Chapter 20 Carbohydrates

Based on
McGraw Hill's *Organic Chemistry*, 5th edition,
Chapter 25

20.1 Photosynthesis and Metabolism

- Carbohydrates are synthesized in green plants by photosynthesis.

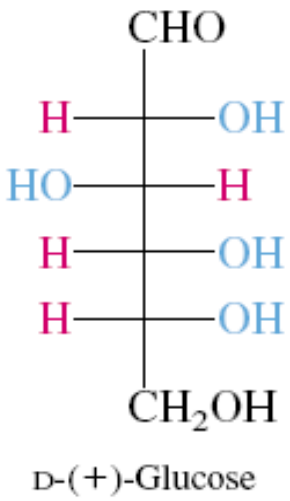
$$xCO_2 + xH_2O \xrightarrow[\text{chlorophyll}]{\text{solar energy}} C_x(H_2O)_y + xO_2$$

- Their energy is released when animals or plants metabolize carbohydrates to carbon dioxide and water.

$$C_x(H_2O)_y + xO_2 \xrightarrow{\text{enzyme}} xCO_2 + xH_2O + \text{energy}$$

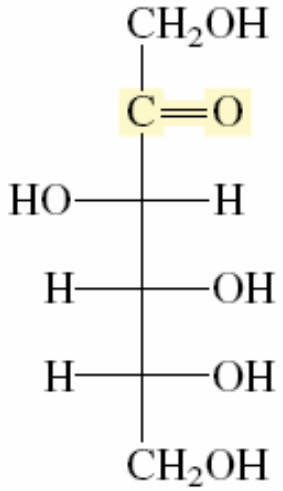
20.2 Carbohydrats

- Carbohydrates are usually defined as ***polyhydroxy aldehydes*** and ***ketones***, or substances that hydrolyze to yield polyhydroxy aldehydes and ketones.



D-(+)-Glucose

polyhydroxy aldehydes



D-Fructose

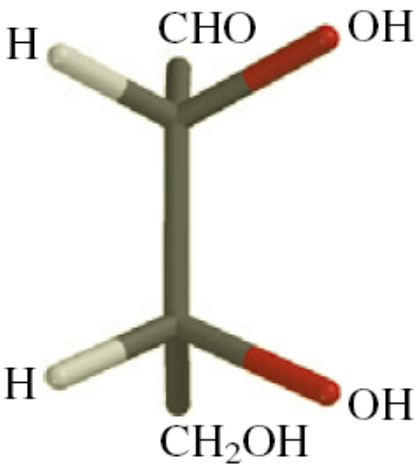
polyhydroxy ketones

20.3 Classification of Carbohydrates

- ***A monosaccharide*** is the simplest carbohydrate that cannot be hydrolyzed into the simpler carbohydrate.
- ***An oligosaccharide*** (*oligos* is a Greek word that in its plural form means “few”) yields 3–10 monosaccharide units on hydrolysis.
- ***Polysaccharides*** are hydrolyzed to more than 10 monosaccharide units.

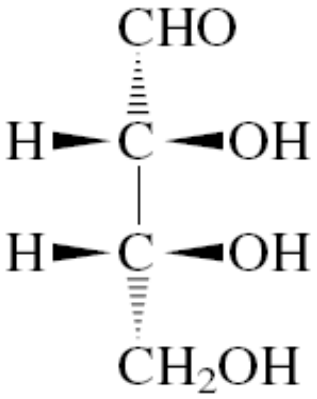
20.4 Fischer Projections

- Fischer determined the structure of glucose in 1900 and won the Nobel Prize in chemistry in 1902.

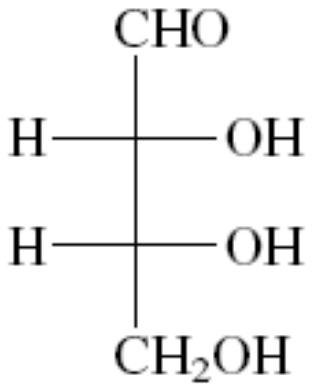


Eclipsed conformation of a tetrose

is equivalent to



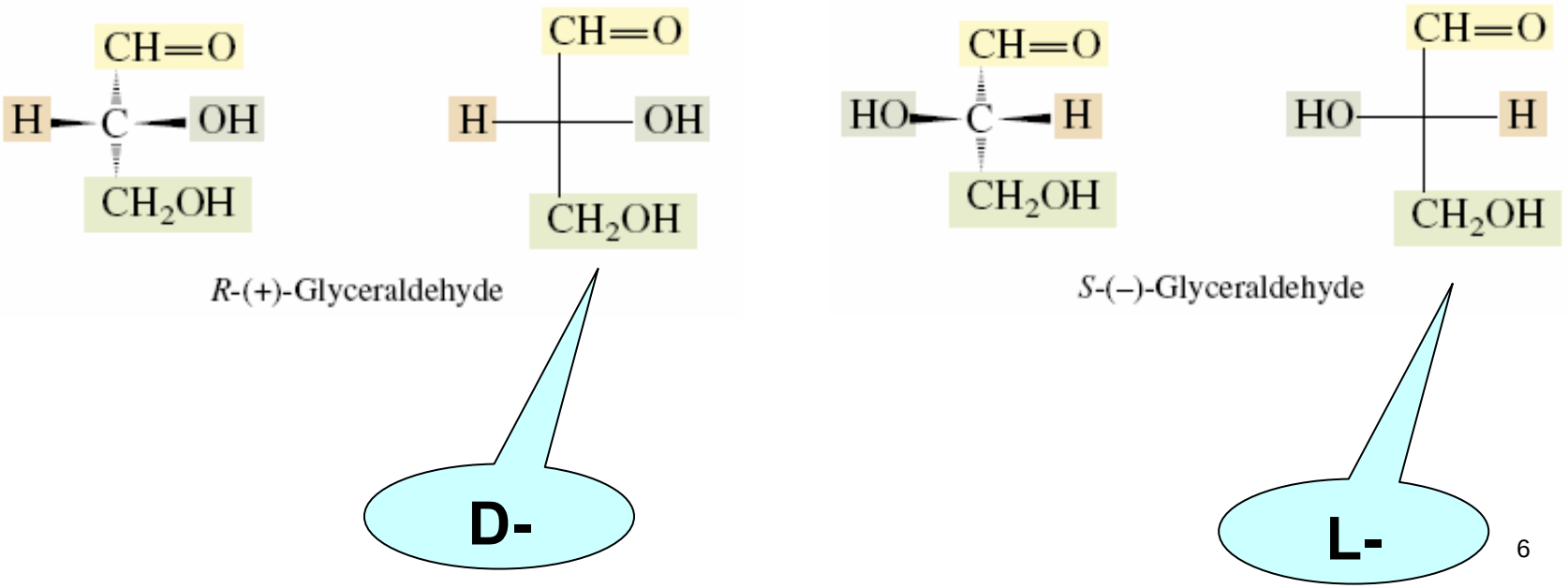
which is written as



Fischer projection of a tetrose

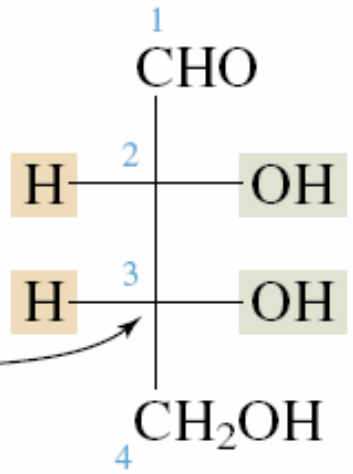
20.5 D-L Notation

- The enantiomers of *glyceraldehyde* (2,3-dihydroxypropanal) are used as fundamental molecules in carbohydrate stereochemistry.
- The absolute configuration of (+)-glyceraldehyde was said to be **D** and that of its enantiomer, (-)-glyceraldehyde, **L**.

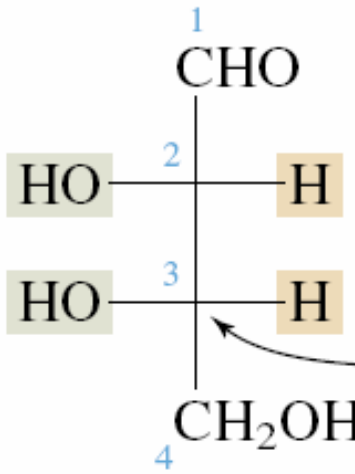


D-L Notation

Highest numbered stereogenic center has configuration analogous to that of D-glyceraldehyde

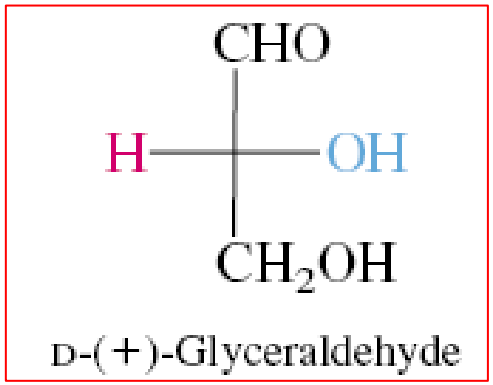


D-Erythrose

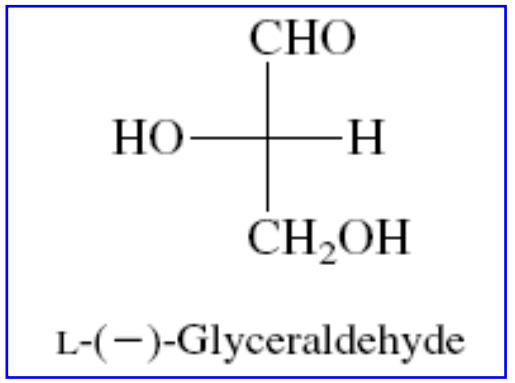


L-Erythrose

Highest numbered stereogenic center has configuration analogous to that of L-glyceraldehyde



D-(+)-Glyceraldehyde

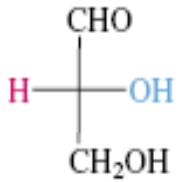


L-(−)-Glyceraldehyde

结论：

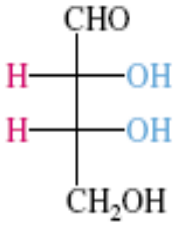
从D（+）甘油醛衍生来的单糖，都属于D型，

从L（-）甘油醛衍生来的单糖，都属于L型。

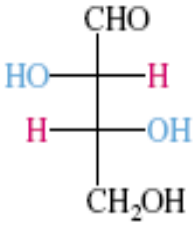


D-(+)-Glyceraldehyde

自然界中的葡萄糖、果糖均为D型

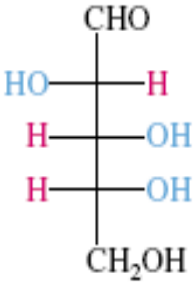


D-(−)-Erythrose

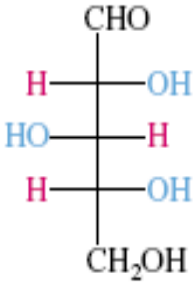


D-(−)-Threose

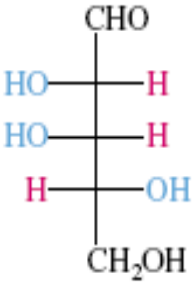
D-(−)-Ribose



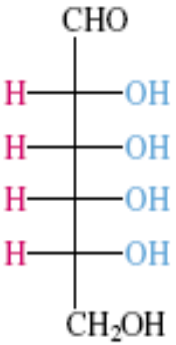
D-(−)-Arabinose



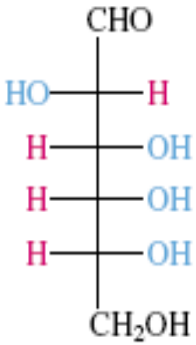
D-(+)-Xylose



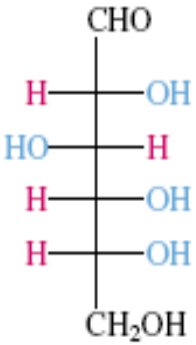
D-(−)-Lyxose



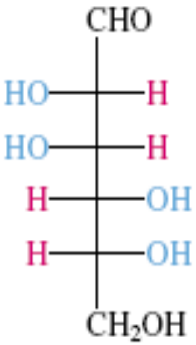
D-(+)-Allose



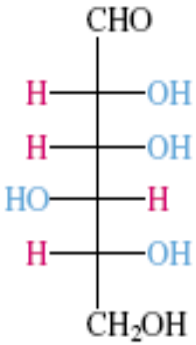
D-(+)-Altrose



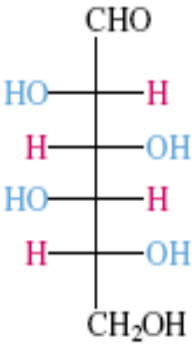
D-(+)-Glucose



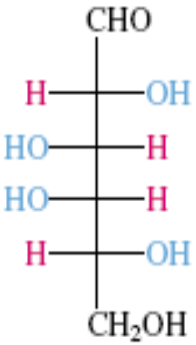
D-(+)-Mannose



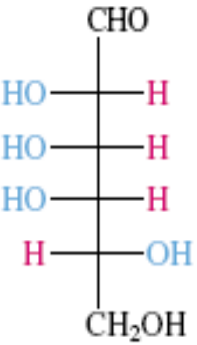
D-(−)-Gulose



D-(−)-Idose



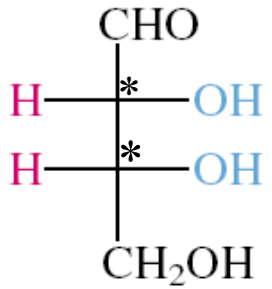
D-(+)-Galactose



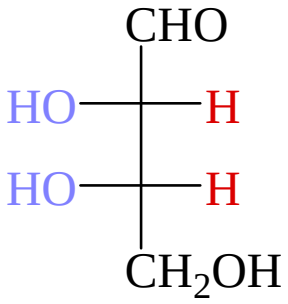
D-(+)-Talose

20.6 D-L Notation: Enantiomer

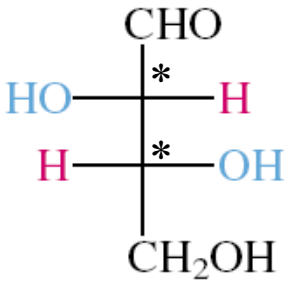
- D- and L-notation are enantiomers of each other.
- For example, aldotetrosesL-(+)-Threose have two stereogenic centers, so four stereoisomers are possible.



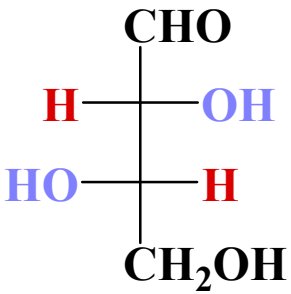
D-(−)-Erythrose



L-(+)-Erythrose

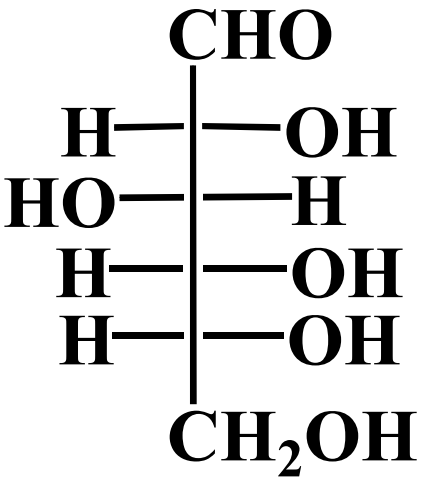


D-(−)-Threose



L-(+)-Threose

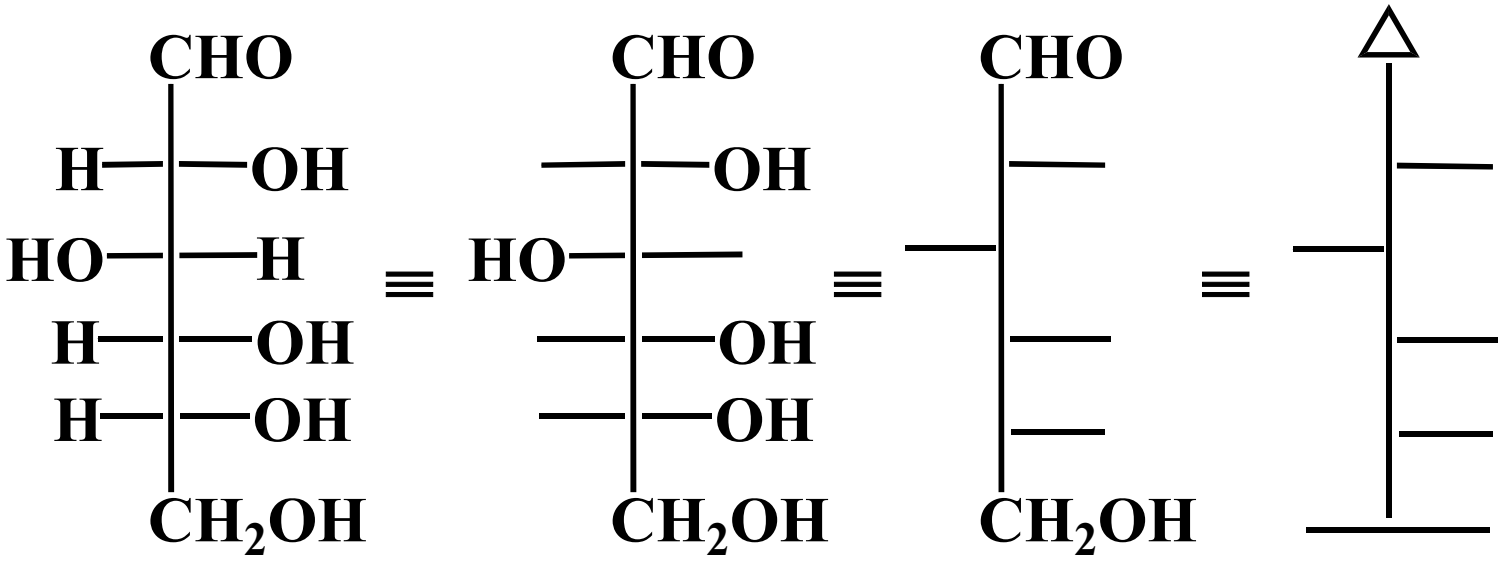
20.7 D-L Notation / R-S Notation



D–(+)– 葡萄糖

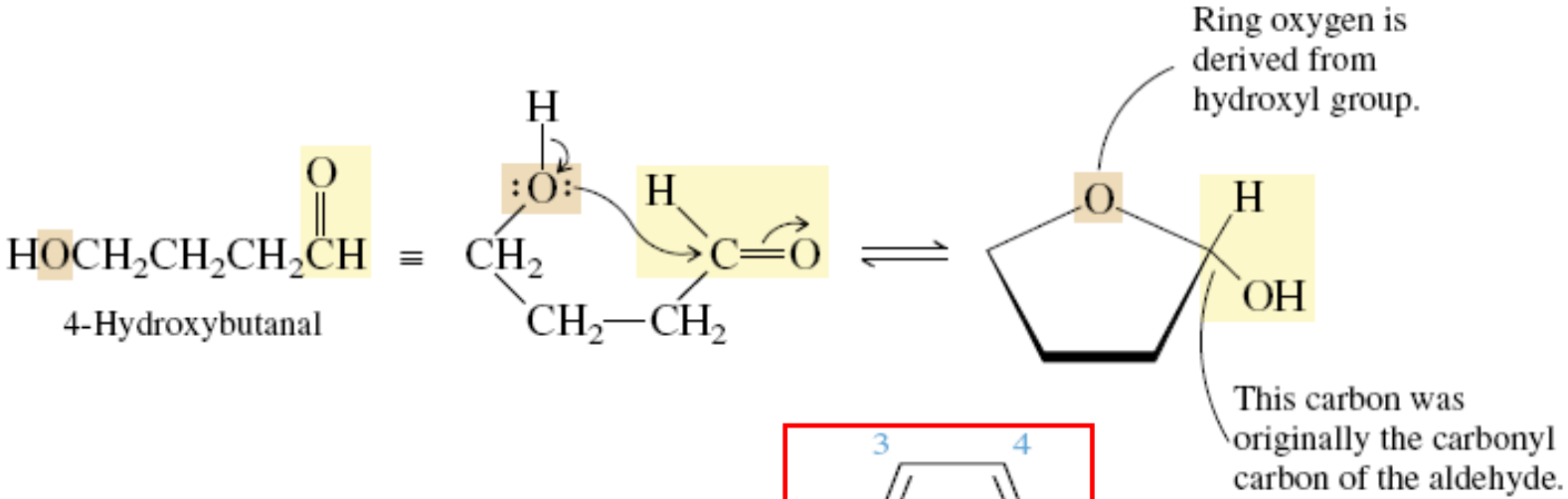
（2R，3S，4R，5R–2，3，4，5，6–五羟基己醛）

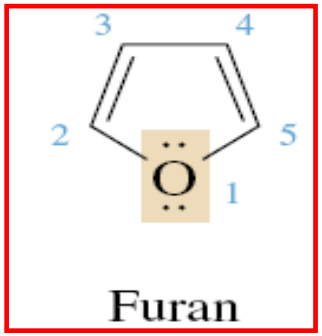
20.8 Write the Fischer Projection



20.9 A Cyclic Hemiacetal

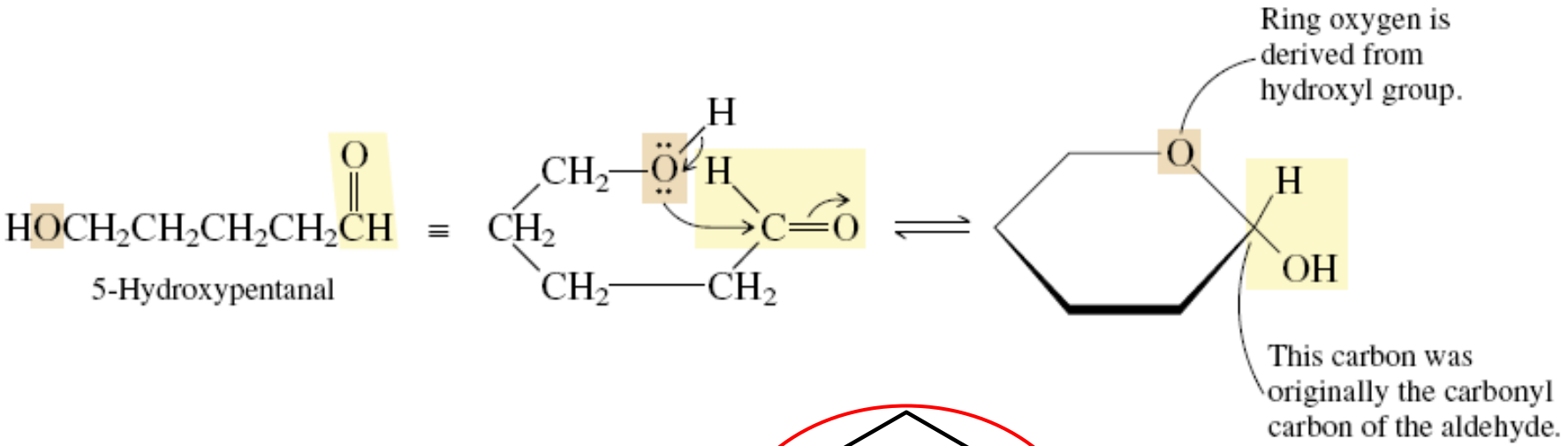
- nucleophilic addition of an alcohol function to a carbonyl group gives a hemiacetal.
- Five-membered cyclic hemiacetals of carbohydrates are called **furanose** forms

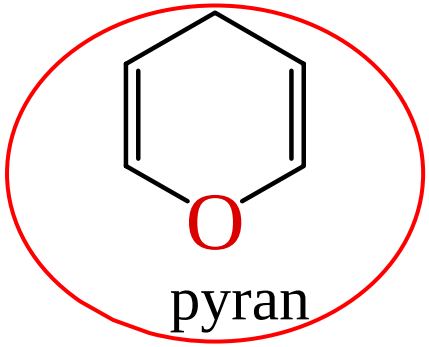




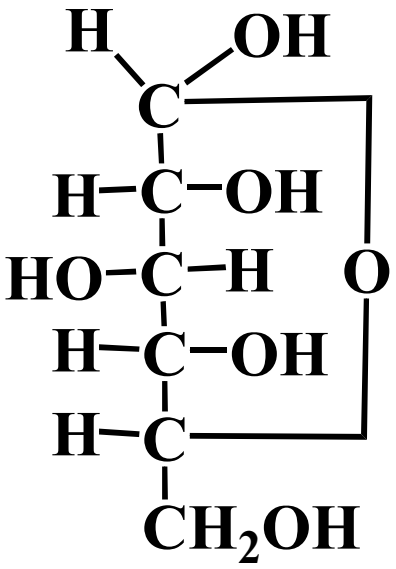
A Cyclic Hemiacetal

- Six-membered cyclic hemiacetals of carbohydrates are called **pyranose** forms

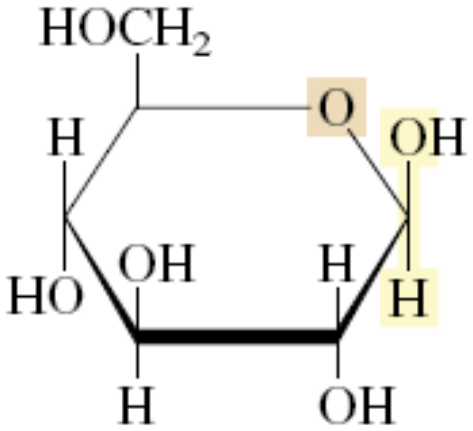




20.10 Cyclic form of D-Glucose



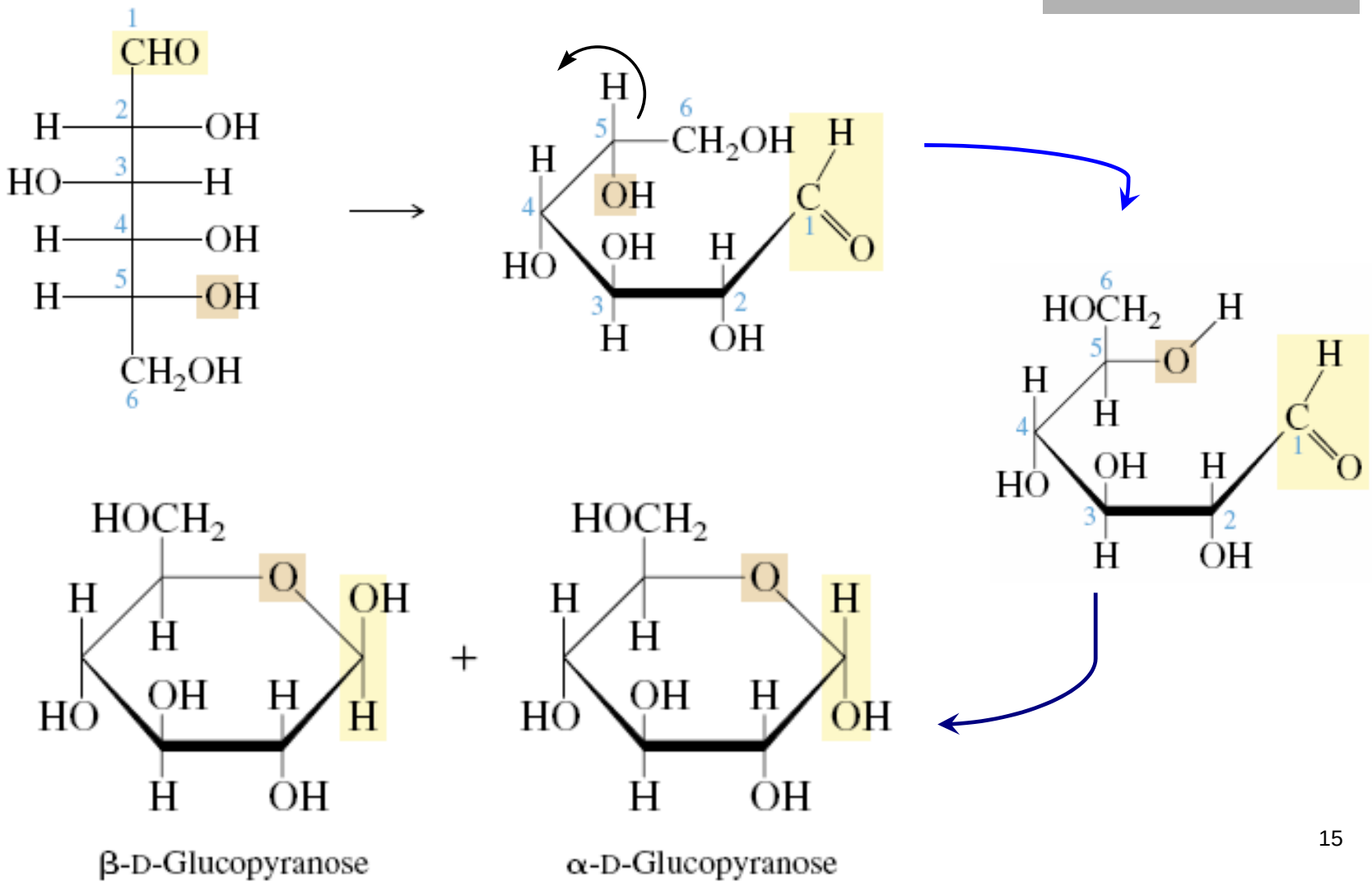
直立环状投影式



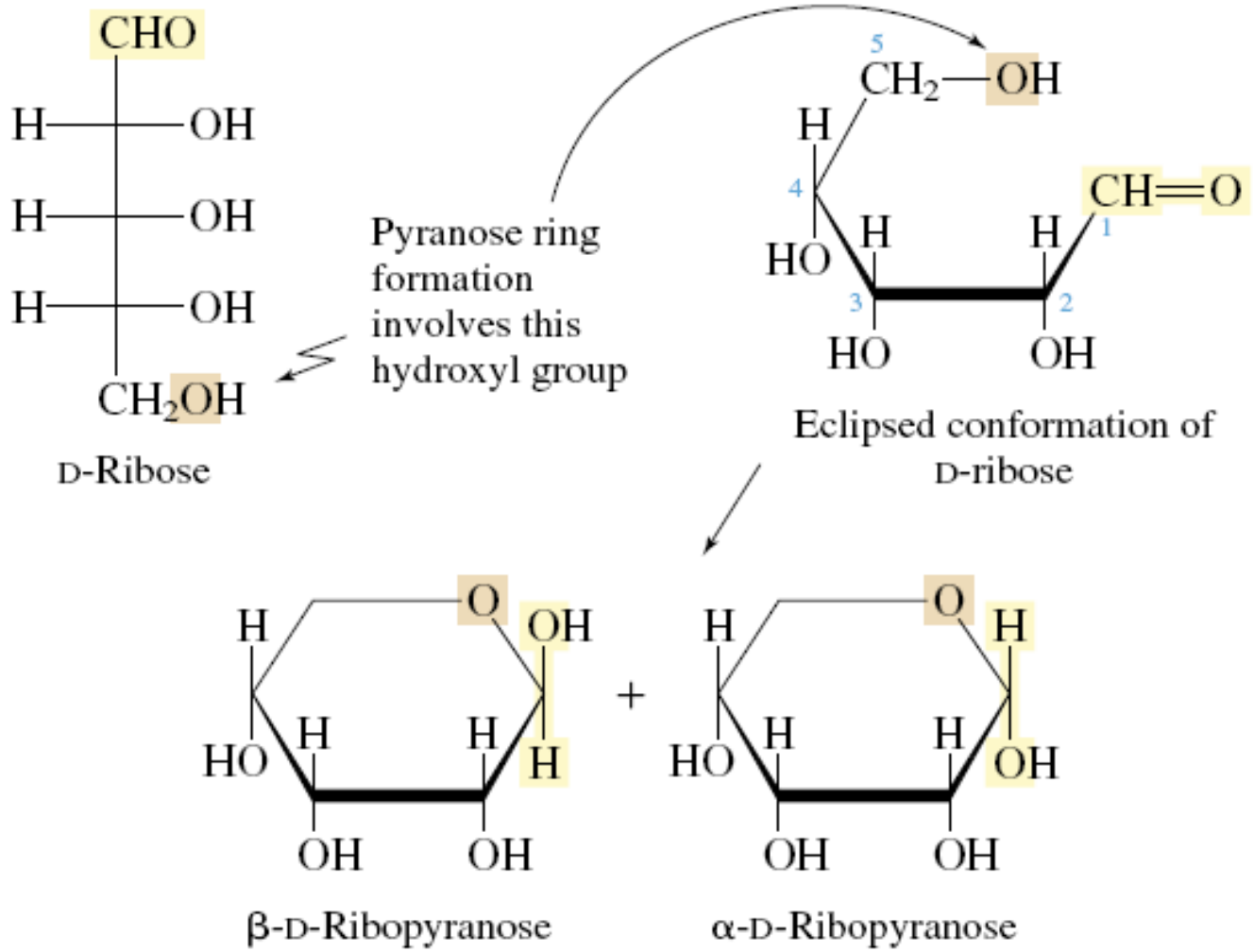
Haworth formulas

(透视式或哈武斯式)

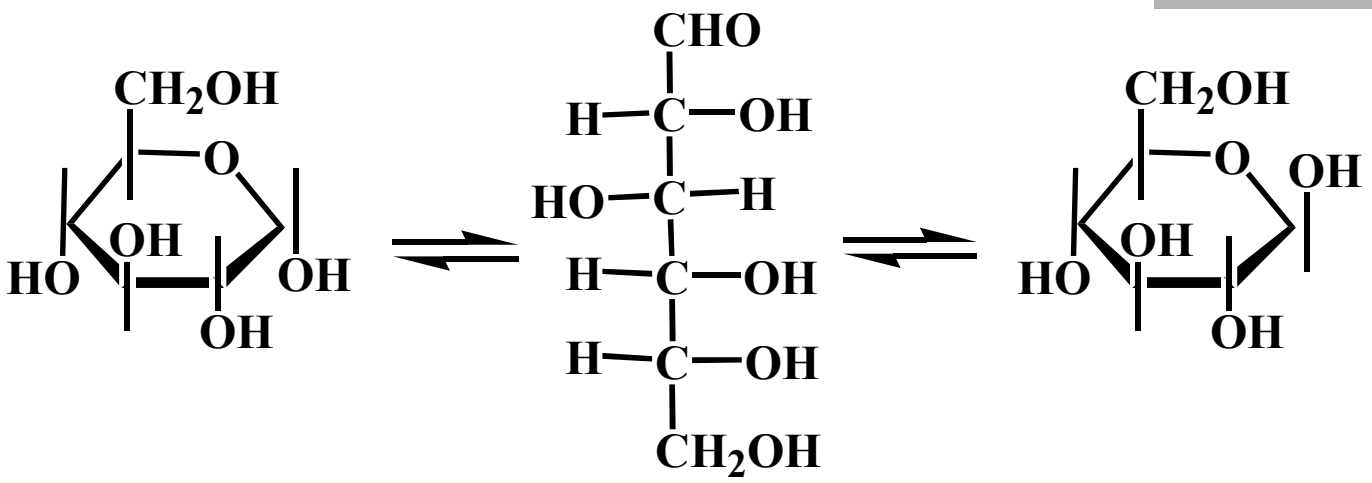
20.11 Write Haworth Formulas: D-Glucose



Write Haworth Formulas: D-Ribose



α- and β-Notation



α-D-葡萄糖 ~37%　　D-(+)-葡萄糖 ~0.1%　　β-D-葡萄糖 ~63%

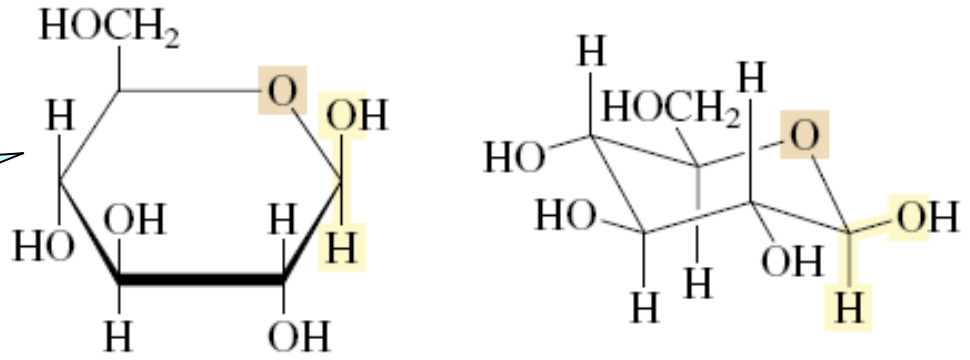
半缩醛碳上的羟基（C1上的羟基）和决定构型的羟基（C5上的羟基）在碳链的同侧，称为α型；

半缩醛碳上的羟基和决定构型的羟基在碳链的异侧的如（V），称为β型。α型和β型是非对映异构体。

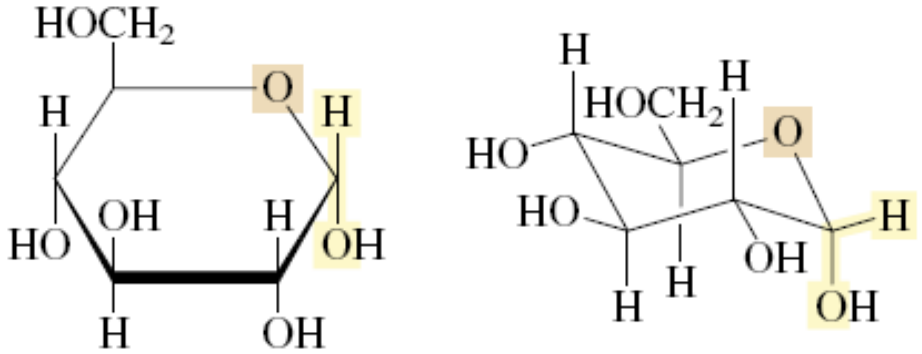
A Chair Conformation

- X-ray crystallographic studies of a large number of carbohydrates reveal that the six-membered pyranose ring of D-glucose adopts a chair conformation

More stable (63%)



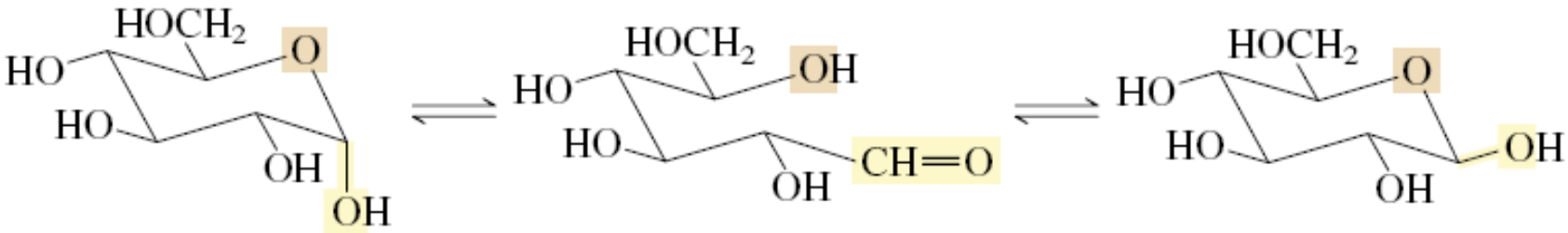
β-D-Glucopyranose



α-D-Glucopyranose

20.12 Mutarotation

- On standing, the rotation of the solution containing the isomer decreases from 112.2° to 52.5°; the rotation of the solution of the isomer increases from 18.7° to the same value of 52.5°. This phenomenon is called **mutarotation.**

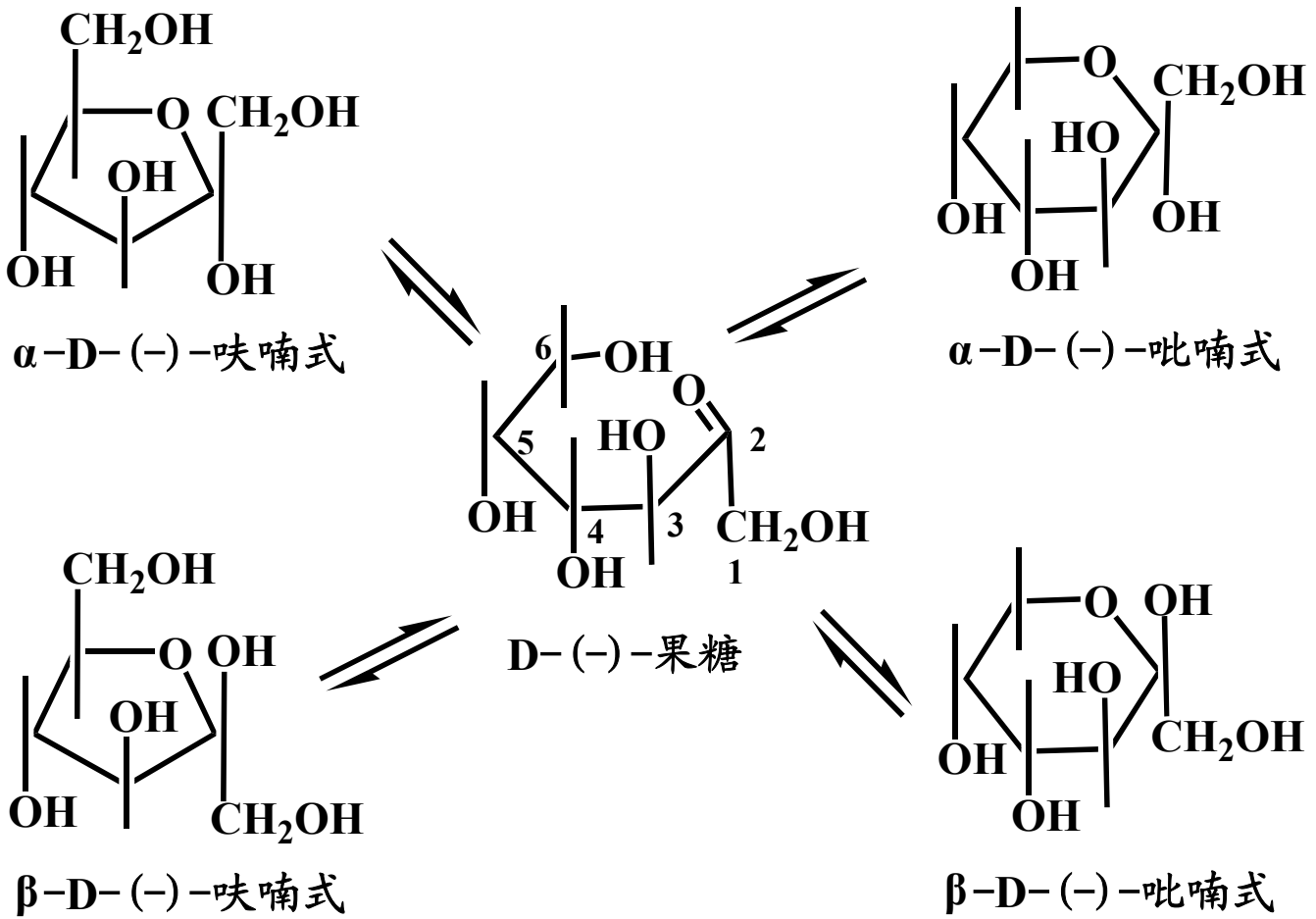


α-D-Glucopyranose (mp 146°C; $[\alpha]_D$ +112.2°)

Open-chain form of D-glucose

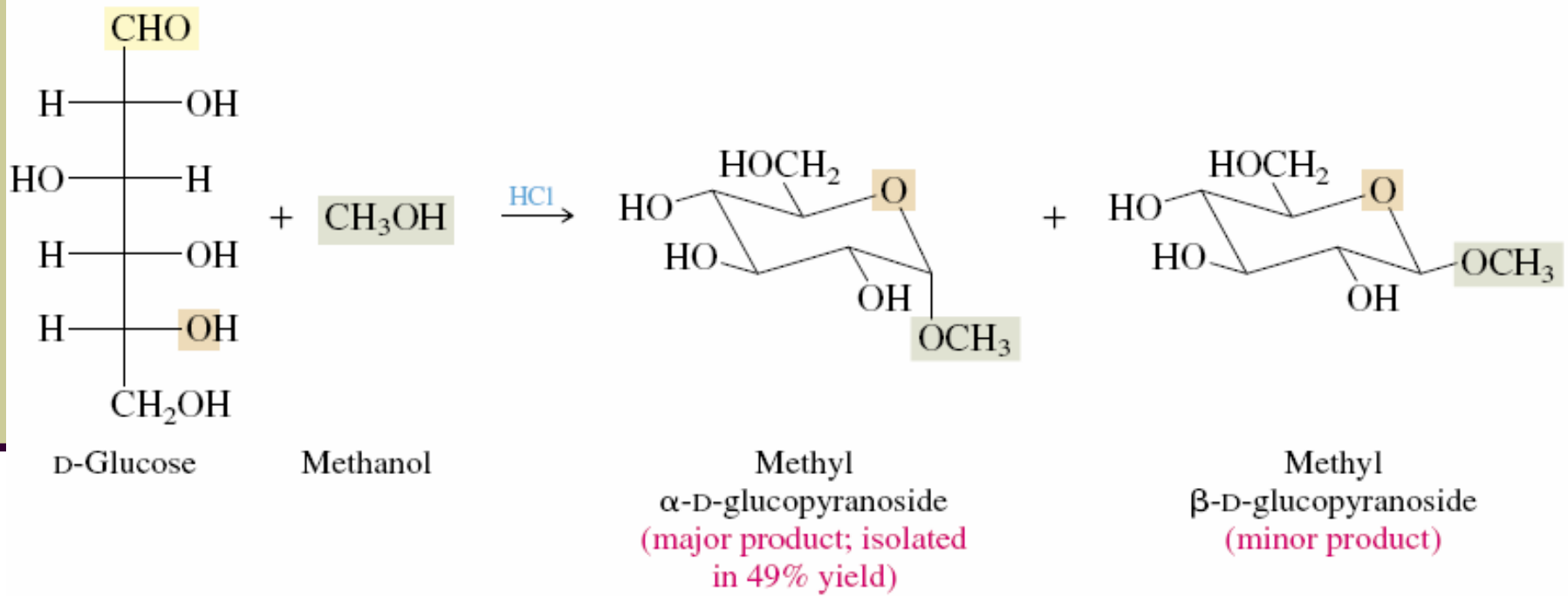
β-D-Glucopyranose (mp 148–155°C; $[\alpha]_D$ +18.7°)

20.13 Write Haworth Formulas: D-Fructose



20.14 Glycosides (苷)

- **Glycosides** are characterized by the replacement of the anomeric hydroxyl group by some other substituent.

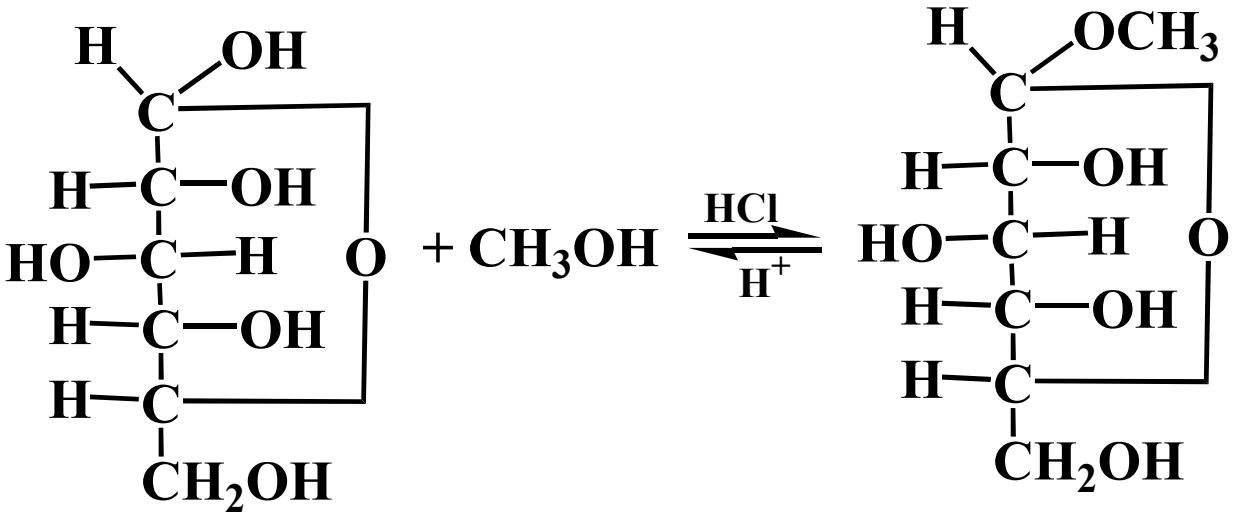


D-Glucose | Methanol | Methyl α-D-glucopyranoside (major product; isolated in 49% yield) | Methyl β-D-glucopyranoside (minor product)

Glycosides (苷)

配糖物（简称为苷）：凡糖的半缩醛式羟基（简称为苷羟基）

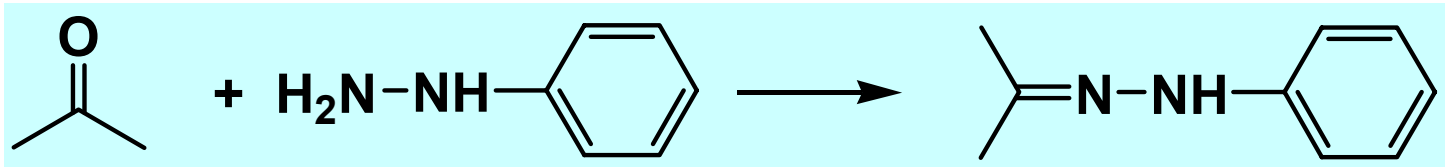
与另一个羟基化合物失水而生成的缩醛。

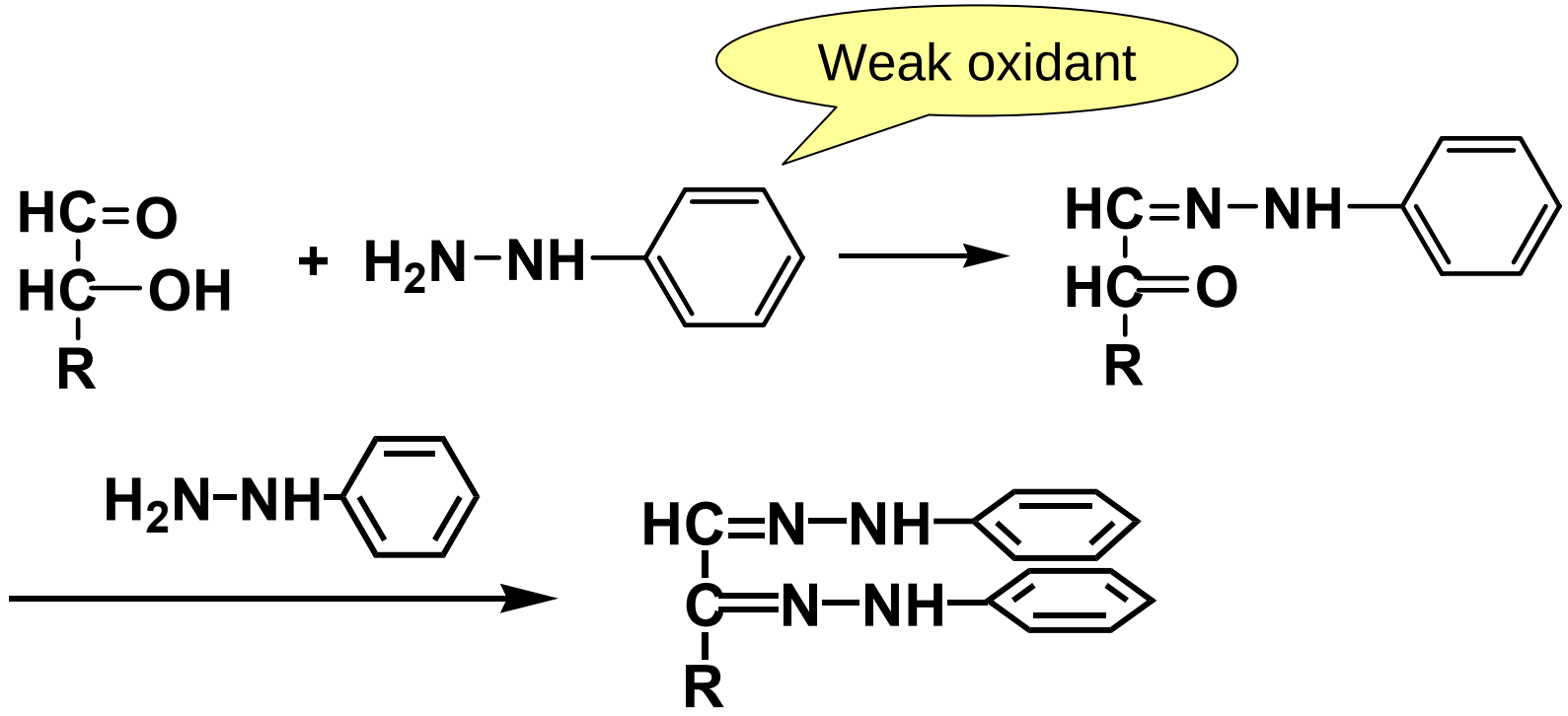


葡萄糖甲苷

苷分解后生成糖和非糖部分（羟基化合物），后者叫做配基或配质，糖的部分叫做糖苷基，全名为某糖某苷。

20.15 Reactions of Monosaccharides: Osazones (脎)

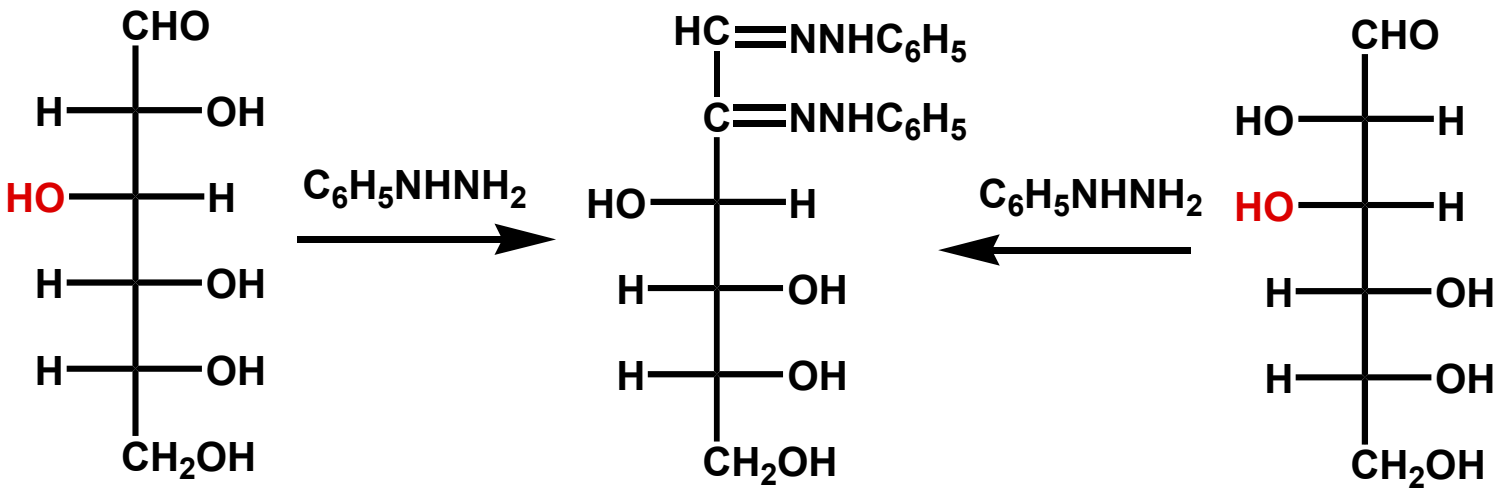




Osazones (脎)

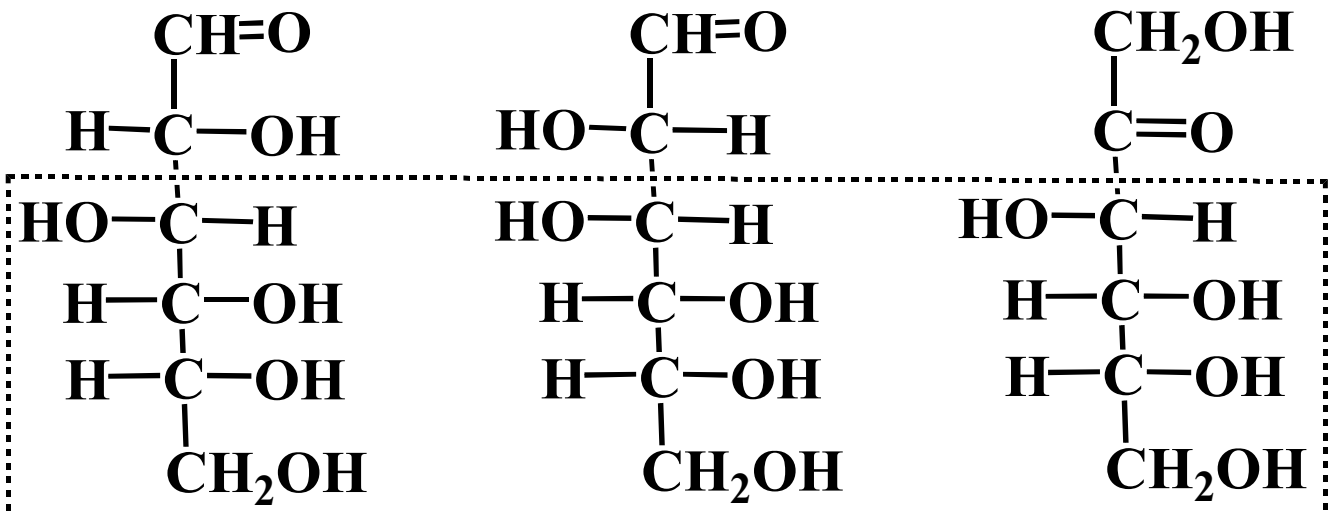
Epimers（差向异构体）

- In general , any pair of diastereomers that differ in configuration at only a sigle tetrahedral stereogenic carbon can be called epimers.



在第二碳上构型不同而其他碳原子构型相同的差向异构体（或叫表里异构体），必然生成同一个脎。

Application of Osazones



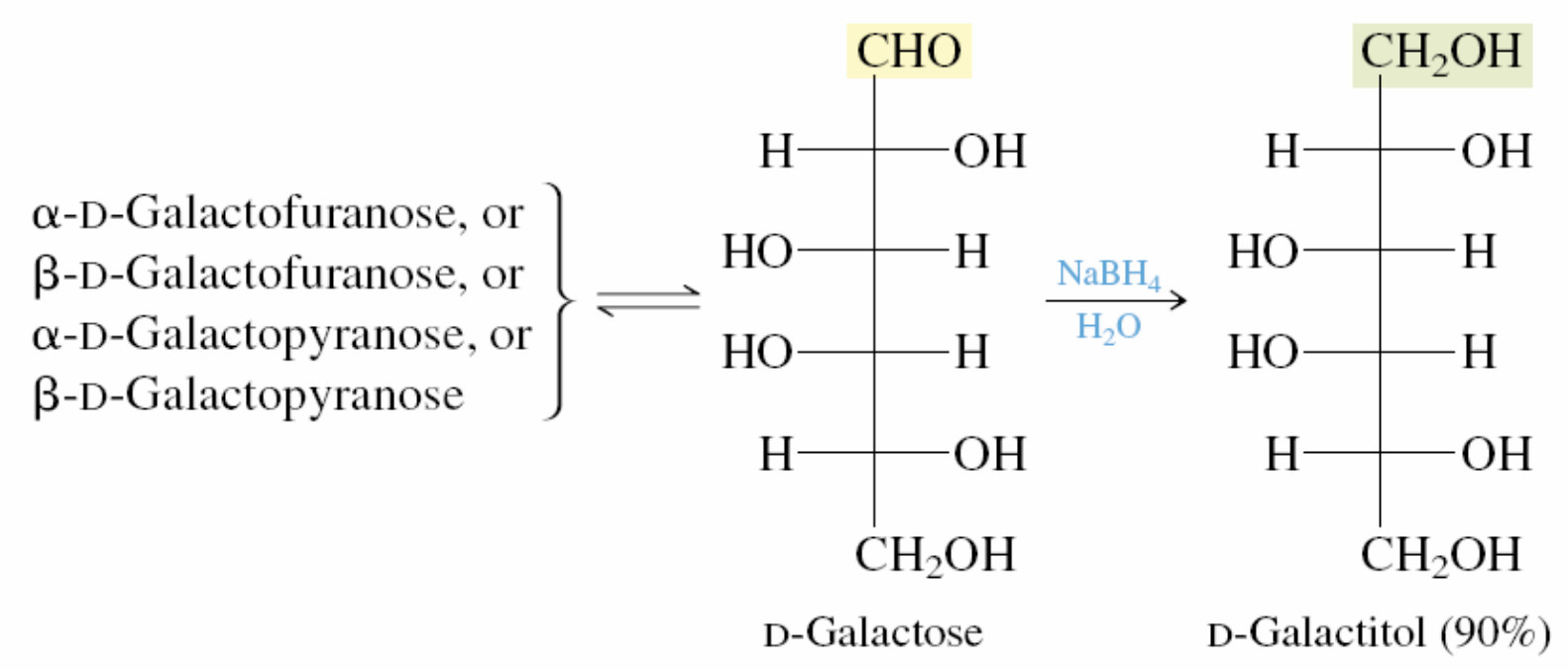
D-(+)- 葡萄糖　D-(+)- 甘露糖　D-(-)- 果糖

应用:

（i）根据糖脎的晶体及生成时间来鉴定糖;

（ii）推测糖的构型

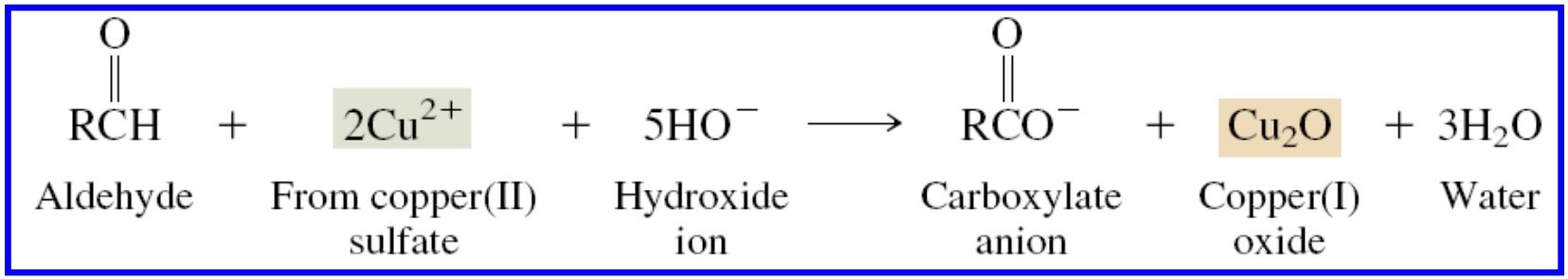
20.16 Reactions of Monosaccharides: Reduction

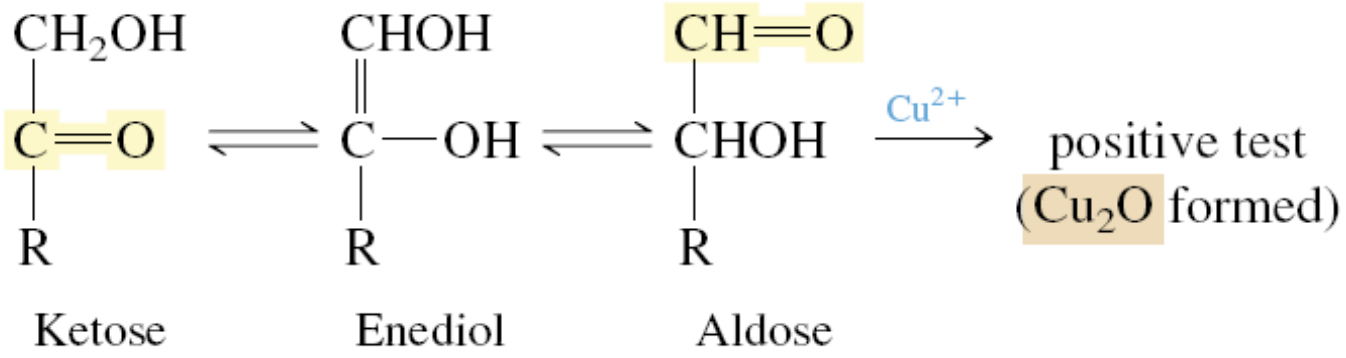


应用：根据其有无旋光性，可以推测糖的构型。

20.17 Reactions of Monosaccharides: Oxidation

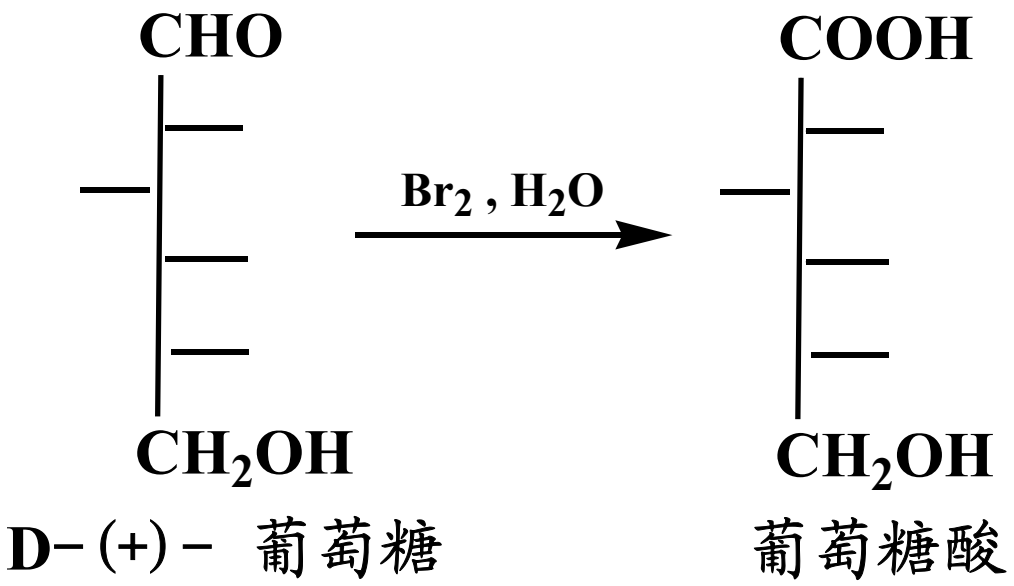
- Carbohydrates that give positive tests with *Benedict's reagent* are termed **reducing sugars**.





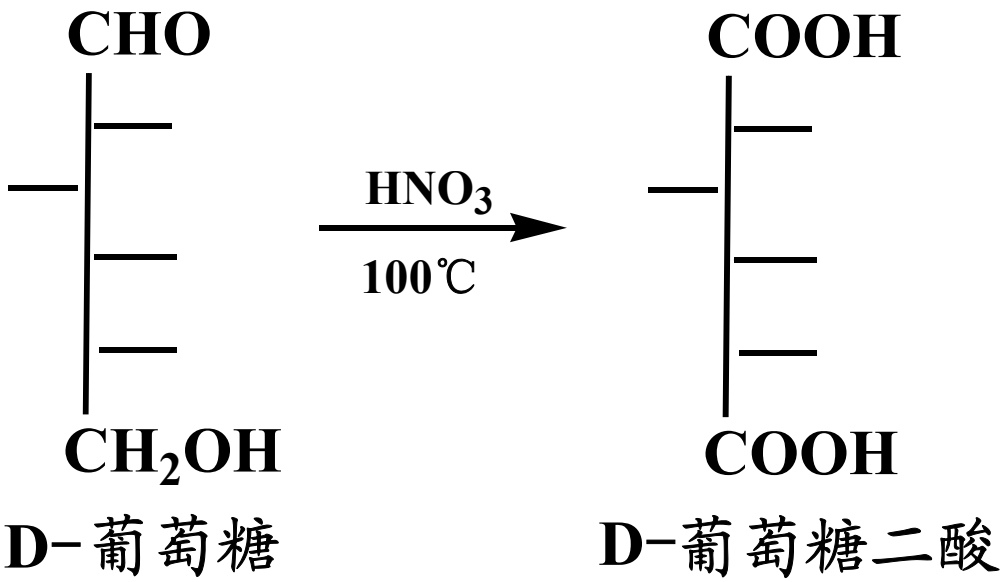
适用范围：醛糖、α-羟基酮

Oxidation of Monosaccharides



应用： 区别醛糖和酮糖。

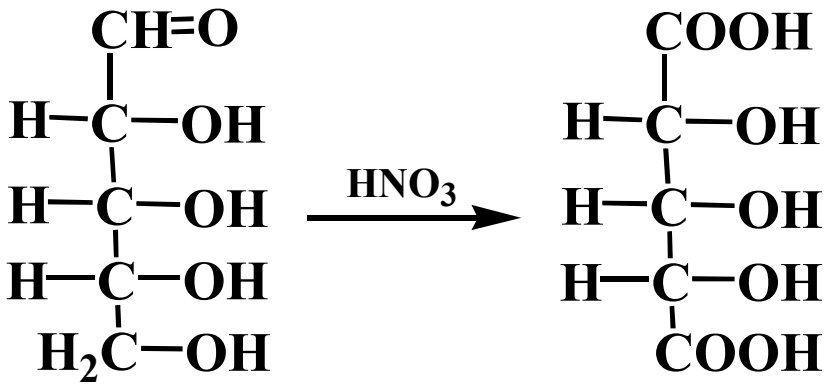
Oxidation of Monosaccharides



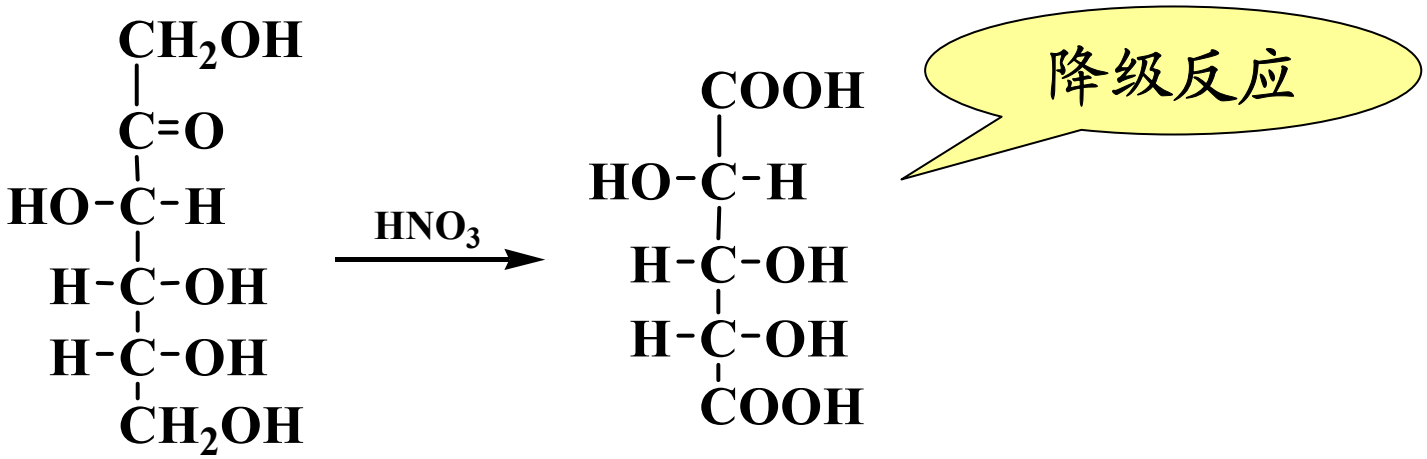
D-葡萄糖　　D-葡萄糖二酸

应用：根据产物的旋光性可以推测糖的构型

Oxidation of Monosaccharides

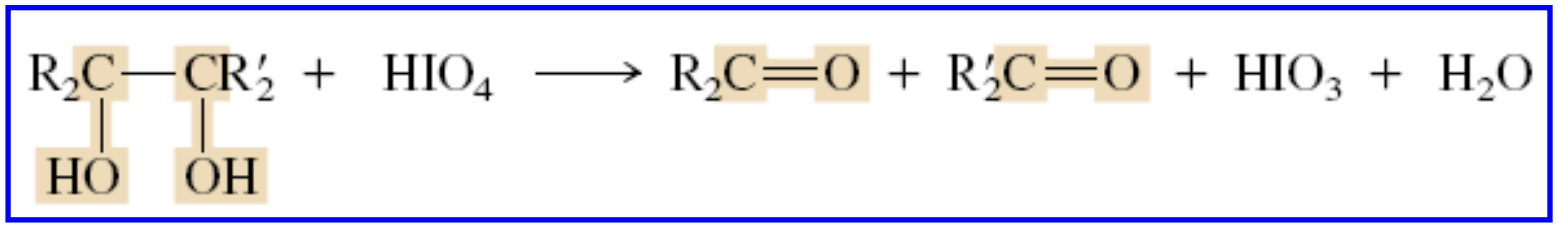


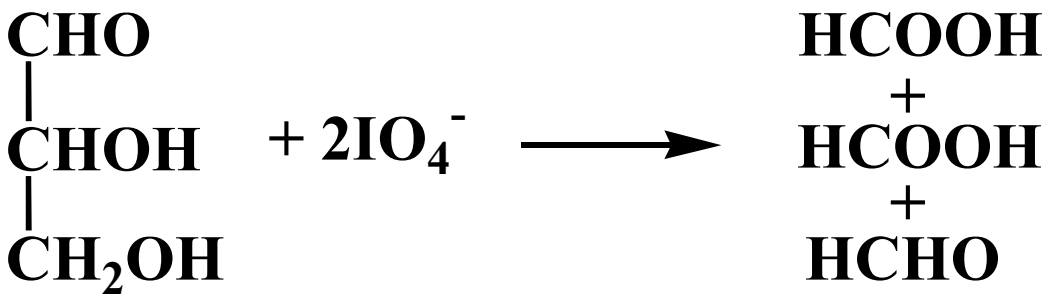
D-核糖　　核糖二酸（无旋光性）



D-果糖　　D-树胶糖二酸(有旋光性）

Oxidation of Monosaccharides

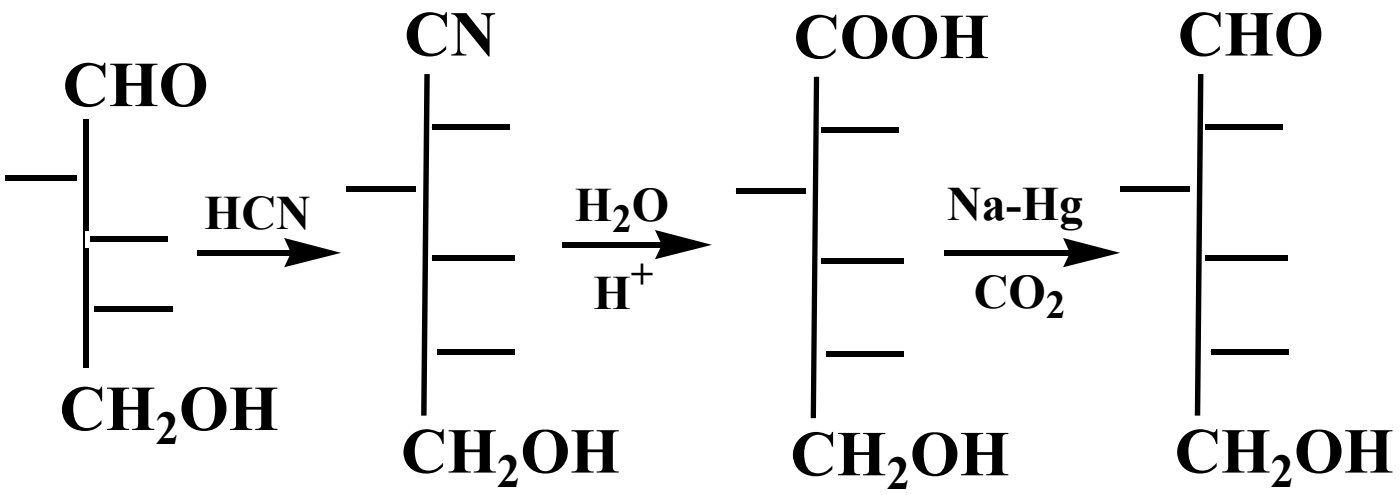




应用：反应常定量进行，是研究糖类结构最有用的手段之一。

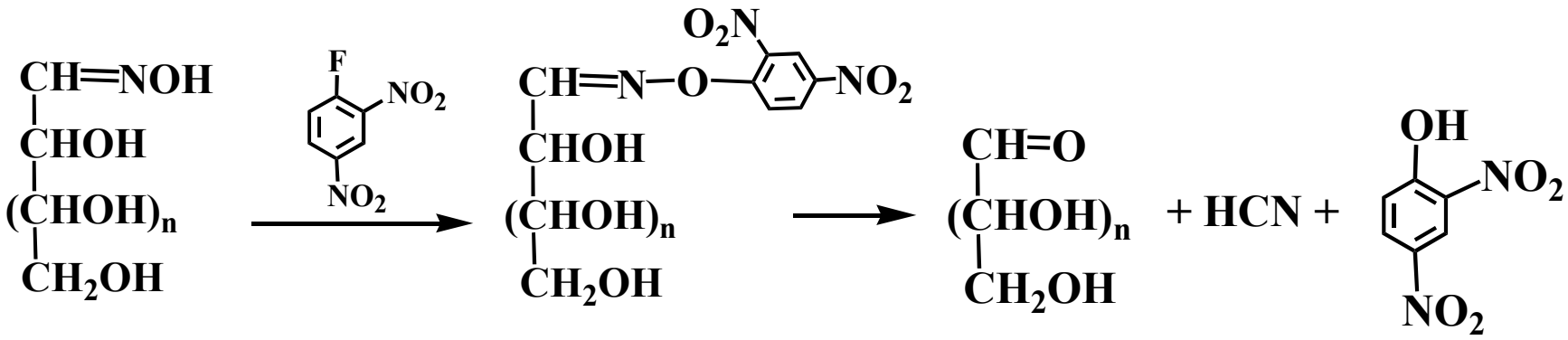
20.18 Cyanohydrin Formation

Chain exension
(递升)



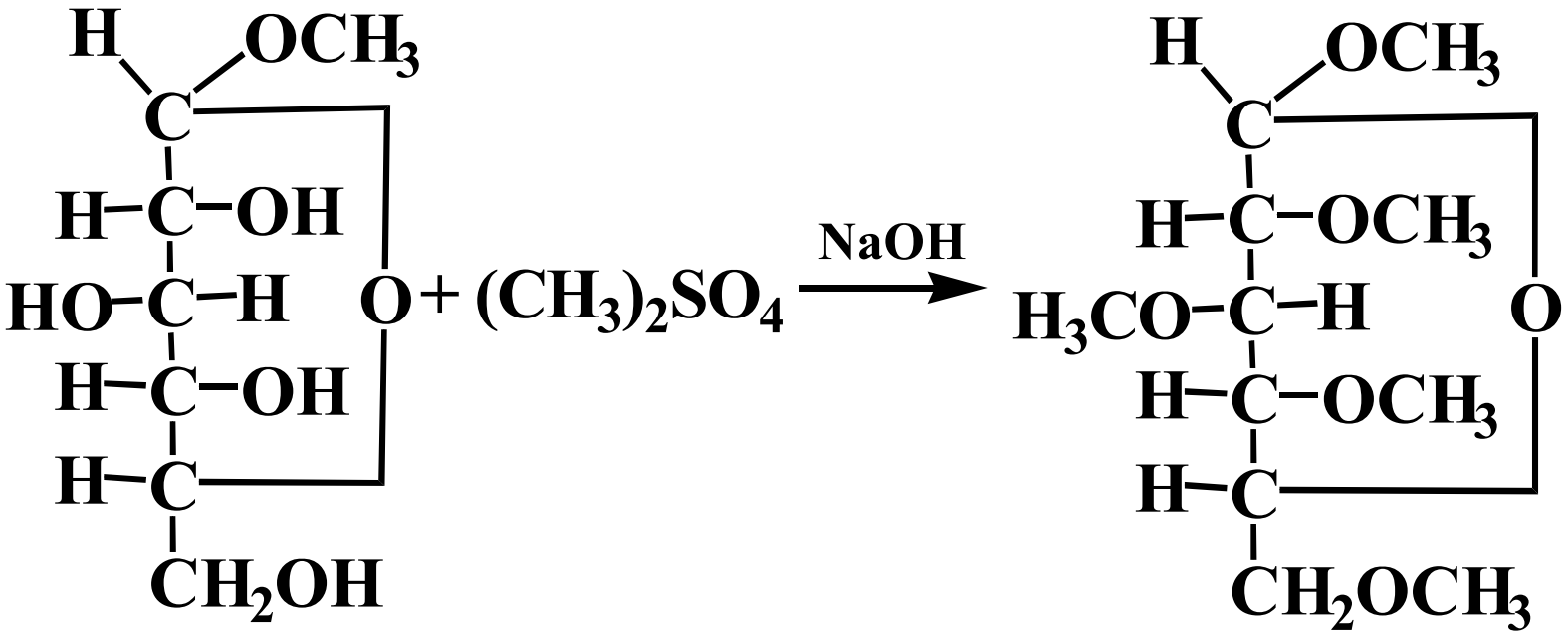
递升：从单糖经与HCN加成而增加一个碳原子后，再水解，还原生成增加一个碳的单糖。

Cyanohydrin Formation



递降：从己糖可减去一个碳原子而成戊糖，或戊糖降一级而成丁糖。其中，生成腈的方法称为沃尔递降法（Wohl Degradation）。

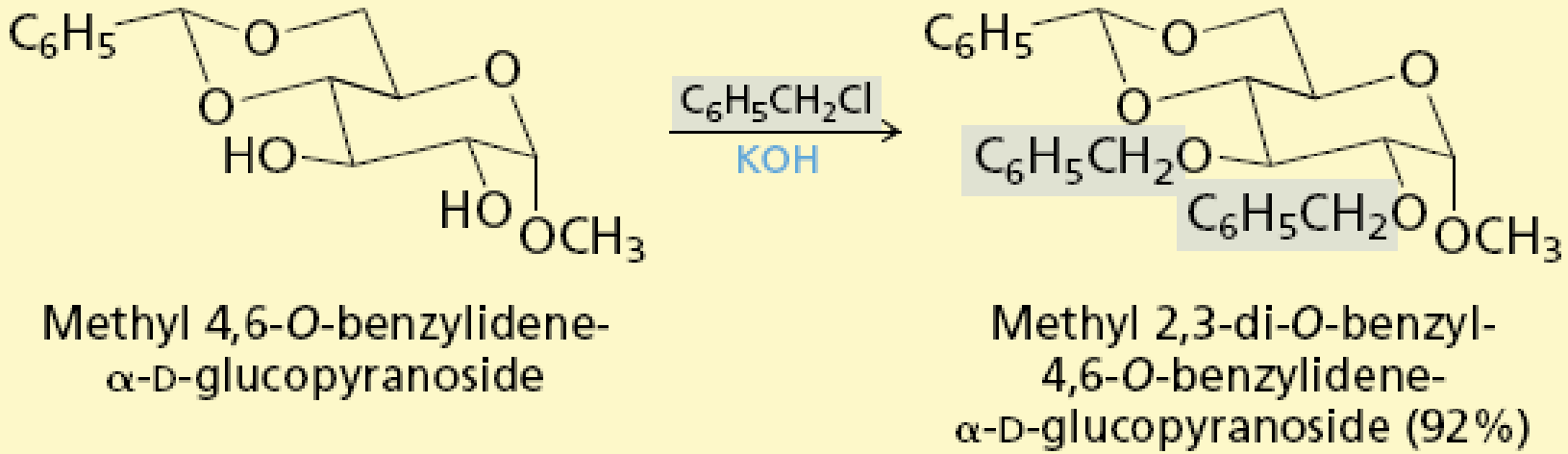
20.19 Reactions of Monosaccharides: Alkylation



葡萄糖甲苷

O–五甲基葡萄糖

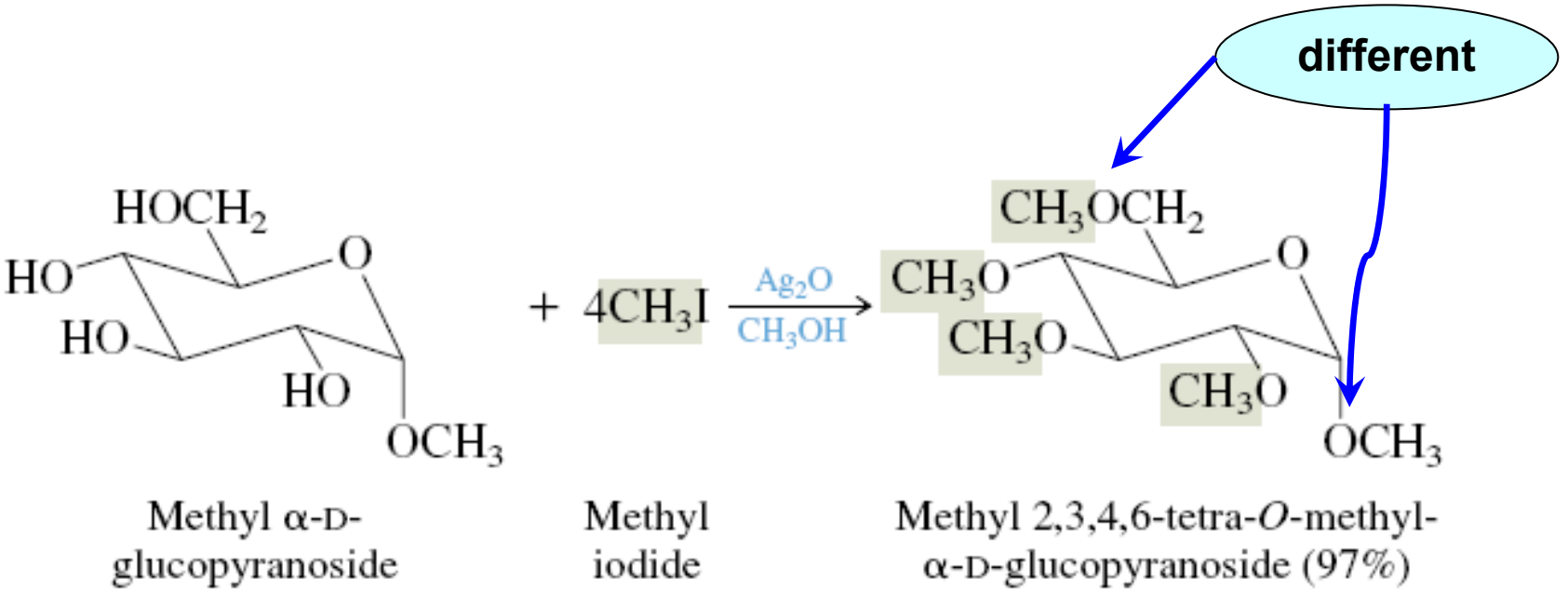
Alkylation of Monosaccharides



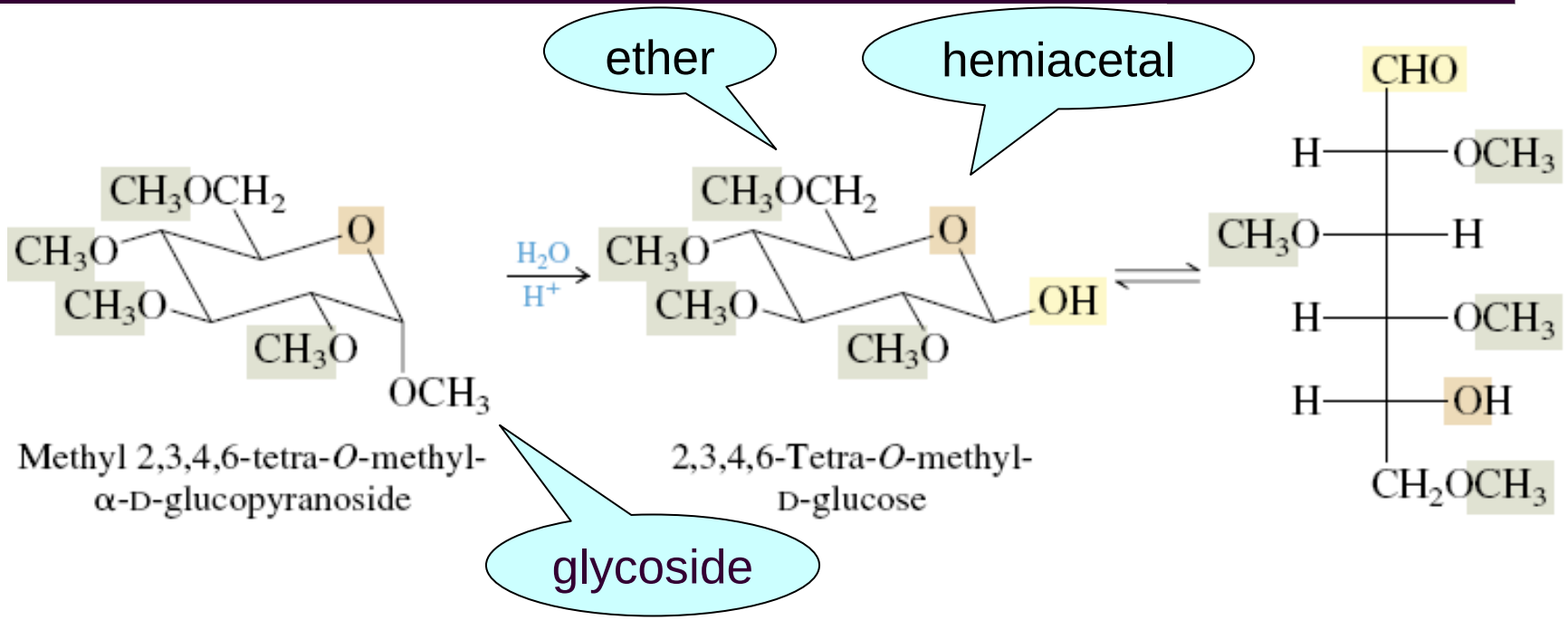
Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside

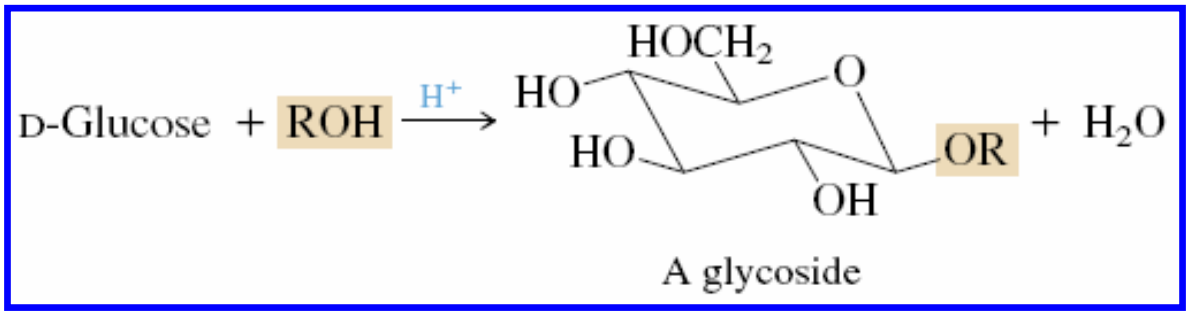
Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (92%)

Alkylation of Monosaccharides

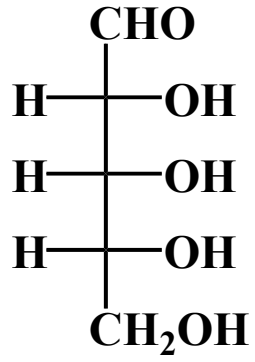


20.20 Difference of C-O bond in Monosaccharide

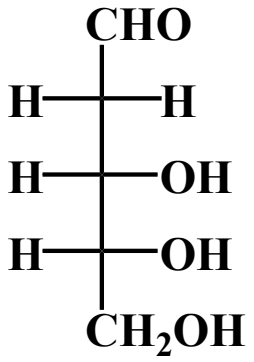




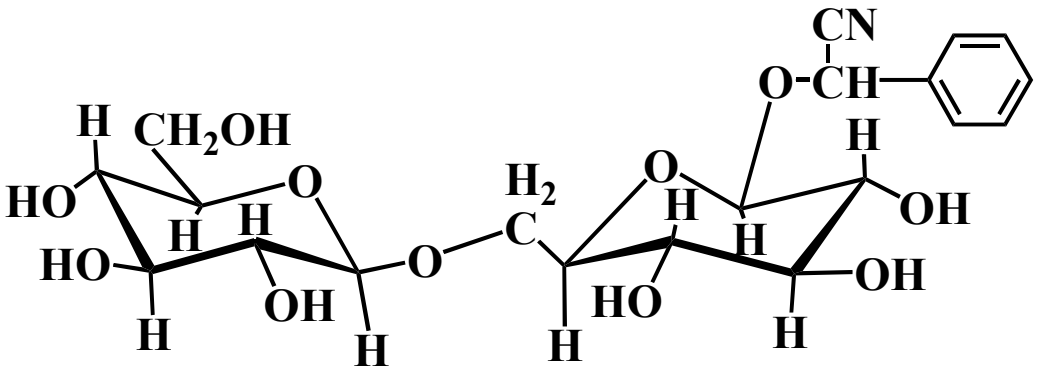
20.21 Some Monosaccharides



D–(–)–核糖



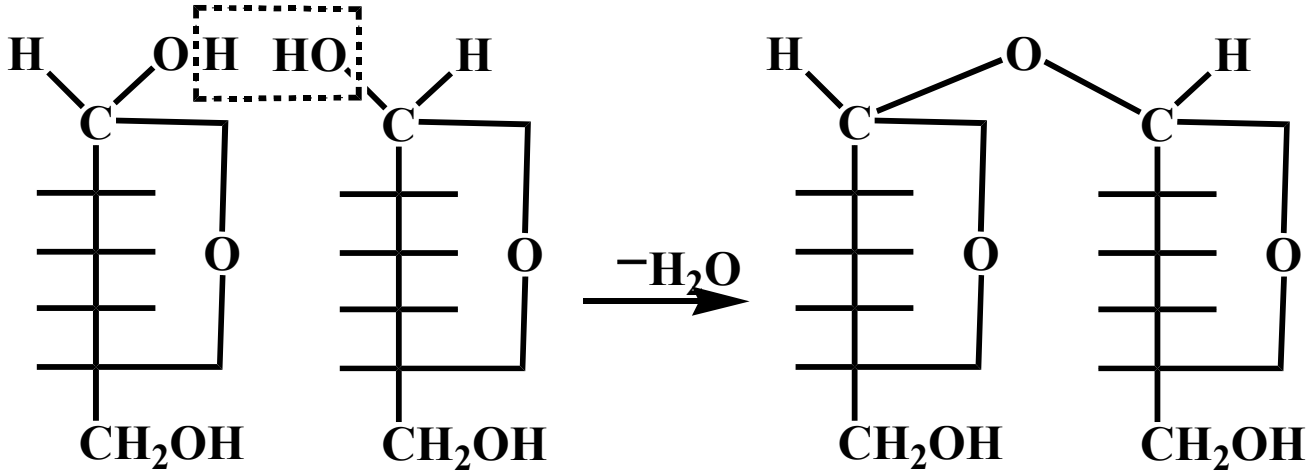
D–(–)–脱氧核糖



糖苷

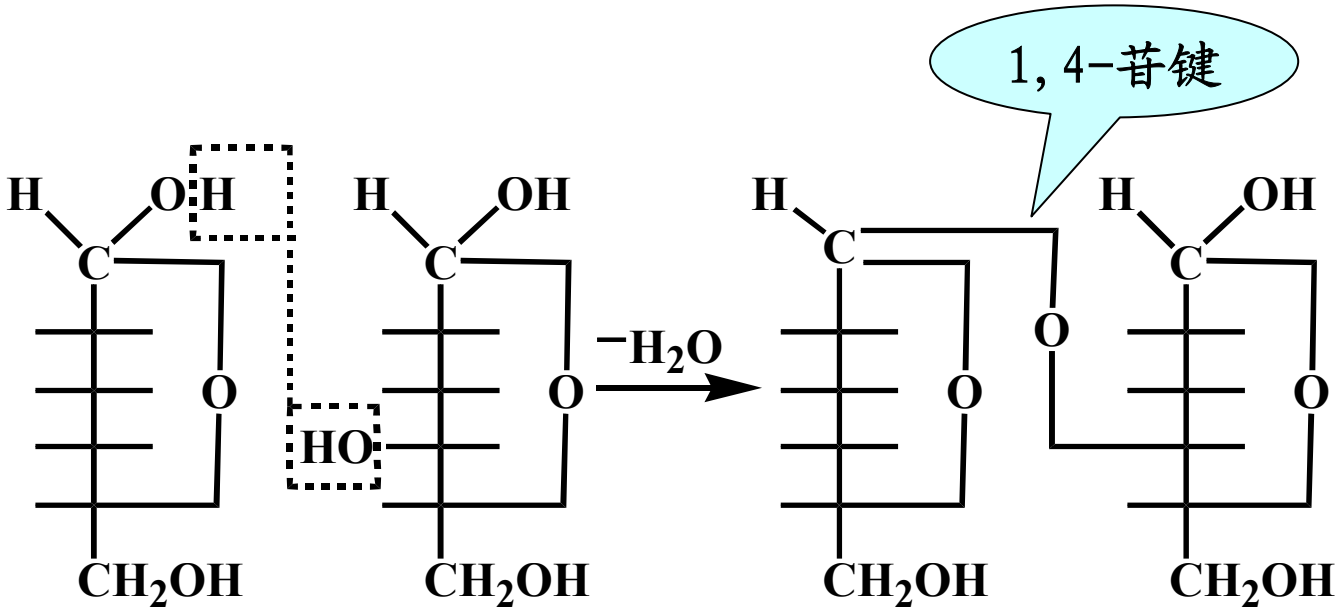
20.22 Disaccharides

- A **disaccharide** on hydrolysis is cleaved to two monosaccharides, which may be the same or different.



（1）通过两个单糖分子的半缩醛羟基脱去一分子水而互相连接而成双糖

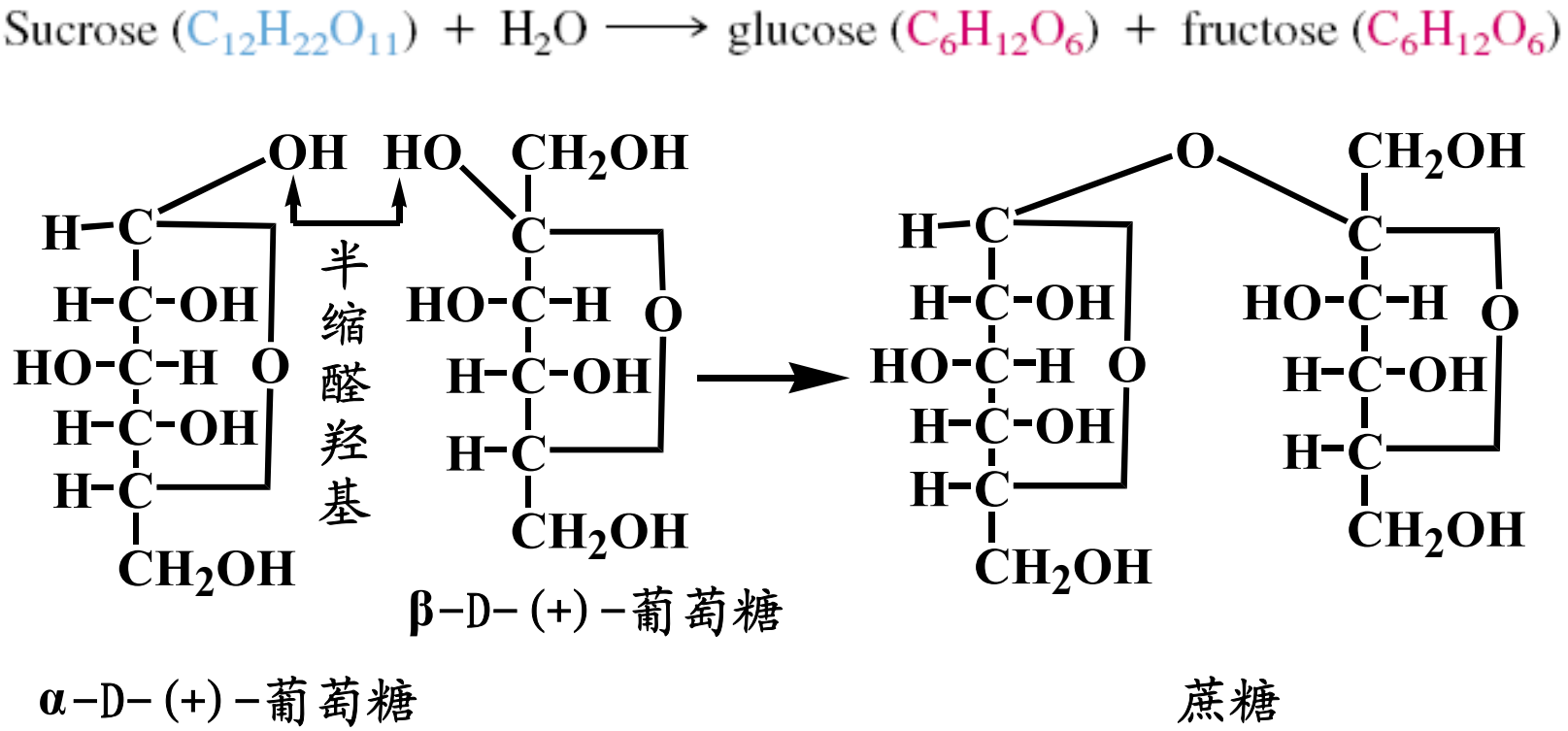
Disaccharides



（2）通过第一个单糖分子的半缩醛羟基与第二个单糖分子中 的醇羟基（如C4的羟基）脱去一分子水而相互连接的双糖

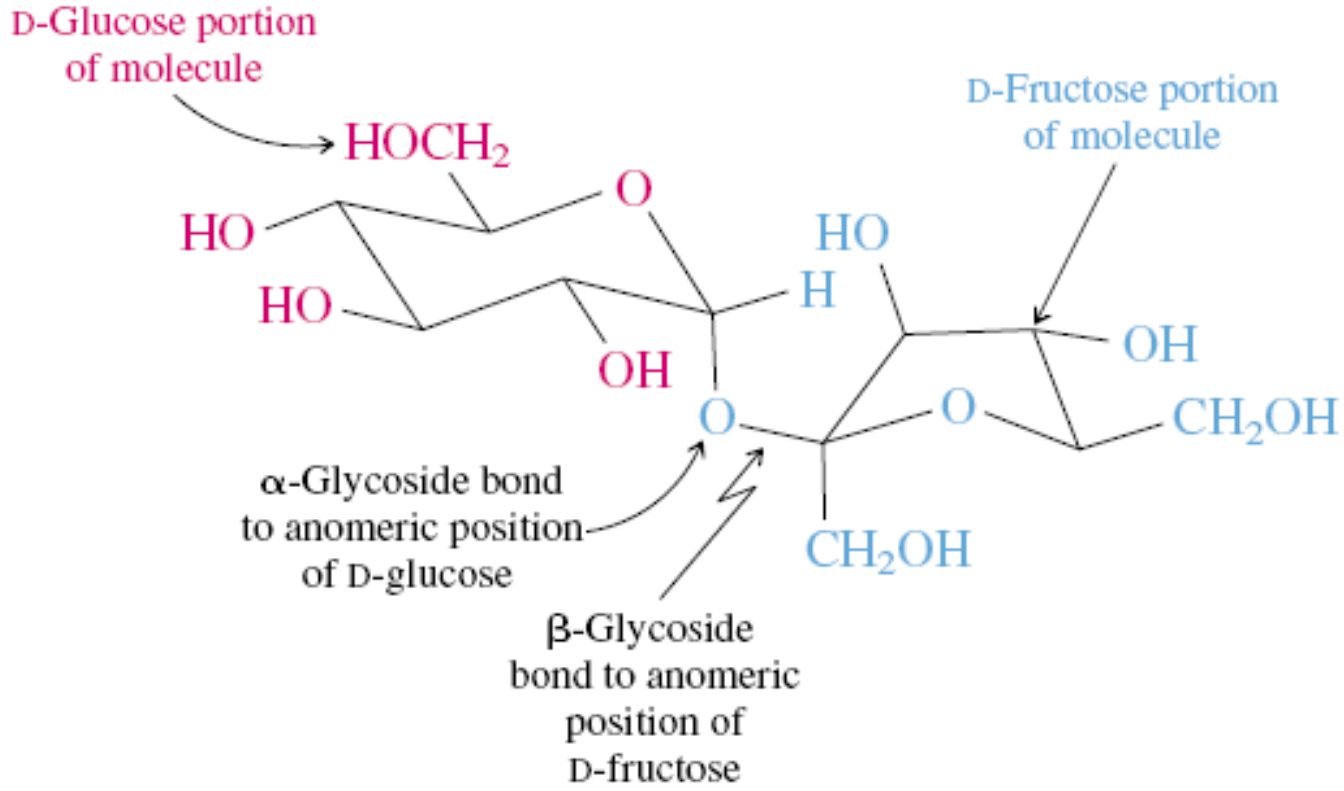
20.23 Sucrose

- *Sucrose* is a disaccharide that yields one molecule of glucose and one of fructose on hydrolysis.



Sucrose

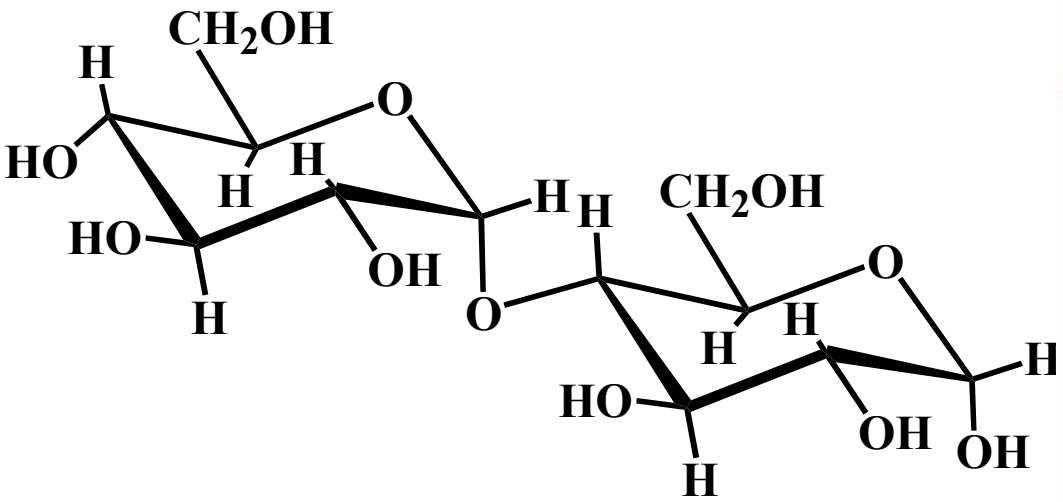
葡萄糖的C1是α型，而果糖的C2是β型，构象式:

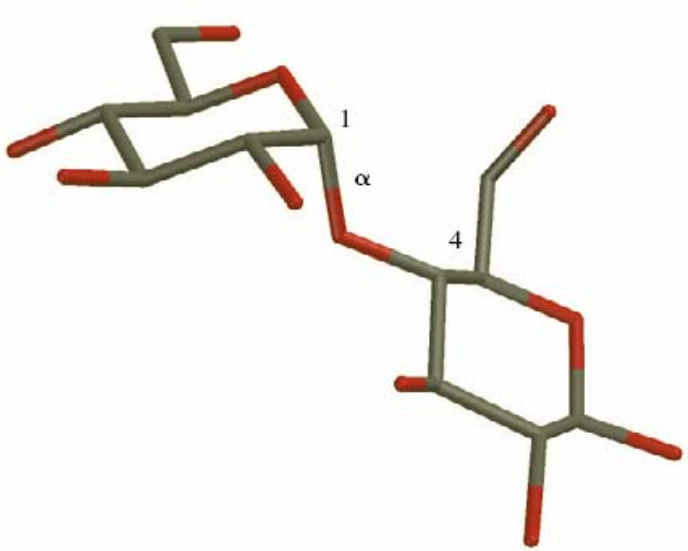


蔗糖不能生成糖脎，没有变旋现象，不和托伦试剂及费林试剂作用即没有还原性，是非还原性双糖。

20.24 Maltose

由两分子D-葡萄糖组成，是α型的:

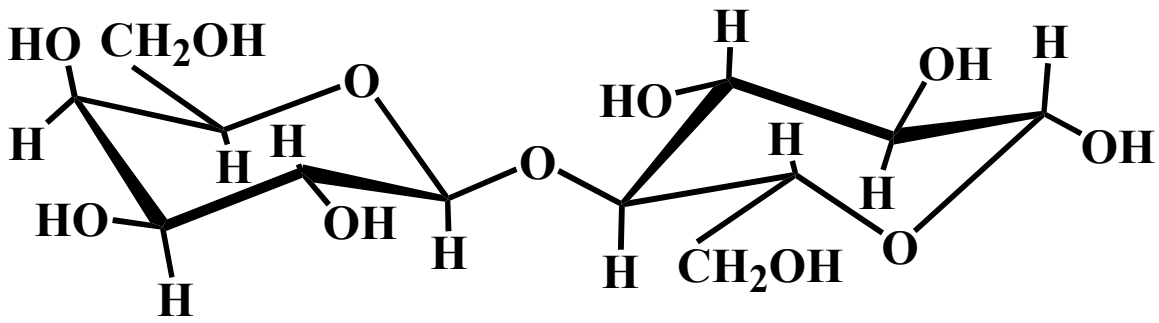




麦芽糖能生成糖脎，能与托伦试剂或费林试剂作用，即有还原性，称为还原性双糖。

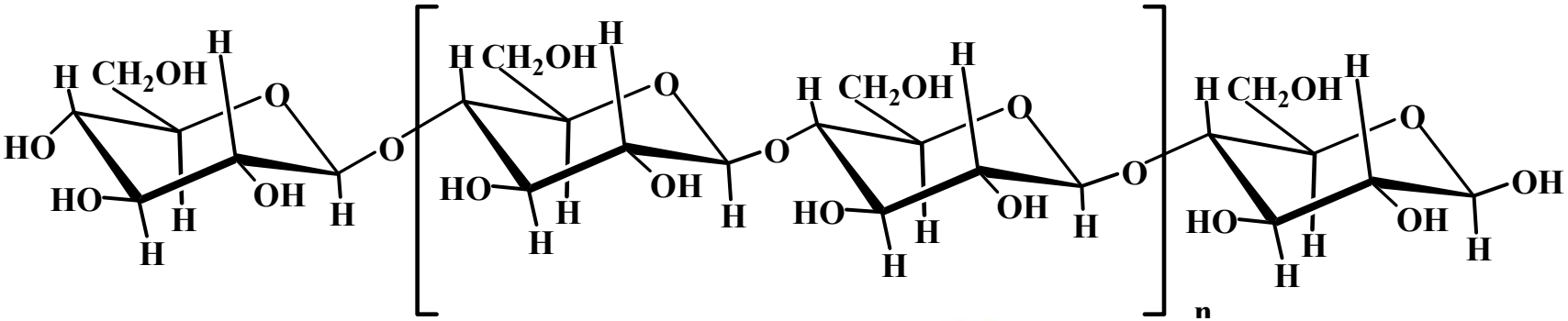
20.25 Lactose

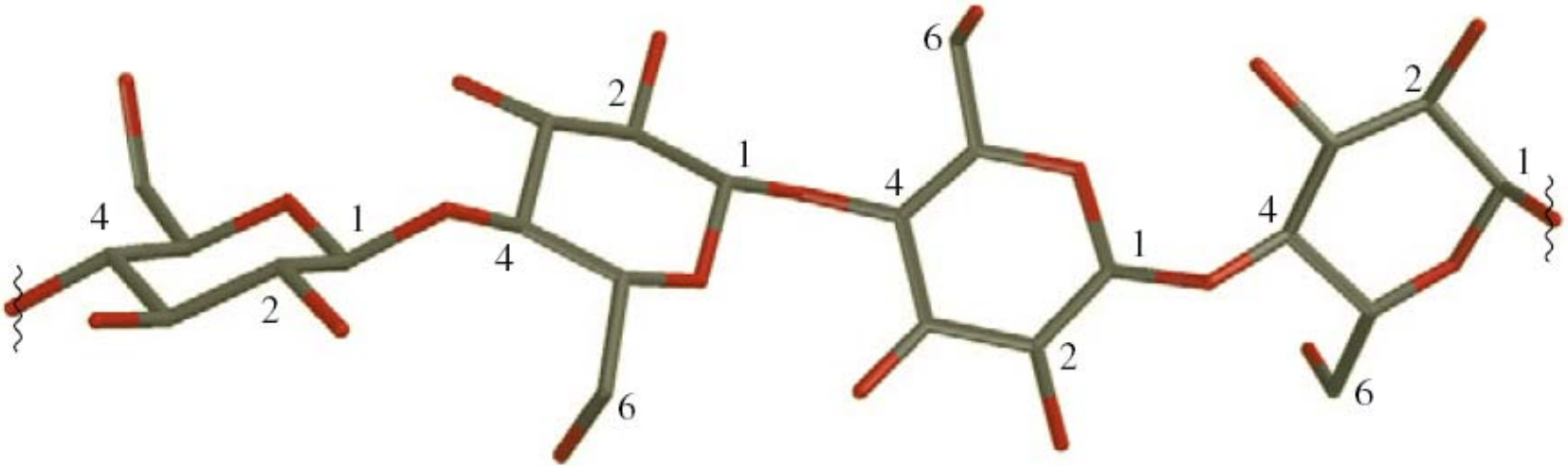
乳糖：是还原性糖，有α和β两种异构体：



20.26 Polysaccharides: Cellulose

纤维素的结构：由多个纤维二糖聚合而成的高聚体。





20.26 Polysaccharides: Starch

- **Starch** is a mixture of a water-dispersible fraction called *amylose* and a second component, *amylopectin.*
- Amylose is a polysaccharide made up of about 100 to several thousand D-glucose units joined by (1,4)-glycosidic bonds：