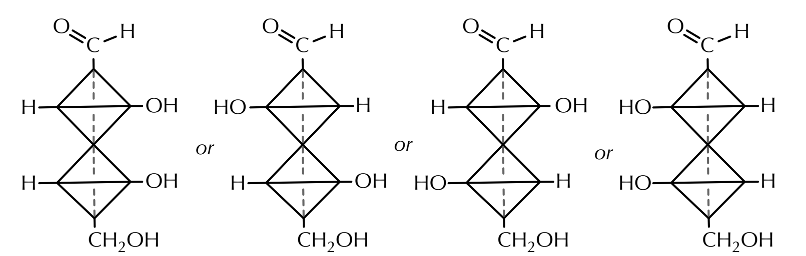
Figure 1606

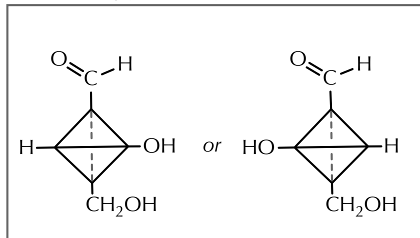
Experimental correlation between the properties of aldotetrose diastereomers from natural glyceraldehyde with the properties of the natural erythrose.

Known: Natural (-)-erythrose $[\alpha]_D$ = -33˚; unknown: which of these four?



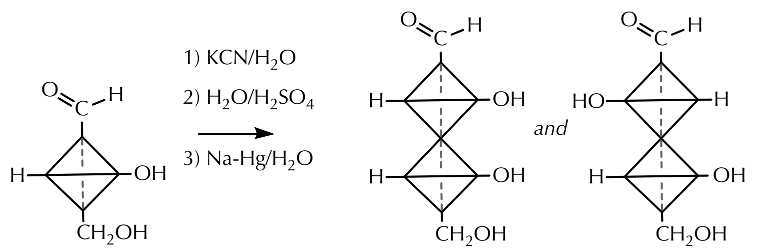
E1 **E2** **E3** **E4**

Natural (+)-glyceraldehyde is one of these two.



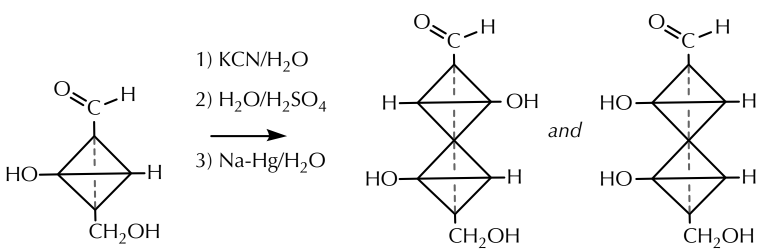
G1 **G2**

If **G1** is (+)-glyceraldehyde, then the Kiliani-Fischer synthesis creates the possible **E1** and **E2** erythroses. If the **E1** end groups are oxidized to carboxylic acids, it becomes optically inactive (*meso*-tartaric acid). If the **E2** end groups are oxidized to carboxylic acids, it becomes an optically active tartaric acid.



G1 **E1** **E2**

If **G2** is (+)-glyceraldehyde, then the Kiliani-Fischer synthesis creates the possible **E3** and **E4** erythroses. If the **E4** end groups are oxidized to carboxylic acids, it becomes optically inactive (*meso*-tartaric acid). If the **E3** end groups are oxidized to carboxylic acids, it becomes an optically active tartaric acid.



G2 **E3** **E4**

experimental results:

(1) Kiliani-Fischer:

Natural (+)-glyceraldehyde creates two products:

one with $[\alpha]_D$ = -33˚, matching natural erythrose, and one with $[\alpha]_D$ = -4˚.

(2) Oxidation of both end groups to carboxylic acids:

The product with $[\alpha]_D$ = -33˚ oxidizes to give optically inactive tartaric acid;

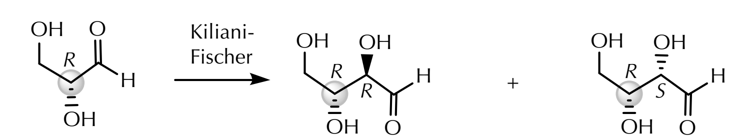
the product with $[\alpha]_D$ = -4˚ oxidixes to optically active tartaric acid $[\alpha]_D$ = +13.5˚ (which is the opposite sign of the naturally occuring isomer).

Fischer's conclusion:

Therefore, natural (-)-erythrose is either **E1** or **E4** and does have the same configuration at carbon-3 as in natural glyceraldehyde (whichever one it is, **G1** or **G2**).

Fischer names the previously unknown **E2** (or **E3**) as (-)-threose, a partial anagram of erythrose.

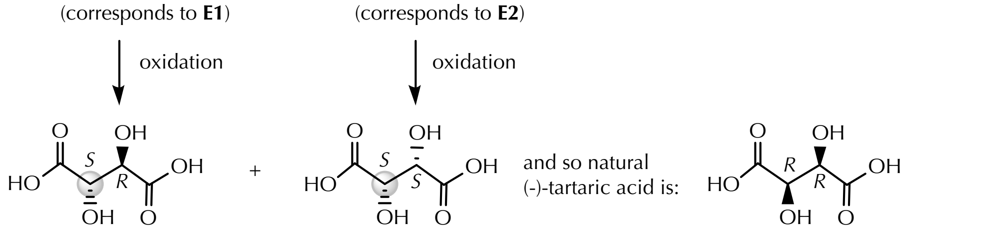
In modern terms, we learn in 1951 that natural glyceraldehyde is the (R)-stereoisomer:



(+)-glyceraldehyde
(*R*)-2,3-dihydroxypropanal
(corresponds to **G1**)

(-)-erythrose
(2*R*,3*R*)-2,3,4-trihydroxybutanal
(corresponds to **E1**)

(-)-threose
(2*S*,3*R*)-2,3,4-trihydroxybutanal
(corresponds to **E2**)



meso-tartaric acid
erythraric acid
(2*R*,3*S*)-2,3-dihydroxybutanedioic acid

(+)-tartaric acid
(2*S*,3*S*)-2,3-dihydroxybutanedioic acid

(-)-tartaric acid
(2*R*,3*R*)-2,3-dihydroxybutanedioic acid