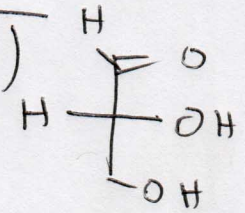
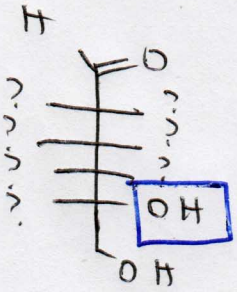
5/16/12 0. Glucose is an aldohexose

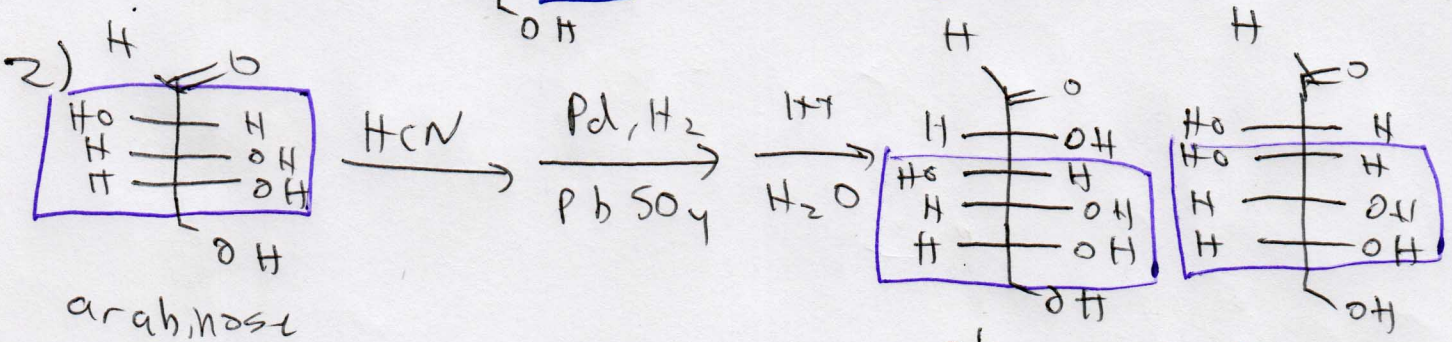
1. Assumption of D configuration
2. Glucose + Mannose are epimers that can be synthesized from arabinose
3. Arabinaric acid is optically active
4. Glucaric + mannaric acids are optically active
5. D-glucose + L-gulose form the same aldaric acid

1) 

Fischer guessed the configuration of D-glyceraldehyde.



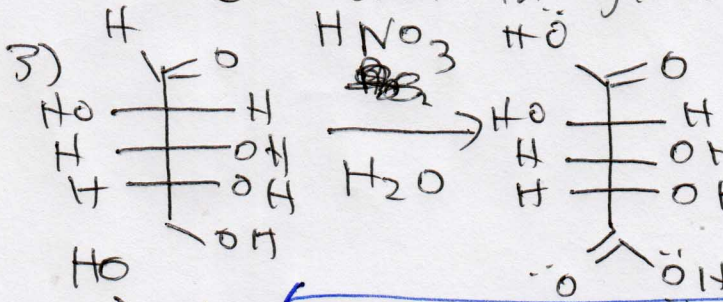
∴ The last stereocenter in glucose is assumed and was a guess

2) 

arabinose

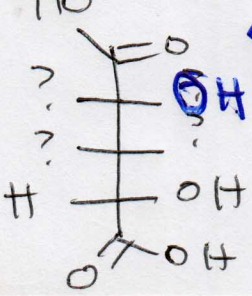
glucose + mannose

Since glucose + mannose can be synthesized from arabinose, if the configuration of a stereocenter in arabinose is established, the configuration of a a stereocenter in glucose + mannose is established.

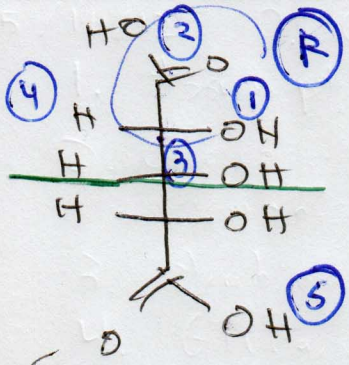
3) 

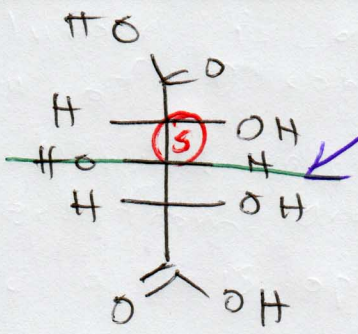
← an aldaric acid → arabinaric acid

Arabinaric acid is optically active.



The only way this compound can be optically inactive is if it is meso, which would require an internal mirror plane

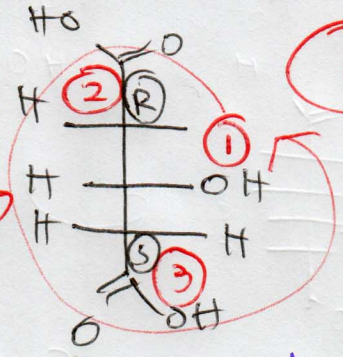




pseudostereocenter – r, s

A carbon that does produce stereoisomers but cannot formally assigned a configuration of R or S since two of the carbon's substituents are equivalent, R > S

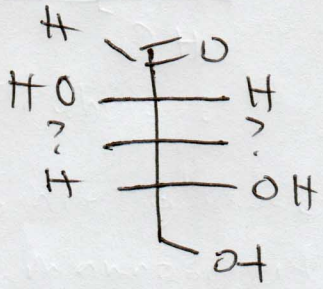
both are meso, because of the configuration of the top stereocenter.



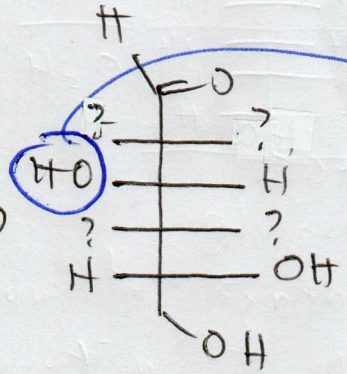
pointed towards

To determine the pseudo configuration of pseudostereocenter, R is given priority over S.

Since both of these compounds are meso, neither can be D-arabinose.

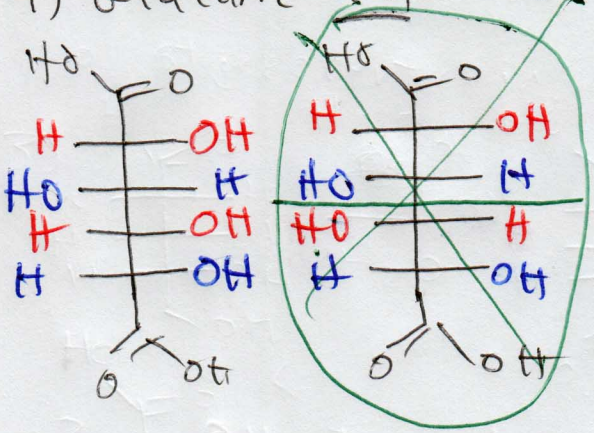


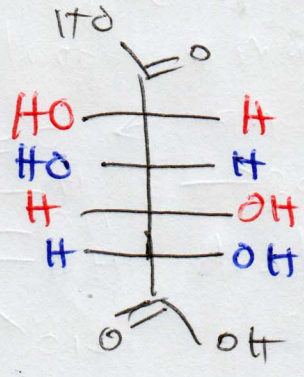
KFCE

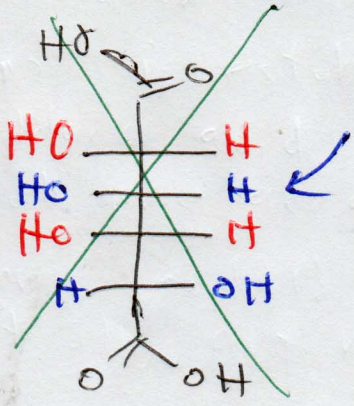


now established

4) Glucaric and mannaric acids are optically active.



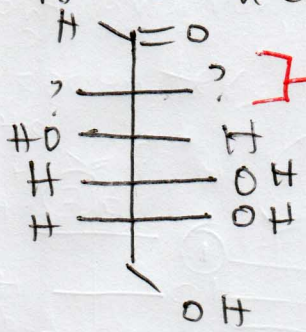




established

meso → cannot be ~~stereo~~ the aldaric acid of glucose & mannose

Glucose ~~&~~ and mannose have the same configuration for the 3rd stereocenter; they only differ by the 1st stereocenter. Therefore, if the 3rd stereocenter is shown to be incorrect for either compound, it is incorrect for both. This is why two compounds were eliminated as possibilities when one of the two was shown to be meso (upon oxidation).



→ only one SC left undetermined

5) Two sugars make the same aldaric acid as glucose.