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. Arabinose acid is optically active
4. Glucaric + mannaric acids are optically active
5. D-glucose + L-gulose form the same aldonic acid.

1) Fischer guessed that the configuration of D-glyceraldehyde.

2) The last stereocenter in glucose is assumed and was a guess.

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

4) 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.
pseudo stereocenter - 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, RSS

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

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

4) Glucaric and mannanic acids are optically active.

Meso → cannot be the aldonic acid of glucose and 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 aldonic acid as glucose.

Mannose

SAME!