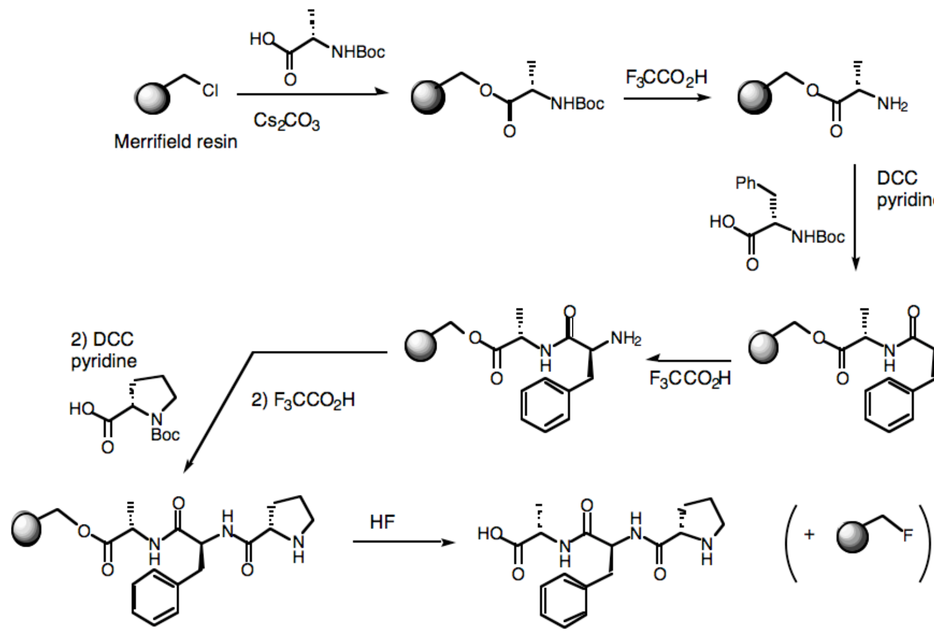
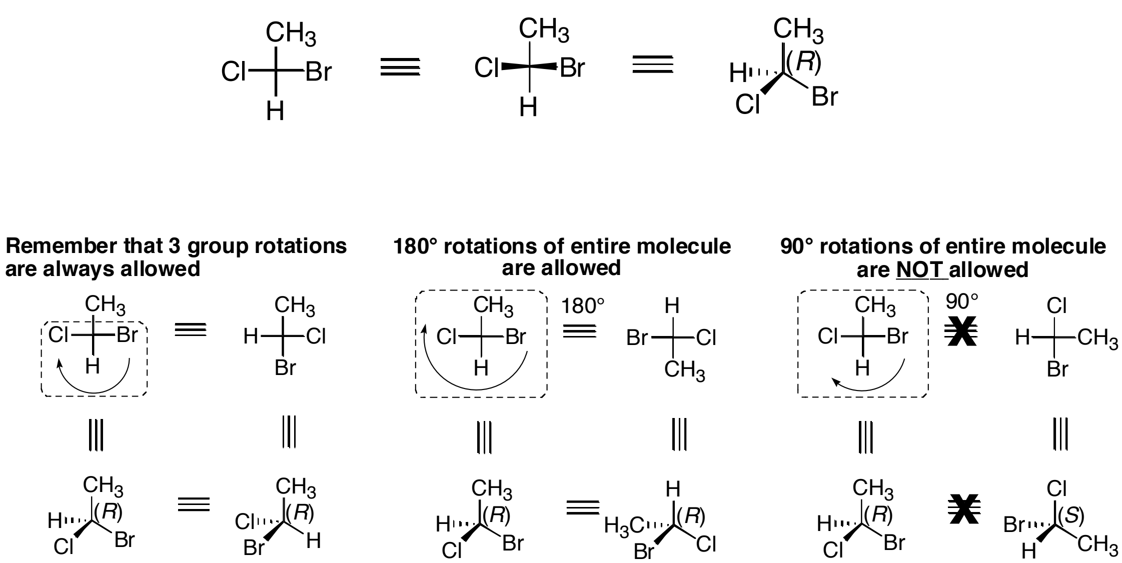
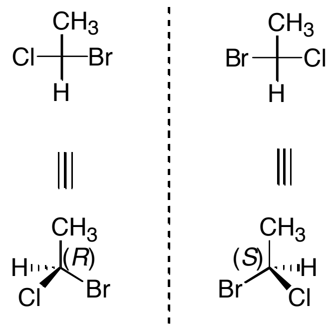
Solid Phase Peptide Synthesis



Fischer Projections revisited

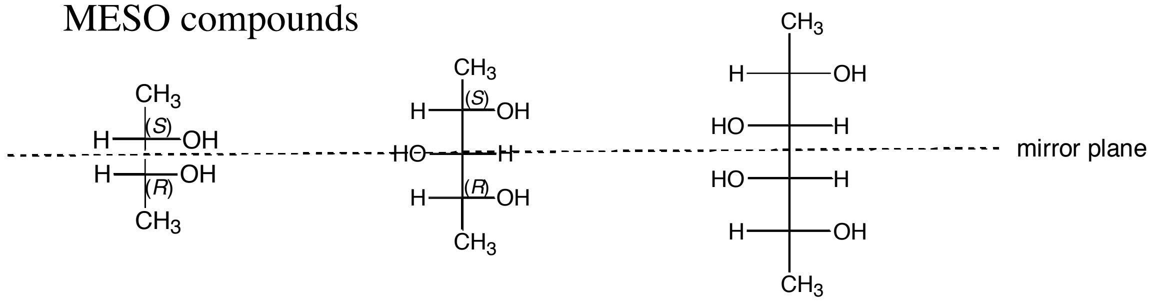


mirror images are enantiomers

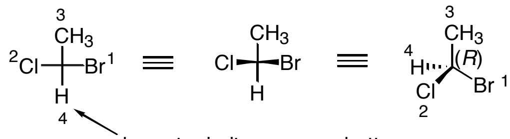


identification of meso compounds by a horizontal mirror plane

MESO compounds

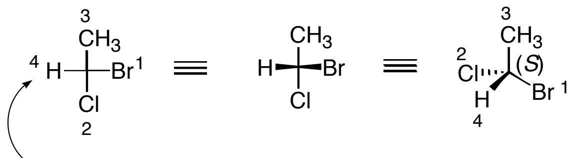


a Helpful way to assign stereochemistry



lowest priority group on bottom

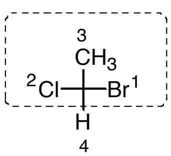
notice that
lowest priority group (H)
is in the back



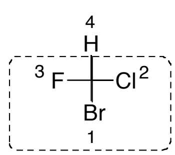
lowest priority group on side

notice that
lowest priority group (H)
is in the front

If the lowest priority group is on the top or bottom: assign 'as normal'

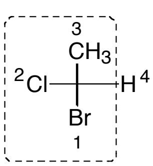


clockwise = *R*

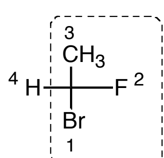


counterclockwise = *S*

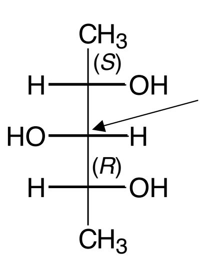
BUT If the lowest priority group is on the SIDE: make the OPPOSITE ASSIGNMENT



clockwise = *S*
(opposite of the 'normal
assignment)

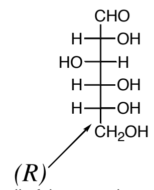


counterclockwise = *R*
(opposite of the 'normal
assignment)



not a stereocenter

Carbohydrates: $C_nH_{2n}O$



all of the natural sugars have *R* configuration at this stereo-center.

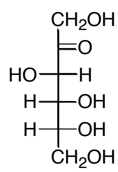
sugar

D-glucose: an aldohexose

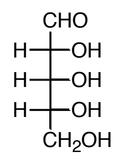
aldehyde — six carbon

Dextrorotatory = D
- *(R)* configuration for sugars

Levorotatory = L
- *(S)*-configuration for sugars



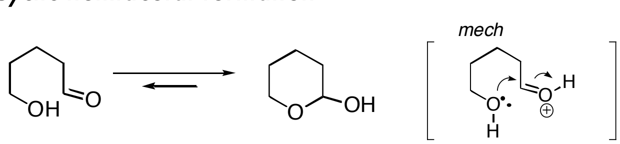
D-fructose: a ketohexose



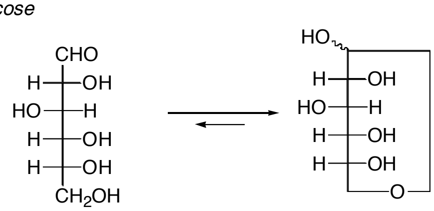
D-ribose: an aldopentose

Open chain sugars can equilibrate with cyclic hemiacetals

Cyclic hemiacetal formation



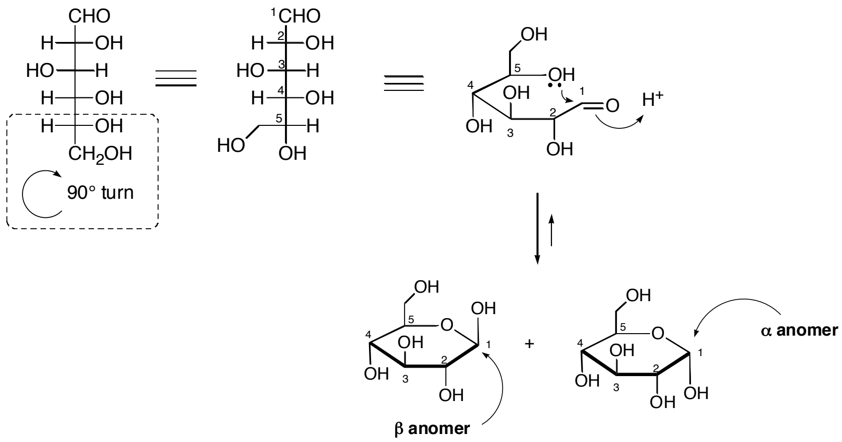
glucose



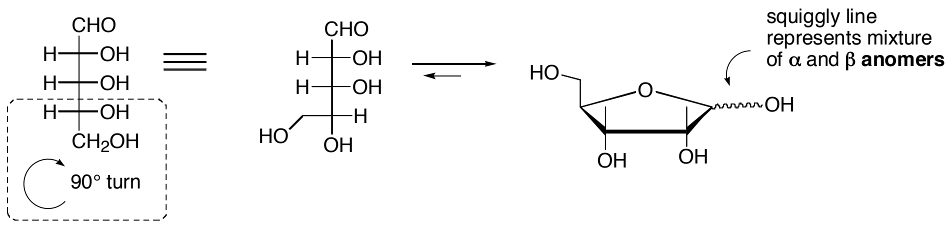
OK, so this is how they drew it back in the 1800's

Haworth Projections

For glucose

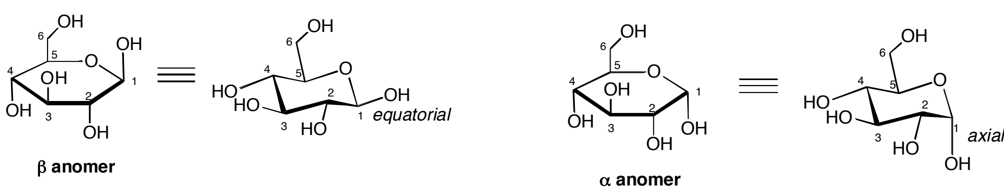


For ribose

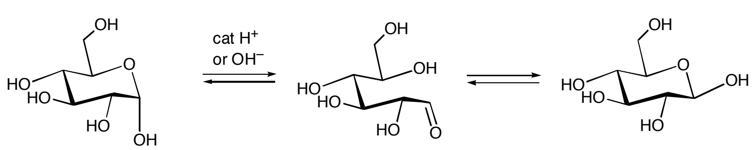


Converting Haworth Projections to Chair Projections

For glucose



Mutarotation of glucose



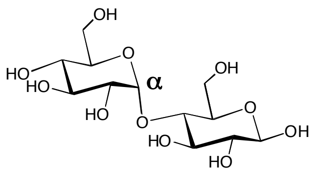
α_D = +112

H_2O

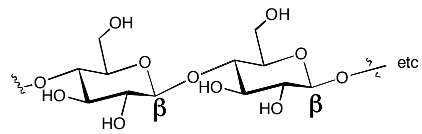
α_D = +52

Oligosaccharides and Polysaccharides

a disaccharide



maltose (beer): a glucose dimer



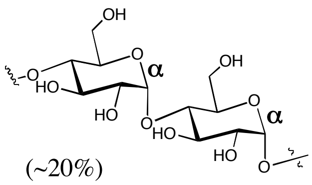
cellulose : a glucose polymer

highly linear strucrture: very effective for intrastrand H-bonding

insoluble: cell walls

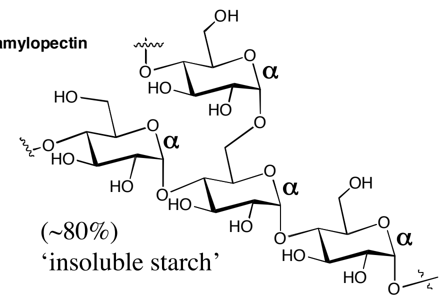
starch: two components

amylose



(~20%)
'soluble starch'

amylopectin

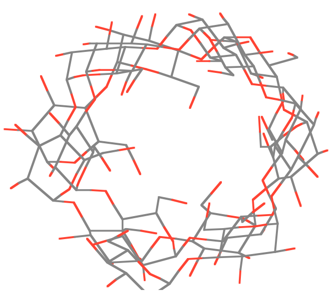


(~80%)
'insoluble starch'

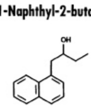
Oligosaccharides and Polysaccharides

Amylose is highly helical

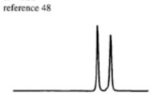
end view



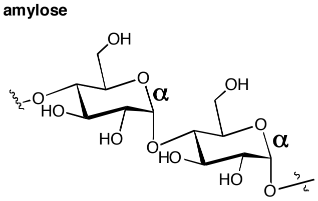
1-Naphthyl-2-butanol

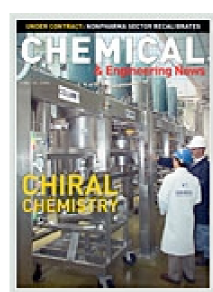


Column = (S,S)-ULMO
25 cm x 4.6 mm
Mobile Phase = (95/5) Heptane/IPA
Flow Rate = 1.0 mL/min
Detection = UV 215 nm
Run Time = 6 min
k'_1 = 0.80
α = 1.35
reference 48



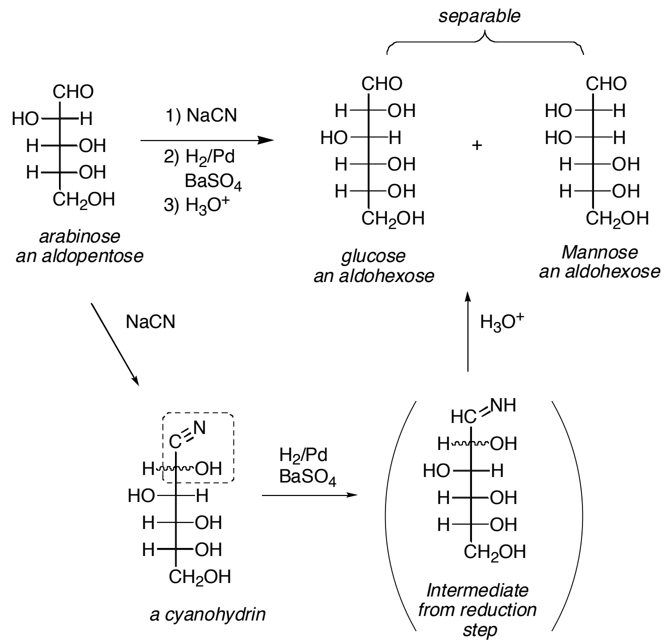
amylose





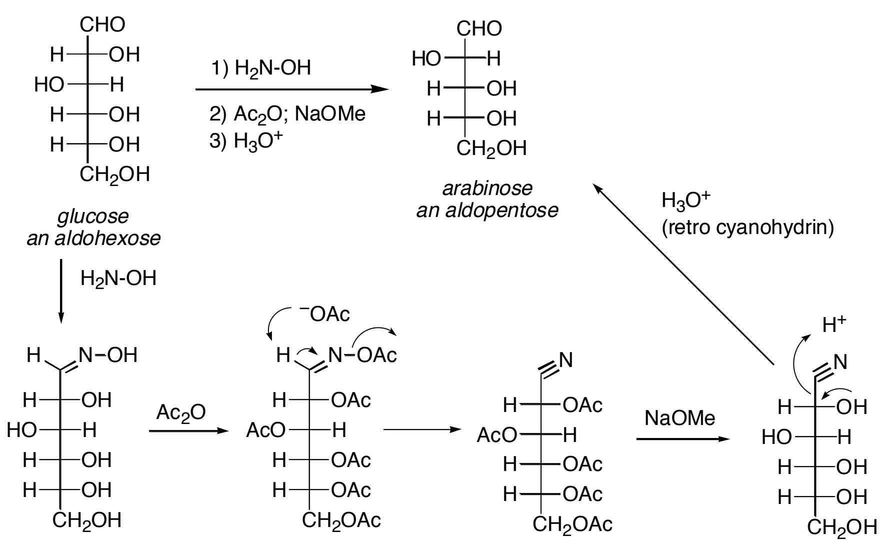
Some reactions of sugars

Kiliani Fischer Synthesis

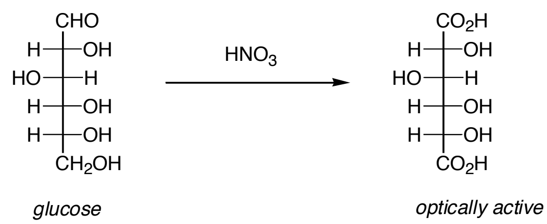


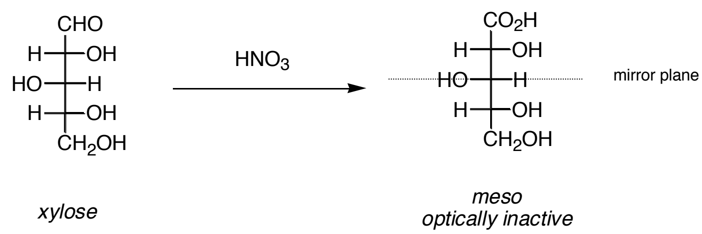
Some reactions of sugars

Wohl Degradation



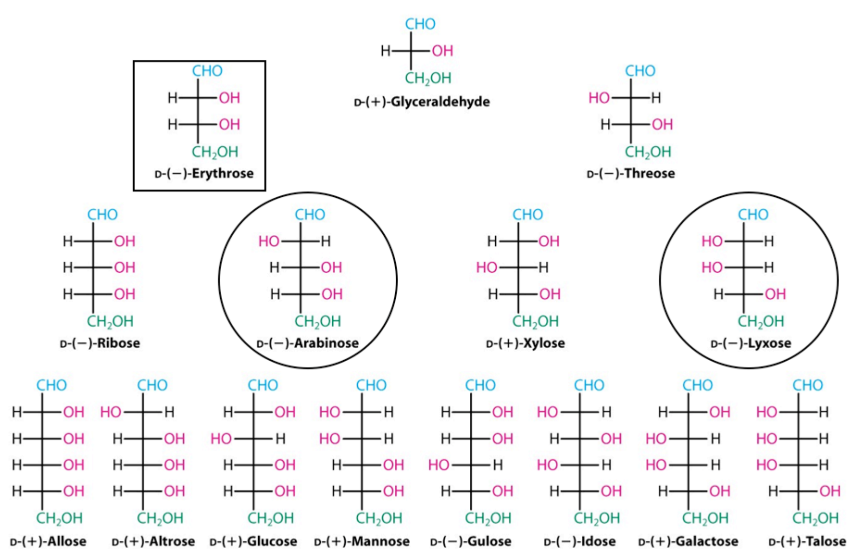
Oxidation of sugars





The Fischer Proof

1. An aldopentose is oxidized by HNO_3 to give an optically active diacid. Wohl degradation of that same aldopentose gives an aldotetrose. This aldotetrose provides an optically inactive diacid upon HNO_3 oxidation. Identify the aldopentose.



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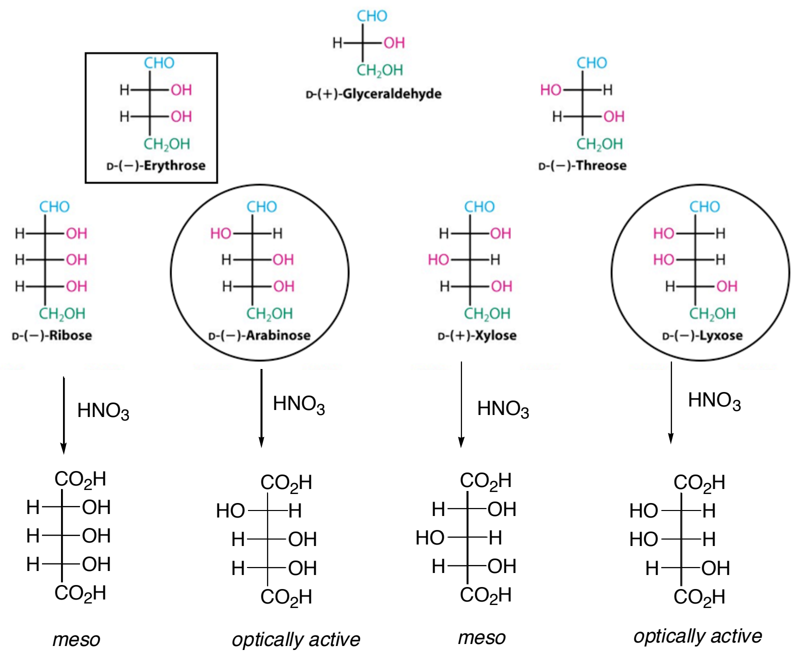

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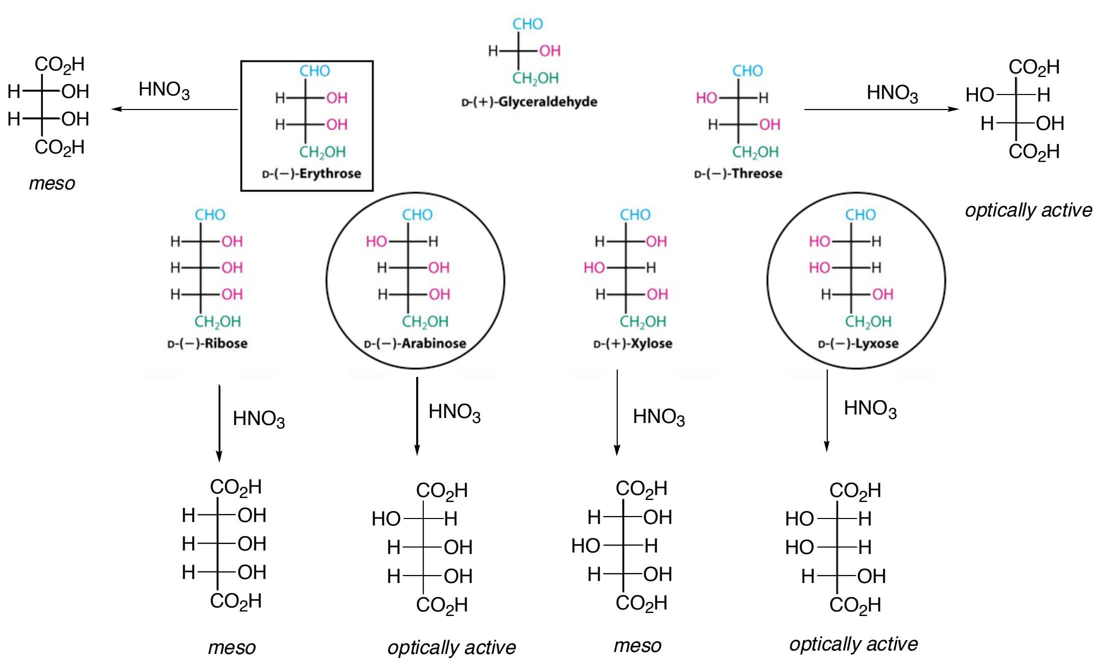

The Fischer Proof

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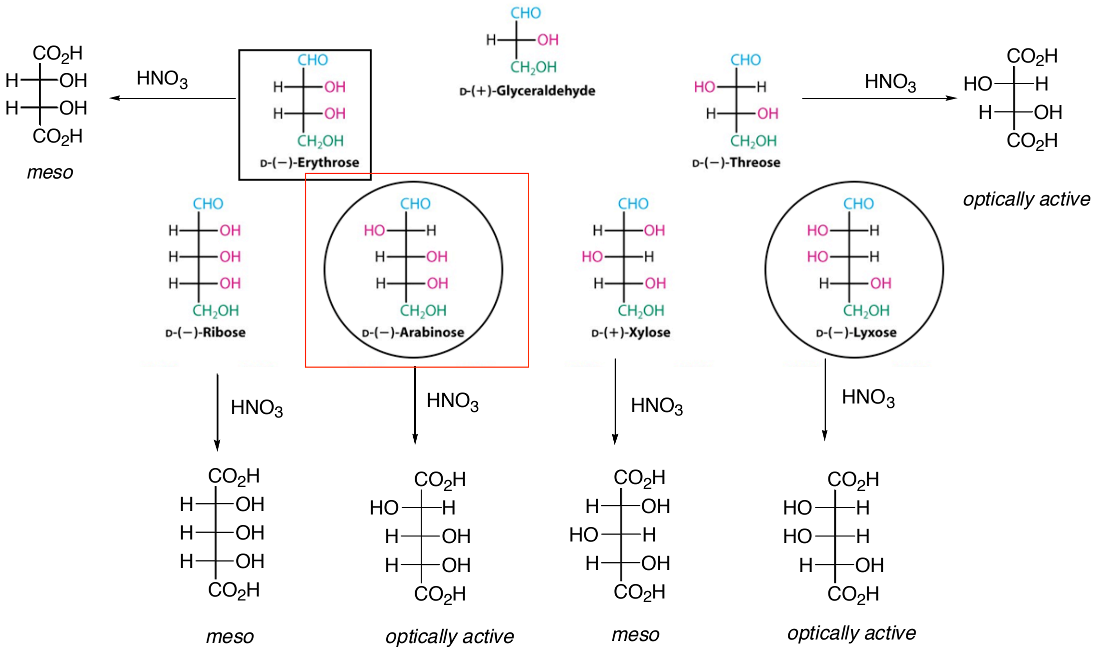

The Fischer Proof: Fischer used this type of analysis for all of the Sugars, starting from a good guess for glyceraldehyde

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