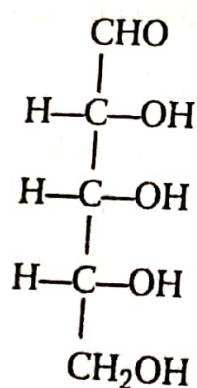


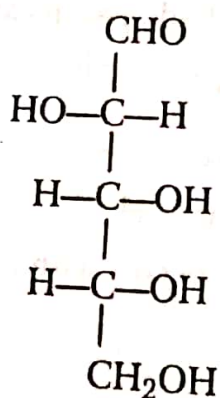
### 5.4.4 Structure Determination of D-Glucose

The above structure has four unlike asymmetric carbon atoms (shown by asterisks). This representation of glucose is incomplete because it does not give us any idea about the spatial arrangement of the —OH and H atoms around these four asymmetric carbon atoms. A specific procedure is applied to find out the configuration around each chiral carbon atom, and it was given by Emil Fischer.

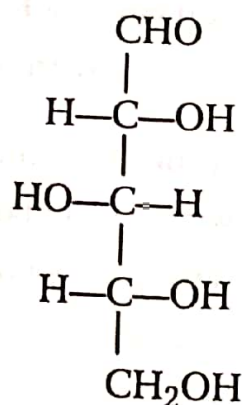
A key compound in this determination is D-arabinose, an alopentose, which must have one of the following structures (I-IV).



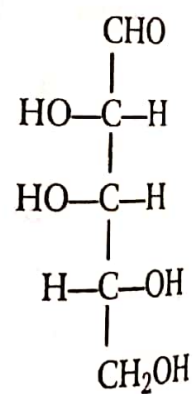
I.



II.

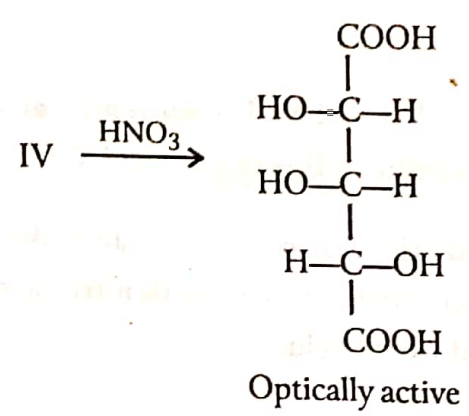
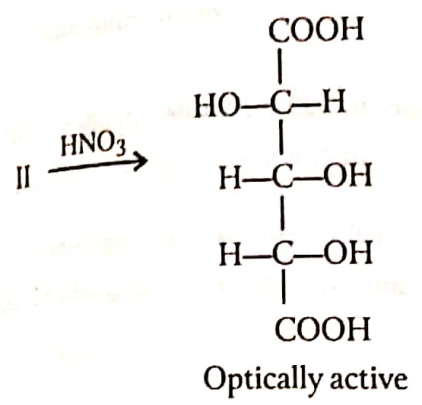
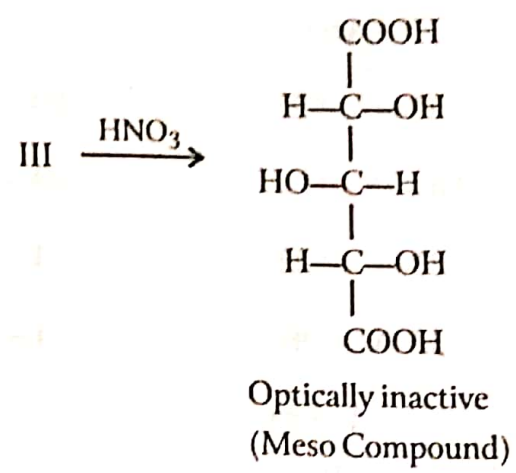
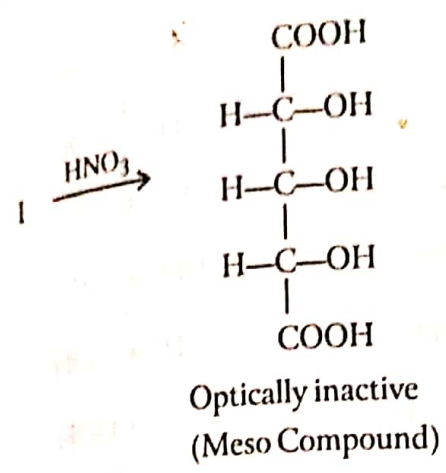


III.

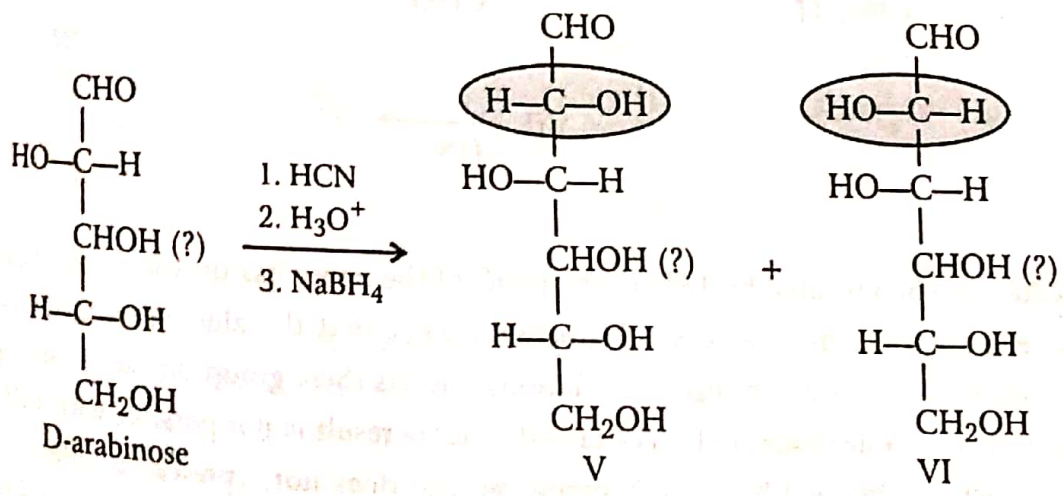


IV.

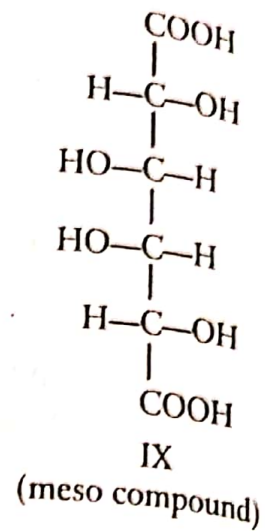
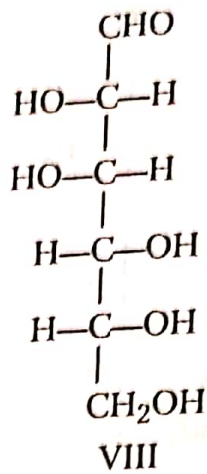
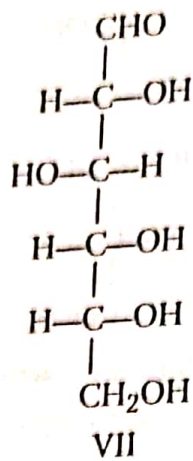
It is known, that oxidation of D-arabinose with nitric acid gives an optically active dicarboxylic acid. Under these condition I and III would have given optically inactive meso di acids. It is important to note that the meso compounds are those which contain two or more asymmetric centres but are optically inactive. These contain an internal plane of symmetry which bisects the molecule into two equal halves such that one half of the molecule forms the mirror image of the other half. Moreover, meso compounds are optically inactive because the optical activity due to one half is compensated by the optical activity of the other half.



D-Arabinose is therefore either II or IV, and can be represented with configuration in doubt at C-3 for the time being. When D-arabinose is subjected to the Kiliani-Fischer synthesis, it gives two sugars, glucose and mannose. These sugars differ only in configuration at C-2, which is the new asymmetric centre created in the chain-extension. Structures V and VI must therefore represent glucose and mannose. The next step is to determine the configuration at C-4 and then decide which is glucose and which is mannose.

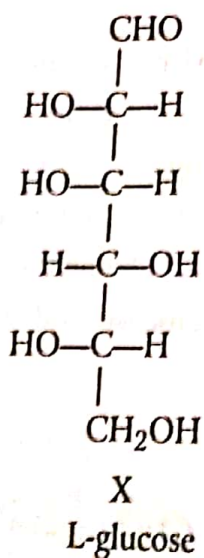


Both glucose and mannose on oxidation with nitric acid give diacids which are optically active. This means that the hydroxyl group at C-4 is on the right, as in VII and VIII. If it would have been on the left, VII would have yielded an optically inactive meso diacid, IX.

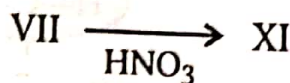
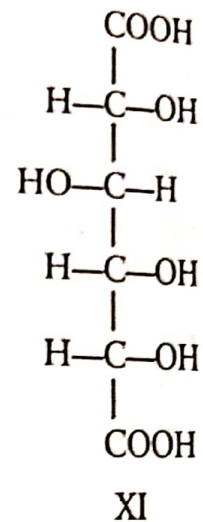
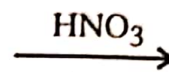
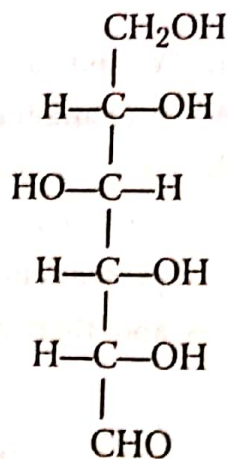


Structure VII and VIII, then represent D-glucose and D-mannose. It only remains to decide whether VII is glucose and VIII is mannose, or the other way around.

To decide this last point, one can make use of another aldohexose, L-glucose, X. This compound when oxidized with nitric acid yields the same dicarboxylic acid (XI) as that obtained from D-glucose.



Rotation  
 $\equiv$   
 by  
 $180^\circ$



L-Glucose when rotated by  $180^\circ$  in the plane of the paper has the same configuration at the asymmetric centres as does D-glucose, except that the aldehyde and the primary alcohol groups are interchanged. Oxidation converts these groups to the carboxyl groups and thus the same diacid (XI) is obtained. Such a result is not possible with VIII, since the structure obtained by interchanging the end does not represent a different sugar. Hence D-glucose is represented by structure VII, and D-mannose by structure VIII. It follows from the above discussion that the structure of D-glucose is

