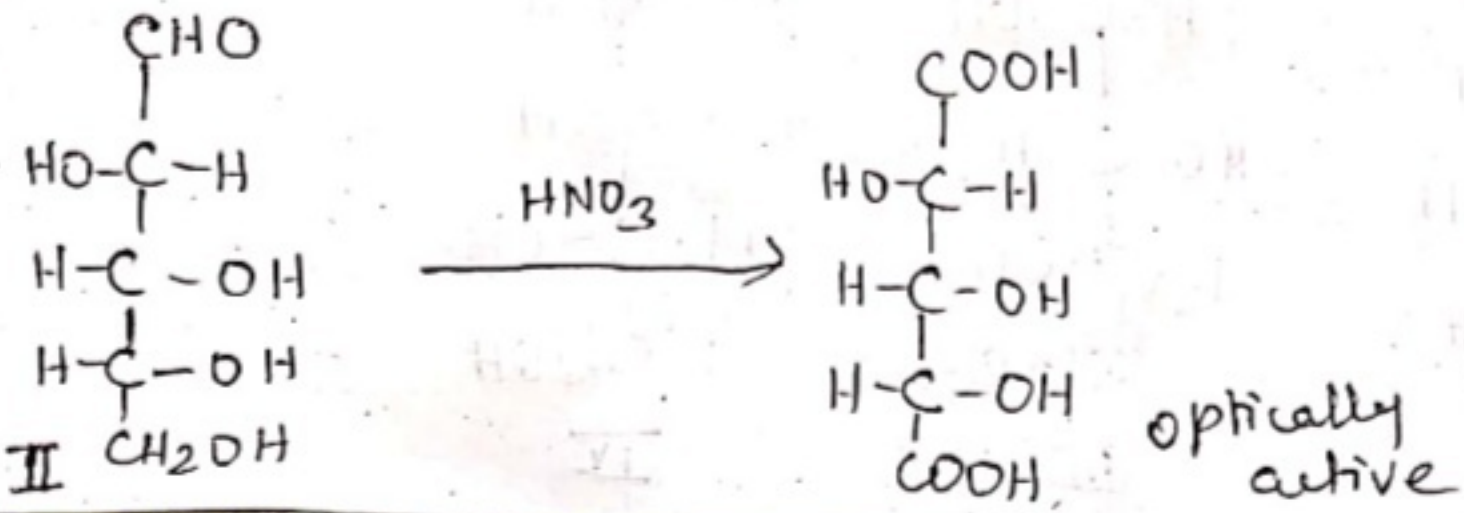
* Oxidation of D-arabinose with HNO_3 gives an optically active dicarboxylic acid.
* Under these conditions I and III would have given Optically inactive meso diacids.
* They contain a plane of symmetry such that one half Of the molecule form the minor image of the other half.
* They are optically inactive because the optical activity due to one half is counter balanced by the optical activity of the other half.



I

Optically inactive (Meso compound)

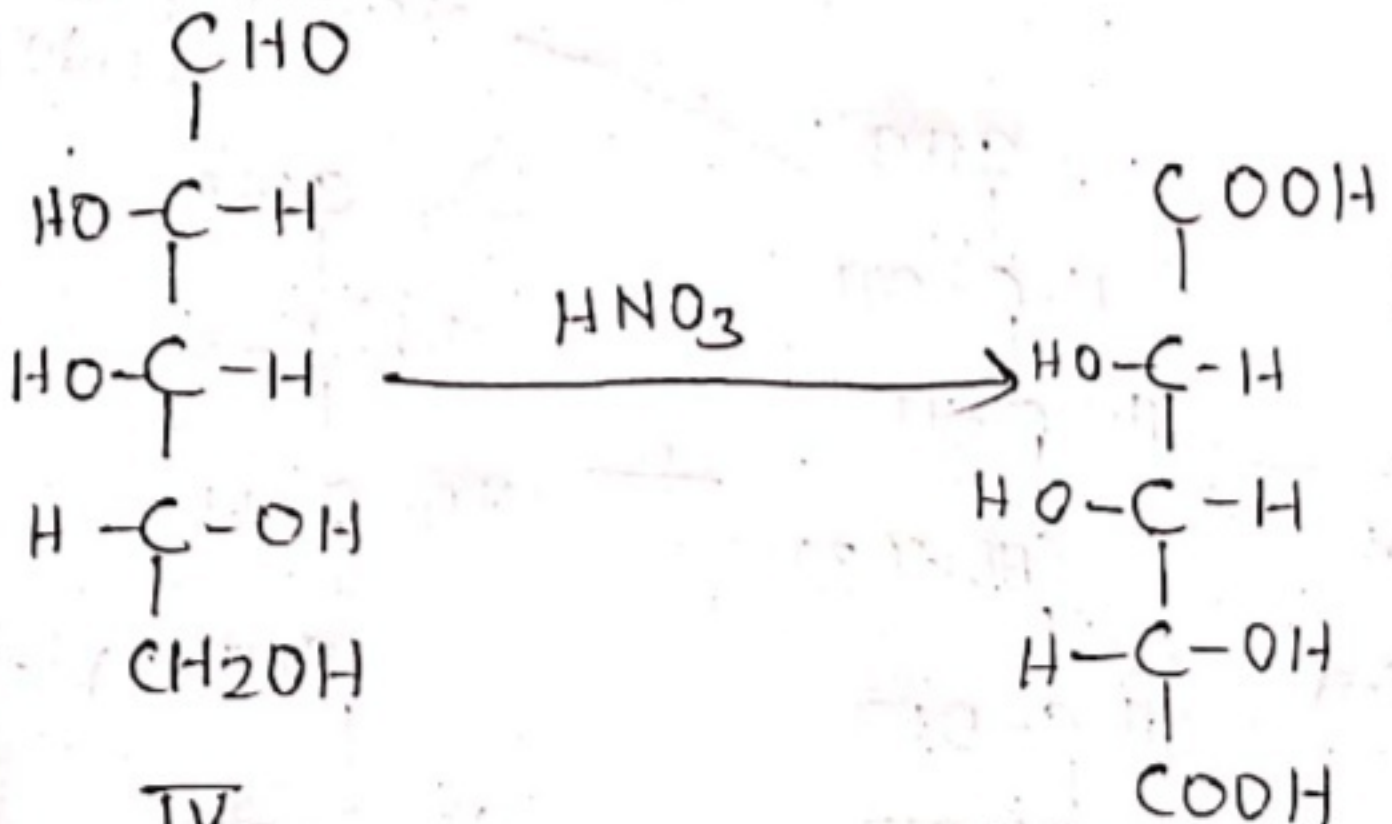
Optically inactive (Meso compound)



II

optically active

3.



IV

COOH

Optically active

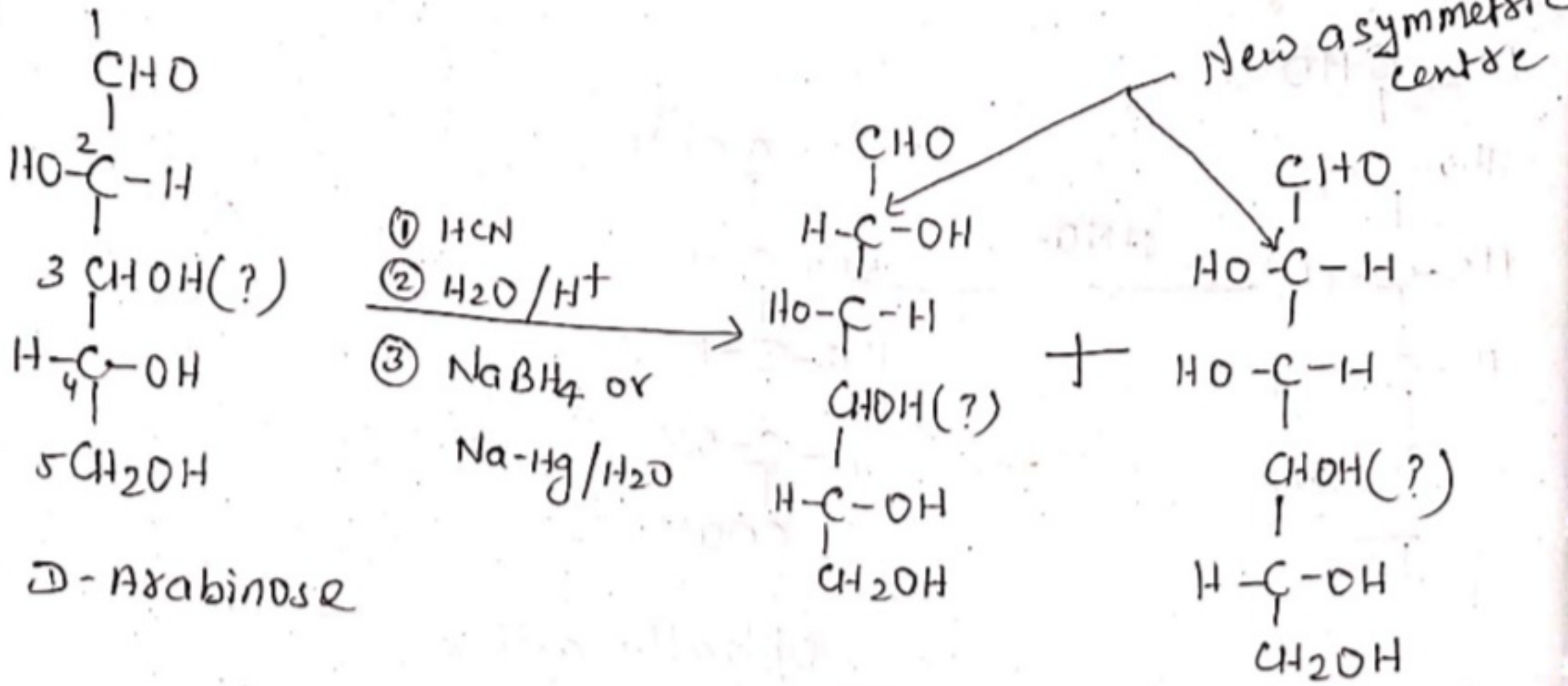
* D-arabinose is therefore either II or IV and can be represented with configuration in doubt at C-3 for the time being.

* When D- arabinose is subjected to the Kiliani Fischer Synthesis, it gives two sugars, glucose and mannose.

* These sugars differ only in configuration at C-2 which is the new assymetric centre created in the chain extension.

* Structure V and VI must therefore represent glucose and mannose.

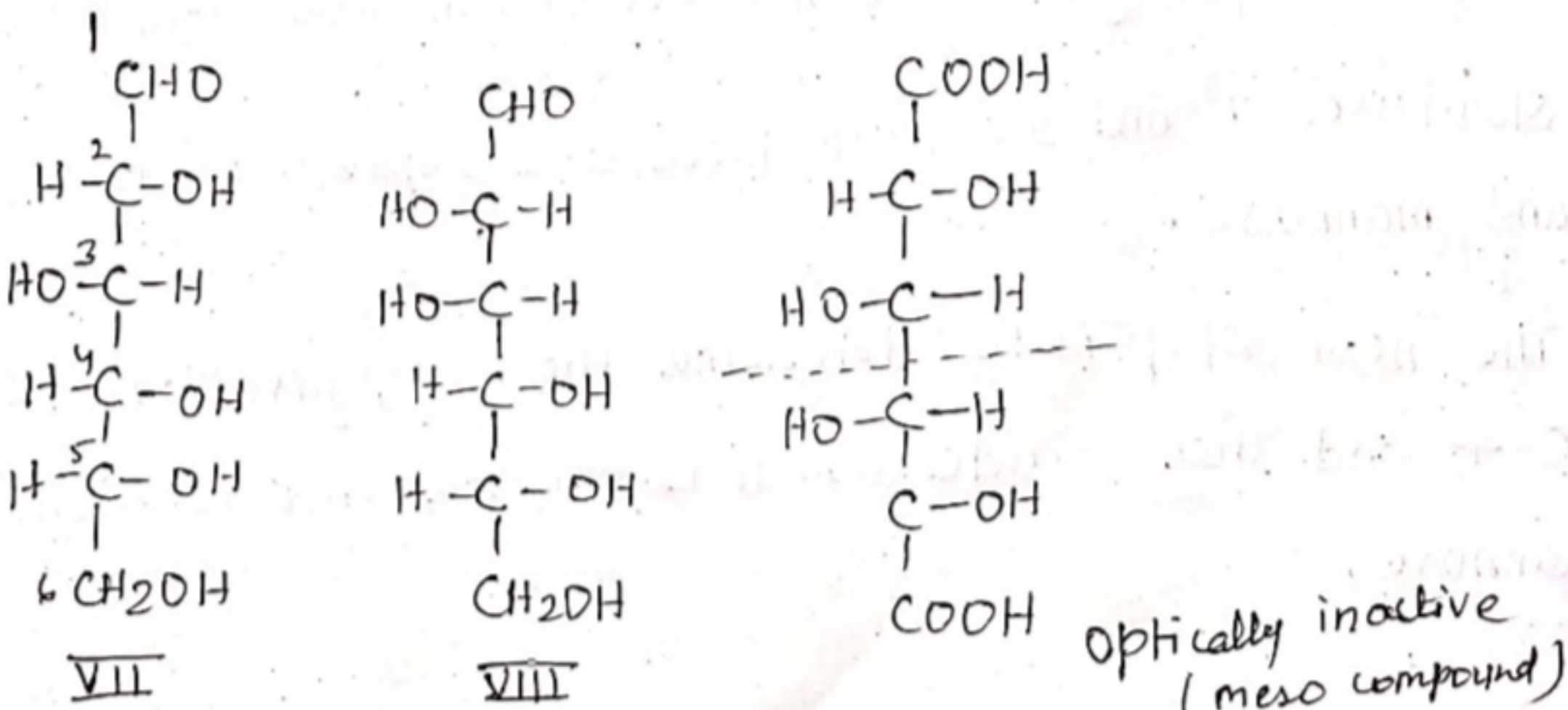
* The next step is to determine the configuration at C-4 and then decide which is glucose and which is mannose.



V VI

Both glucose and mannose on oxidation with HNO_3 give diacids which are optically active. This means that the hydroxyl group C-4 is on the right- as in VII & VIII.

If it were on the left, VII would have yielded an optically inactive meso diacid, IX



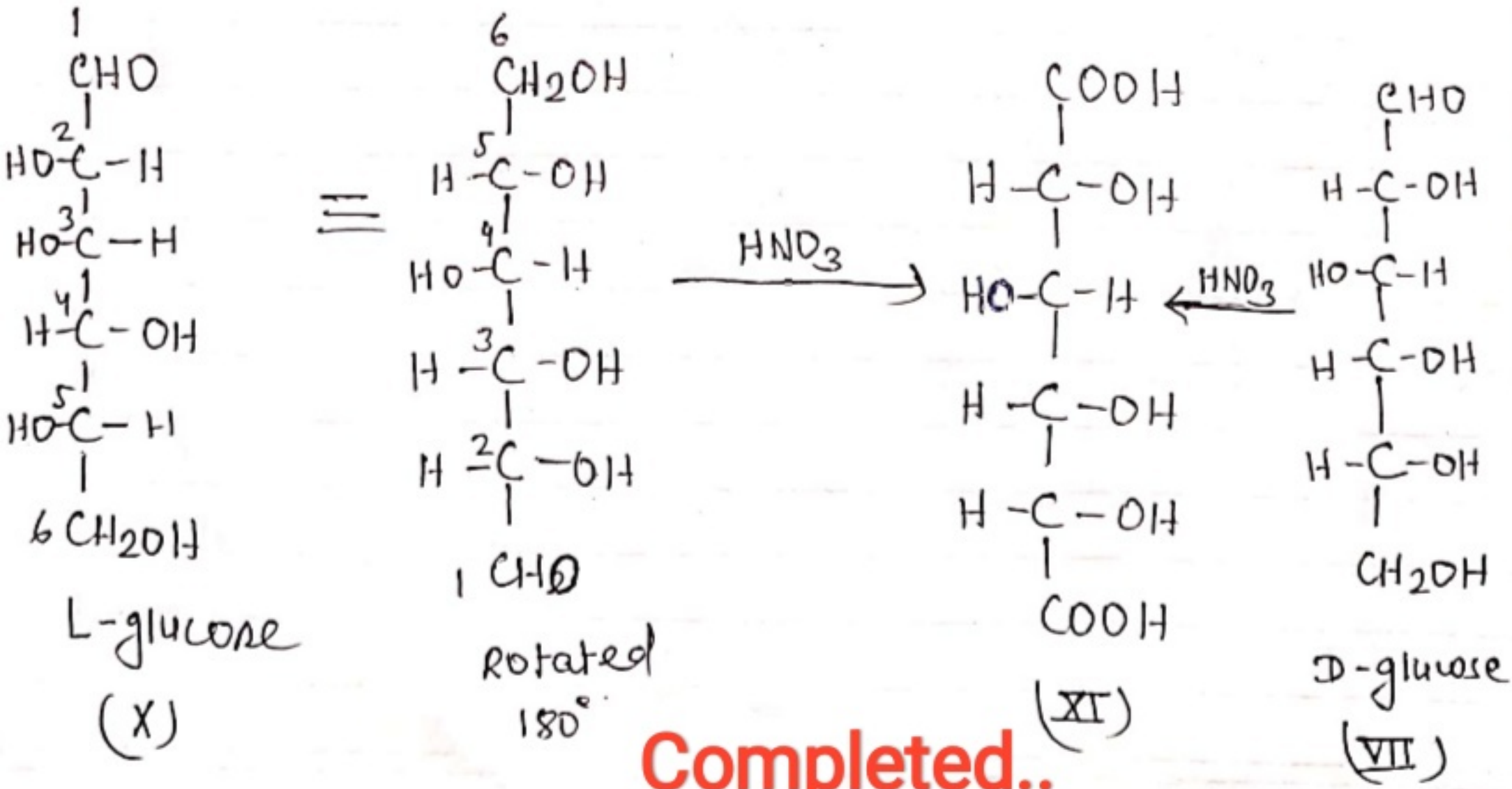
VII VIII

Structure VII and VIII then represent D-glucose and D-mannose.

It only remains to decide whether VII is glucose and VIII is mannose.

To decide this last point we make use of another aldohexose L-glucose, X.

This compound when oxidised with HNO_3 yields the same dicarboxylic acid (XI) as that obtained from D-glucose.



Completed..