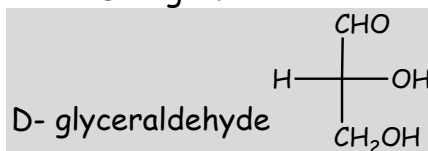


Fischer Proof of Glucose

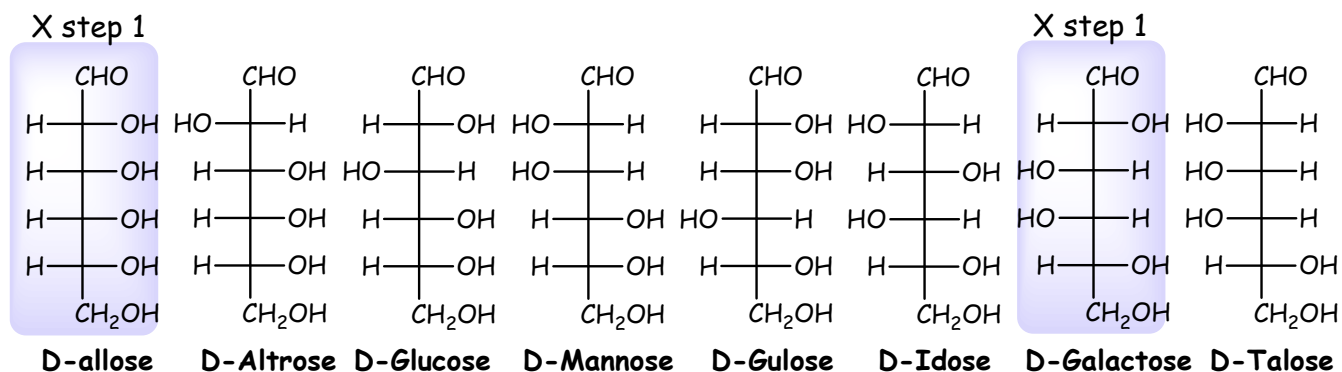
Fischer started his proof in about 1888. This was about a decade after the tetrahedral nature of carbon was proposed and he had the following methods at his disposal:

- Melting points
- Ability to measure optical rotations
- Several reactions of carbohydrates

Fischer knew that glucose was an aldohexoses and that there were 16 stereoisomers possible (8 D-sugars and 8 L-sugars). Fischer arbitrarily assigned the stereochemistry of glyceraldehyde as shown and designated it a D-sugar.

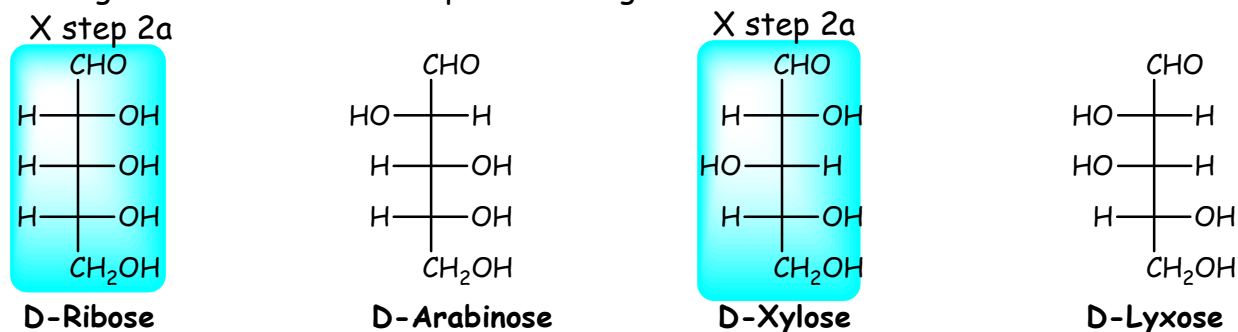


1. Oxidation of D-glucose (structure unknown at the time) with nitric acid gives an optically active aldaric acid. Thus, D-glucose cannot be allose or galactose, both of which would give optically inactive aldaric acids.



2a. Ruff degradation of (+)-glucose gives an aldopentose; oxidation of this pentose with nitric acid gives an optically active aldaric acid. Therefore, this pentose cannot be ribose or xylose (optically inactive aldaric acids).

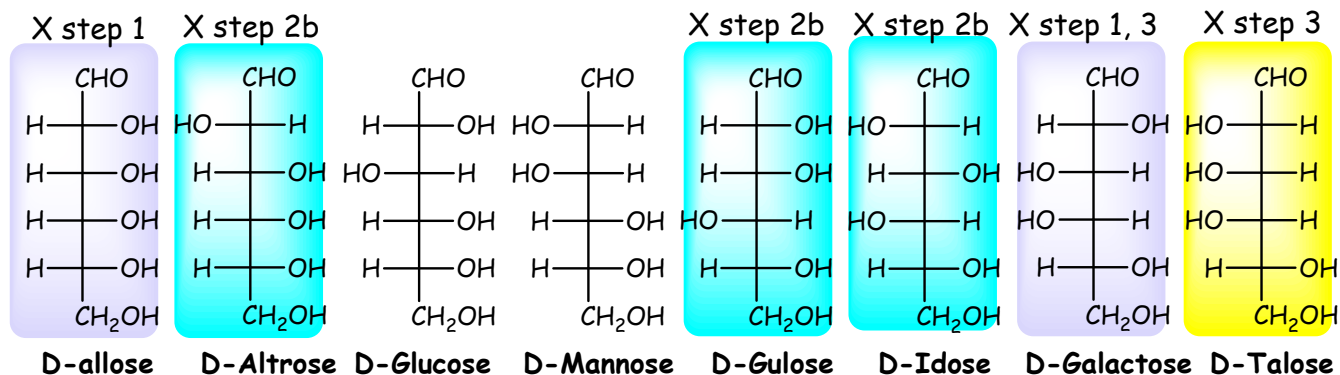
2b. If not ribose or xylose, then glucose cannot be allose/altrose or gulose/idose since these give a meso structure upon Ruff degradation.



Fischer Proof of Glucose

3. Kiliani-Fischer chain lengthening of arabinose gives glucose and mannose both of which give optically active aldaric acids upon oxidation with nitric acid. Since ribose and xylose were eliminated previously, arabinose must have structure that matches D-arabinose or D-Lyxose. However, Lyxose would be converted to galactose and talose and only one of these (talose) would give as optically active aldaric acid, not both.

Therefore, arabinose must have structure shown and that leaves only two possibilities for glucose: glucose or mannose.



4. Fischer had developed a method to interconvert the ends of a carbohydrate so that the CH_2OH group was converted to an aldehyde and the aldehyde was converted to a CH_2OH group. Fischer reasoned that if the structure of glucose was as shown, interconversion would produce a new sugar, an L-sugar. If the structure of mannose was as shown, then interconversion would produce the same sugar. Fischer carried out the interconversion of both and indeed, glucose provided a new sugar which proved the structure as shown on the sugar tree.

