

Produced by honeybees from the nectar of flowers, honey is primarily a mixture of the two simple sugars fructose and glucose. Image copyright Olga Langerova, 2010. Used under license from Shutterstock.com

25

碳水化合物——糖









葡萄糖
Glucose

蔗糖
Sucrose

植物细胞壁
纤维素（多糖）
Cellulose

提供能量
Energy

生活中常见的糖类

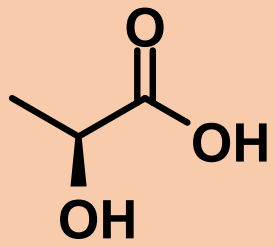
糖的一些生物功能

25.0 糖的定义

- 人们发现俗名为糖（sugar）的化合物，一般分子式都为 $C_n(H_2O)_m$，因此在名称上，将碳水化合物和糖进行混用。
- 然而后来发现，不是所有糖都是 $C_n(H_2O)_m$，也不是所有满足 $C_n(H_2O)_m$ 的都是糖。
- 我们给糖下一个精确的定义：糖是本身或水解以后为多羟基醛或酮的一类物质。

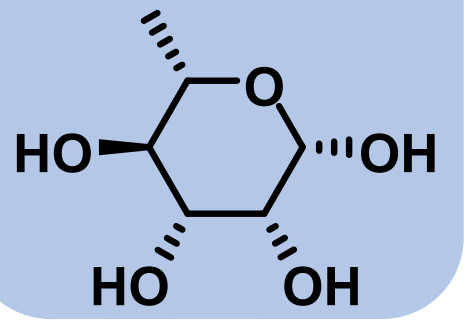
乳酸

$C_3H_6O_3$



鼠李糖

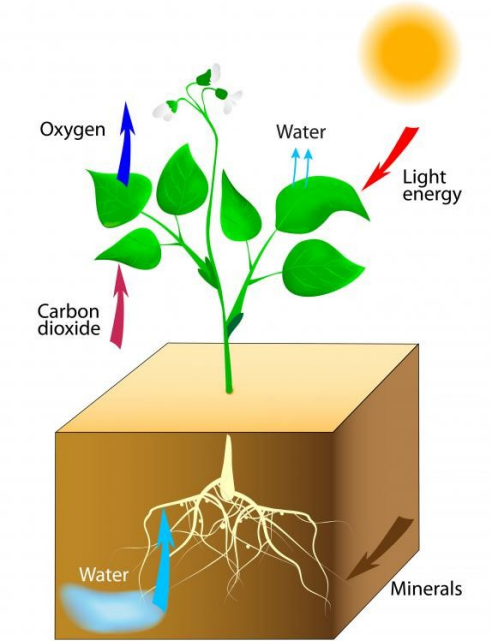
$C_6H_{12}O_5$

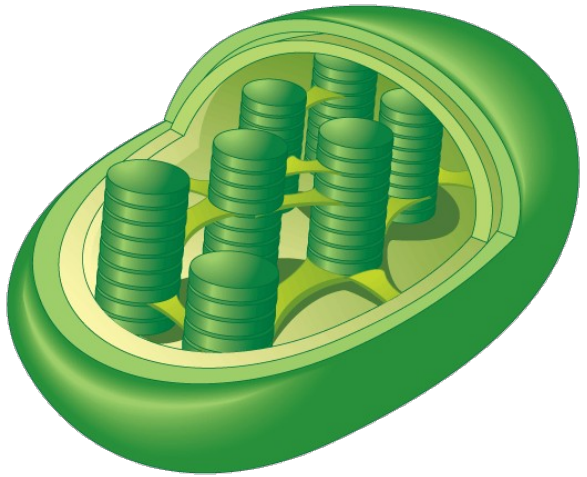


25.0 糖的定义

- 糖是怎样产生的？

$$6\,CO_2 + 6\,H_2O \xrightarrow{\text{Sunlight}} 6\,O_2 + \underbrace{C_6H_{12}O_6}_{\textbf{Glucose}} \longrightarrow \text{Cellulose, starch}$$



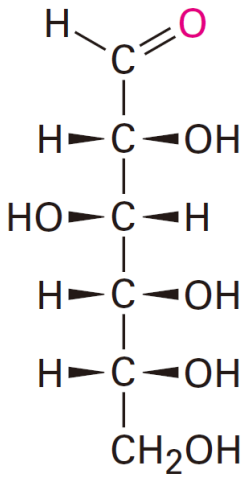


叶绿体

25.1 糖的分类

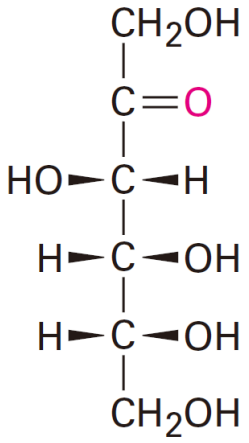
- 分为单糖，寡糖和多糖。单糖就是较简单的，不能再水解的多羟基醛或者多羟基酮及其衍生物。依据水解得到单糖的数目，分为寡糖（几个至十几个）和多糖（上千个）。

一些单糖



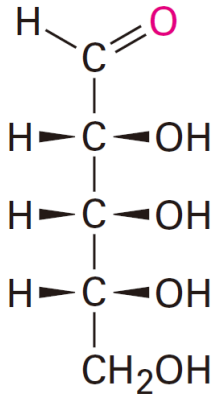
Glucose
(an aldohexose)

葡萄糖(六碳醛糖)



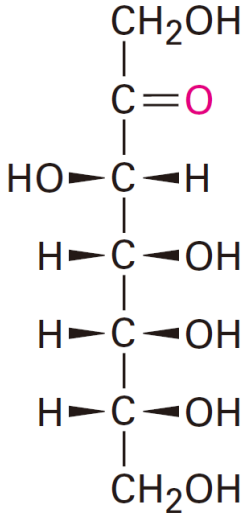
Fructose
(a ketohexose)

果糖(六碳酮糖)



Ribose
(an aldopentose)

核糖(五碳醛糖)

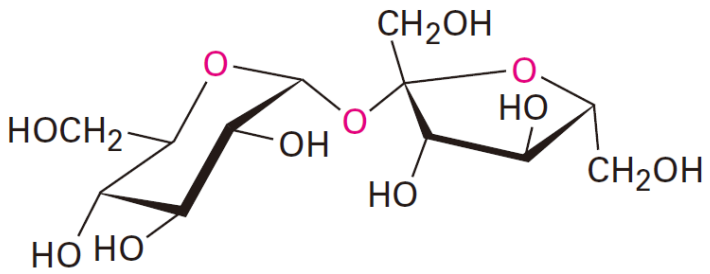


Sedoheptulose
(a ketoheptose)

景天庚糖(七碳酮糖)

25.1 糖的分类

二糖和多糖



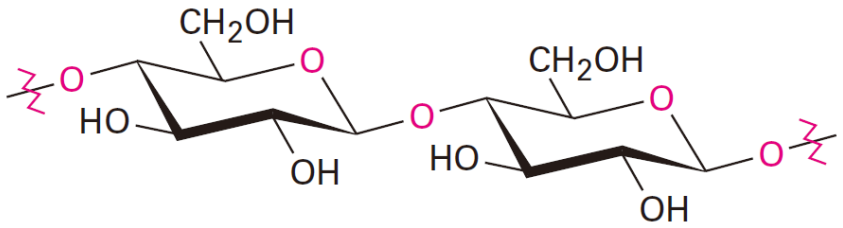
H_3O^+

葡萄糖 + 果糖

1 Glucose + 1 Fructose



Sucrose
(a disaccharide) 蔗糖(二糖)



H_3O^+

~3000 Glucose



上千个葡萄糖



Cellulose
(a polysaccharide)

纤维素(多糖)

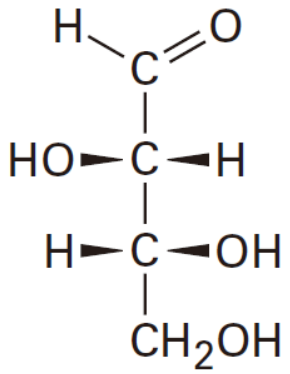
25.1 糖的分类

- 练习

Problem 25.1

Classify each of the following monosaccharides:

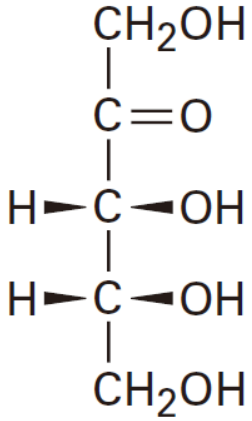
(a)



Threose

苏阿糖

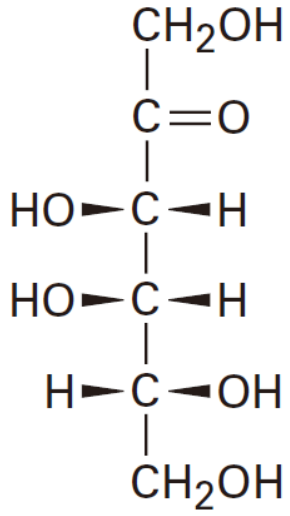
(b)



Ribulose

核酮糖

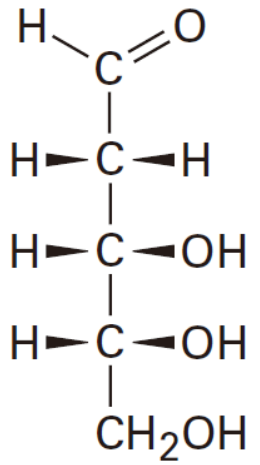
(c)



Tagatose

塔格糖

(d)

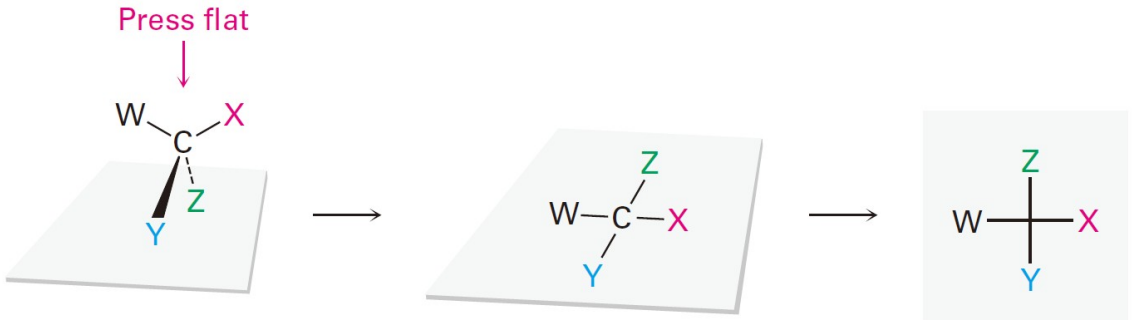


2-Deoxyribose

2-脱氧核糖

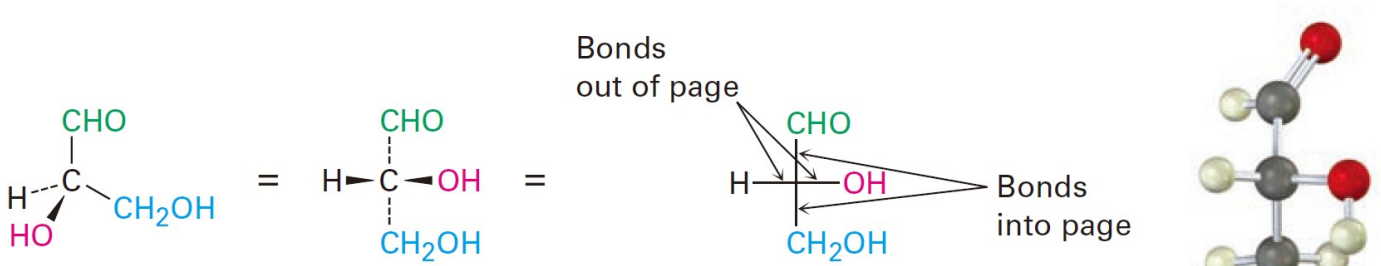
25.2 糖的立体化学

- Fisher 投影式



Fischer projection

For example, (*R*)-glyceraldehyde, the simplest monosaccharide, can be drawn as in **Figure 25.1**.

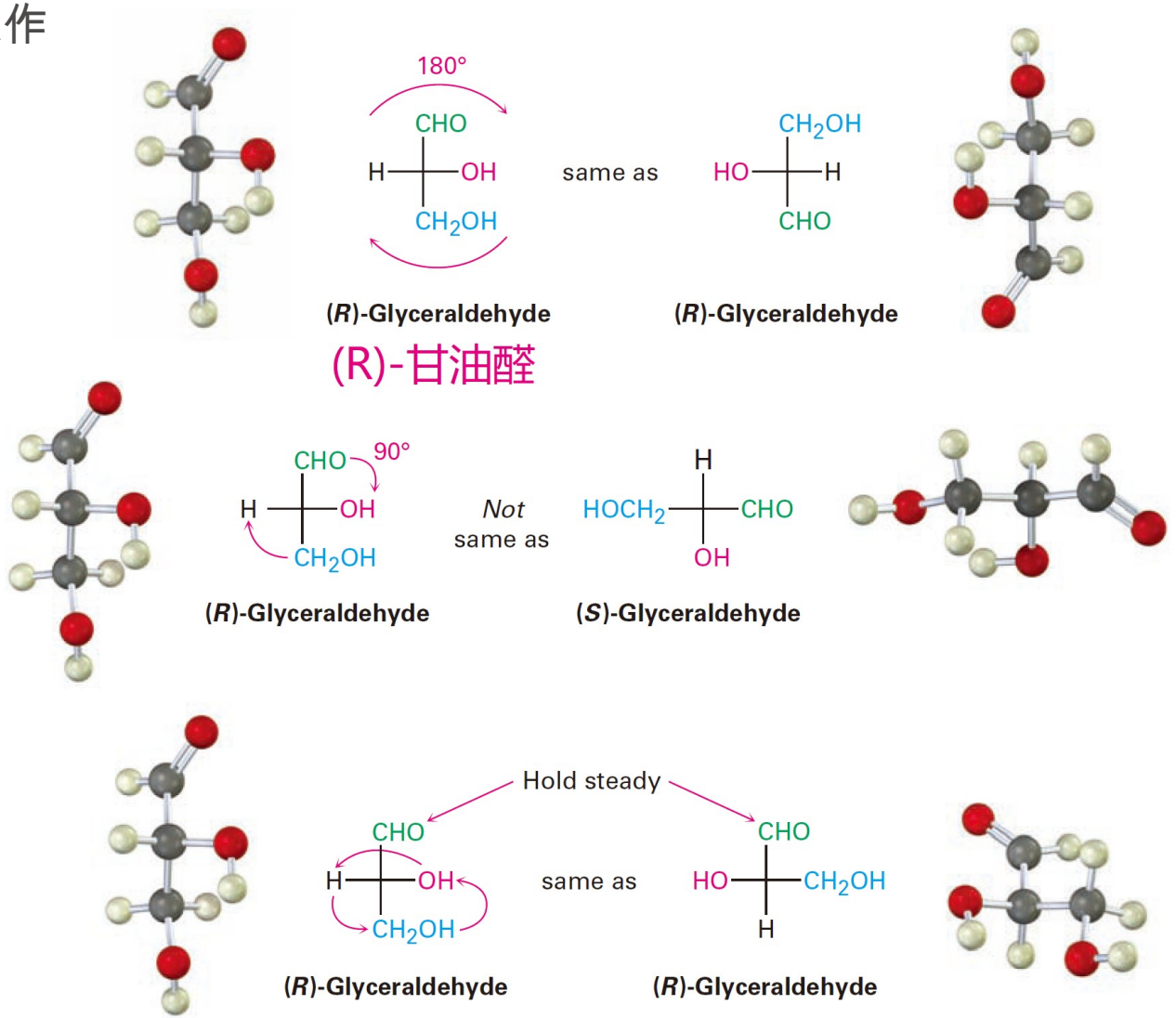


(*R*)-Glyceraldehyde (Fischer projection)

(R)-甘油醛

25.2 糖的立体化学

- Fisher 投影式的操作



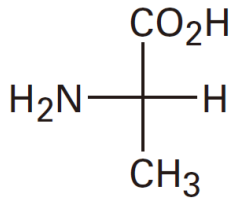
25.2 糖的立体化学

- 练习

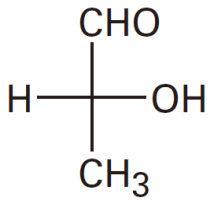
Problem 25.2

Convert each of the following Fischer projections into a tetrahedral representation, and assign *R* or *S* stereochemistry:

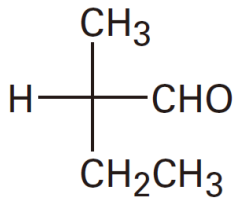
(a)



(b)

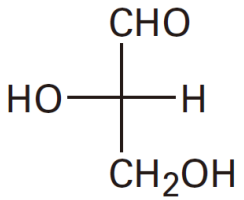


(c)

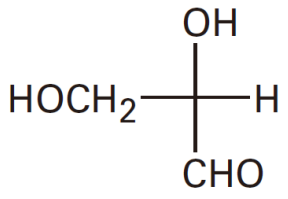


Problem 25.3

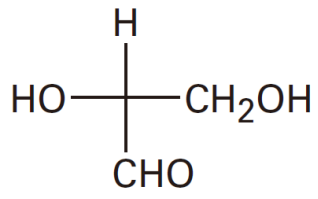
Which of the following Fischer projections of glyceraldehyde represent the same enantiomer?



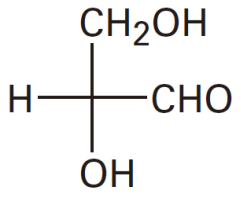
A



B



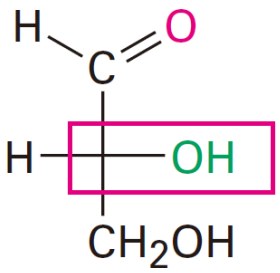
C



D

25.3 糖的 DL 构型分类

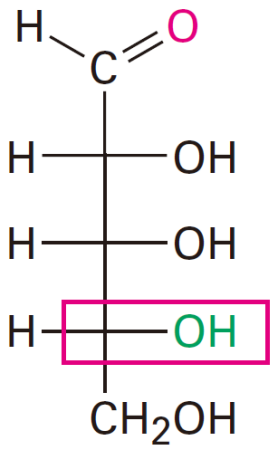
- R 甘油醛写成 Fisher 投影式（保持最高氧化态在上），其手性碳上的羟基在右边，我们规定，这种构型为 D 型。以 D 型甘油醛为基准，从下数第二个羟基（即从下数第一个手性碳上的羟基）和其一致的为 D 构型糖，相反即为 L 构型。



D-Glyceraldehyde
[(*R*)-(+)-glyceraldehyde]

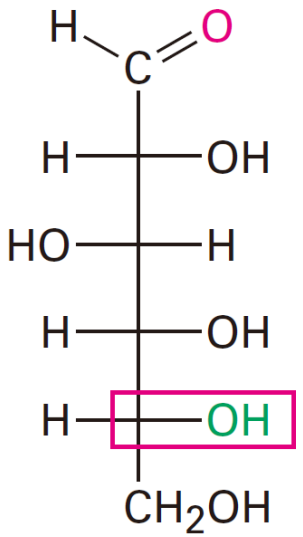
D-甘油醛

羟基向右



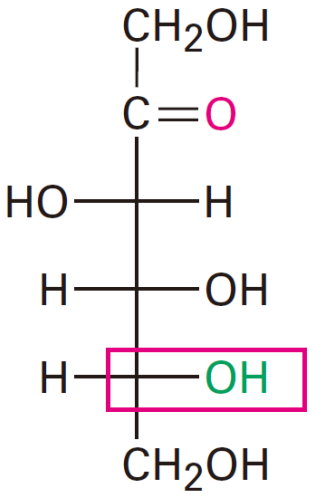
D-Ribose

D-核糖



D-Glucose

D-葡萄糖

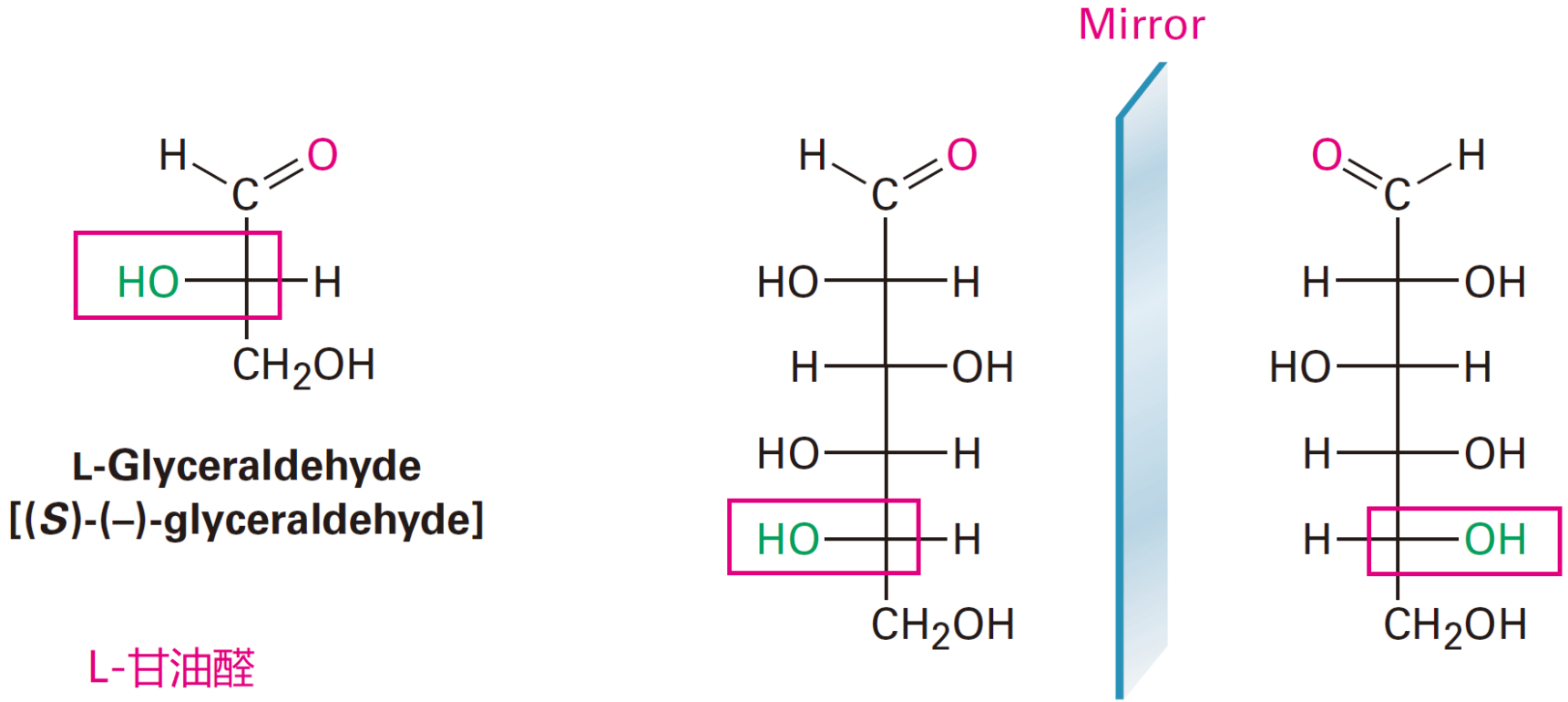


D-Fructose

D-果糖

25.3 糖的 DL 构型分类

- D 构型和 L 构型互为镜面对称



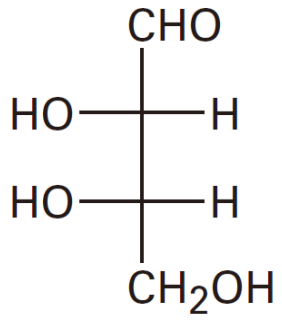
25.3 糖的 DL 构型分类

- 练习

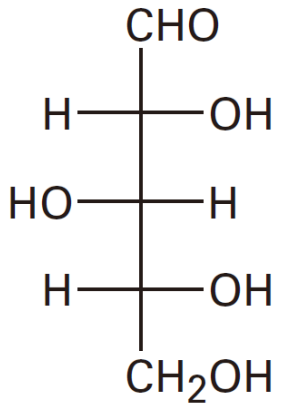
Problem 25.6

Assign *R* or *S* configuration to each chirality center in the following monosaccharides, and tell whether each is a D sugar or an L sugar:

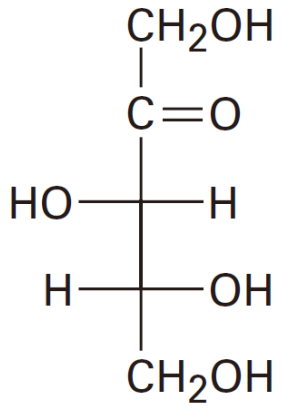
(a)



(b)



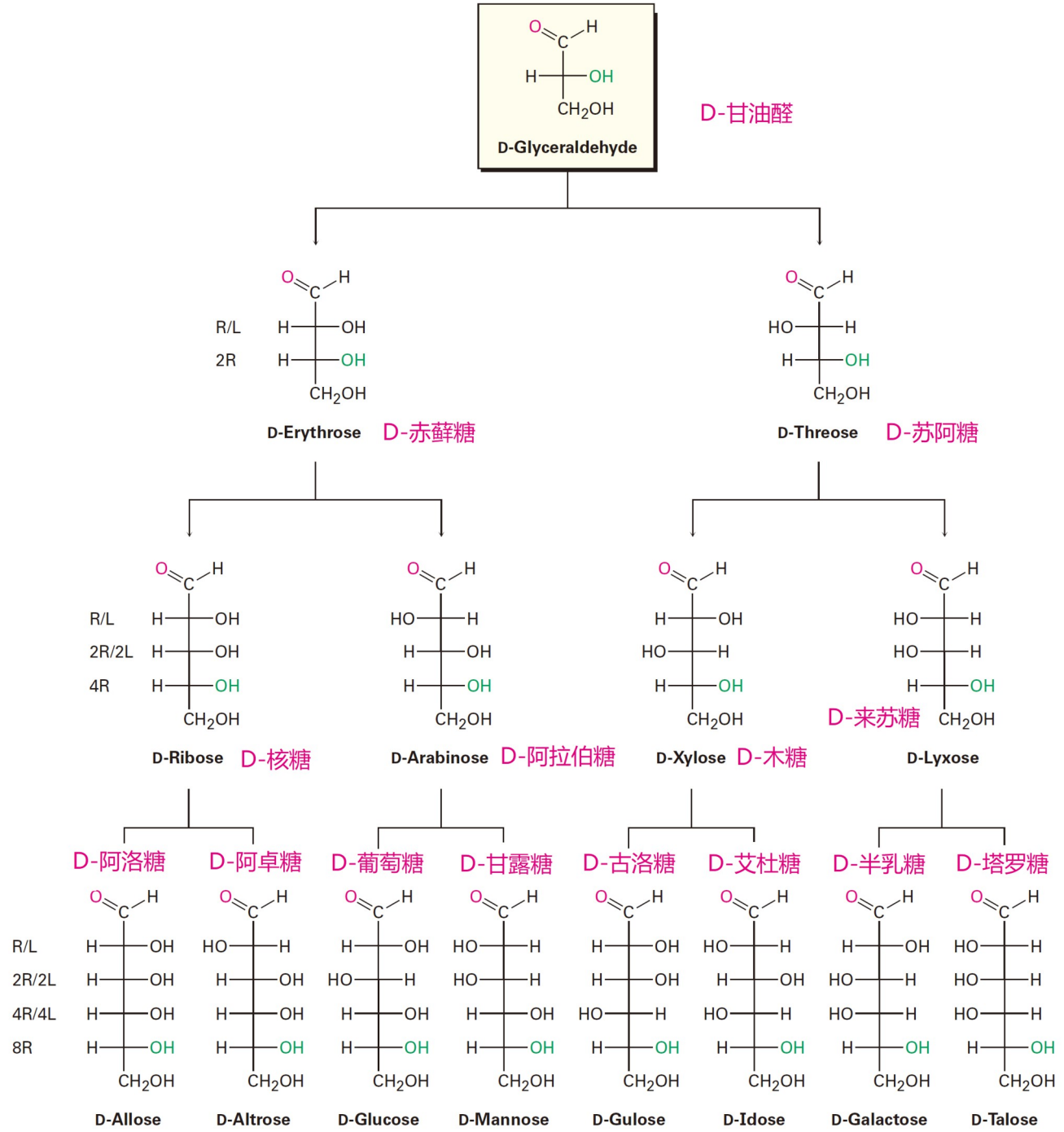
(c)



Problem 25.7

(+)-Arabinose, an aldopentose that is widely distributed in plants, is systematically named (2*R*,3*S*,4*S*)-2,3,4,5-tetrahydroxypentanal. Draw a Fischer projection of (+)-arabinose, and identify it as a D sugar or an L sugar.

25.4 糖的构型


D-Glyceraldehyde
D-甘油醛
R/L
2R
D-Erythrose
D-赤藓糖
D-Threose
D-苏阿糖
R/L
2R/2L
4R
D-Ribose
D-核糖
D-Arabinose
D-阿拉伯糖
D-Xylose
D-木糖
D-来苏糖
D-Lyxose
D-阿洛糖
D-阿卓糖
D-葡萄糖
D-甘露糖
D-古洛糖
D-艾杜糖
D-半乳糖
D-塔罗糖
R/L
2R/2L
4R/4L
8R
D-Allose
D-Altrose
D-Glucose
D-Mannose
D-Gulose
D-Idose
D-Galactose
D-Talose

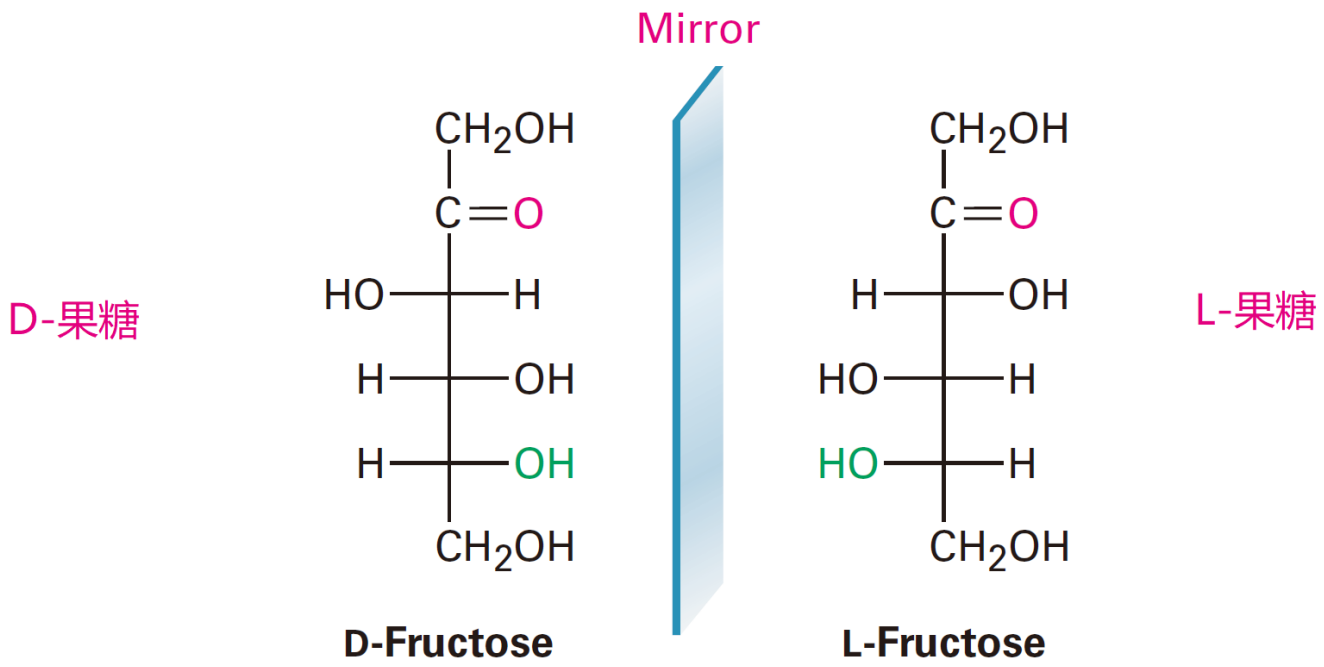
25.4 糖的构型

Draw a Fischer projection of L-fructose.

Strategy

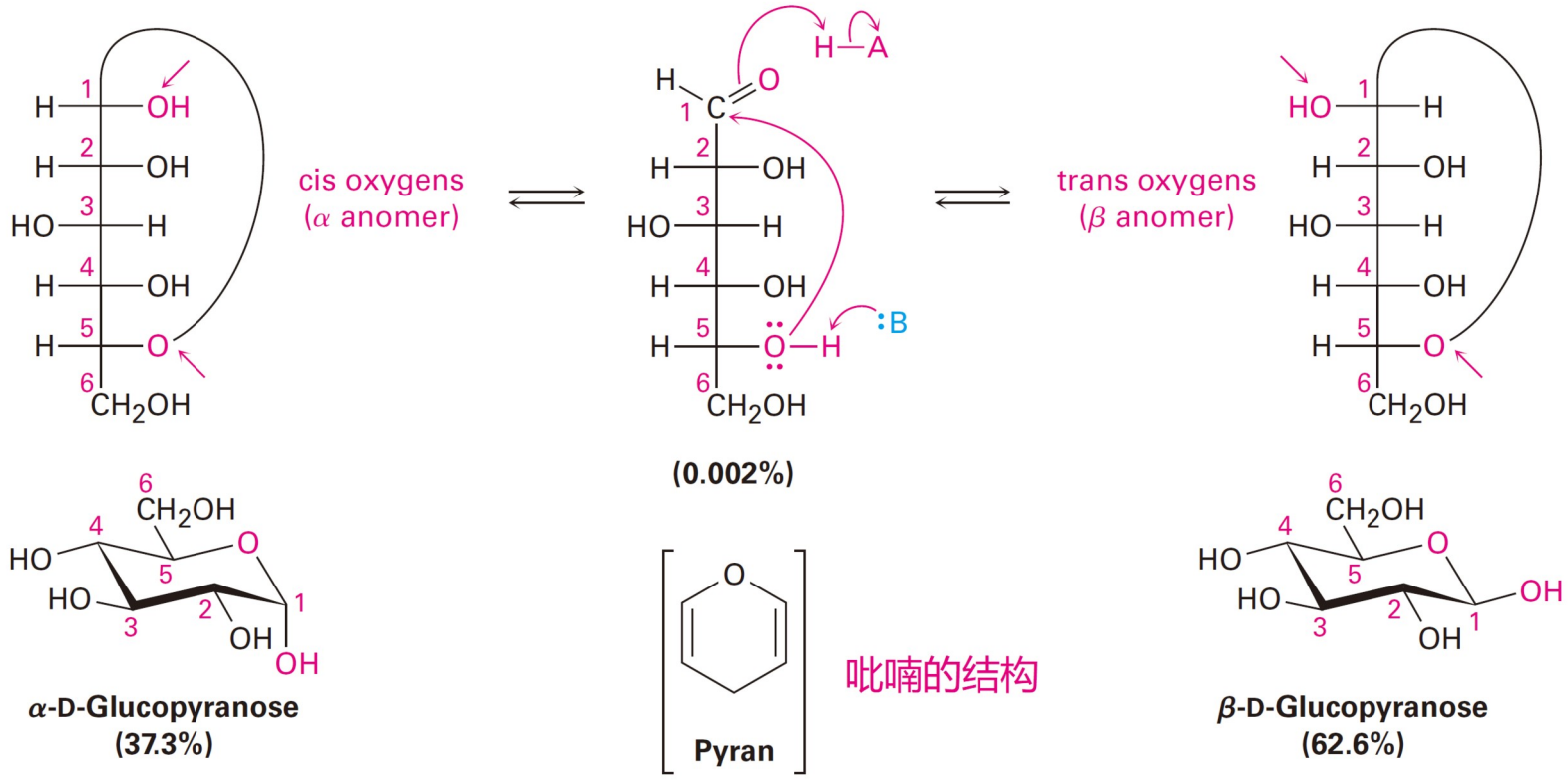
Because L-fructose is the enantiomer of D-fructose, simply look at the structure of D-fructose and reverse the configuration at each chirality center.

Solution



25.5 单糖的环状结构

- 在葡萄糖结构中，5 号碳上的羟基进攻 1 号碳的醛基，得到环状的半缩醛结构。这样一个含有氧原子的六元环，我们称之为吡喃葡萄糖。如图所示固定六元环的其他取代基都在平伏键上，此时如果半缩醛的羟基在直立键上，称为 alpha 构型，若在平伏键上，则为 beta 构型。
- 从 Fisher 投影式来看，1 号碳半缩醛的羟基在右为 alpha ，左为 beta 。

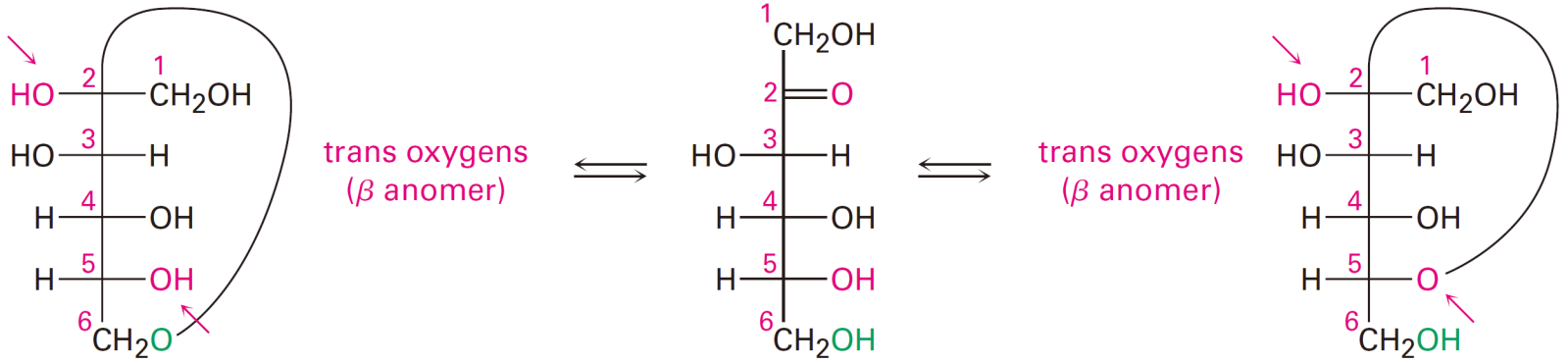


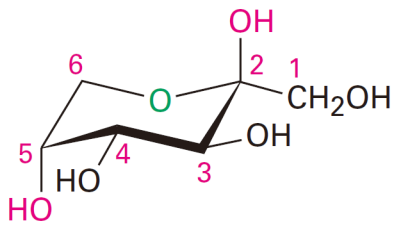
alpha-D-吡喃葡萄糖

beta-D-吡喃葡萄糖

25.5 单糖的环状结构

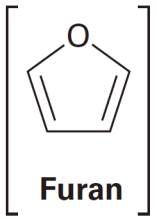
- 在果糖结构中，由于羰基在 2 号碳，这时如果 6 号碳上的羟基进攻 2 号碳的酮羰基，则得到含氧六元环，为吡喃糖；若 5 号碳上的羟基进攻 2 号碳的酮羰基，则得到含氧五元环，为呋喃糖。两种情况都是 beta 端基异构体占优势。



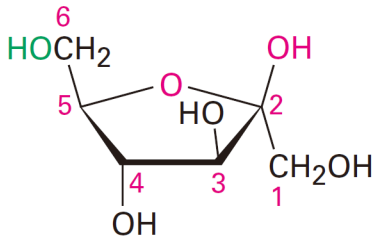


β-D-Fructopyranose (70%)
(+2% α anomer)

beta-D-吡喃果糖



呋喃的结构

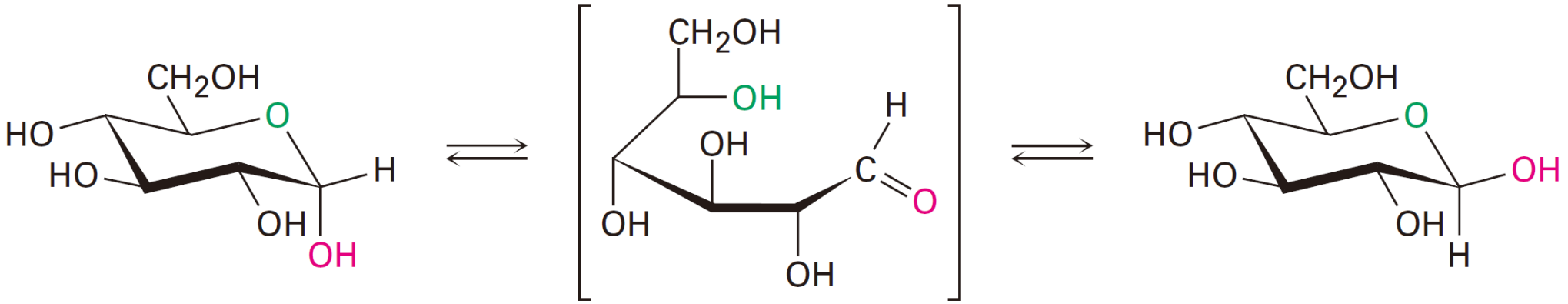


β-D-Fructofuranose (23%)
(+5% α anomer)

beta-D-呋喃果糖

25.5 单糖的环状结构

- 在溶液中，环状葡萄糖结构的 alpha 构型和 beta 构型可以相互转化，这个过程称为变旋光作用。



α-D-Glucopyranose
$[\alpha]_D$ = +112.2

alpha-D-吡喃葡萄糖

熔点 146 °C

β-D-Glucopyranose
$[\alpha]_D$ = +18.7

beta-D-吡喃葡萄糖

熔点 150 °C

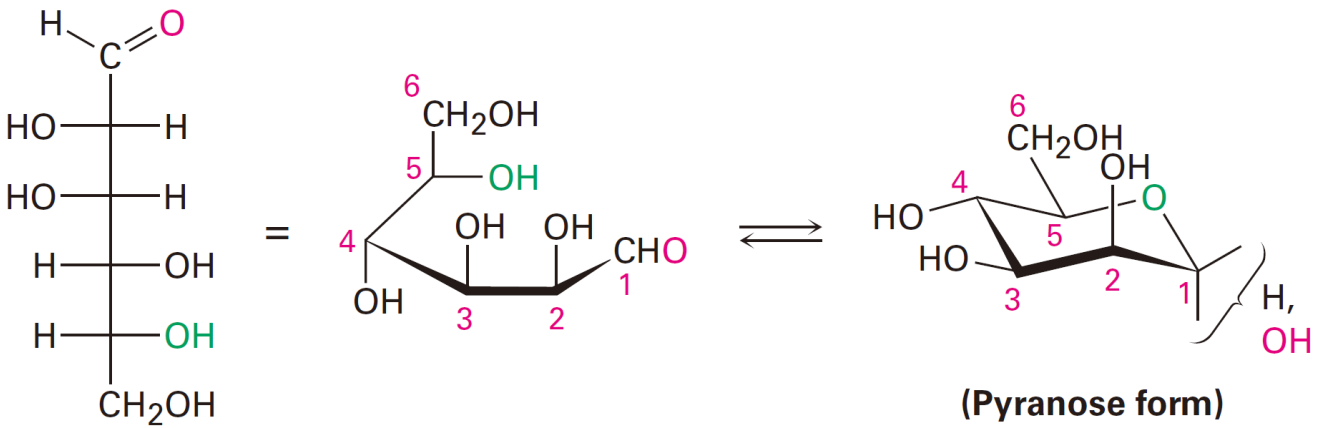
25.5 单糖的环状结构

- 例题 D-Mannose differs from D-glucose in its stereochemistry at C2. Draw D-mannose in its chairlike pyranose form.

Strategy

First draw a Fischer projection of D-mannose. Then lay it on its side, and curl it around so that the —CHO group (C1) is on the right front and the —CH_2OH group (C6) is toward the left rear. Now, connect the —OH at C5 to the C1 carbonyl group to form the pyranose ring. In drawing the chair form, raise the leftmost carbon (C4) up and drop the rightmost carbon (C1) down.

Solution



D-Mannose **(Pyranose form)**

D-甘露糖 alpha or beta-D-吡喃甘露糖

25.5 单糖的环状结构

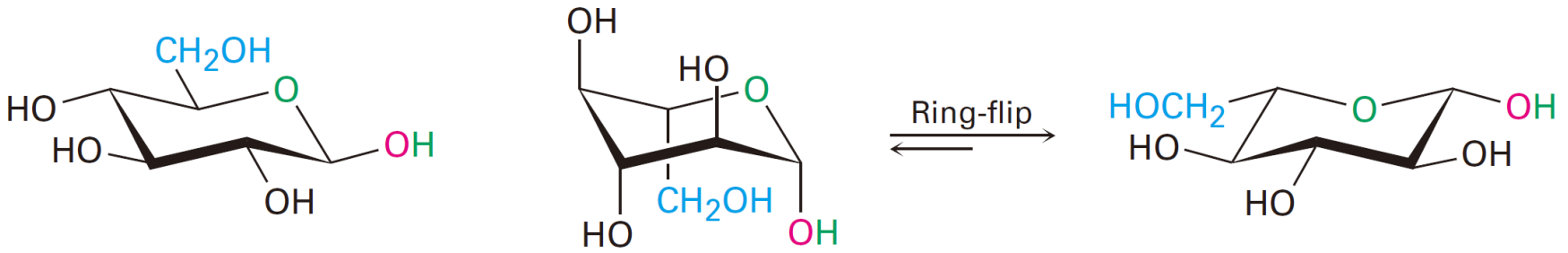
- 例题

Draw β-L-glucopyranose in its more stable chair conformation.

Strategy

It's probably easiest to begin by drawing the chair conformation of β-D-glucopyranose. Then draw its mirror-image L enantiomer by changing the stereochemistry at every position on the ring, and carry out a ring-flip to give the more stable chair conformation. Note that the $-CH_2OH$ group is on the bottom face of the ring in the L enantiomer as is the anomeric −OH.

Solution



β-D-Glucopyranose

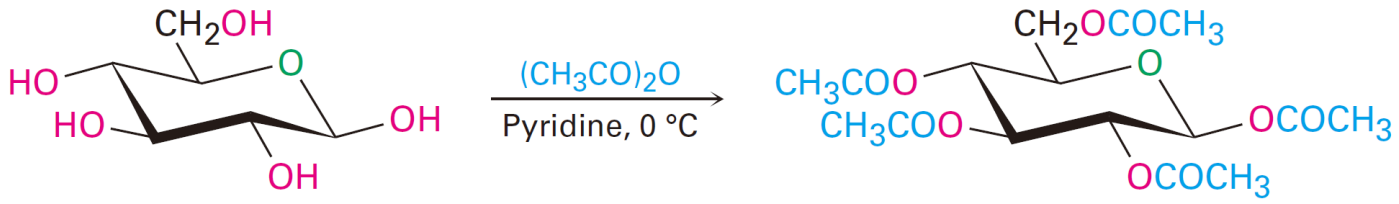
beta-D-吡喃葡萄糖

β-L-Glucopyranose

beta-L-吡喃葡萄糖

25.6 单糖的化学反应

- 酯化和醚化 **Ester and Ether Formation**

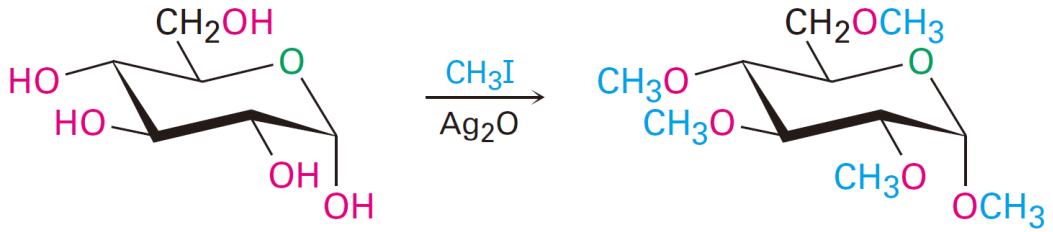


β-D-Glucopyranose

beta-D-吡喃葡萄糖

Penta-*O*-acetyl-β-D-glucopyranose (91%)

beta-D-吡喃葡萄糖-五乙酸酯



α-D-Glucopyranose

alpha-D-吡喃葡萄糖

α-D-Glucopyranose pentamethyl ether (85%)

alpha-D-吡喃葡萄糖-五甲基醚

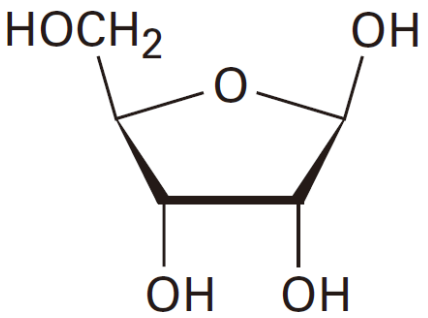
25.6 单糖的化学反应

- 练习

Problem 25.16

Draw the products you would obtain by reaction of β-D-ribofuranose with:

(a) CH_3I, Ag_2O **(b)** $(CH_3CO)_2O$, pyridine



β-D-Ribofuranose

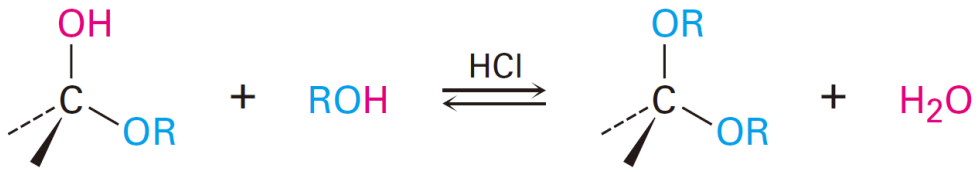
beta-D-呋喃核糖

25.6 单糖的化学反应

- 糖苷化——糖的环状形式的半缩醛形成缩醛

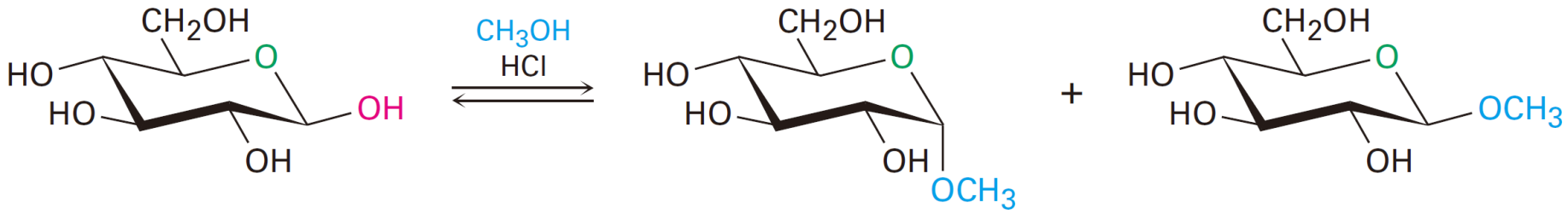
Glycoside Formation
(糖苷)

回顾



A hemiacetal
半缩醛

An acetal
缩醛



β-D-Glucopyranose
(a cyclic hemiacetal)
beta-D-吡喃葡萄糖
(环状半缩醛)

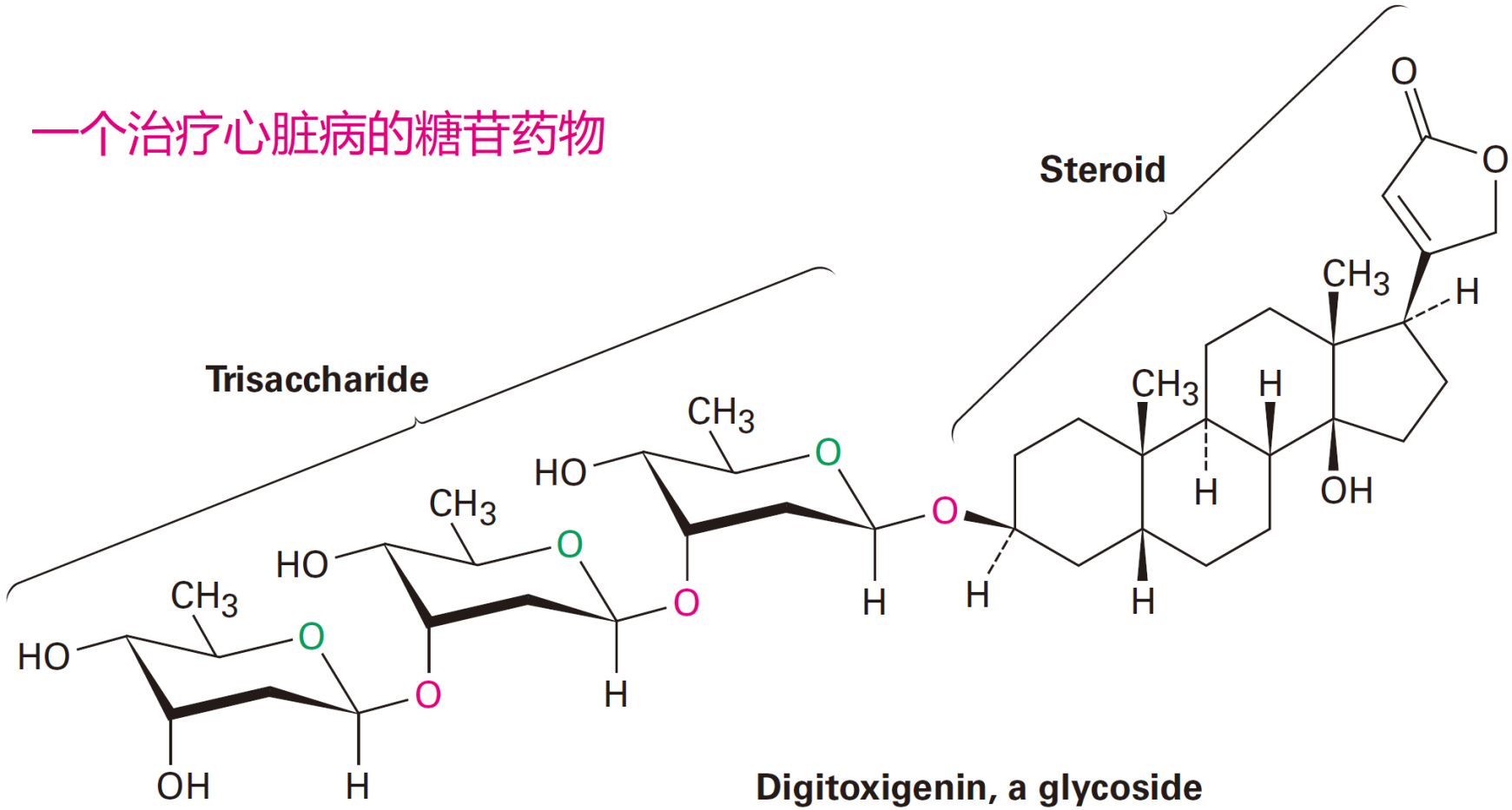
Methyl α-D-glucopyranoside
(66%)
甲基-alpha-D-吡喃葡萄糖苷

Methyl β-D-glucopyranoside
(33%)
甲基-beta-D-吡喃葡萄糖苷

25.6 单糖的化学反应

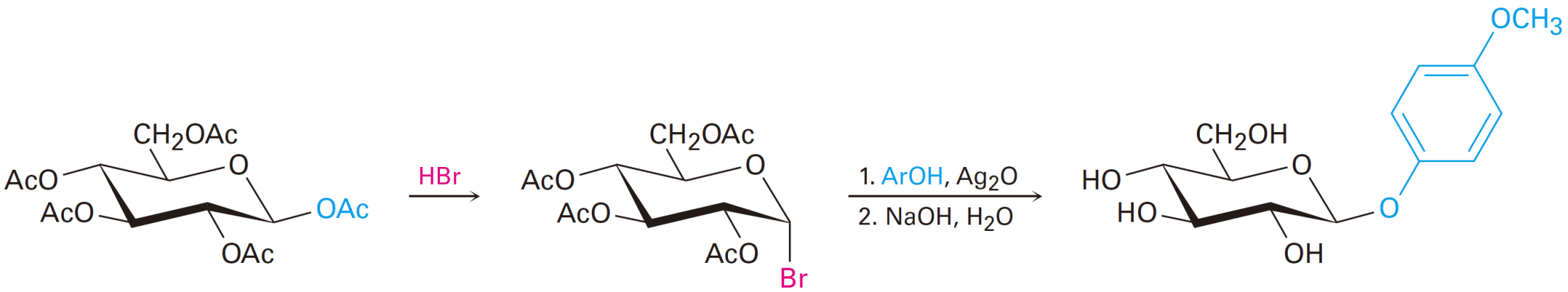
- 糖苷药物

一个治疗心脏病的糖苷药物



25.6 单糖的化学反应

- 糖苷化中的邻基参与



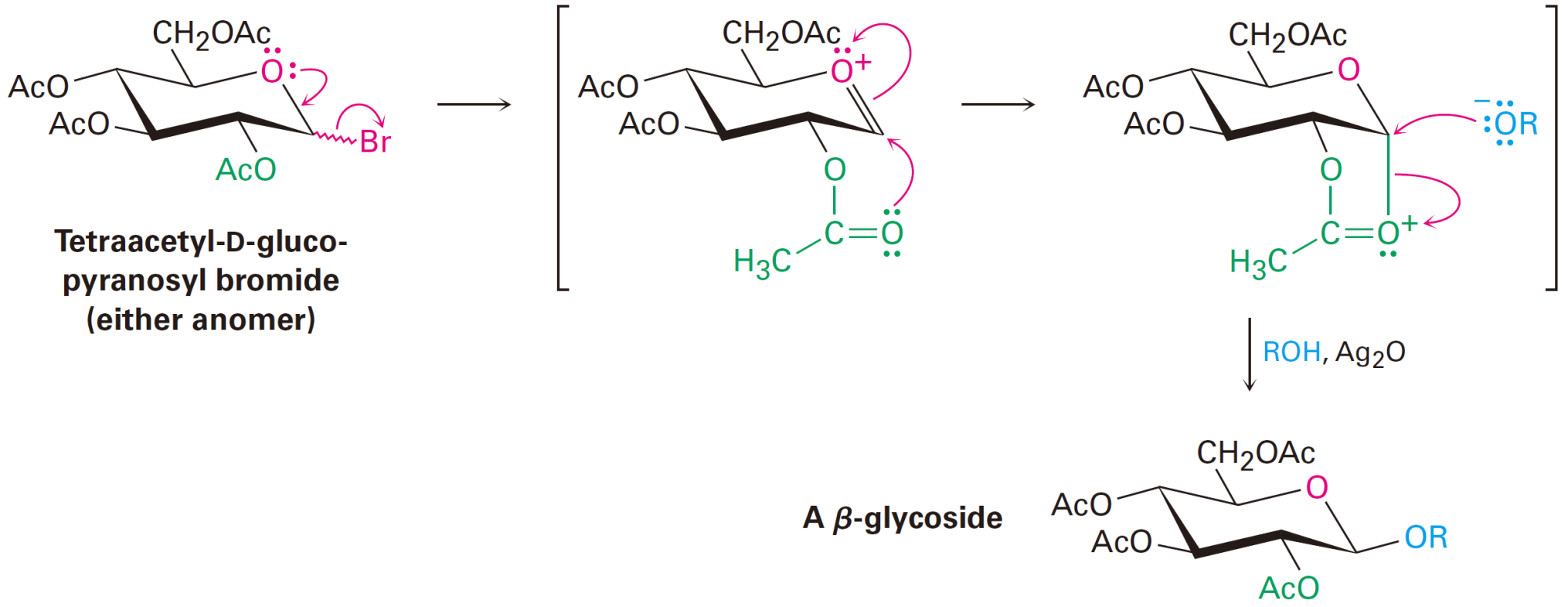
Pentaacetyl-β-D-glucopyranose

Tetraacetyl-α-D-gluco-pyranosyl bromide

Methylarbutin

25.6 单糖的化学反应

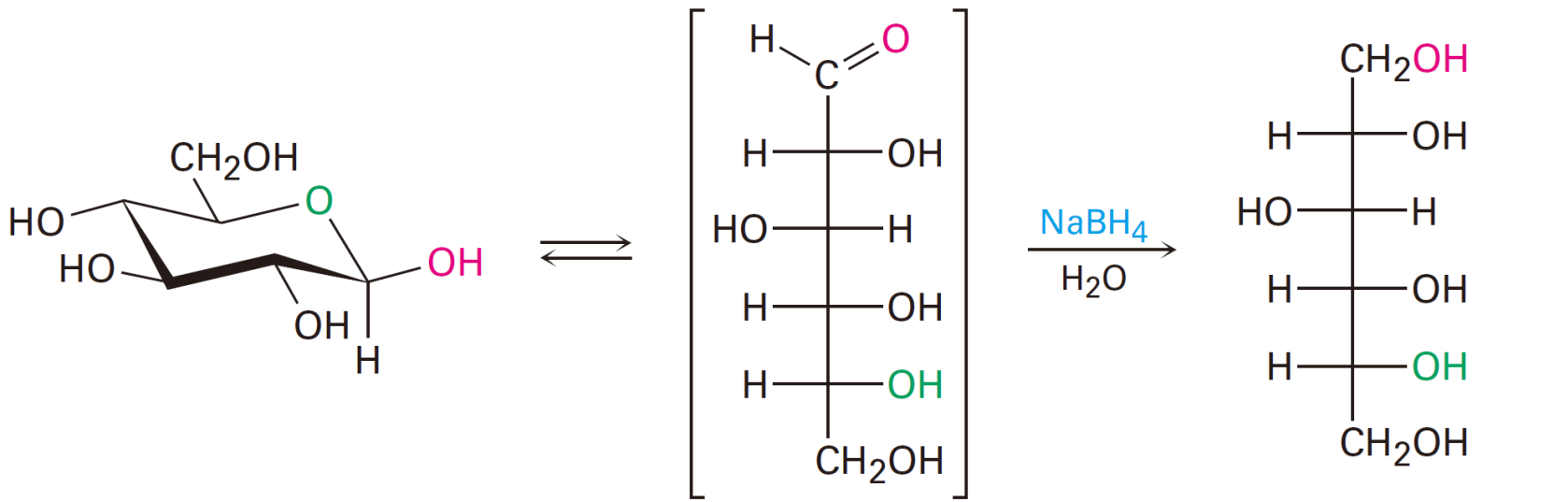
- 糖苷化中的邻基参与



25.6 单糖的化学反应

- 单糖的还原。用 $NaBH_4$ 还原糖中的醛基得到醇。

Reduction of Monosaccharides (单糖)



β-D-Glucopyranose

beta-D-吡喃葡萄糖

D-Glucose

D-葡萄糖

D-Glucitol (D-sorbitol), an alditol

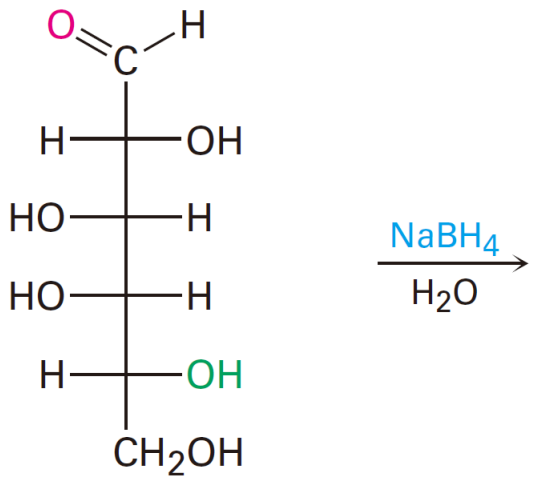
D-山梨醇

25.6 单糖的化学反应

- 练习

Problem 25.17

Reduction of D-glucose leads to an optically active alditol (D-glucitol), whereas reduction of D-galactose leads to an optically inactive alditol. Explain.



D-Galactose

D-半乳糖

$\xrightarrow[H_2O]{NaBH_4}$

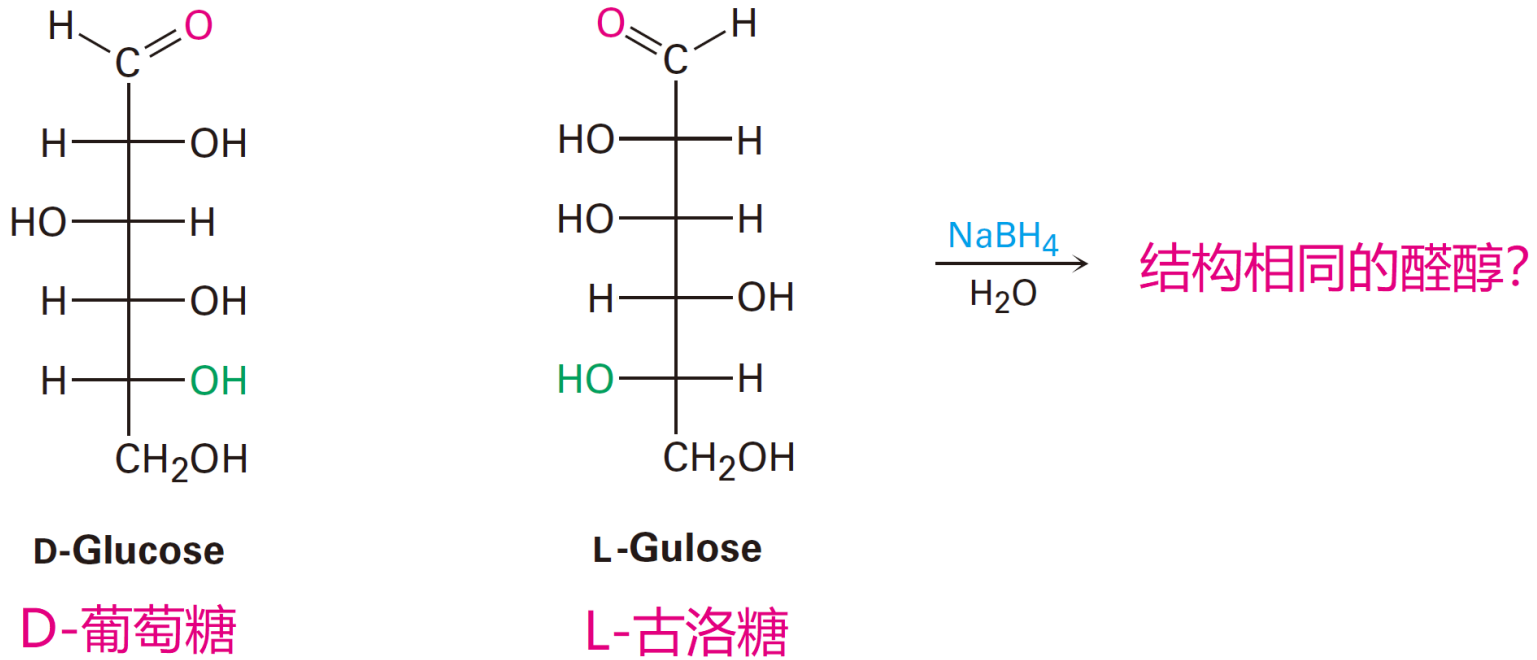
得到一个没有光学活性的醛醇(alditol)，为什么?

25.6 单糖的化学反应

- 练习

Problem 25.18

Reduction of L-gulose with $NaBH_4$ leads to the same alditol (D-glucitol) as reduction of D-glucose. Explain.



D-Glucose

D-葡萄糖

L-Gulose

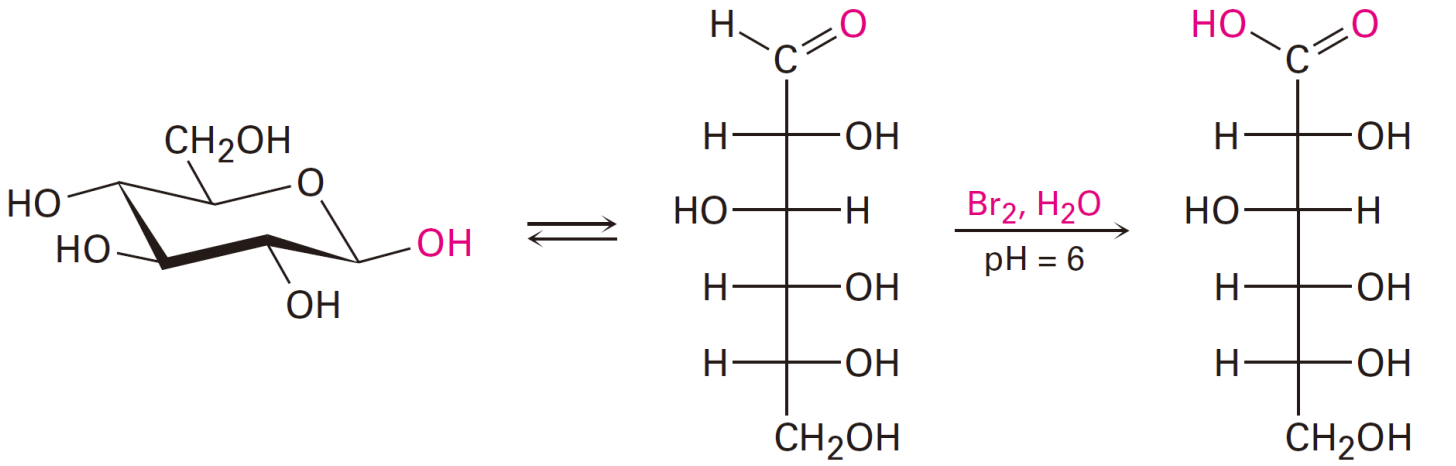
L-古洛糖

25.6 单糖的化学反应

- 单糖的氧化。这里糖中的醛基被 pH=6 的溴水氧化为羧酸，注意醇不受影响。

Oxidation of Monosaccharides（单糖）

Like other aldehydes, aldoses are easily oxidized to yield the corresponding carboxylic acids, called **aldonic acids**. A buffered solution of aqueous Br_2 is often used for the purpose.



D-Glucose

D-葡萄糖

D-Gluconic acid
(an aldonic acid)

D-葡萄糖酸

25.6 单糖的化学反应

- 除了溴水以外，其他氧化剂还有托伦试剂以及本尼迪特试剂。
- 能够被氧化剂氧化的糖叫还原糖。

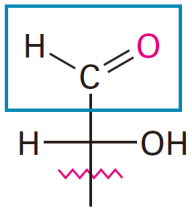
Historically, the oxidation of an aldose with either Ag^+ in aqueous ammonia (called Tollens' reagent) or Cu^{2+} with aqueous sodium citrate (Benedict's reagent) formed the basis of simple tests for what are called **reducing sugars**.

(还原糖)

其他氧化试剂

Ag^+, NH_3/H_2O Tollen 托伦试剂

Cu^{2+}, 柠檬酸钠水溶液 Benedict 本尼迪特试剂



An aldose

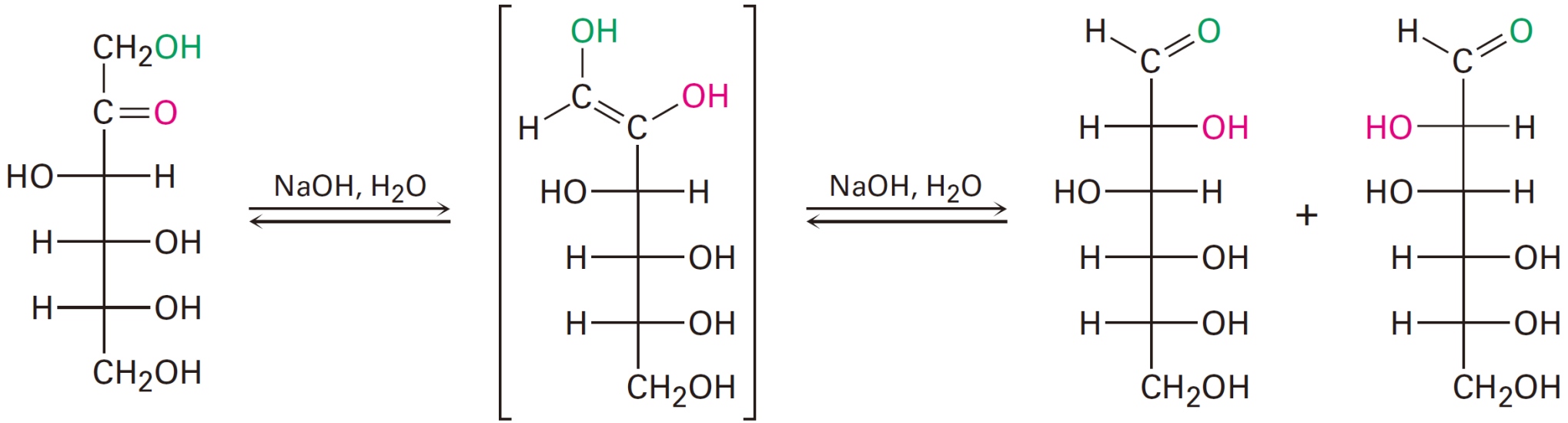
醛糖

所有醛糖都是还原糖

有一些简单的酮糖也是还原糖，因为...

25.6 单糖的化学反应

- D- 果糖是一个酮糖，在碱性条件下，异构化为一对醛糖。虽然酮糖不能被氧化，但是其在碱性水溶液中会转化为醛糖，就可以被氧化了。



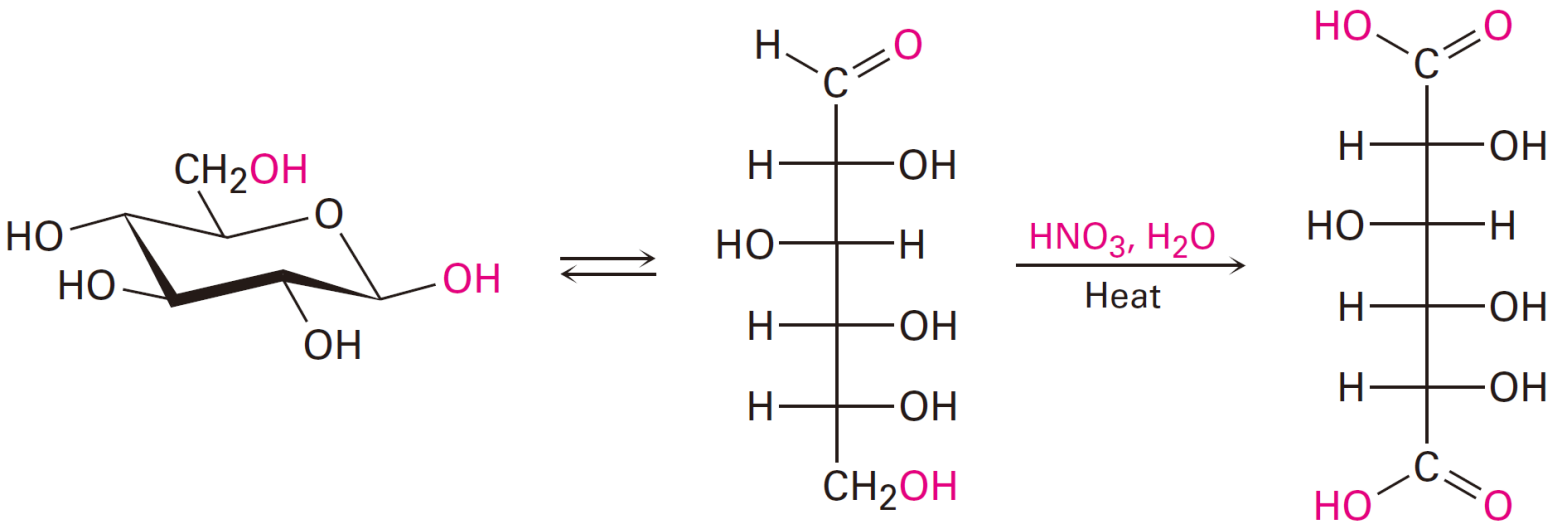
D-Fructose **An enediol** **D-Glucose** **D-Mannose**

D-果糖　烯二醇　D-葡萄糖　D-甘露糖

25.6 单糖的化学反应

- 在更强的氧化剂条件下，如硝酸的水溶液加热条件，醛和一级醇都被氧化为羧酸，注意二级醇不变。

If warm dilute HNO_3 (nitric acid) is used as the oxidizing agent, an aldose is oxidized to a dicarboxylic acid called an **aldaric acid**. Both the aldehyde carbonyl and the terminal $-CH_2OH$ group are oxidized in this reaction.



D-Glucose

D-葡萄糖

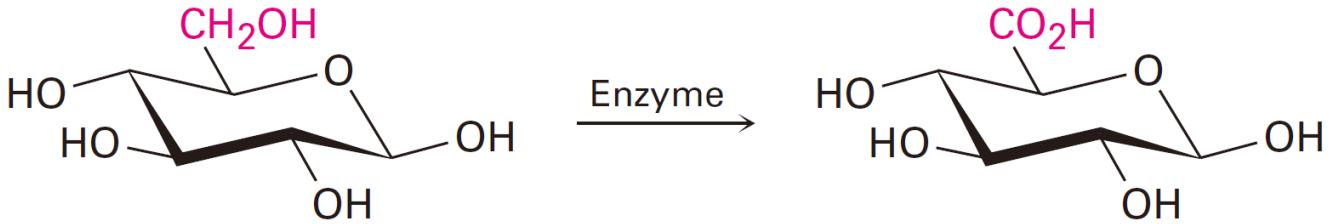
D-Glucaric acid
(an aldaric acid)

D-葡萄糖二酸

25.6 单糖的化学反应

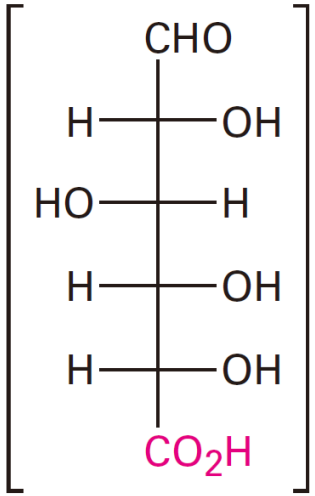
- 当然，生物体内的酶有很强的专一性，在特定氧化酶作用下，糖中的一级醇被氧化为酸，而醛不受影响。

Finally, if only the $-CH_2OH$ end of the aldose is oxidized without affecting the $-CHO$ group, the product is a monocarboxylic acid called a **uronic acid.** The reaction can only be done enzymatically; no chemical reagent is known that can accomplish this selective oxidation in the laboratory.



D-Glucose

D-Glucuronic acid (a uronic acid)



D-葡萄糖

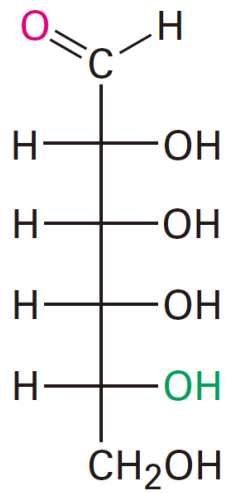
D-葡萄糖醛酸

25.6 单糖的化学反应

- 练习

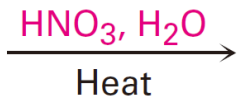
Problem 25.19

D-Glucose yields an optically active aldaric acid on treatment with HNO_3, but D-allose yields an optically inactive aldaric acid. Explain.



D-Allose

D-阿洛糖

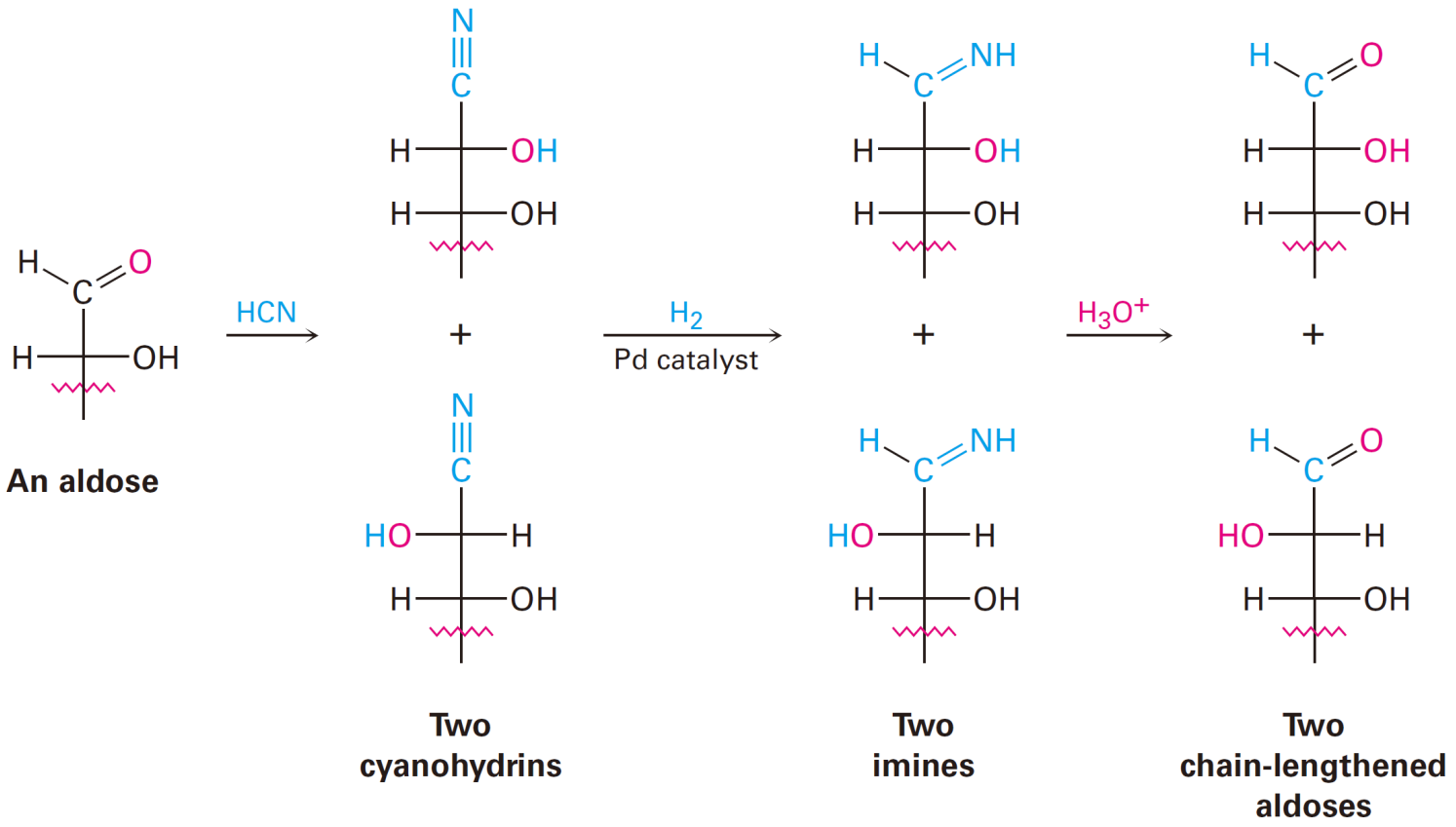


非光学活性的醛糖二酸

25.6 单糖的化学反应

- 克利安尼 - 费歇尔合成（Kiliani-Fischer 合成）是糖化学中一个常用的增碳反应。

Chain Lengthening: The Kiliani–Fischer Synthesis

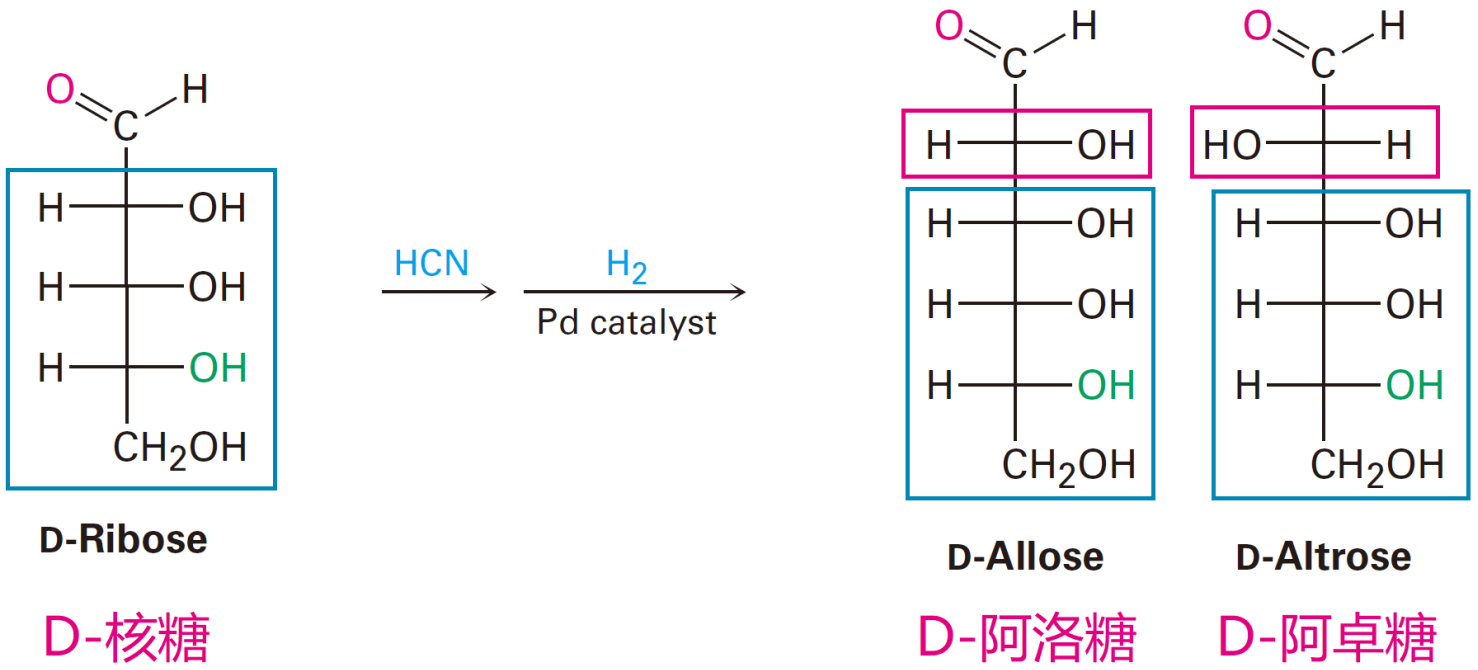


25.6 单糖的化学反应

- 练习

Problem 25.21

What product(s) would you expect from Kiliani–Fischer reaction of D-ribose?



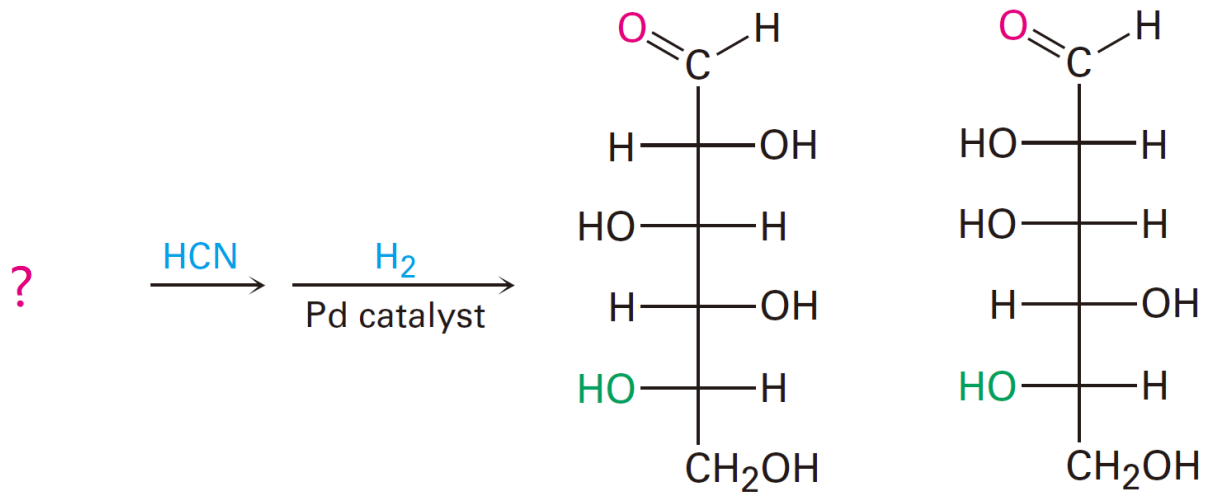
D-核糖　　D-阿洛糖　　D-阿卓糖

25.6 单糖的化学反应

- 练习

Problem 25.22

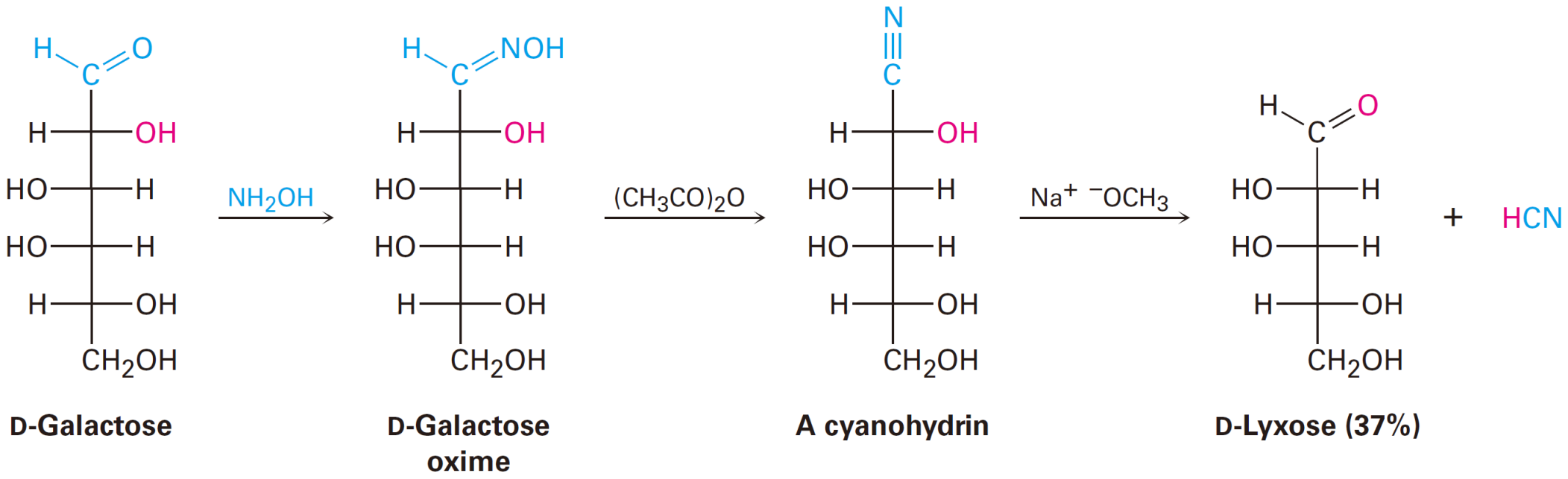
What aldopentose would give a mixture of L-gulose and L-idose on Kiliani–Fischer chain extension?



25.6 单糖的化学反应

- 佛尔递降反应 (Wohl degradation) 是糖化学中使醛糖碳链缩短的常用反应之一，由 Alfred Wohl 于 1893 年发现

Chain Shortening: The Wohl Degradation

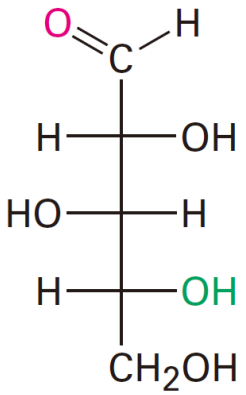


25.6 单糖的化学反应

- 练习

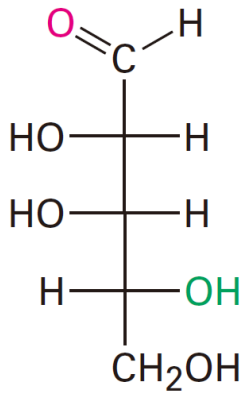
Problem 25.23

Two of the four D aldopentoses yield D-threose on Wohl degradation. What are their structures?



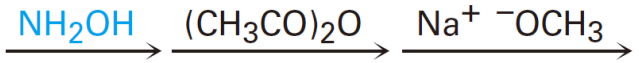
D-Xylose

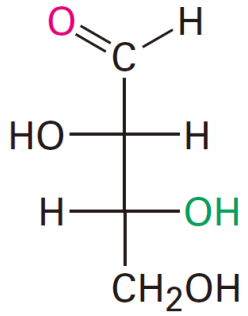
D-木糖



D-Lyxose

D-来苏糖

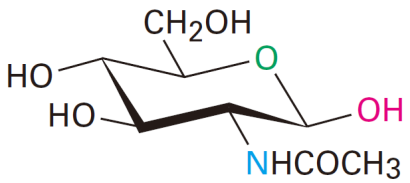


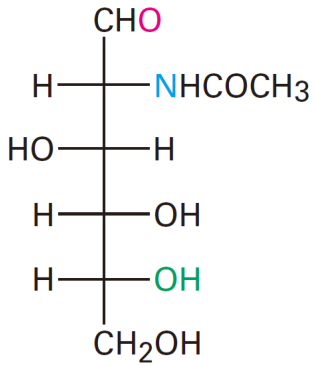


D-Threose

D-苏阿糖

25.7 八种重要的单糖



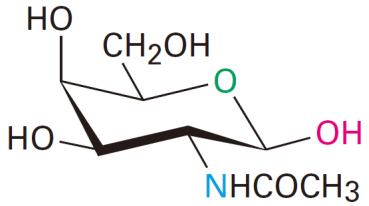


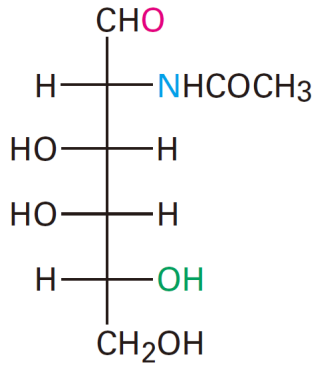
***N*-Acetyl-D-glucosamine (2-acetamido-2-deoxy-D-glucose)**

N-乙酰基氨基葡萄糖

(维骨力)

(膝盖)关节修复



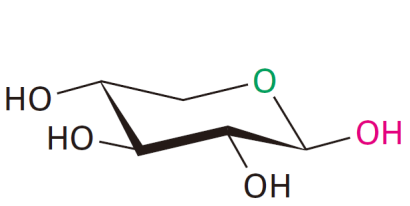


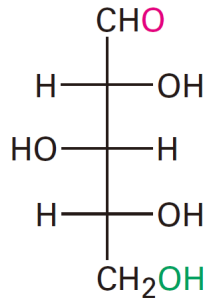
***N*-Acetyl-D-galactosamine (2-acetamido-2-deoxy-D-galactose)**

N-乙酰基氨基半乳糖

(软骨糖胺)

构成细胞的糖蛋白

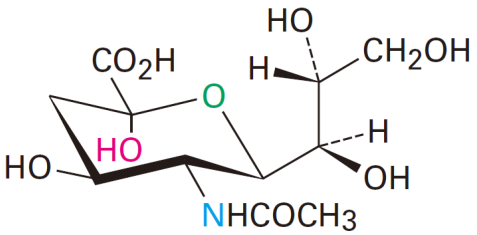


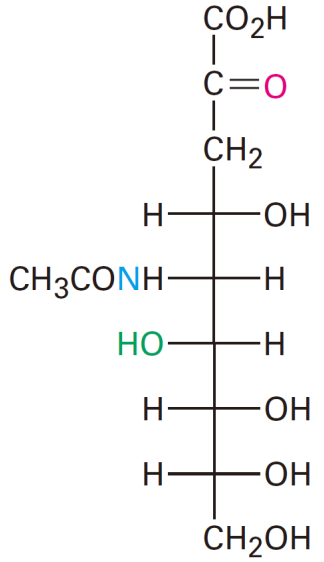


D-Xylose

木糖

无热量甜味剂





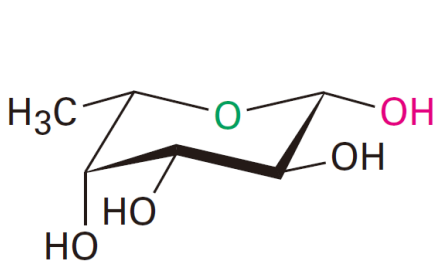
***N*-Acetyl-D-neuraminic acid**

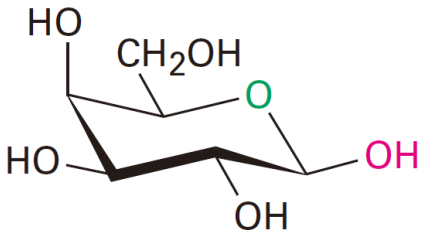
N-乙酰基甘露糖胺丙酮酸

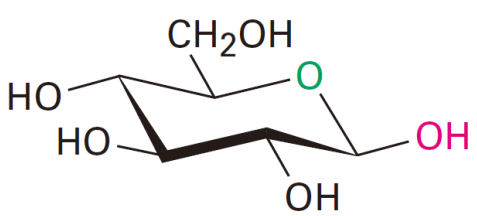
(神经氨酸)

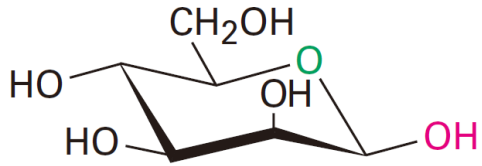
糖蛋白和神经节苷脂

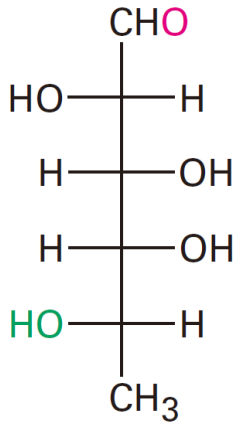
25.7 八种重要的单糖







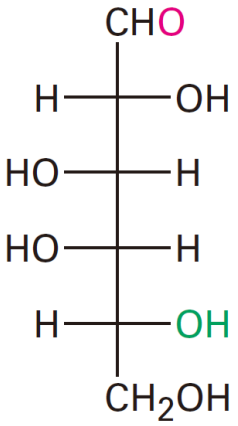




L-Fucose
(6-deoxy-L-galactose)

岩藻糖

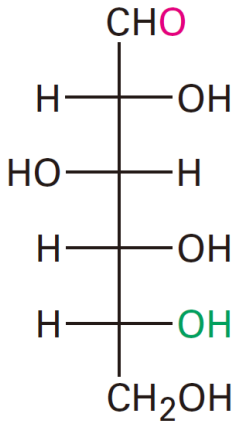
神经传导 免疫调节



D-Galactose

半乳糖

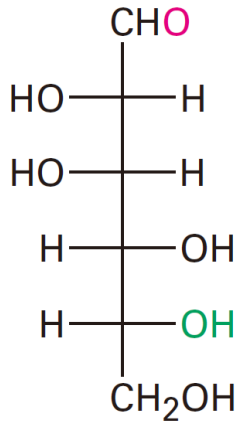
乳糖的组成部分



D-Glucose

葡萄糖

能量来源



D-Mannose

甘露糖

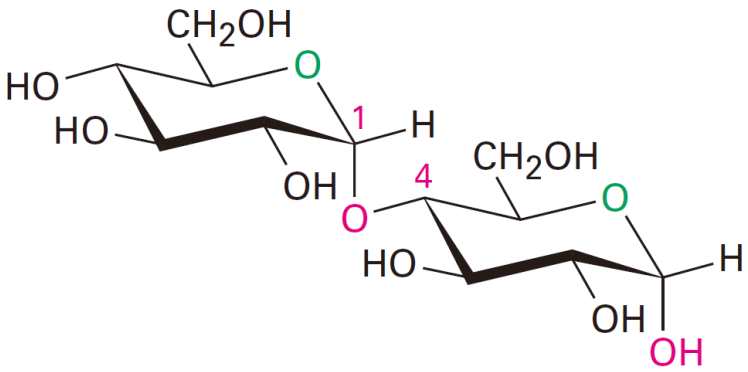
合成糖蛋白 调节免疫系统

25.8 二糖

- 二糖，顾名思义，它水解后得到两个单糖。如下图中麦芽糖和纤维二糖。它们水解后都得到两个葡萄糖。

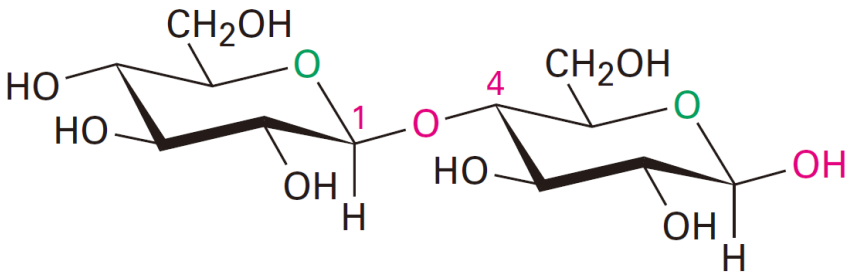
Maltose and Cellobiose





Maltose, a 1→4-α-glycoside 1,4-alpha 糖苷键
[4-*O*-(α-D-glucopyranosyl)-α-D-glucopyranose]

麦芽糖



Cellobiose, a 1→4-β-glycoside 1,4-beta 糖苷键
[4-*O*-(β-D-glucopyranosyl)-β-D-glucopyranose]

纤维二糖

咀嚼馒头会有甜味是为什么？

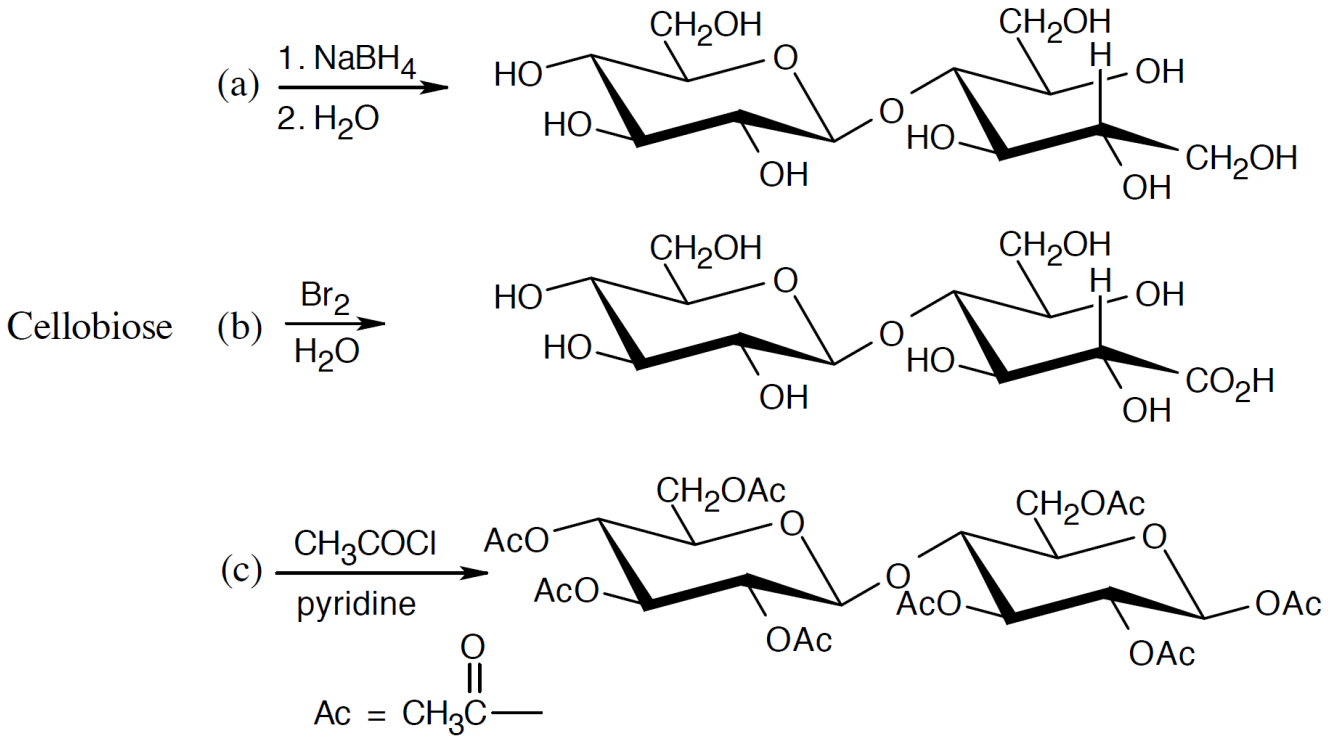
25.8 二糖

- 练习

Problem 25.25

Show the product you would obtain from the reaction of cellobiose with the following reagents:

(a) $NaBH_4$ **(b)** Br_2, H_2O **(c)** CH_3COCl, pyridine

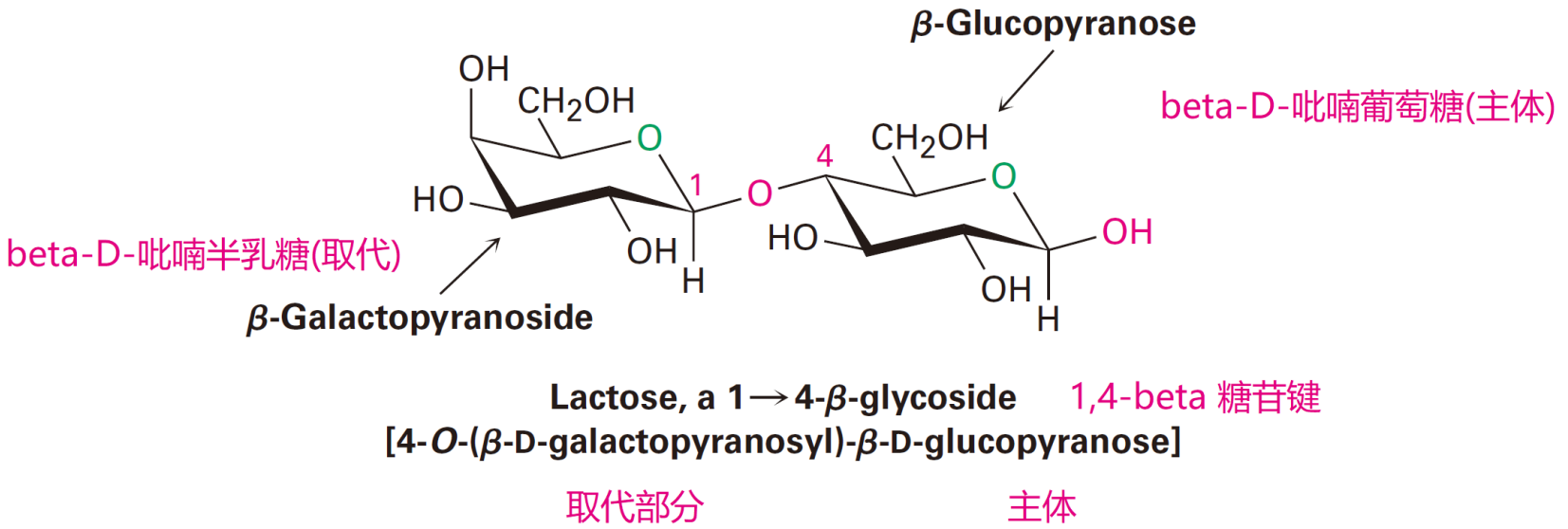


25.8 二糖

- 乳糖水解后得到一分子葡萄糖和一分子半乳糖。

Lactose 乳糖

Lactose is a disaccharide that occurs naturally in both human and cow's milk. It is widely used in baking and in commercial milk formulas for infants.



Lactose, a 1→4-β-glycoside 1,4-beta 糖苷键
[4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranose]

取代部分 主体



为什么有人喝牛奶会拉肚子？怎么办？

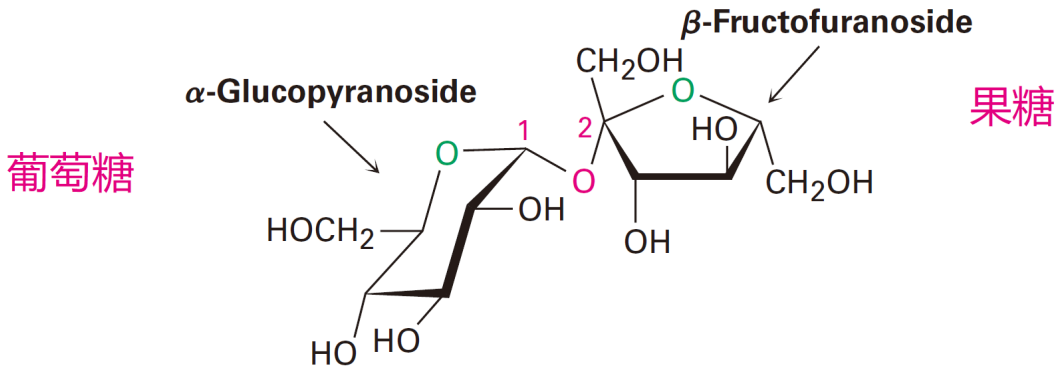
答：可以喝酸奶...

25.8 二糖

- 蔗糖，由一个葡萄糖和一个果糖组成。红糖是粗制蔗糖，白糖是精制蔗糖。注意，这里两个糖是由 1, 2 糖苷键连接。

Sucrose 蔗糖

Sucrose, or ordinary table sugar, is probably the most abundant pure organic chemical in the world. Whether from sugar cane (20% sucrose by weight) or sugar beets (15% by weight), and whether raw or refined, all table sugar is sucrose.



Sucrose, a 1→2-glycoside
[2-*O*-(α-D-glucopyranosyl)-β-D-fructofuranoside]



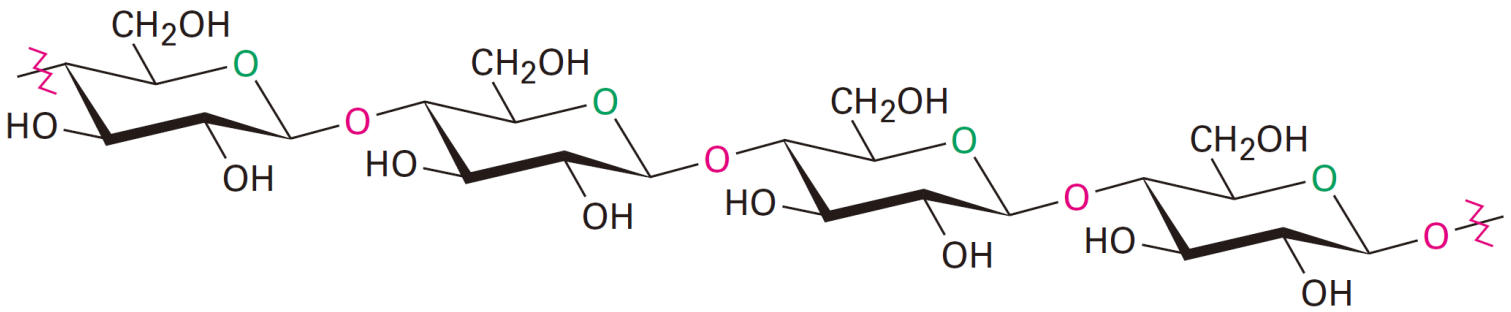
红糖比白糖甜度低，营养更全面。

25.9 多糖

- 纤维素，水解以后得到寡聚纤维素，彻底水解得到葡萄糖。棉花是自然界中最纯的纤维素。纤维素中葡萄糖的连接方式是 1, 4-beta 糖苷键。

Cellulose

Cellulose consists of several thousand D-glucose units linked by 1→4-β-glycoside bonds like those in cellobiose. Different cellulose molecules then interact to form a large aggregate structure held together by hydrogen bonds.



Cellulose, a 1→4-*O*-(β-D-glucopyranoside) polymer

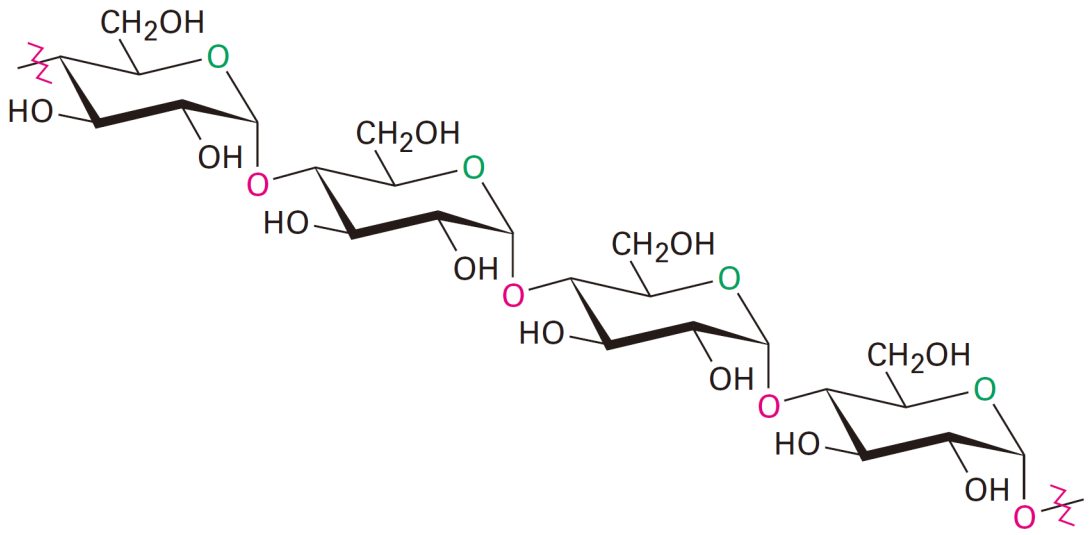


25.9 多糖

- 淀粉水解以后得到麦芽糖（二糖），彻底水解得到葡萄糖。淀粉中葡萄糖的连接方式是 1, 4-alpha 糖苷键。

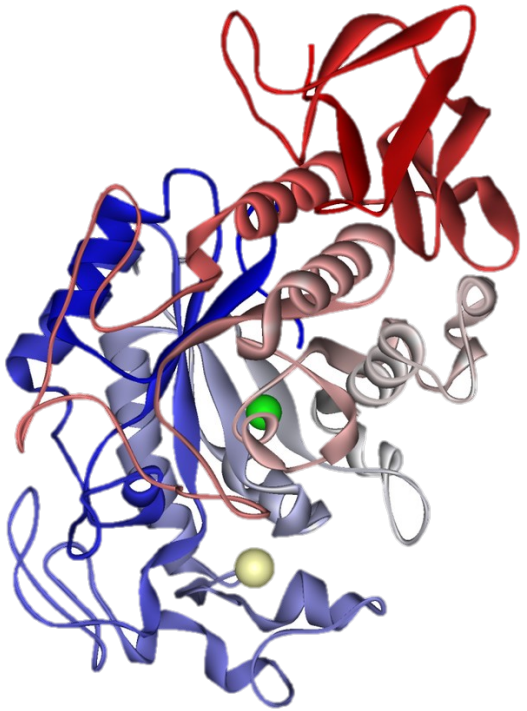
Starch and Glycogen

Potatoes, corn, and cereal grains contain large amounts of *starch,* a polymer of glucose in which the monosaccharide units are linked by 1→4-α-glycoside bonds like those in maltose. Starch can be separated into two fractions: amylose and amylopectin. Amylose accounts for about 20% by weight of starch and consists of several hundred glucose molecules linked together by 1→4-α-glycoside bonds.





同样是多糖，为什么人只能吃淀粉，而不能吃纤维素呢？而牛羊等食草动物可以？



人类唾液中的 α– 淀粉酶



链丝菌属水解纤维素酶

作业

- 25.35, 25.38, 25.43, 25.44, 25.49, 25.61, 25.66, 25.67ab