Hogeschool van Arnhem en Nijmegen
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# Course bi5b chemistry: Chapter 21 carbohydrates (koolwaterstoffen)



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# Reference

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Fundamentals of General, Organic, and Biological

# Chemistry

Seventh Edition

John McMurry
*Cornell University*

David S. Ballantine
*Northern Illinois University*

Carl A. Hoeger
*University of California, San Diego*

Virginia E. Peterson
*University of Missouri, Columbia*

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(Reference: Chapter 21 from McMurry et al.)

# Chapter goals

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## CHAPTER GOALS

1. **What are the different kinds of carbohydrates?**
   **THE GOAL:** Be able to define monosaccharides, disaccharides, and polysaccharides, and recognize examples. (◀◀◀ A.)
2. **Why are monosaccharides chiral, and how does this influence the numbers and types of their isomers?**
   **THE GOAL:** Be able to identify the chiral carbon atoms in monosaccharides, predict the number of isomers for different monosaccharides, and identify pairs of enantiomers. (◀◀◀ B.)
3. **What are the structures of monosaccharides, and how are they represented in written formulas?**
   **THE GOAL:** Be able to explain relationships among open-chain and cyclic monosaccharide structures, describe the isomers of monosaccharides, and show how they are represented by Fischer projections and cyclic structural formulas. (◀◀◀ A, B.)
4. **How do monosaccharides react with oxidizing agents and alcohols?**
   **THE GOAL:** Be able to identify reducing sugars and the products of their oxidation, recognize acetals of monosaccharides, and describe glycosidic linkages in disaccharides. (◀◀◀ C, D.)
5. **What are the structures of some important disaccharides?**
   **THE GOAL:** Be able to identify the monosaccharides combined in maltose, lactose, and sucrose, and describe the types of linkages between the monosaccharides. (◀◀◀ A, B, D.)
6. **What are the functions of some important carbohydrates that contain modified monosaccharide structures?**
   **THE GOAL:** Be able to identify the functions of chitin, connective-tissue polysaccharides, heparin, and glycoproteins. (◀◀◀ A.)
7. **What are the structures and functions of cellulose, starch, and glycogen?**
   **THE GOAL:** Be able to describe the monosaccharides and linkages in these polysaccharides, their uses, and their fates in metabolism. (◀◀◀ A, B, D.)

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(Reference: Chapter 21 from McMurry et al.)

# Inhoudsopgave

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(Reference: Chapter 21 from McMurry et al.)

# 21.1 Koolhydraten

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- “Hydraten van koolstof”
- Koolstof omgeven door watermoleculen
- Algemene formule:

$$C_x(H_2O)_y$$

- **Heeft niets met water te maken !!!**

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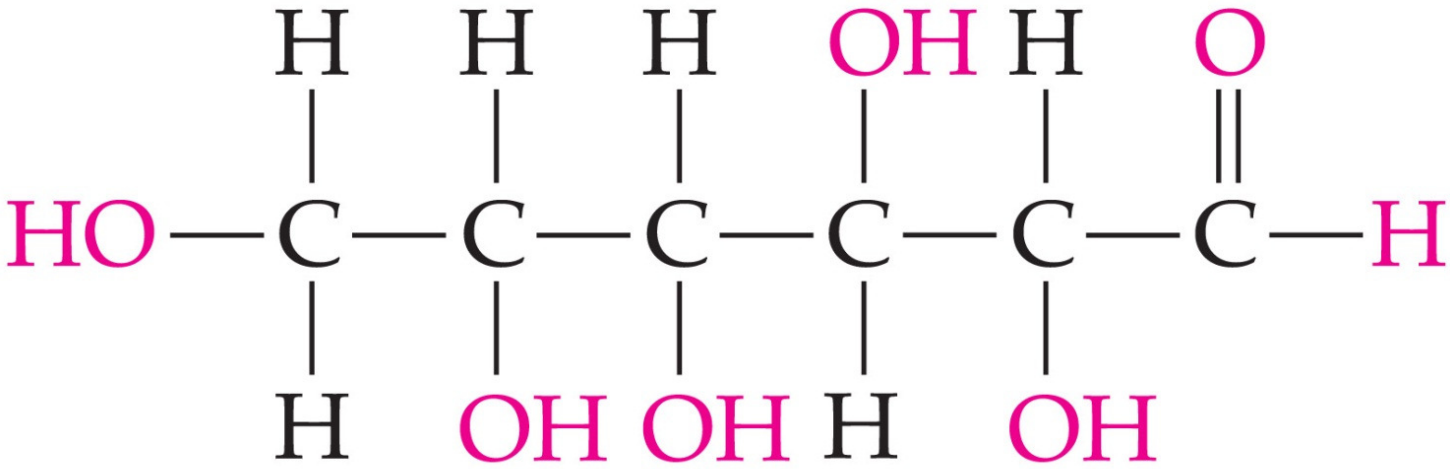
# Glucose




Glucose



$C_6H_{12}O_6$

$C_6(H_2O)_6$



(Reference: Chapter 21 from McMurry et al.)

# 21.1 Koolhydraten

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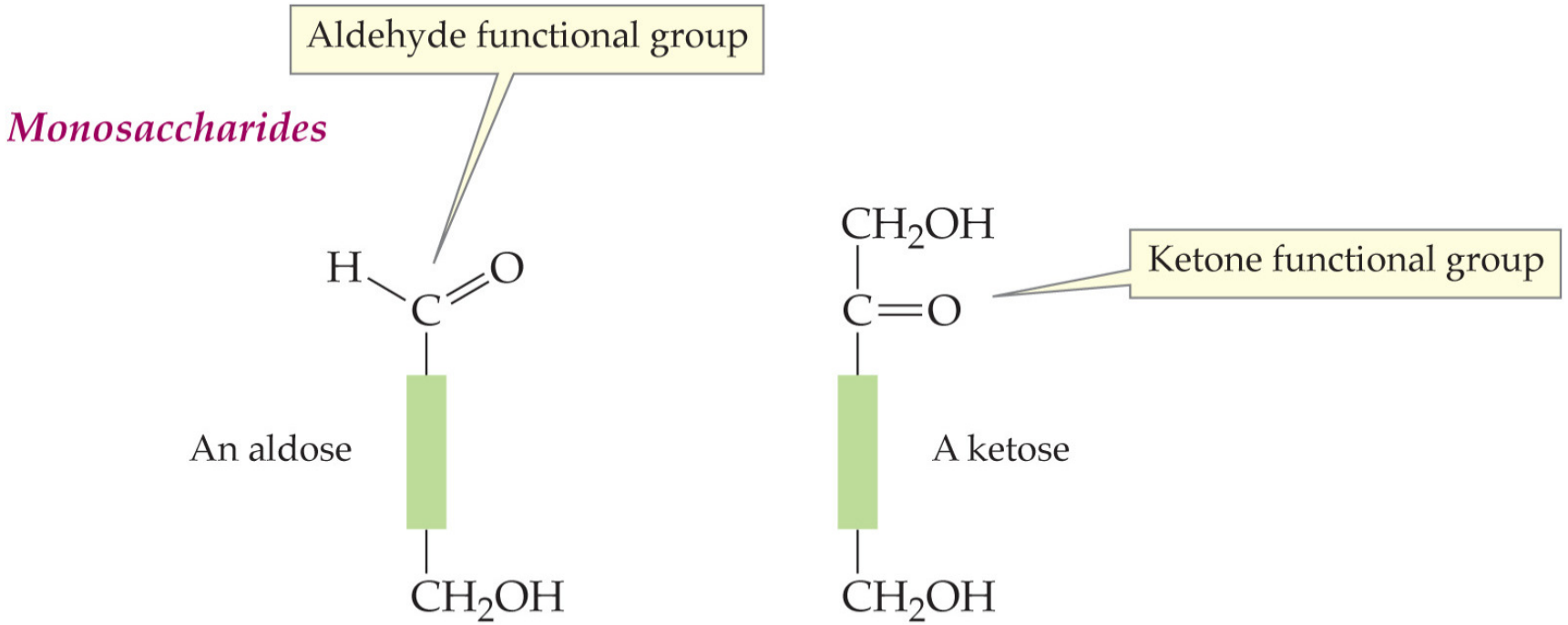
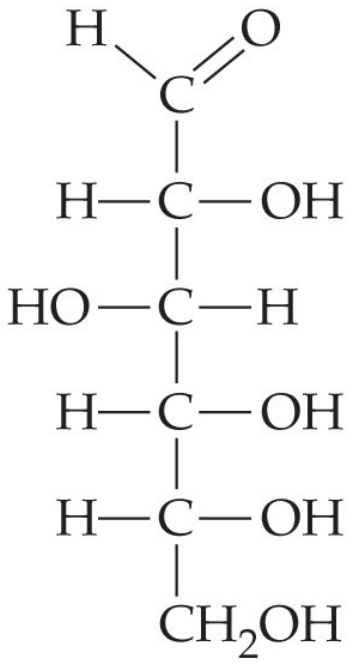
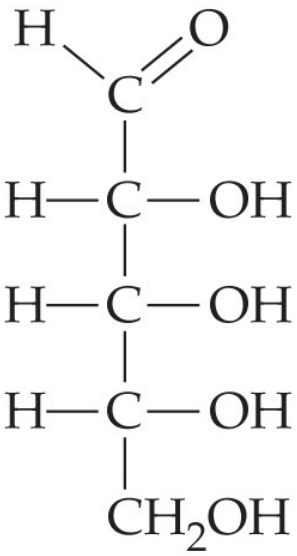
- **polyhydroxy ketonen/aldehydes**
  - **aldose / ketose**
- **monosaccharide**



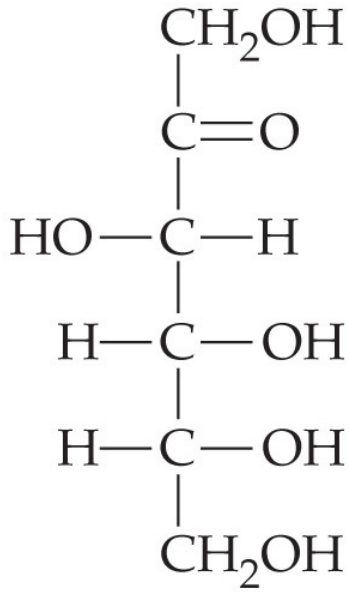
# 21.1 Koolhydraten




Glucose, an aldohexose
(monomer for starch and cellulose;
major source of energy)




Ribose, an aldopentose
(a component of ATP,
coenzymes, and RNA)




Fructose, a ketohexose
(present in corn syrup
and fruit)

# 21.1 Disacharides

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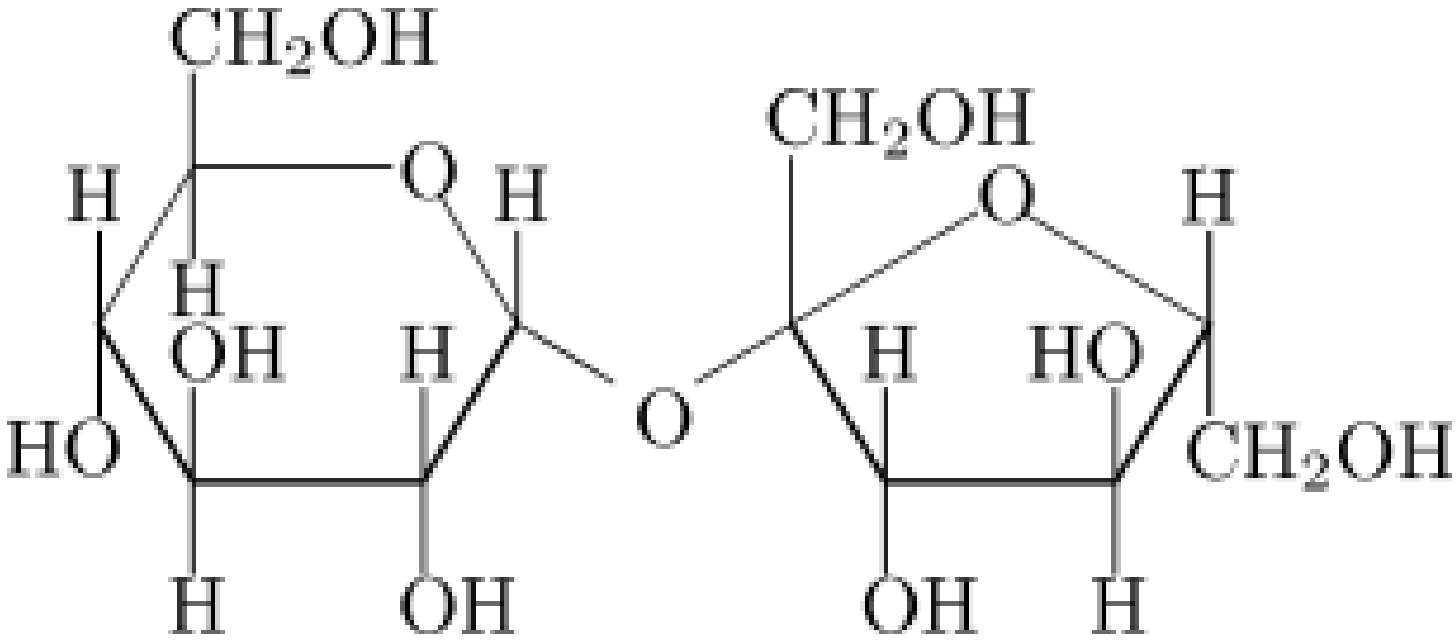
- Opgebouwd uit twee monosacharides
- Sacharose (glucose en fructose)






(Reference: Chapter 21 from McMurry et al.)

# 21.1 Polysacharides

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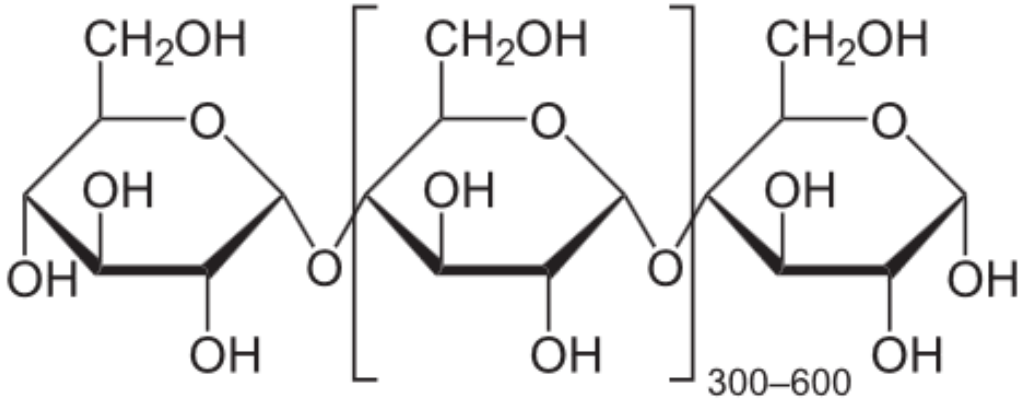
- **polymeer van monosacharides**
  - **zetmeel**
    - ***amylose***
    - **amylopectine**
  - **cellulose**
  - **chitine**
  - **pectine**

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(Reference: Chapter 21 from McMurry et al.)

# 21.1 Worked example 21.1

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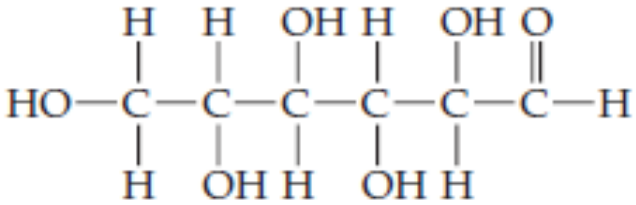
Classify the monosaccharide shown as an aldose or a ketose, and name it according to its number of carbon atoms.



**ANALYSIS** First determine if the monosaccharide is an aldose or a ketose. Then determine the number of carbon atoms present. This monosaccharide is an aldose because an aldehyde group is present. It contains 6 carbon atoms.

**SOLUTION**

The monosaccharide is a 6-carbon aldose, so we refer to it as an aldohexose.

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# 21.1 Problems 21.1 & 21.2

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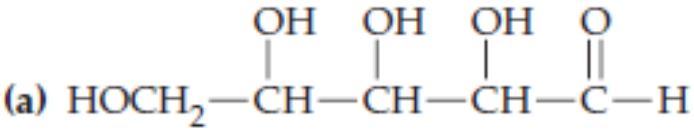
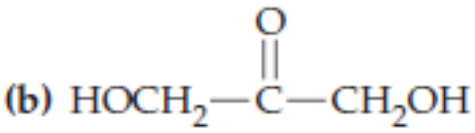
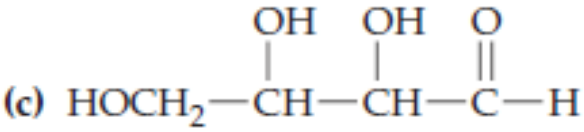
**PROBLEM 21.1**

Classify the following monosaccharides as an aldose or a ketose, and name each according its number of carbon atoms.



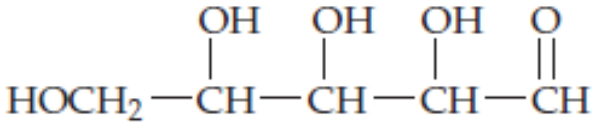




**PROBLEM 21.2**

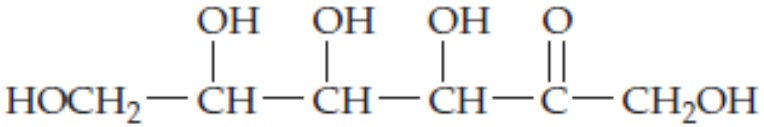
Draw the structures of an aldopentose and a ketohexose.

21.1 (a) aldopentose (b) ketotriose (c) aldotetrose

21.2




An aldopentose




A ketohexose



(Reference: Chapter 21 from McMurry et al.)

# Inhoudsopgave

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(Reference: Chapter 21 from McMurry et al.)

# 21.2 Chirale suikers

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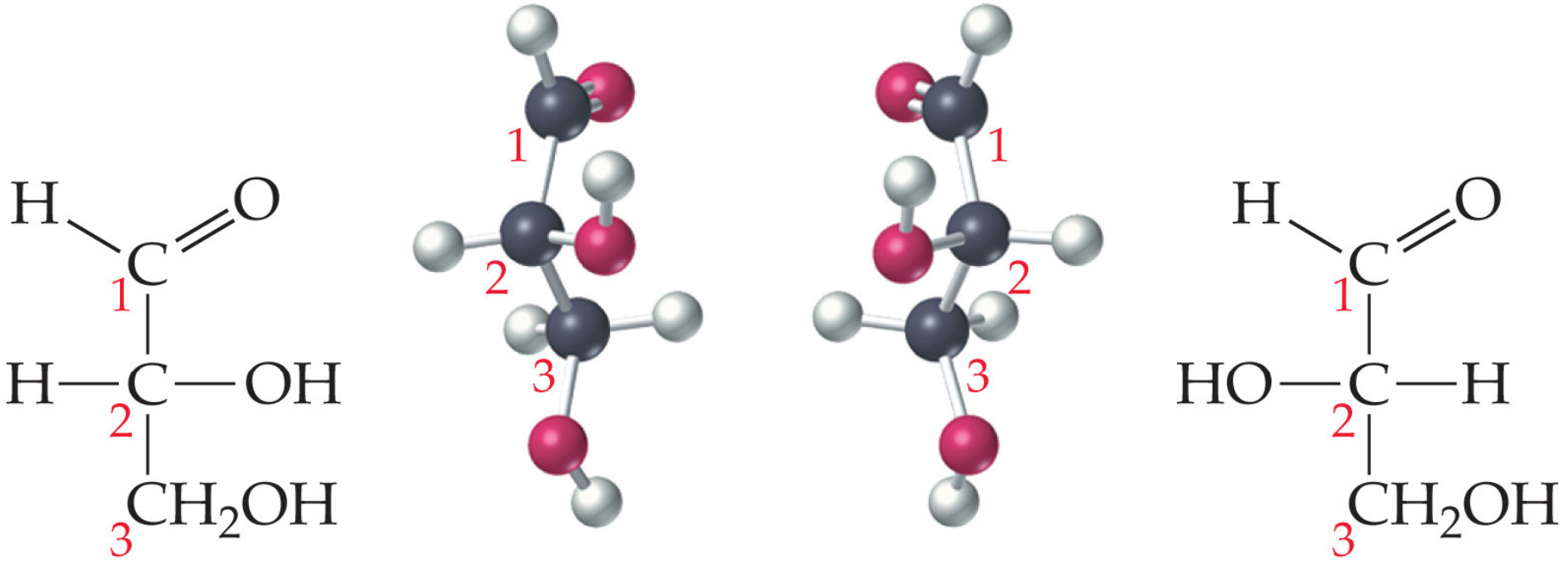
- **Eén chiraal koolstofatoom**




D-Glyceraldehyde
Right-handed

L-Glyceraldehyde
Left-handed

# 21.2 Diastereomeren

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- **Stereo-isomeren**
  - **NIET elkaars spiegelbeeld**
  - **NIET met elkaar tot dekking te brengen**

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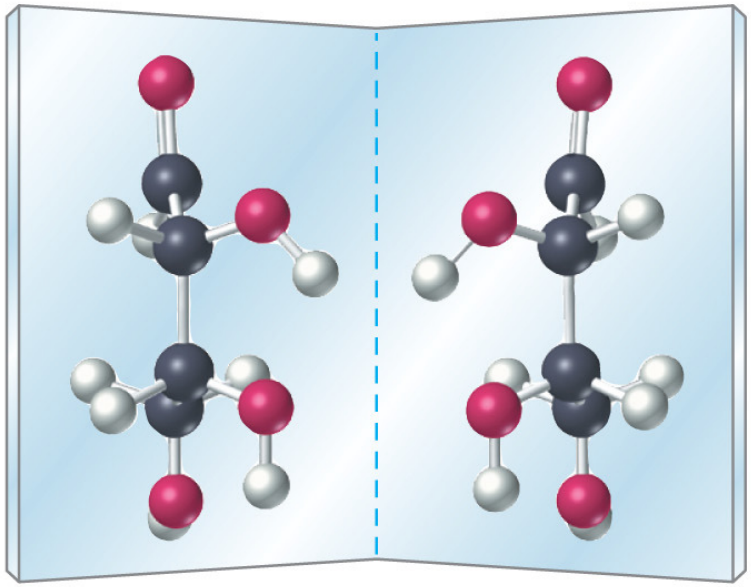
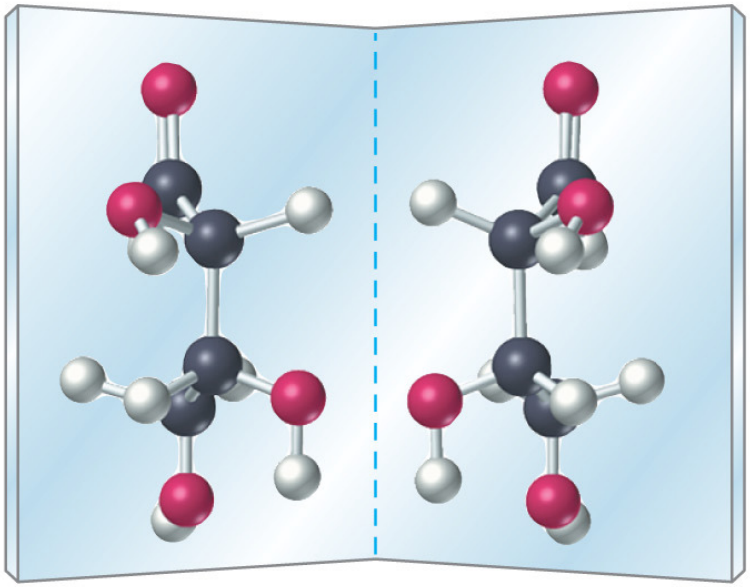
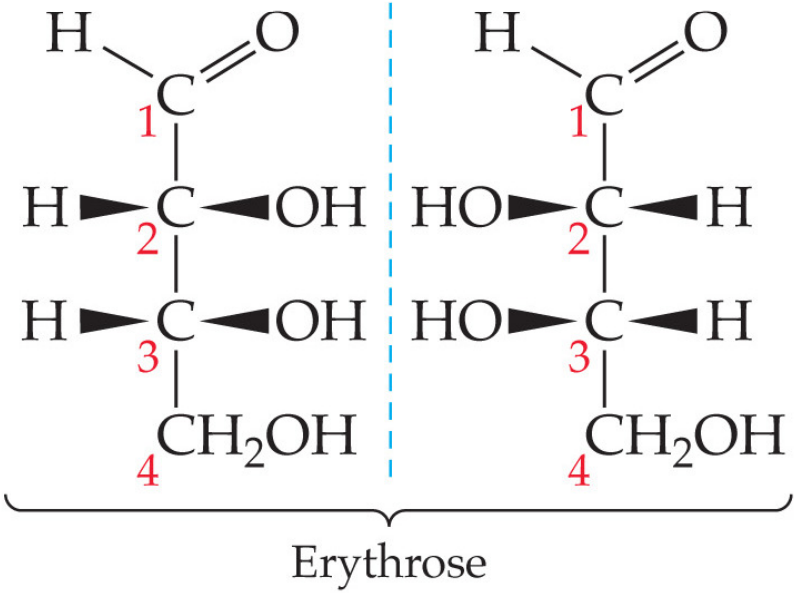
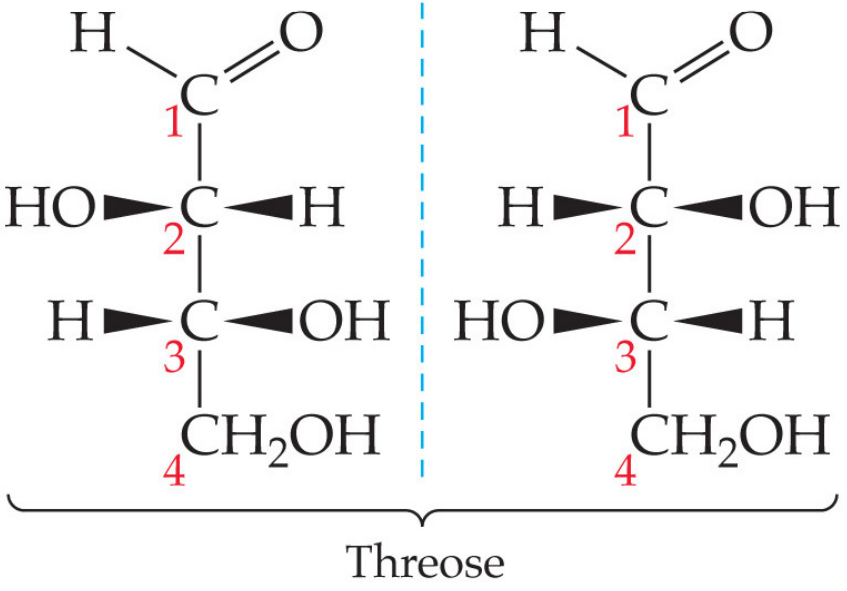
# 21.2 Diastereomeren







# Problems 21.3 – 21.5

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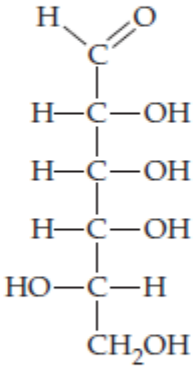
**PROBLEM 21.3**

Aldoheptoses have five chiral carbon atoms. What is the maximum possible number

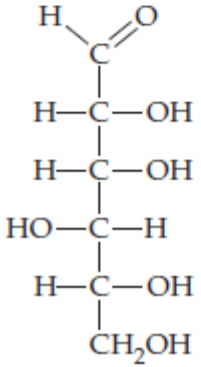
**21.3** 32 stereoisomers **21.4** (d) **21.5** The bottom carbon is not chiral. The orientations of the hydroxyl groups bonded to the chiral carbons must be shown in order to indicate which stereoisomer is pictured.

**PROBLEM 21.5**

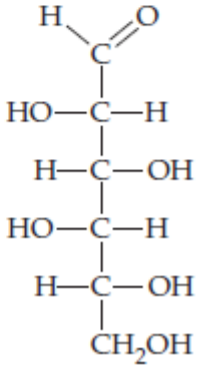
Notice in structures (a)–(d) below that the bottom carbon and its substituents are written as $CH_2OH$ in every case. How does the C in this group differ in each case from the C atoms above it? Why must the locations of the H atoms and —OH groups attached to the carbons between this one and the carbonyl group be shown?



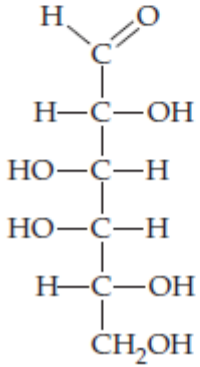
(a)



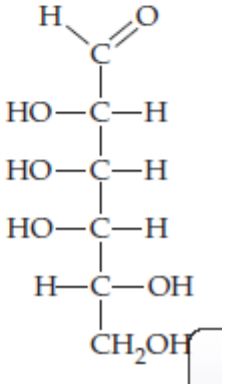
(b)



(c)



(d)



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(Reference: Chapter 21 from McMurry et al.)

# Inhoudsopgave

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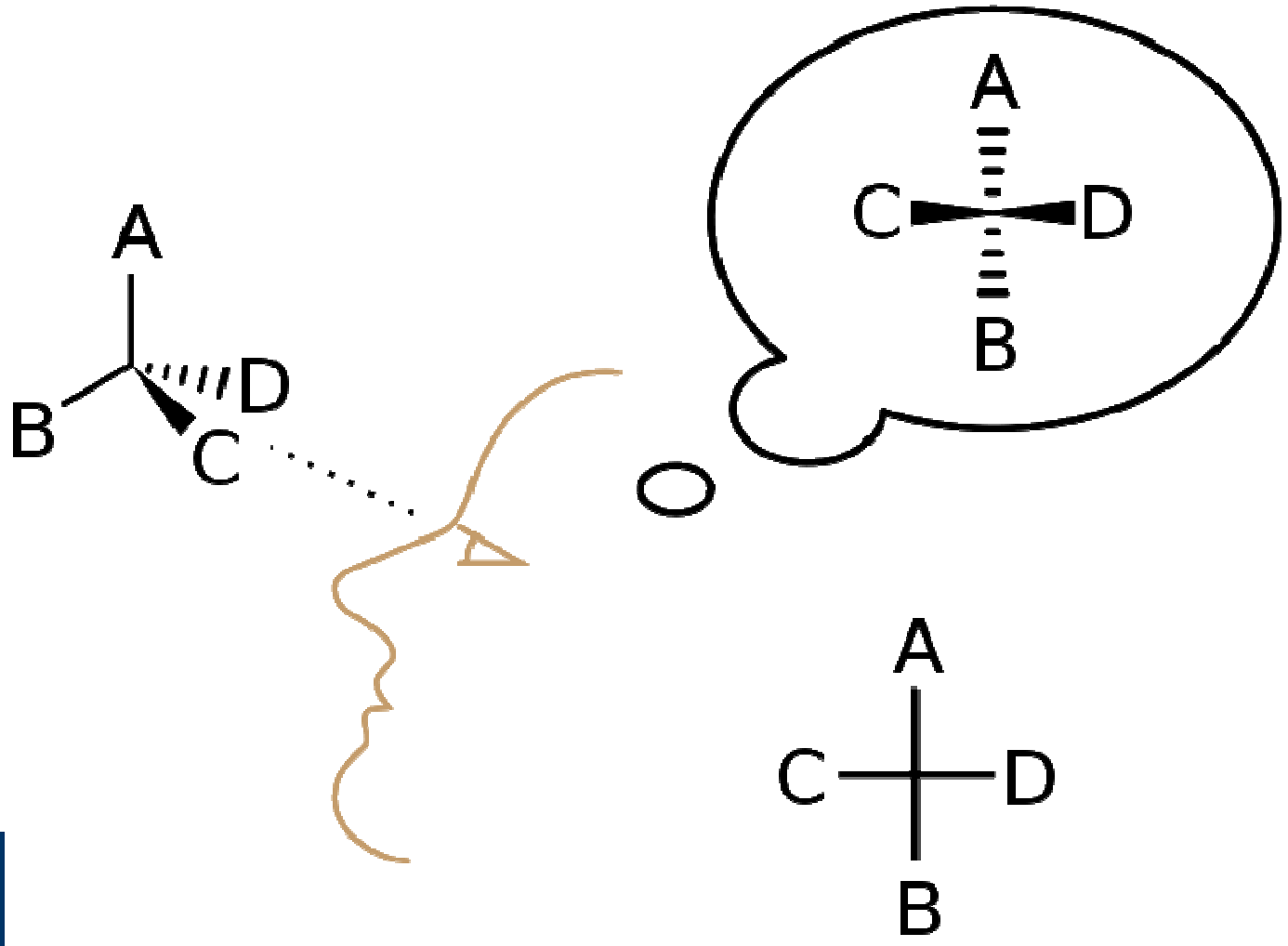
(Reference: Chapter 21 from McMurry et al.)

# 21.3 Fischer-projecties



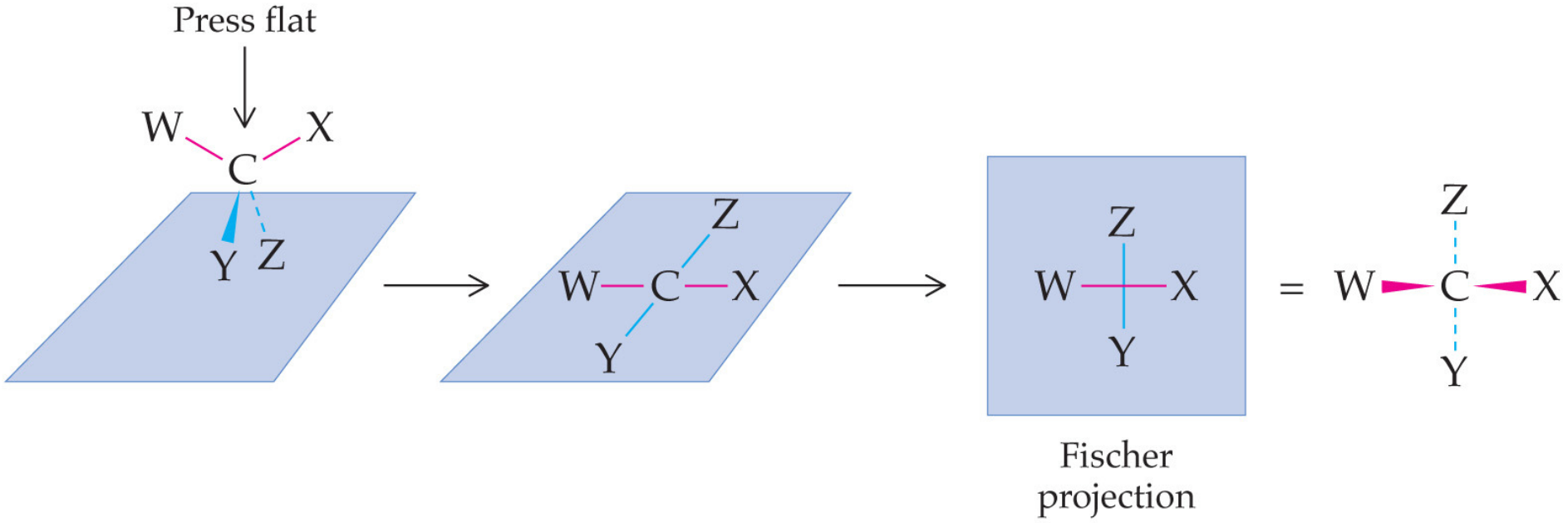





(Reference: Chapter 21 from McMurry et al.)

# 21.3 Fischer-projecties





# 21.3 Fischer-projecties

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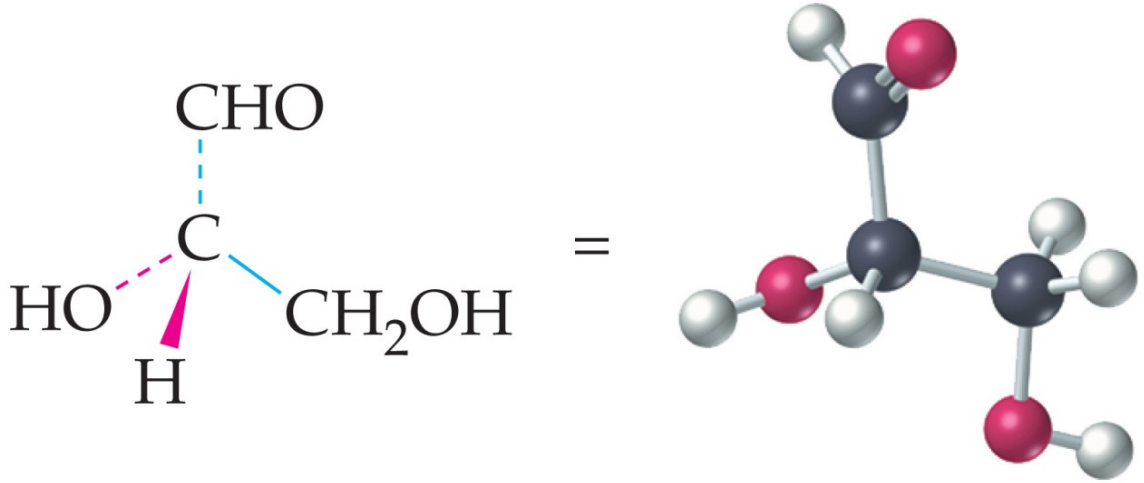
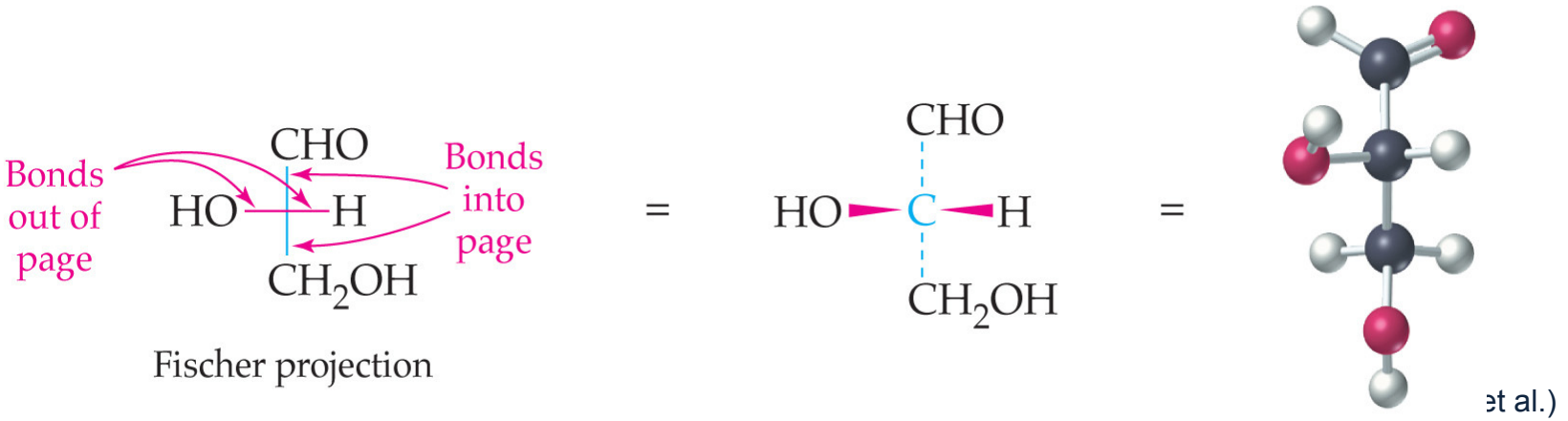


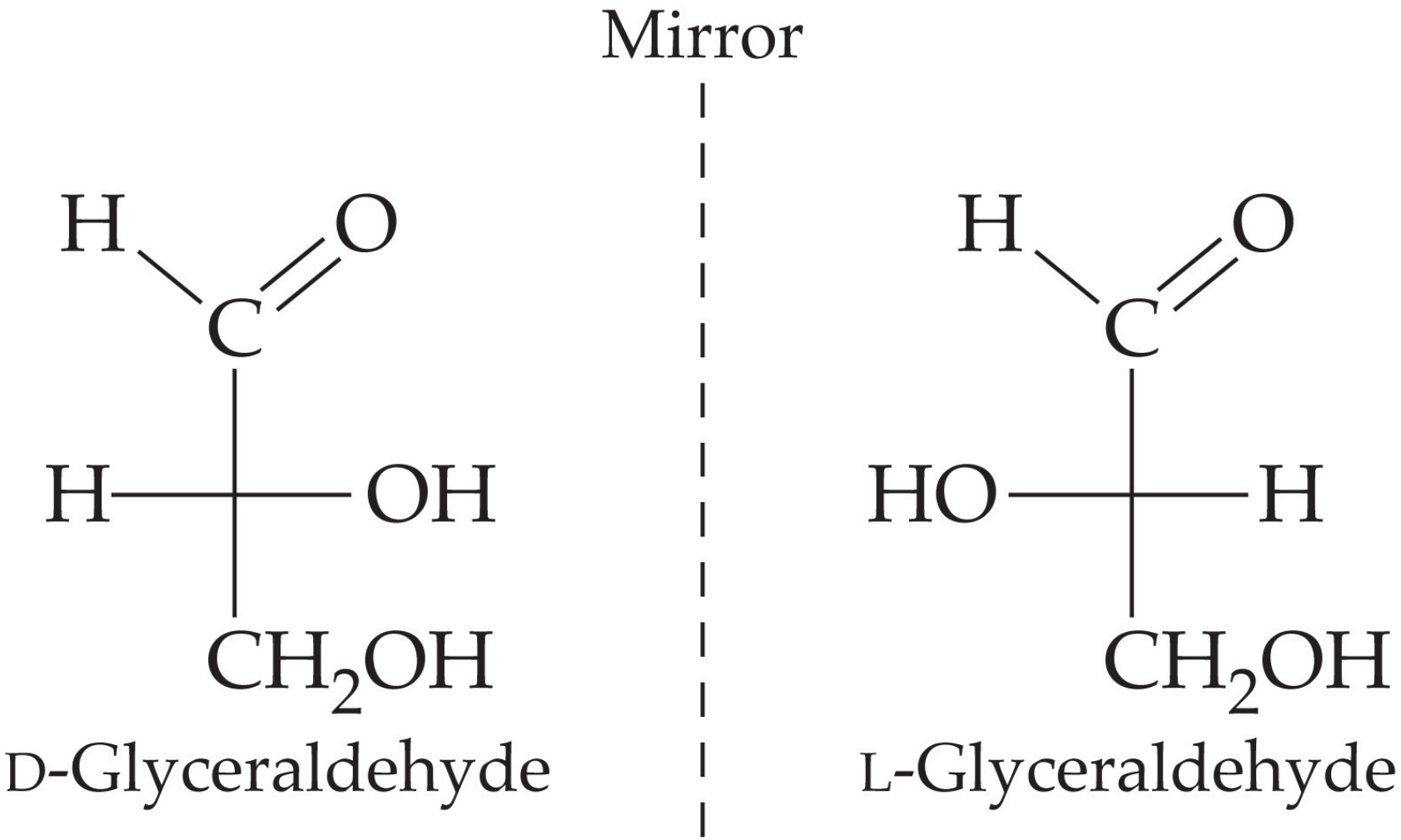



*Fischer projection of a glyceraldehyde enantiomer*



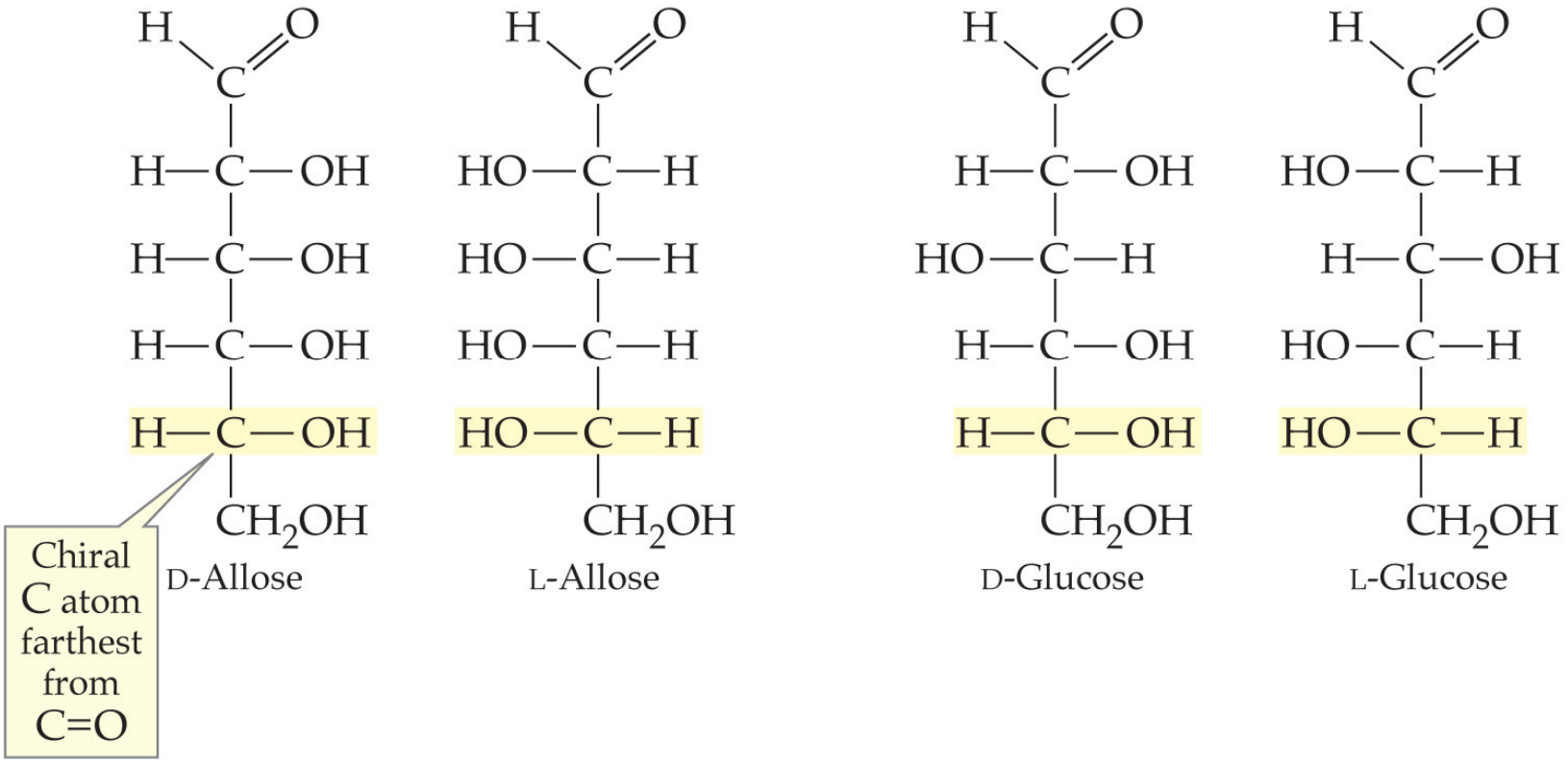

et al.)

# Basis: glyceraldehyde



# Basis: glyceraldehyde

*Two pairs of aldohexose enantiomers*



# Worked example 21.2

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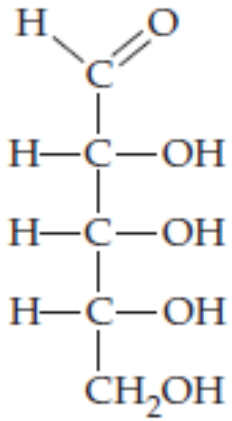
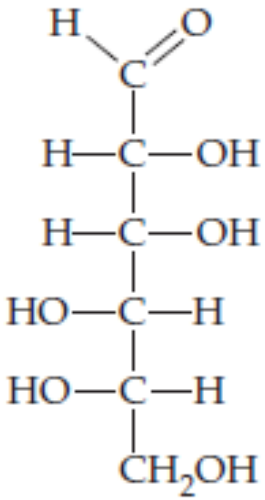
Identify the following monosaccharides as (a) D-ribose or L-ribose, (b) D-mannose or L-mannose.

(a)




(b)




**ANALYSIS** To identify D or L isomers, you must check the location of the —OH group on the chiral carbon atom farthest from the carbonyl group. In a Fischer projection, this is the carbon atom above the bottom one. The —OH group points left in an L enantiomer and right in a D enantiomer.

**SOLUTION**

In (a) the —OH group on the chiral carbon above the bottom of the structure points to the right, so this is D-ribose. In (b) this —OH group points to the left, so this is L-mannose.

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# Problems 21.6

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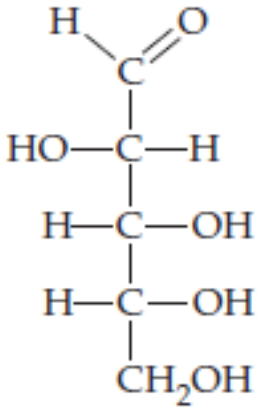
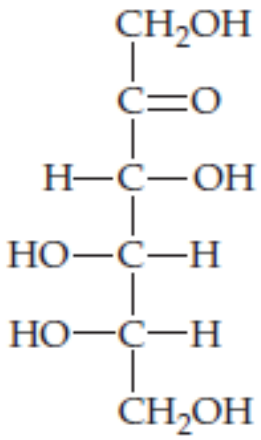
Draw the enantiomer of the following monosaccharides, and in each pair identify the D sugar and the L sugar.

(a)



(b)



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# Problems 21.6

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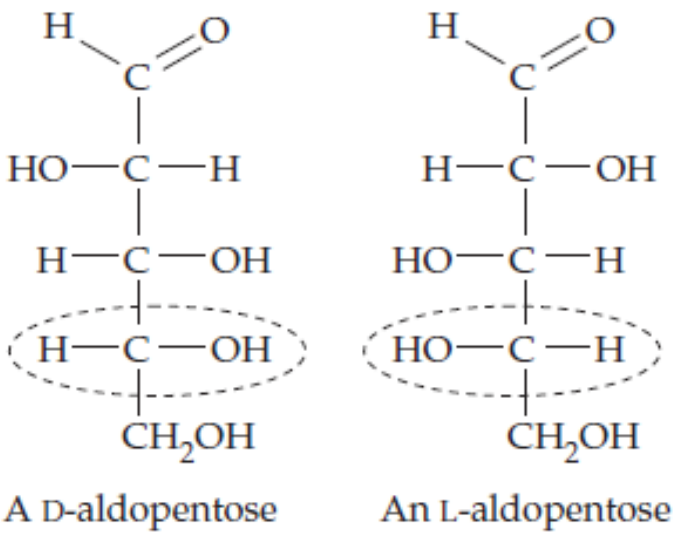
21.6 (a)

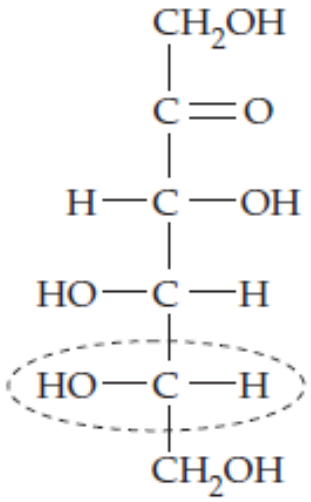


A D-aldopentose

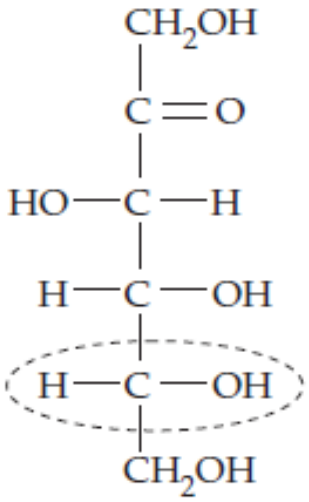


An L-aldopentose

(b)



An L-ketohexose



A D-ketohexose

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(Reference: Chapter 21 from McMurry et al.)

# Inhoudsopgave

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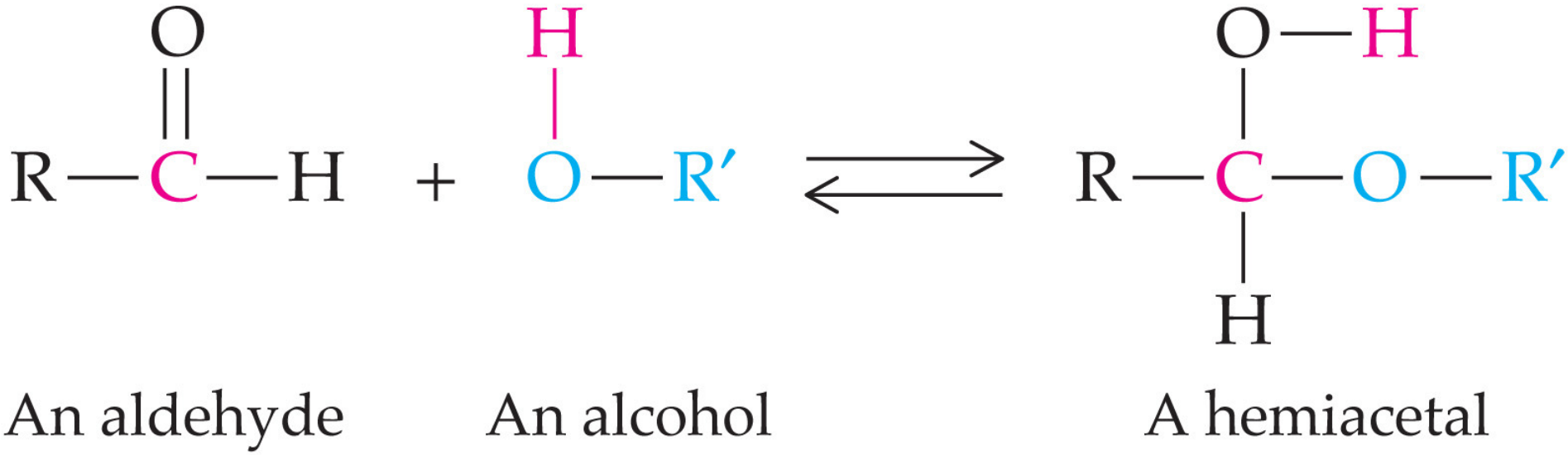
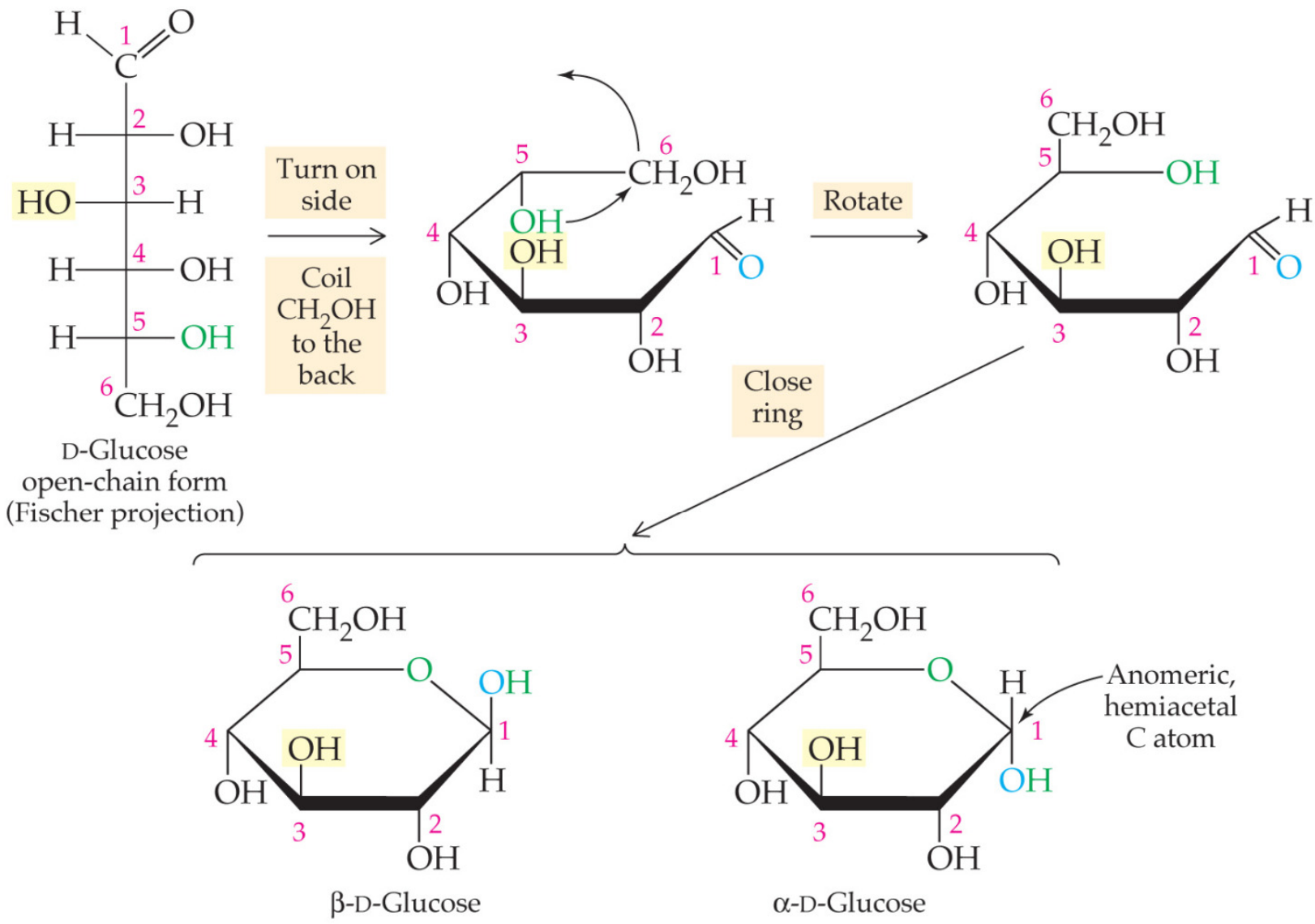
(Reference: Chapter 21 from McMurry et al.)

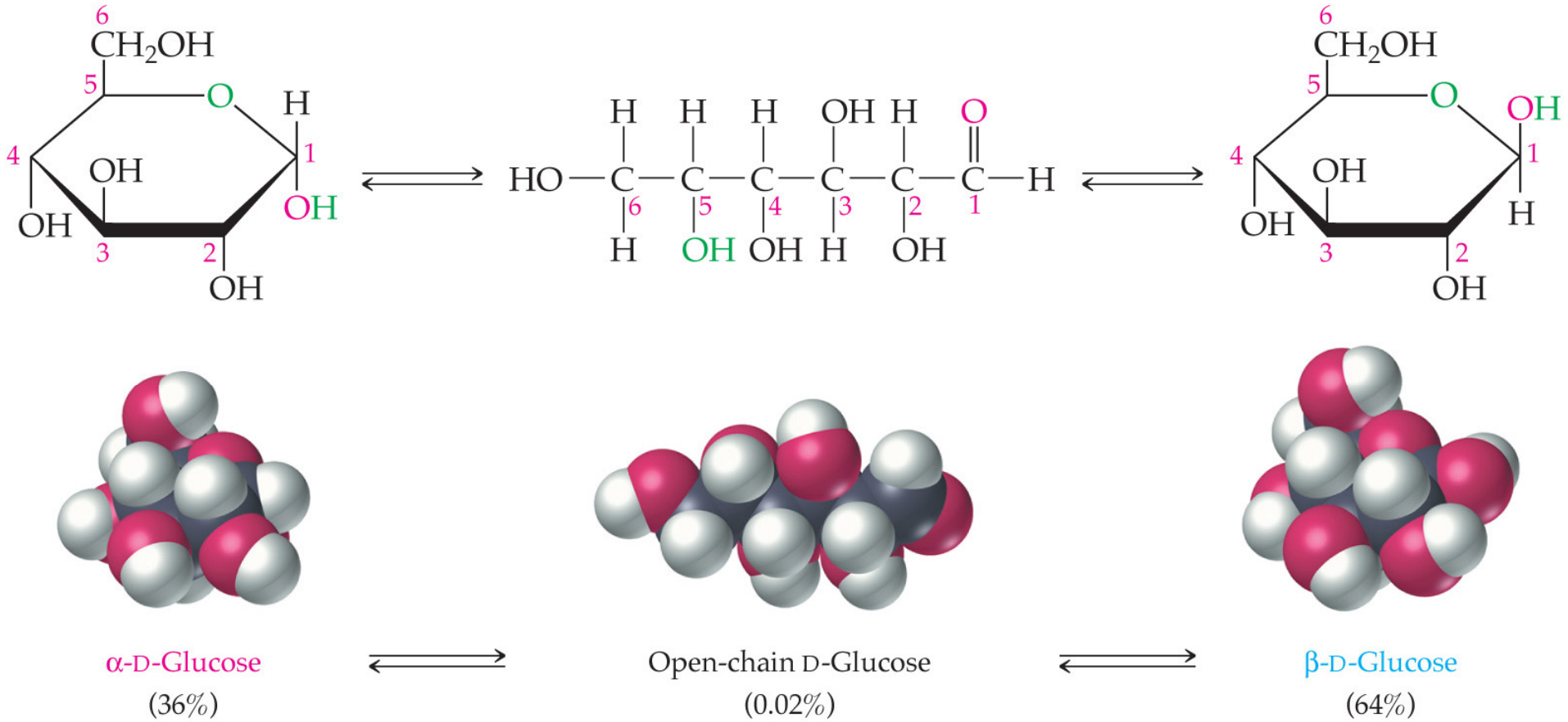
# 21.4 Structuur van monosacharides



# 21.4 Structuur van monosacharides



# 21.4 Mutarotatie



# Worked example 21.3

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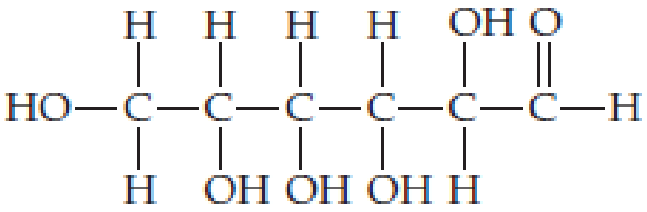
The open-chain form of D-altrose, an aldohexose isomer of glucose, has the following structure. Draw D-altrose in its cyclic hemiacetal form:



D-Altrose

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(Reference: Chapter 21 from McMurry et al.)

# Worked example 21.3

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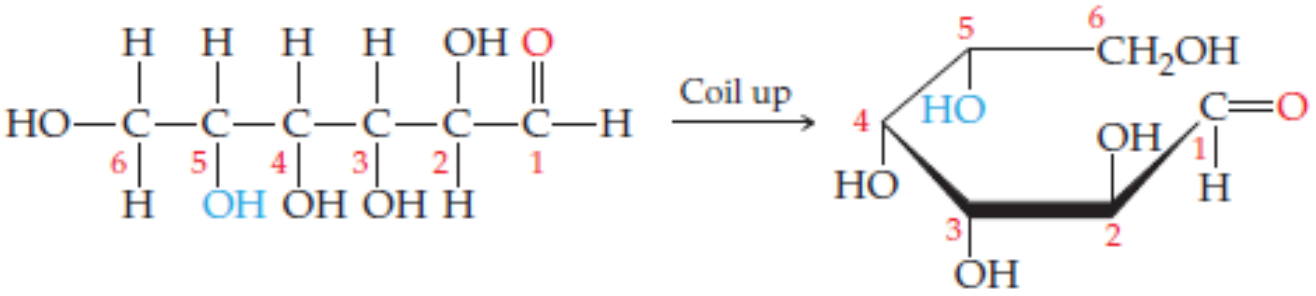
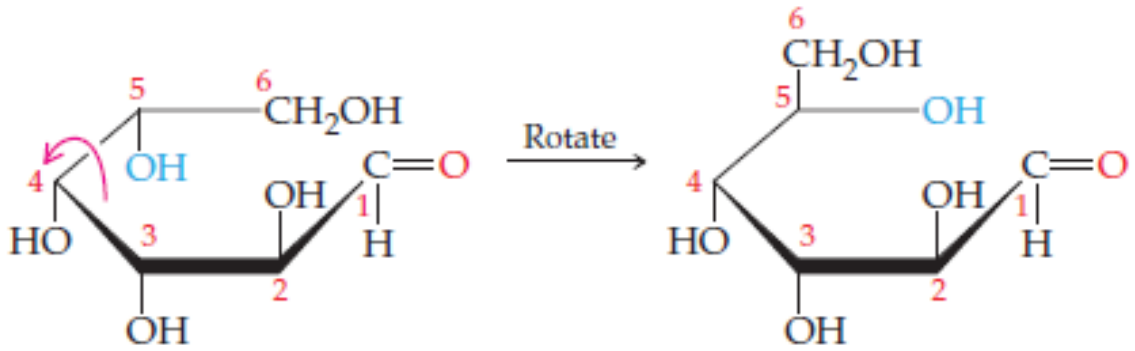
First, coil D-altrose into a circular shape by mentally grasping the end farthest from the carbonyl group and bending it backward into the plane of the paper:




Next, rotate the bottom of the structure around the single bond between C4 and C5 so that the —$CH_2OH$ group at the end of the chain points up and the —OH group on C5 points toward the aldehyde carbonyl group on the right:

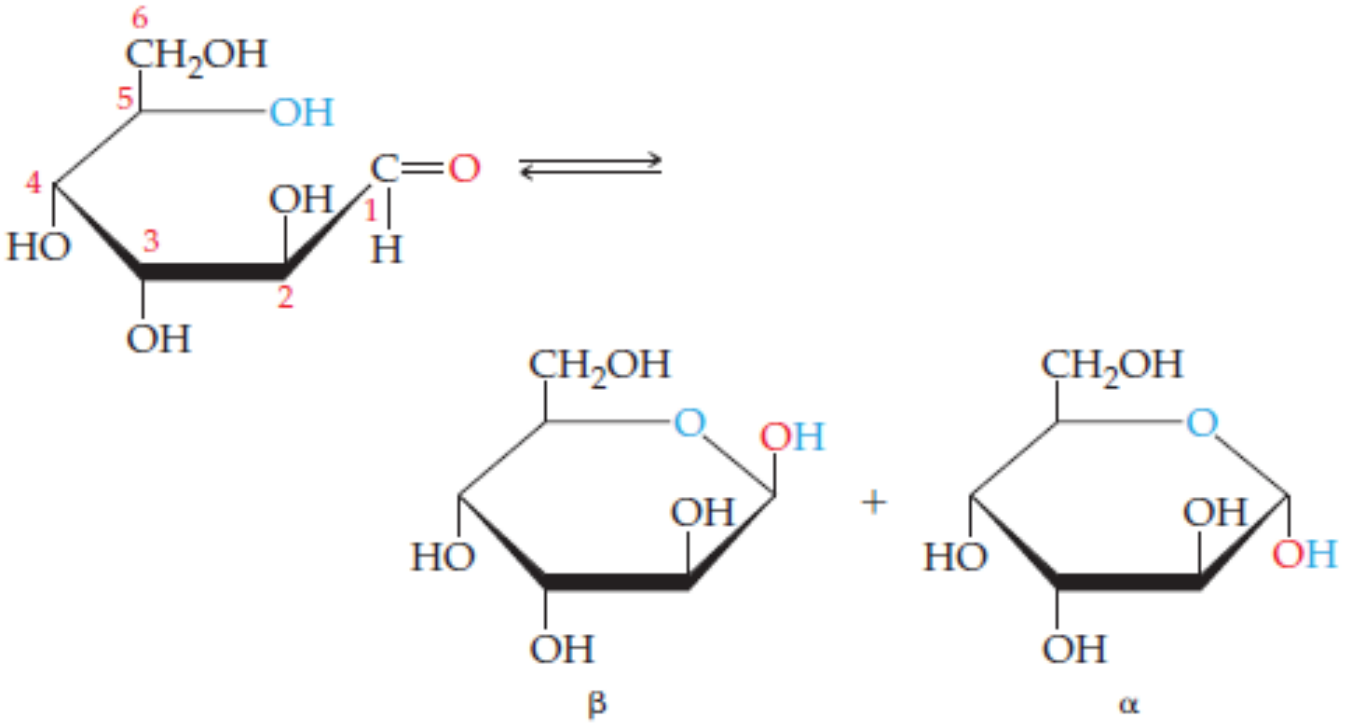





(Reference: Chapter 21 from McMurry et al.)

# Worked example 21.3

Finally, add the —OH group at C5 to the carbonyl C=O to form a hemiacetal ring. The new —OH group formed on C1 can be either up ($\beta$) or down ($\alpha$):






(Reference: Chapter 21 from McMurry et al.)

# Problem 21.8

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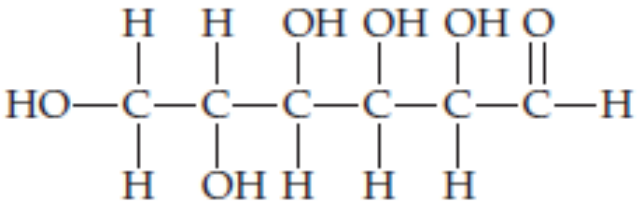
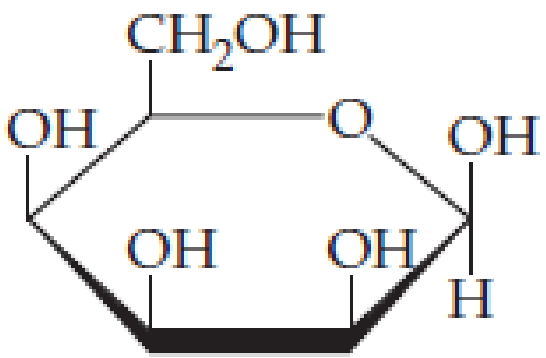
D-Talose, a constituent of certain antibiotics, has the open-chain structure shown below. Draw D-talose in its cyclic hemiacetal form.

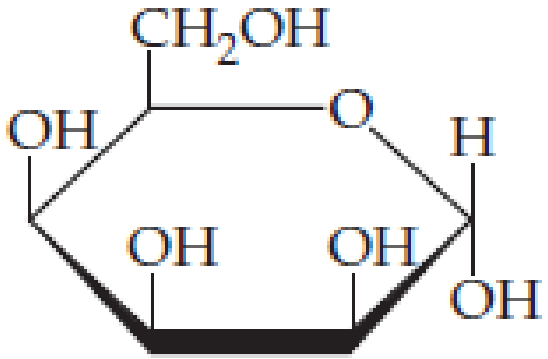



D-Talose

21.8




β-anomer




α-anomer

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(Reference: Chapter 21 from McMurry et al.)

# Problem 21.9

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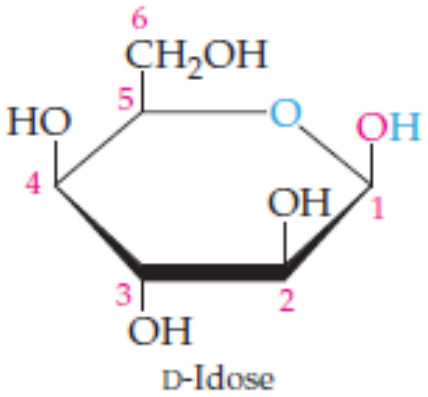
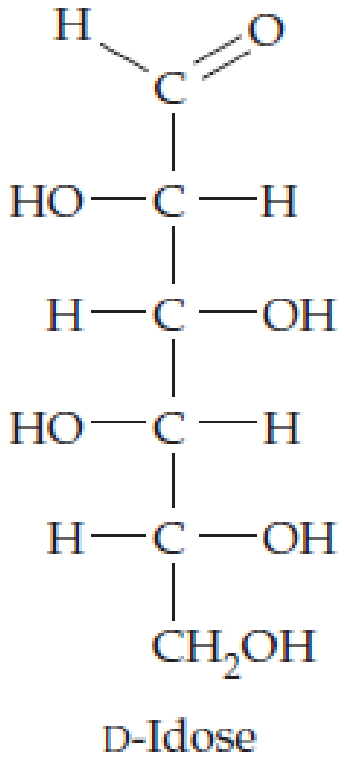
The cyclic structure of D-idose, an aldohexose, is shown below. Convert this to the straight-chain Fischer projection structure.



D-Idose

21.9



D-Idose

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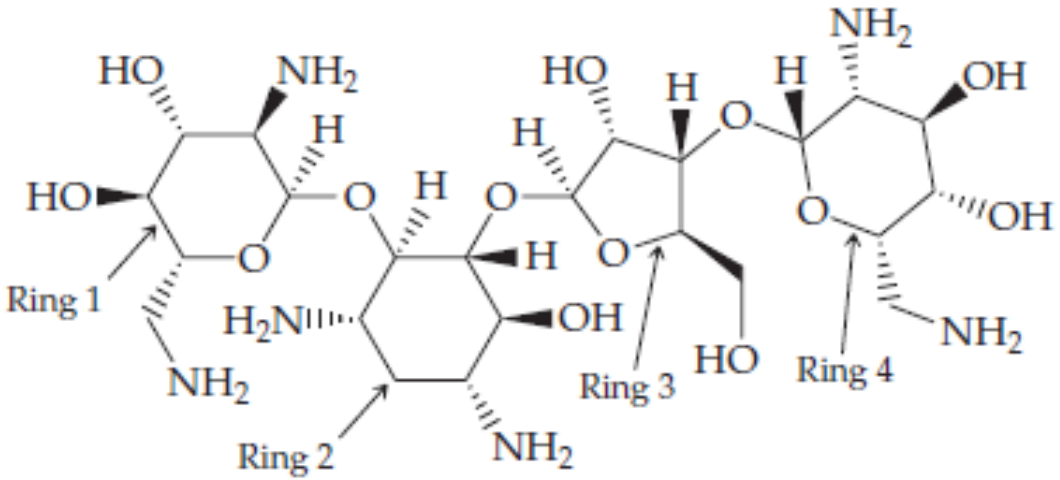
(Reference: Chapter 21 from McMurry et al.)

# Worked example 21.4

Framycetin, a topical antibiotic, is a four-ring molecule consisting of several amino-glycosides—sugars that have some of the —OH groups on the sugars replaced by $-NH_2$ groups—and another ring, with oxygen links between the rings. What sugar or other molecule is each ring derived from?




**ANALYSIS** Look at each ring carefully. Ring 2 does not include an O. It cannot be a sugar. Rings 1, 3, and 4 all contain O as a ring member. Imagine the rings as underivatized sugars, that is with —OH groups instead of $-NH_2$ groups; count the number of carbon atoms in each sugar and draw the sugar form to help identify the sugar.



(Reference: Chapter 21 from McMurry et al.)

# Worked example 21.4

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SOLUTION

Ring 2 has six carbon atoms and no oxygen atoms as part of the ring; it is not a sugar, but is a cyclohexane derivative. Rings 1 and 4 are derived from the aldohexose, glucose, while ring 3 is derived from the aldopentose, ribose.

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(Reference: Chapter 21 from McMurry et al.)

# Key concept problem 21.10

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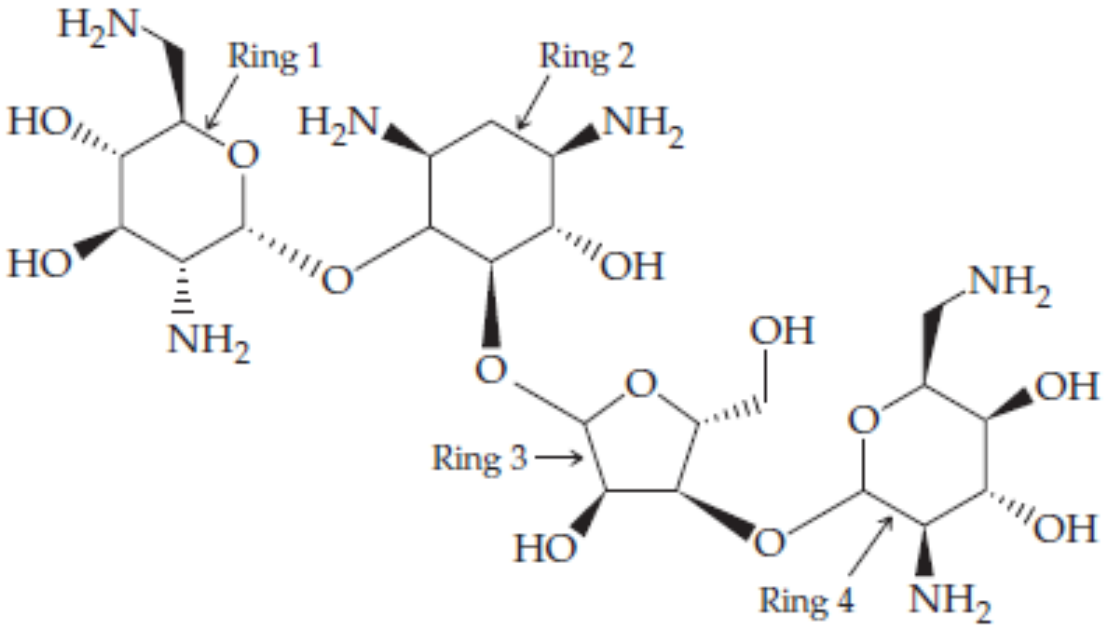
Neomycin is an antibiotic used in topical applications to inhibit the growth of bacteria. It is an aminoglycoside, that is, some of the —OH groups on the sugars have been replaced by $—NH_2$ or R groups. The four rings that constitute neomycin are joined by glycosidic bonds and two of the rings are amino sugars. In the structure shown, identify (a) the amino sugar rings by number, (b) the unmodified sugar ring structure, and (c) the non-sugar ring structure. List how many carbon atoms are in each ring.




**21.10 (a) Rings 1 and 4** (5 carbons) are amino sugars, (b) Ring 3 (4 carbons) is an unmodified sugar, (c) Ring 2 (6 carbons) is a nonsugar.



(Reference: Chapter 21 from McMurry et al.)

# Inhoudsopgave

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(Reference: Chapter 21 from McMurry et al.)

# 21.5 Belangrijke monosacharides

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- Glucose
- Galactose
- Fructose
- Ribose
- 2-Deoxyribose

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(Reference: Chapter 21 from McMurry et al.)

# 21.5 Belangrijke monosacharides

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**TABLE 21.1 Relative Sweetness of Some Sugars and Sugar Substitutes**

| Name | Type | Sweetness |
|---|---|---|
| Lactose | Disaccharide | 16 |
| Galactose | Monosaccharide | 30 |
| Maltose | Disaccharide | 33 |
| Glucose | Monosaccharide | 75 |
| Sucrose | Disaccharide | 100 |
| Fructose | Monosaccharide | 175 |
| Cyclamate | Artificial | 3000 |
| Aspartame | Artificial | 15,000 |
| Saccharin | Artificial | 35,000 |
| Sucralose | Artificial | 60,000 |

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(Reference: Chapter 21 from McMurry et al.)

# 21.5 Glucose

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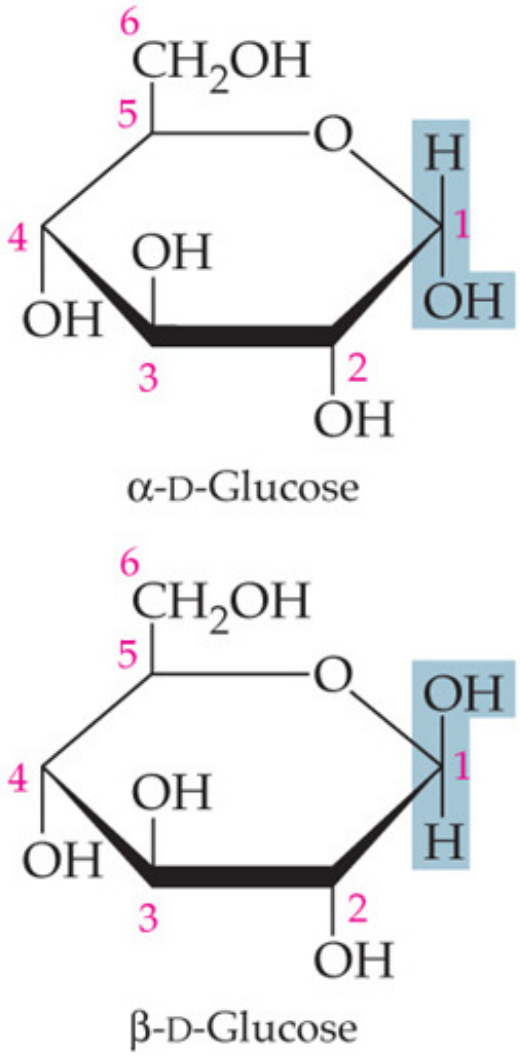
*Anomers*

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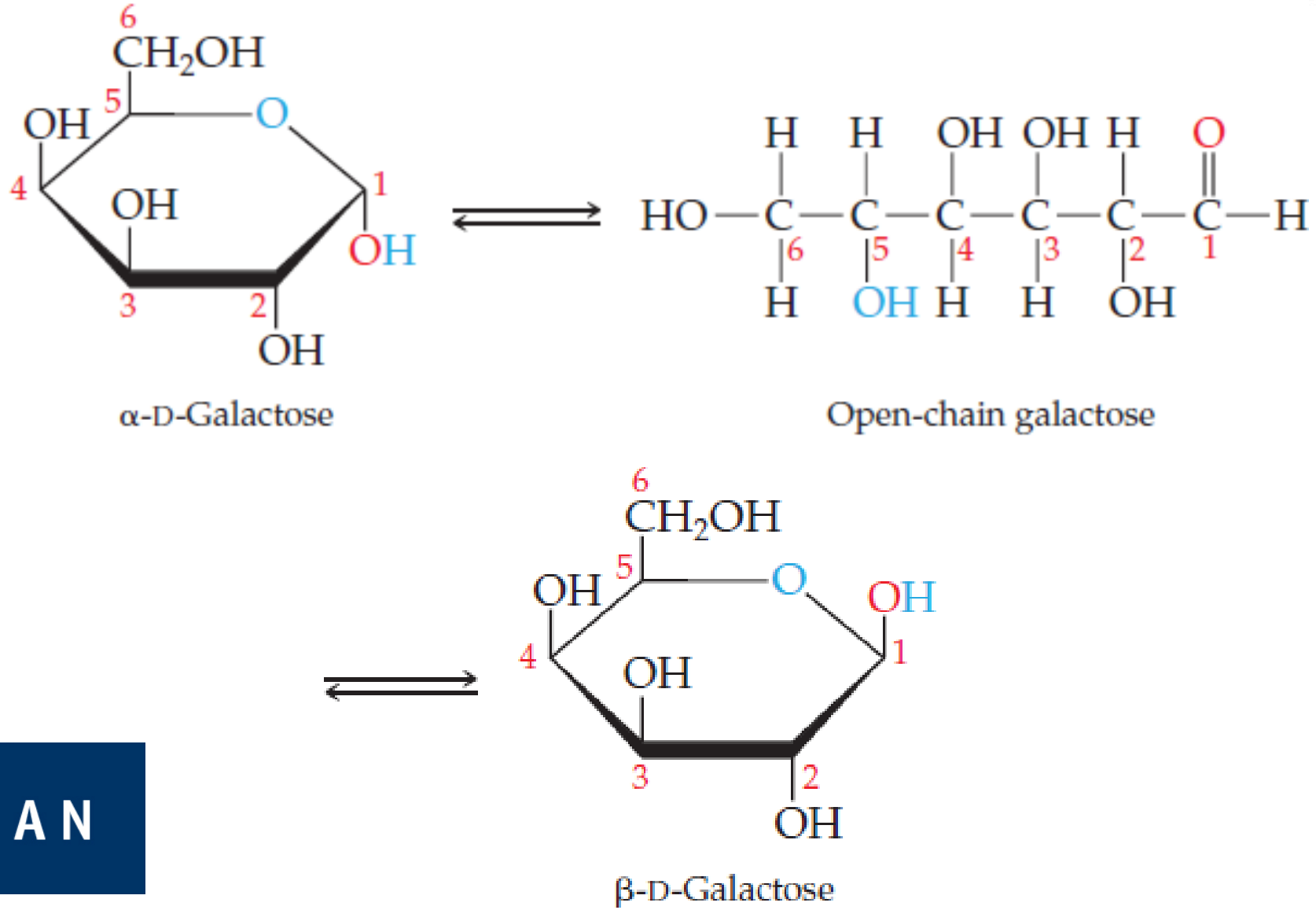
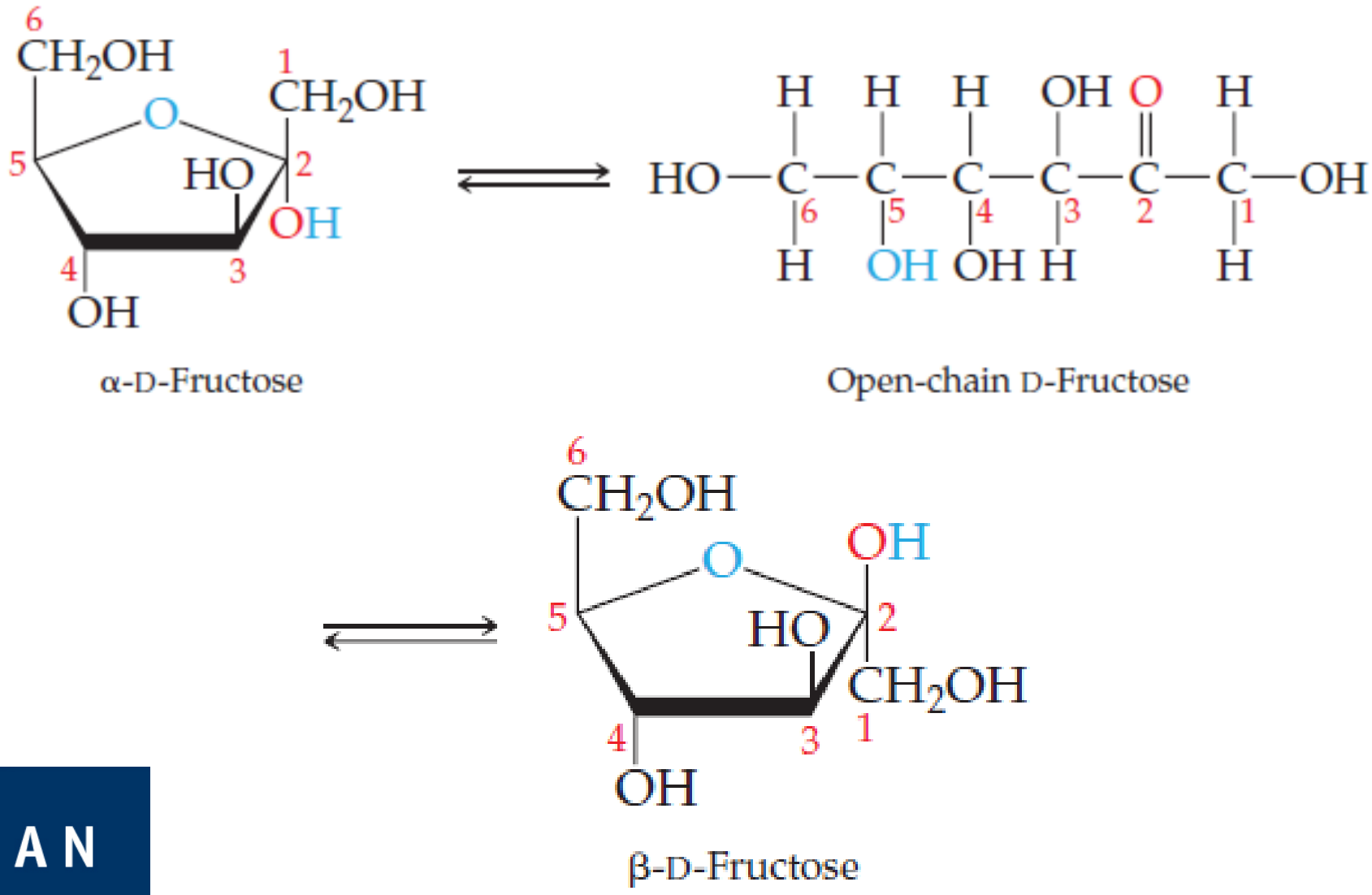
(Reference: Chapter 21 from McMurry et al.)

# 21.5 Galactose



# 21.5 Fructose

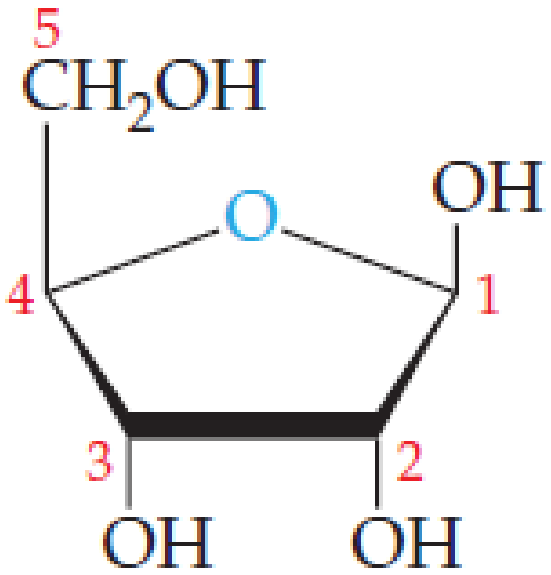




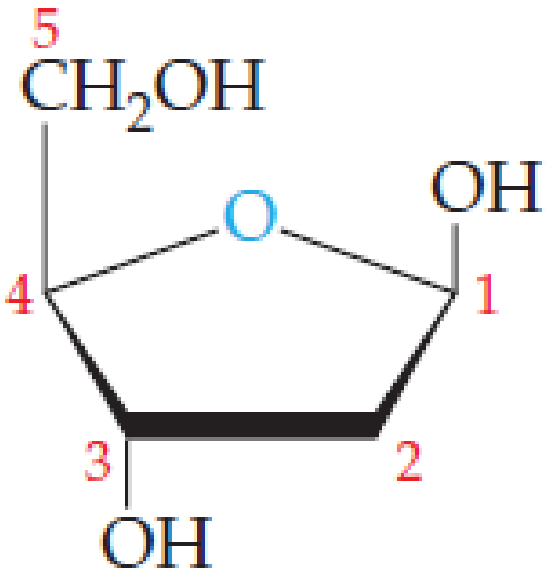

(Reference: Chapter 21 from McMurry et al.)

# 21.5 Ribose & 2-Deoxyribose






β-D-Ribose




β-D-2-Deoxyribose

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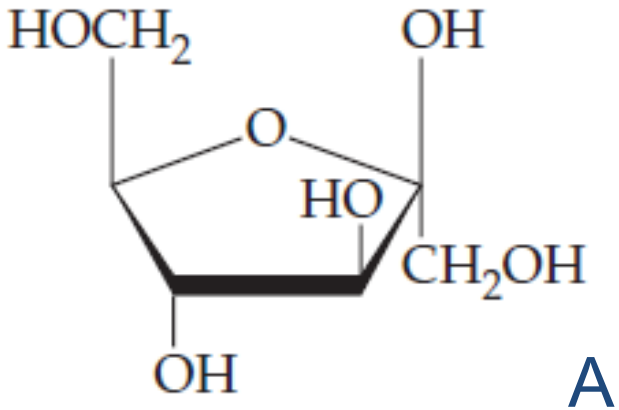
(Reference: Chapter 21 from McMurry et al.)

# Problem 21.11




A monosaccharide hemiacetal

Vragen:

- Nummer de C-atomen
- Identificeer het anomerische C-atom
- Is dit de α of β anomeer?

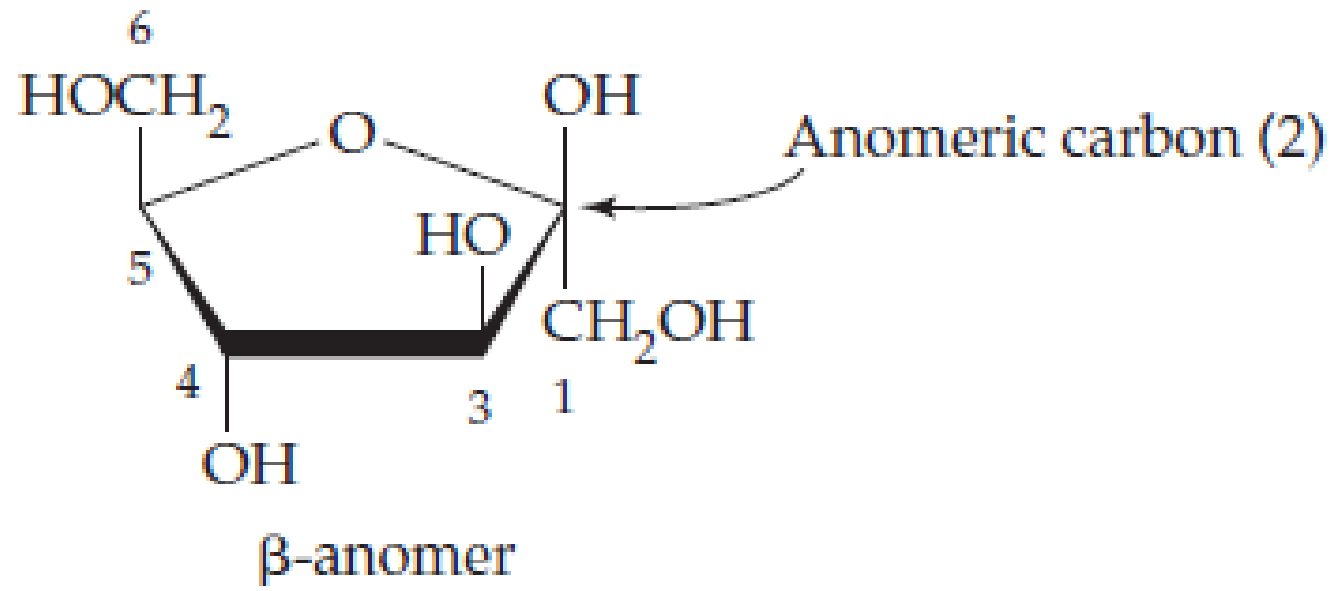


(Reference: Chapter 21 from McMurry et al.)

# Problem 21.11



21.11




β-anomer



(Reference: Chapter 21 from McMurry et al.)

# Problem 21.12

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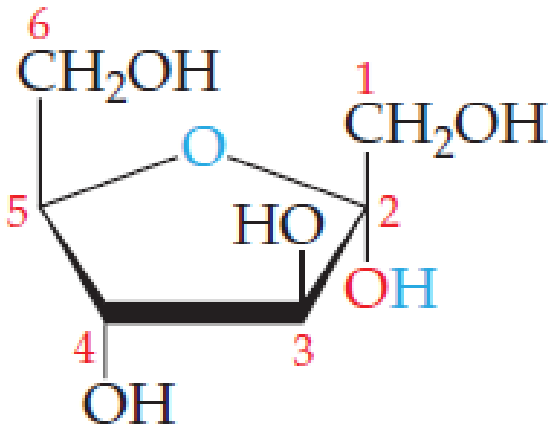
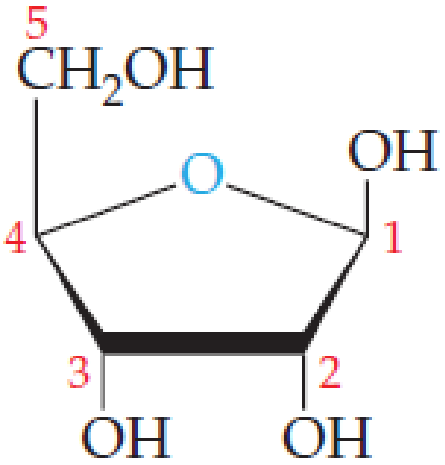
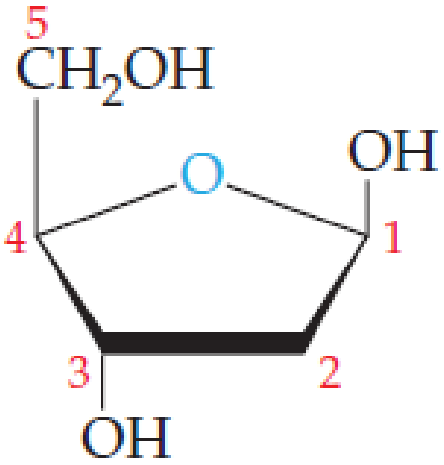
## Identificeer de chirale koolstofatomen in onderstaande structuren




α-D-Fructose




β-D-Ribose




β-D-2-Deoxyribose

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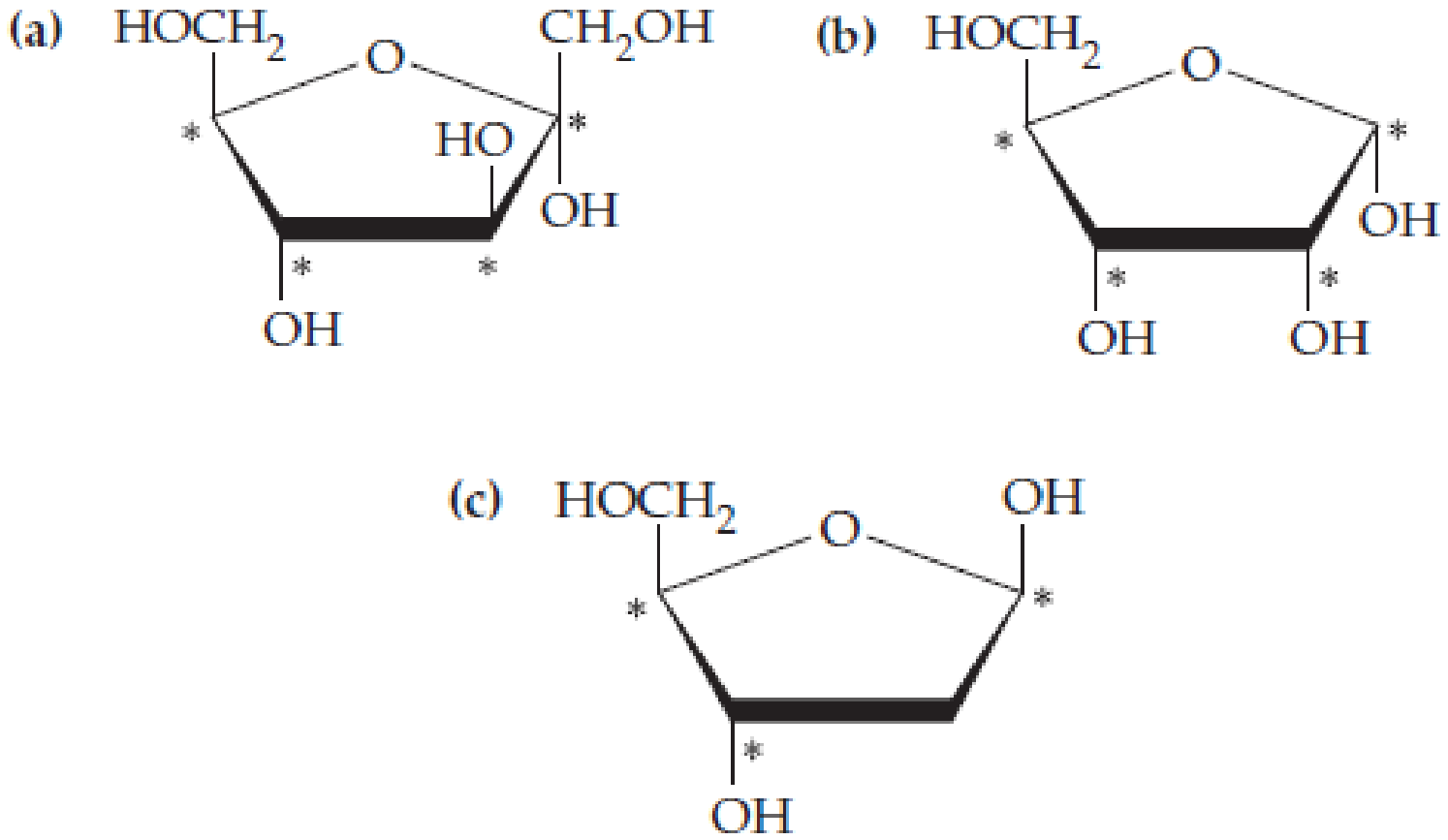
(Reference: Chapter 21 from McMurry et al.)

# Problem 21.12



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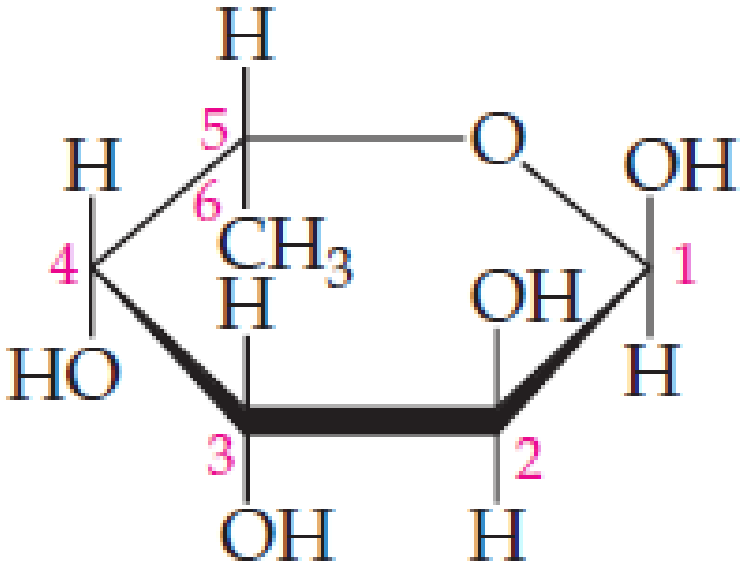
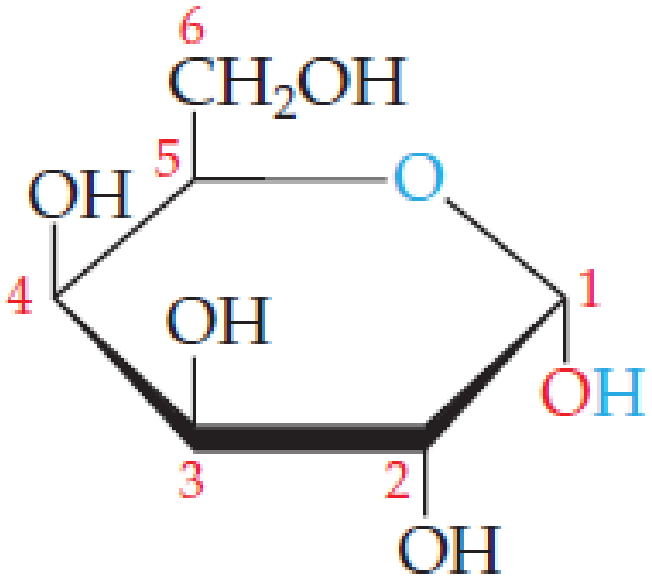
(Reference: Chapter 21 from McMurry et al.)

# Problem 21.13






L-Fucose




Galactose

- Is L-fucose an α of β anomeer?
- Vergelijk met galactose. Waar ontbreekt -OH?
- Is 6-deoxy-l-galactose de correcte naam voor fucose? Leg uit!

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(Reference: Chapter 21 from McMurry et al.)

# Inhoudsopgave

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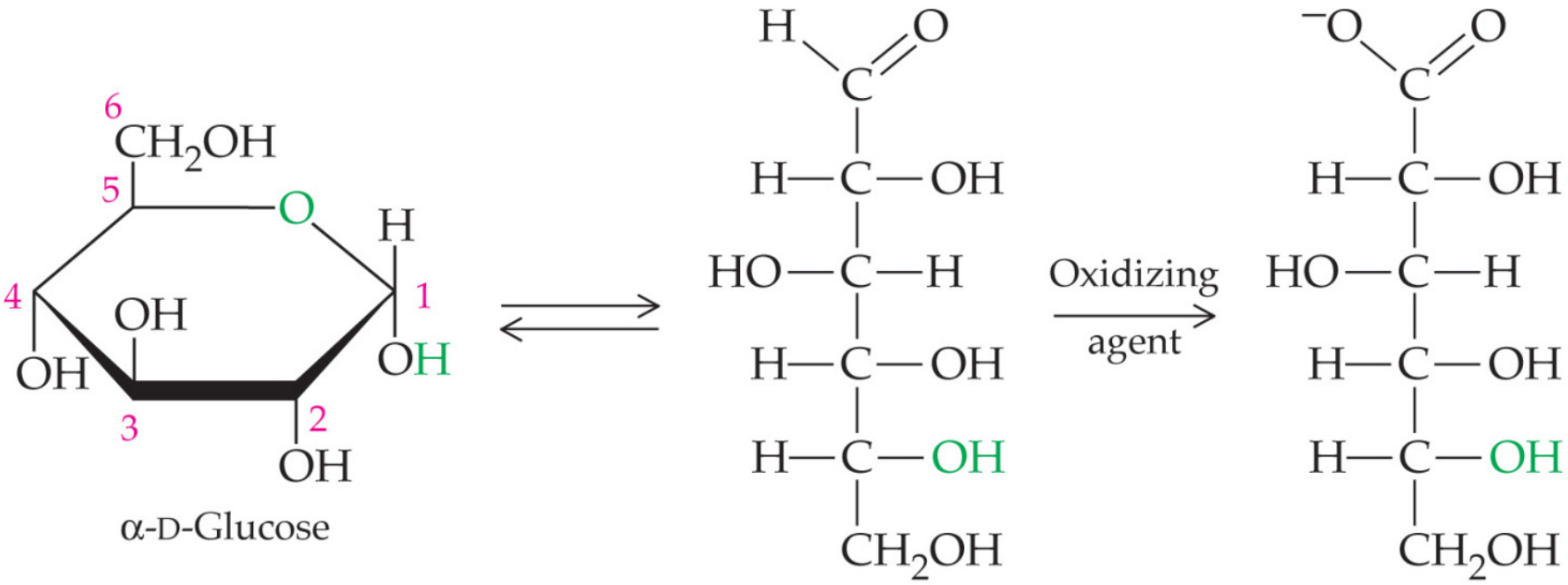
(Reference: Chapter 21 from McMurry et al.)

# 21.6 Reacties van monosacharides

- **Reducerende suiker**
  - **reageren met oxiderende stoffen**



# 21.6 Reacties van monosacharides

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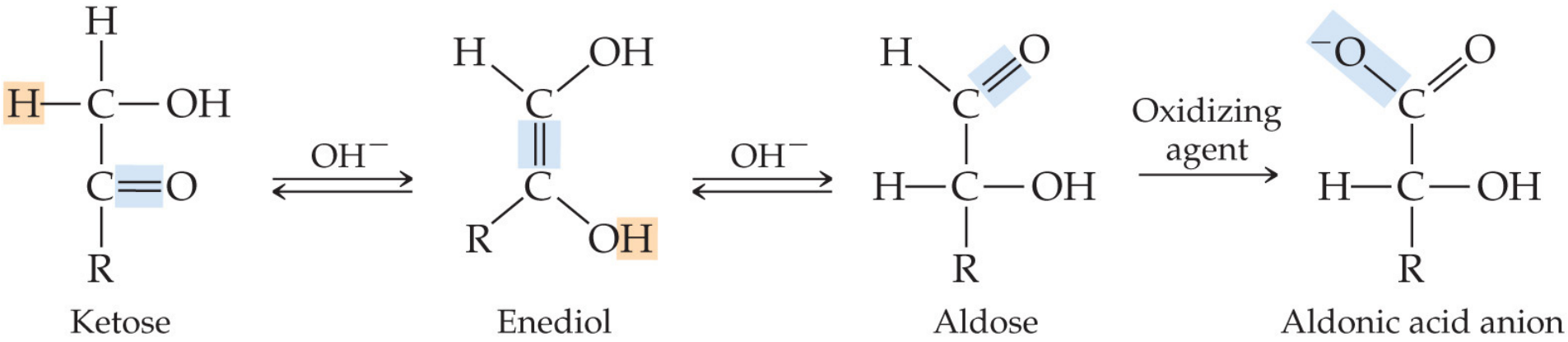
## Basisch milieu

- **In basisch milieu zijn alle suikers (ook ketoses) te oxideren.**



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# 21.6 Reacties van monosacharides

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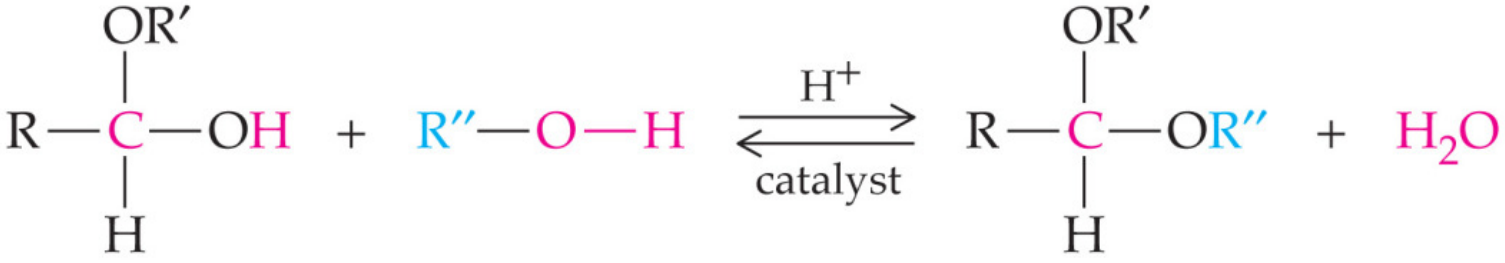
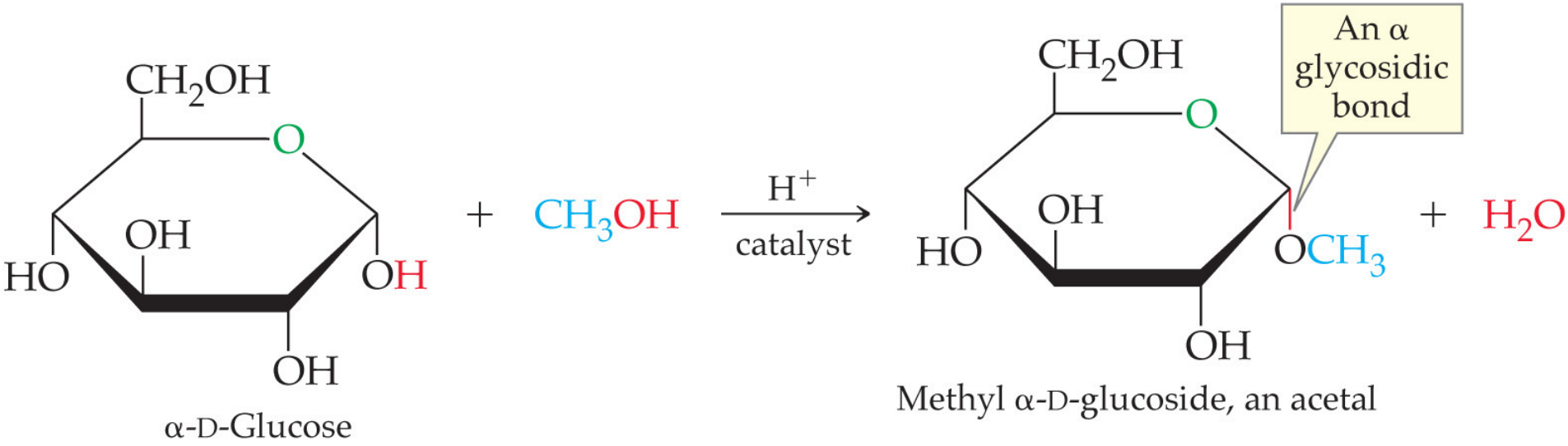
## Glycoside






*Formation of a glycoside*



# 21.6 Reacties van monosacharides

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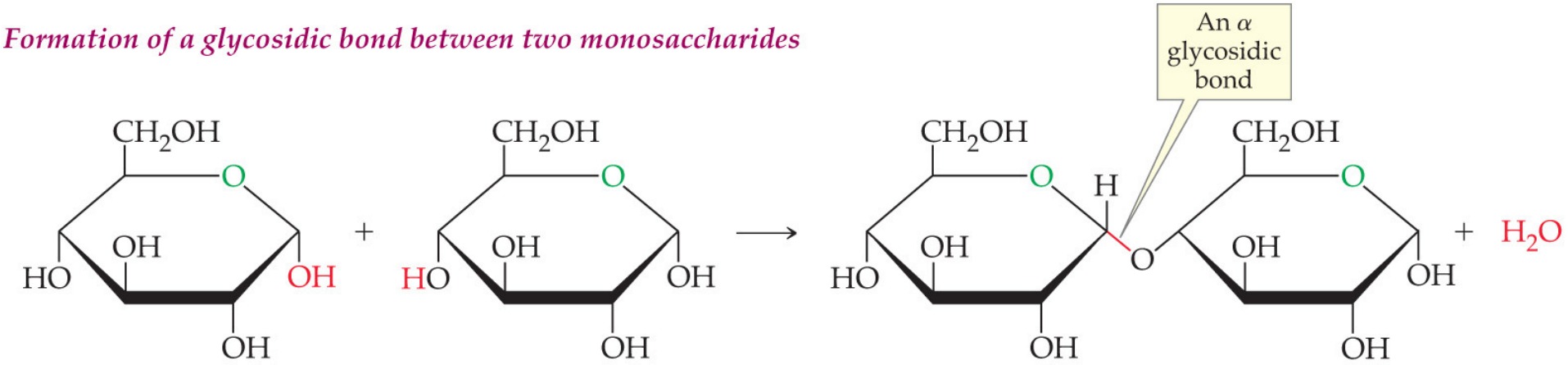
## Vorming disacharide

*Formation of a glycosidic bond between two monosaccharides*



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(Reference: Chapter 21 from McMurry et al.)

# 21.6 Reacties van monosacharides

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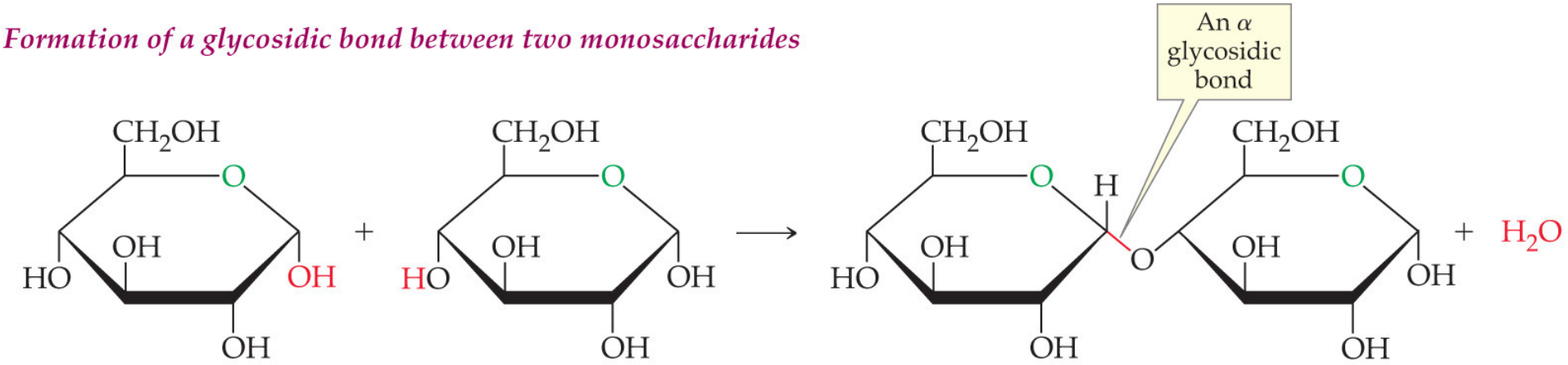
## Hydrolyse disacharide

*Formation of a glycosidic bond between two monosaccharides*



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(Reference: Chapter 21 from McMurry et al.)

# 21.6 Reacties van monosacharides

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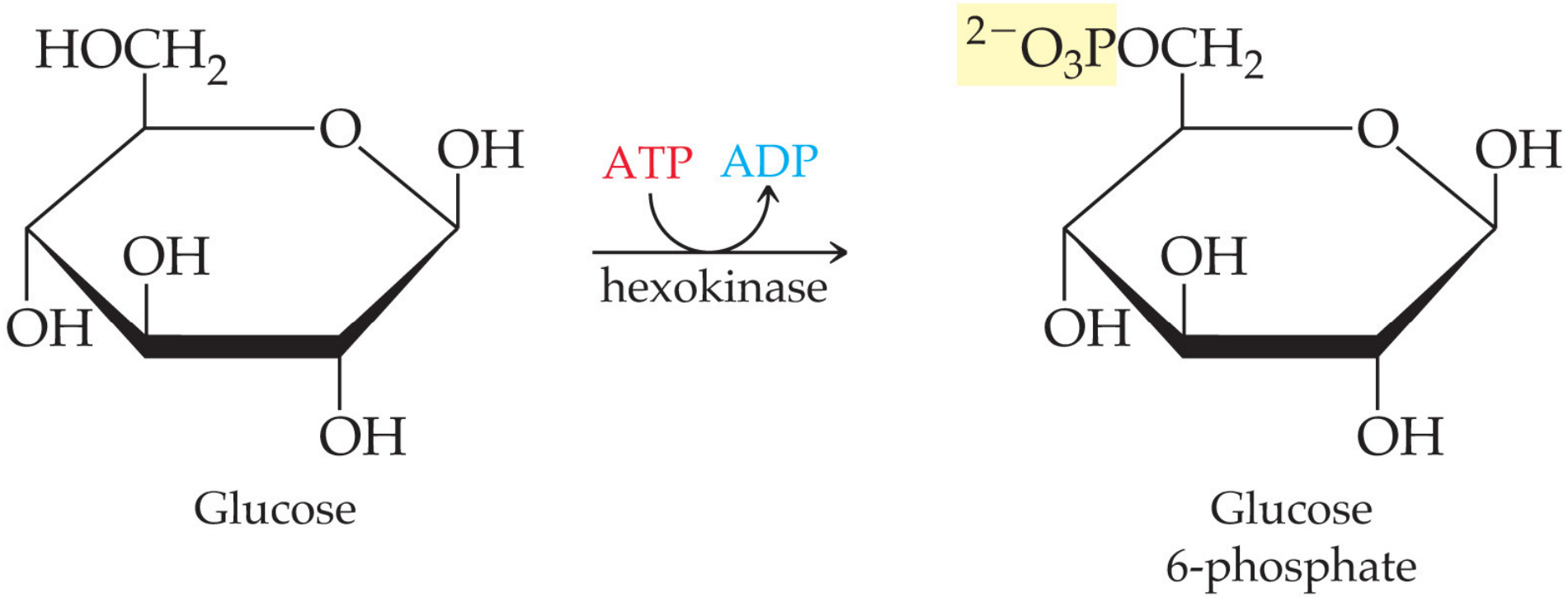
## Fosfaatesters van alcoholen



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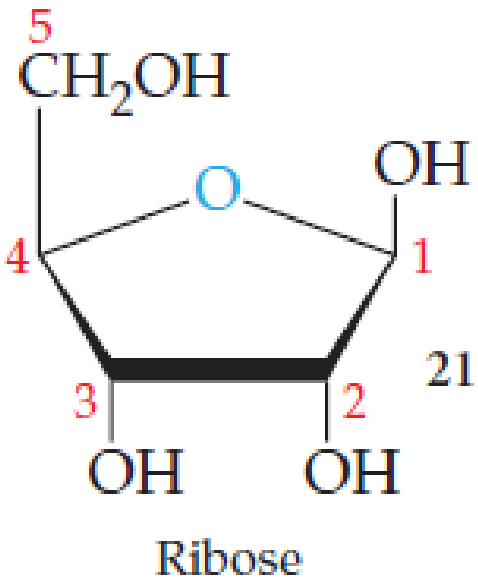
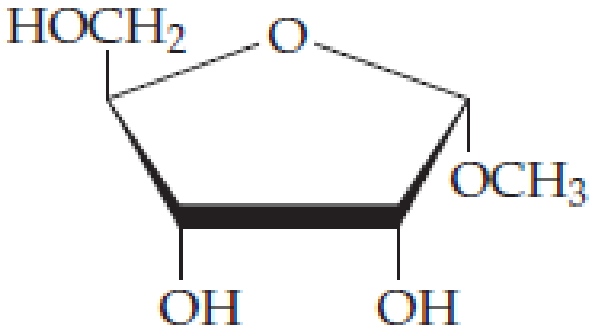
# Problem 21.15

- **Teken de α en β anomeren die ontstaan na een reactie van ribose met methanol.**
- **Hebben we we acetaal of een hemiacetaal?**



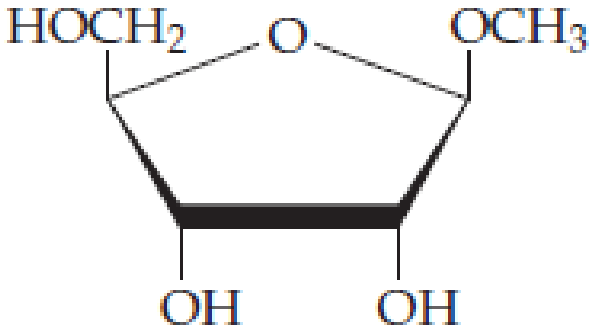
Ribose

21.15



Methyl α-D-riboside

Acetaal



Methyl β-D-riboside



(Reference: Chapter 21 from McMurry et al.)

# Inhoudsopgave

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(Reference: Chapter 21 from McMurry et al.)

# 21.7 Disacharides

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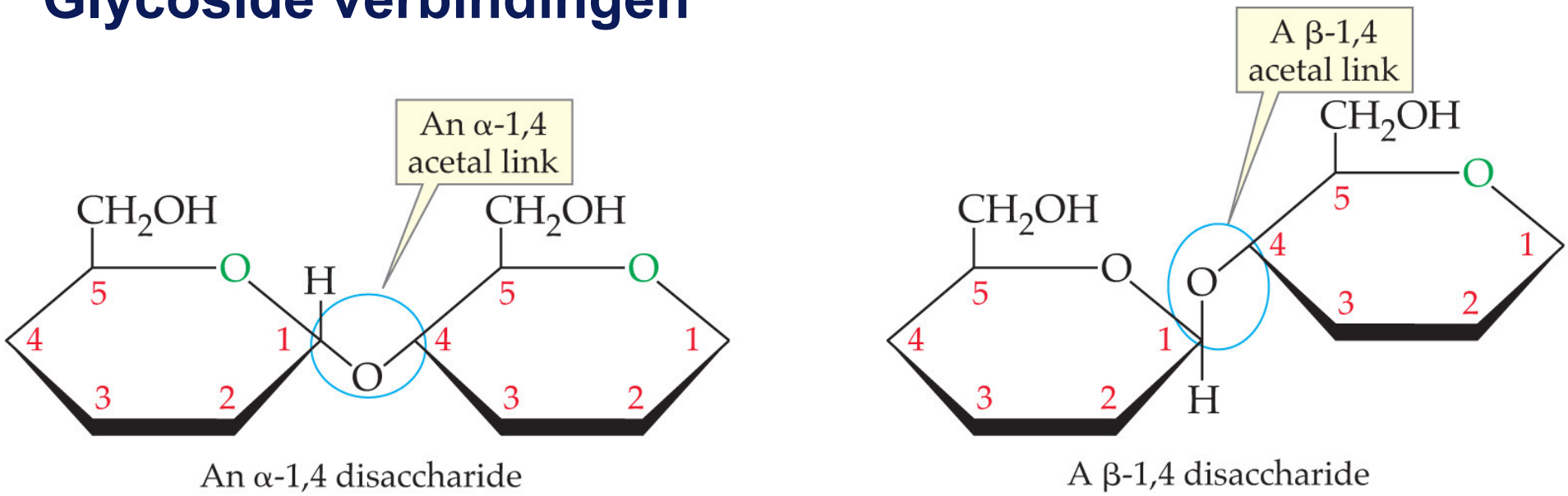
## Glycoside verbindingen



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# 21.7 Disacharides

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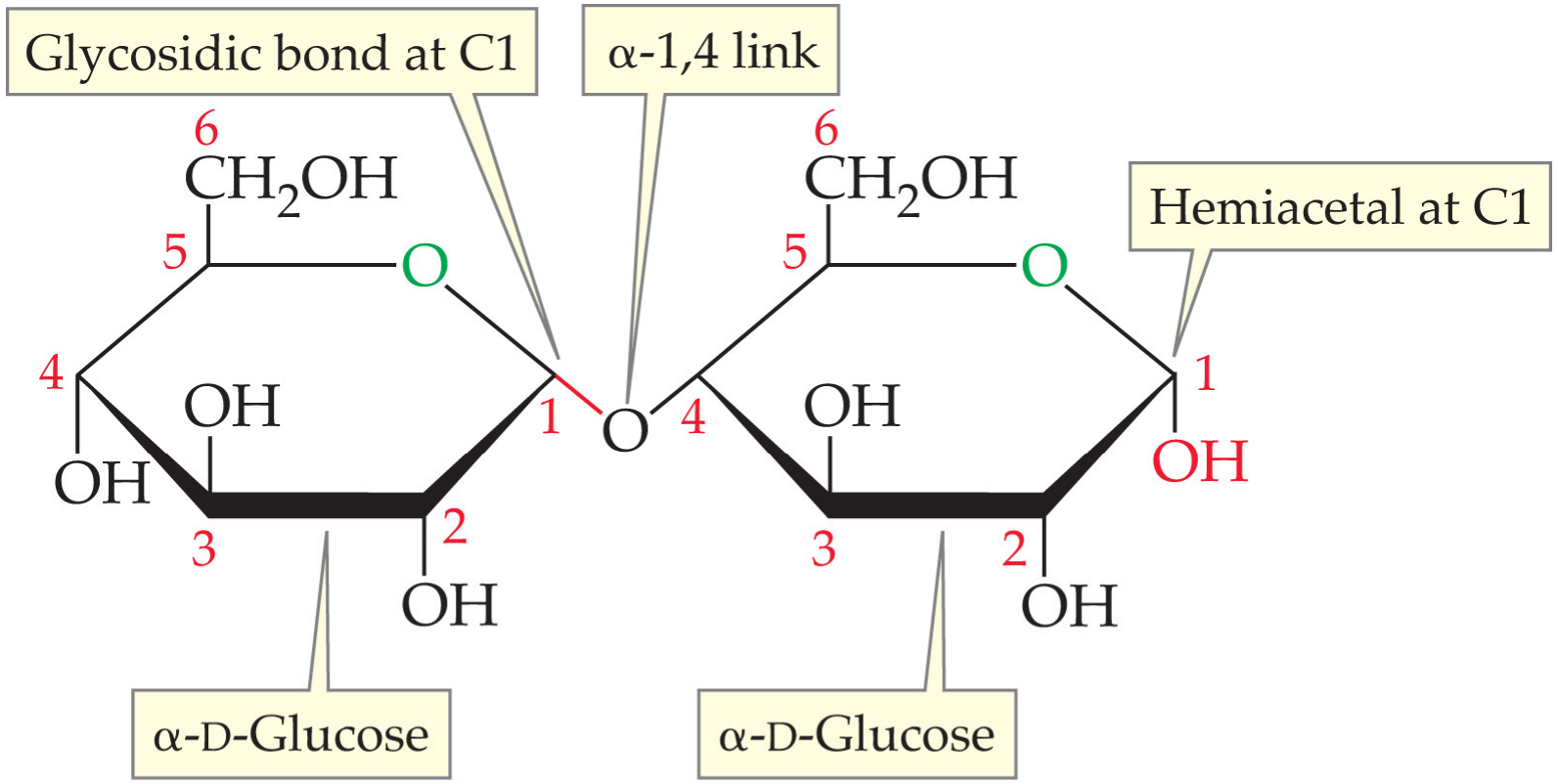
## Maltose




Maltose



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# 21.7 Disacharides

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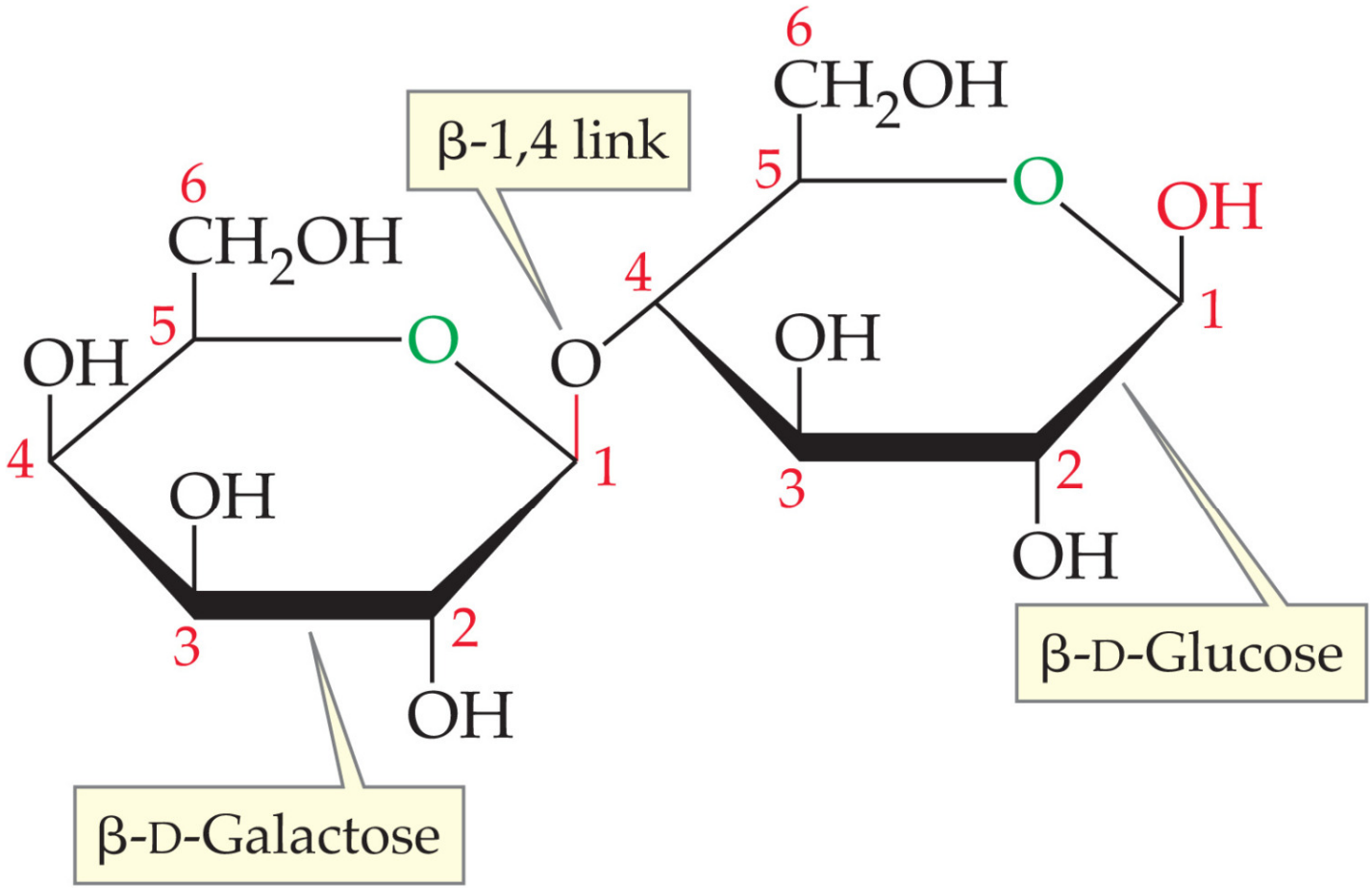
## Lactose (melksuiker)

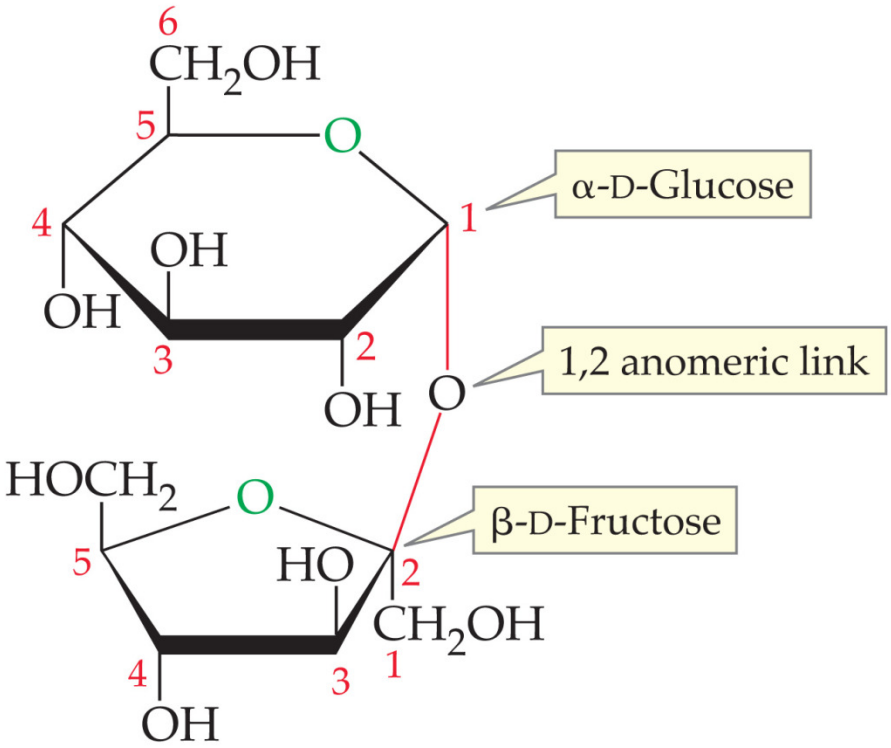



Lactose

# 21.7 Disacharides

## Sucrose (tafelsuiker)

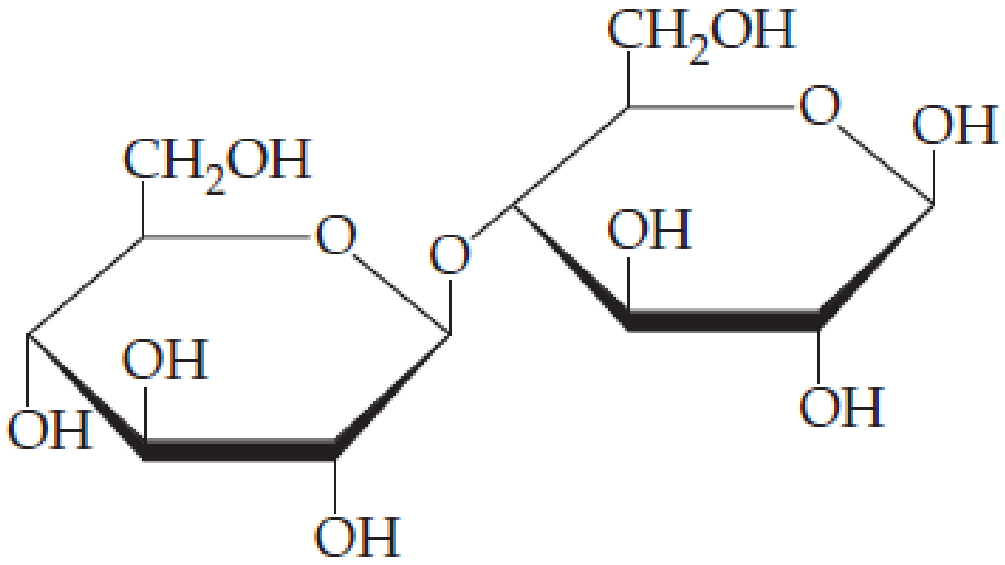
- Géén hemiacetaal-groep omdat de twee anomere C-atomen gekoppeld zijn.
- Géén reducerende suiker.




Sucrose

# Worked example 21.5

The disaccharide cellobiose can be obtained by enzyme-catalyzed hydrolysis of cellulose. Do you expect cellobiose to be a reducing or a nonreducing sugar?




Cellobiose

# Worked example 21.5

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**ANALYSIS** To be a reducing sugar, a disaccharide must contain a hemiacetal group, that is, a carbon bonded to one —OH group and one —OR group. The ring at the right in the structure above has such a group.

**SOLUTION**

Cellobiose is a reducing sugar.

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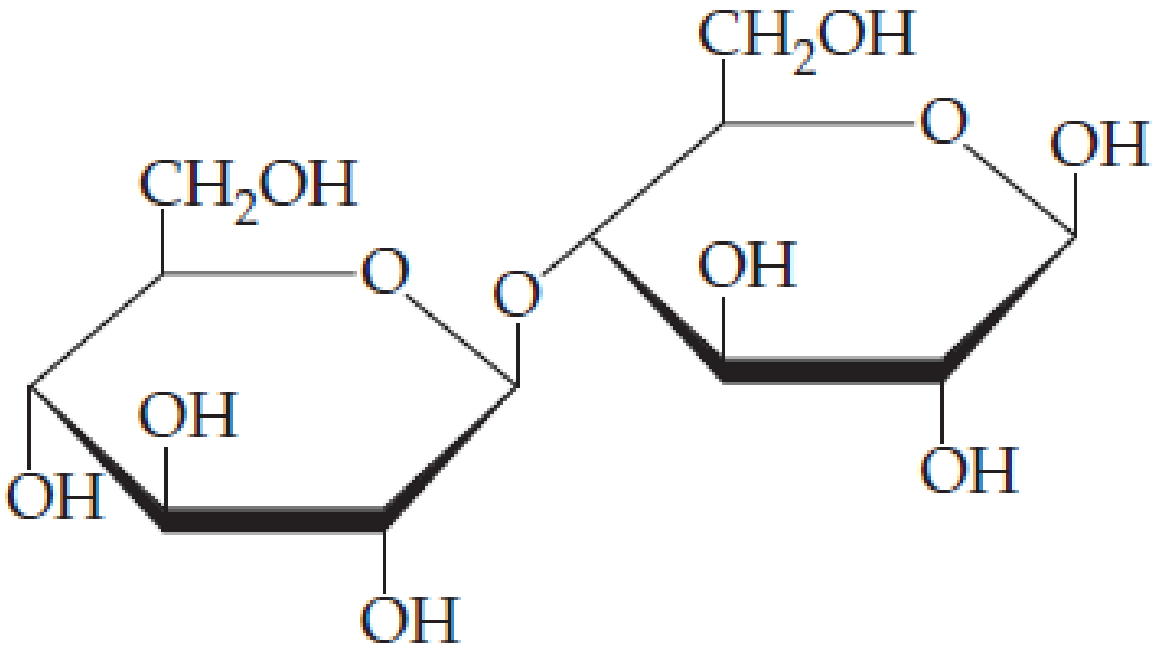
# Problem 21.16






Cellobiose

**Hoe classificeer je de link tussen beide monosacharides?**

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21.16 a $\beta$-1,4 glycosidic link



(Reference: Chapter 21 from McMurry et al.)

# Problem 21.17

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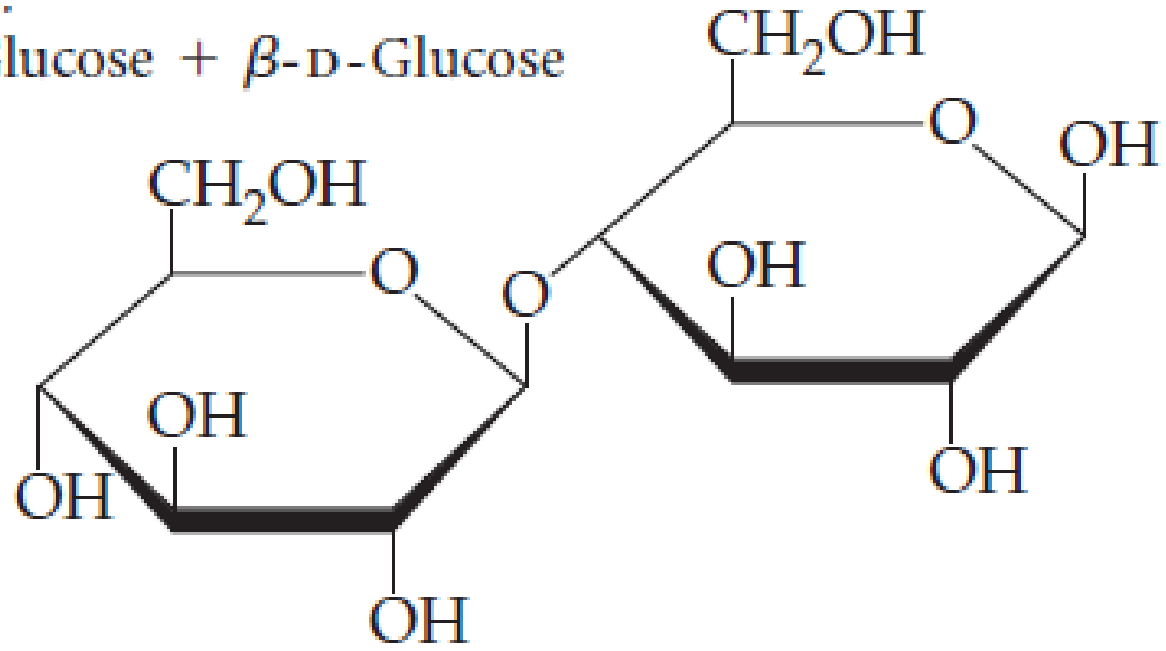
21.17 β-D-Glucose + β-D-Glucose




Cellobiose

- **Welke 2 monosacharides krijg je na hydrolyse van cellobiose?**
- **Wat zijn de namen van de individuele monosacharides?**

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(Reference: Chapter 21 from McMurry et al.)

# Inhoudsopgave

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(Reference: Chapter 21 from McMurry et al.)

# 21.9 Belangrijke polysachariden

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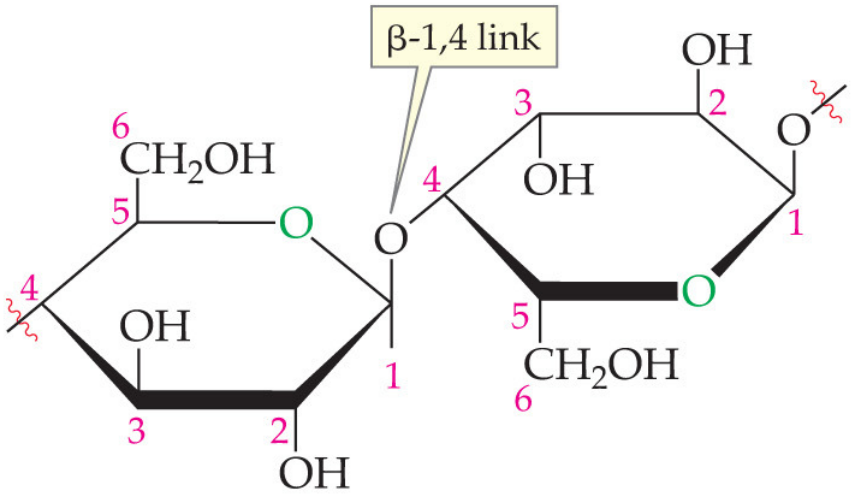
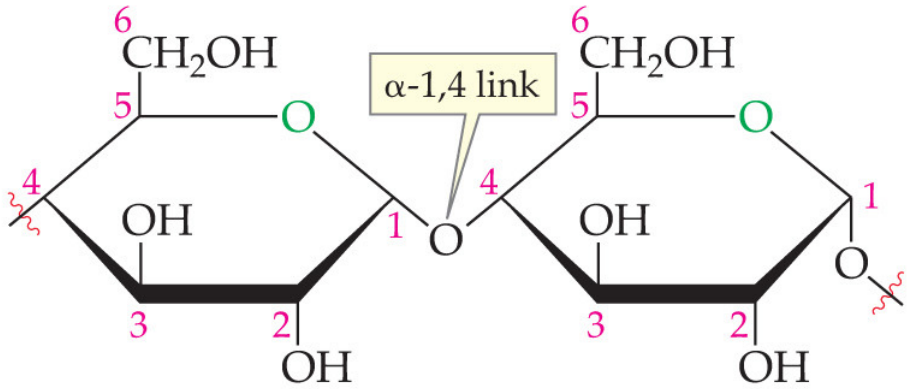
## Cellulose, zetmeel en glycogeen




Cellulose repeating unit




Starch and glycogen repeating unit



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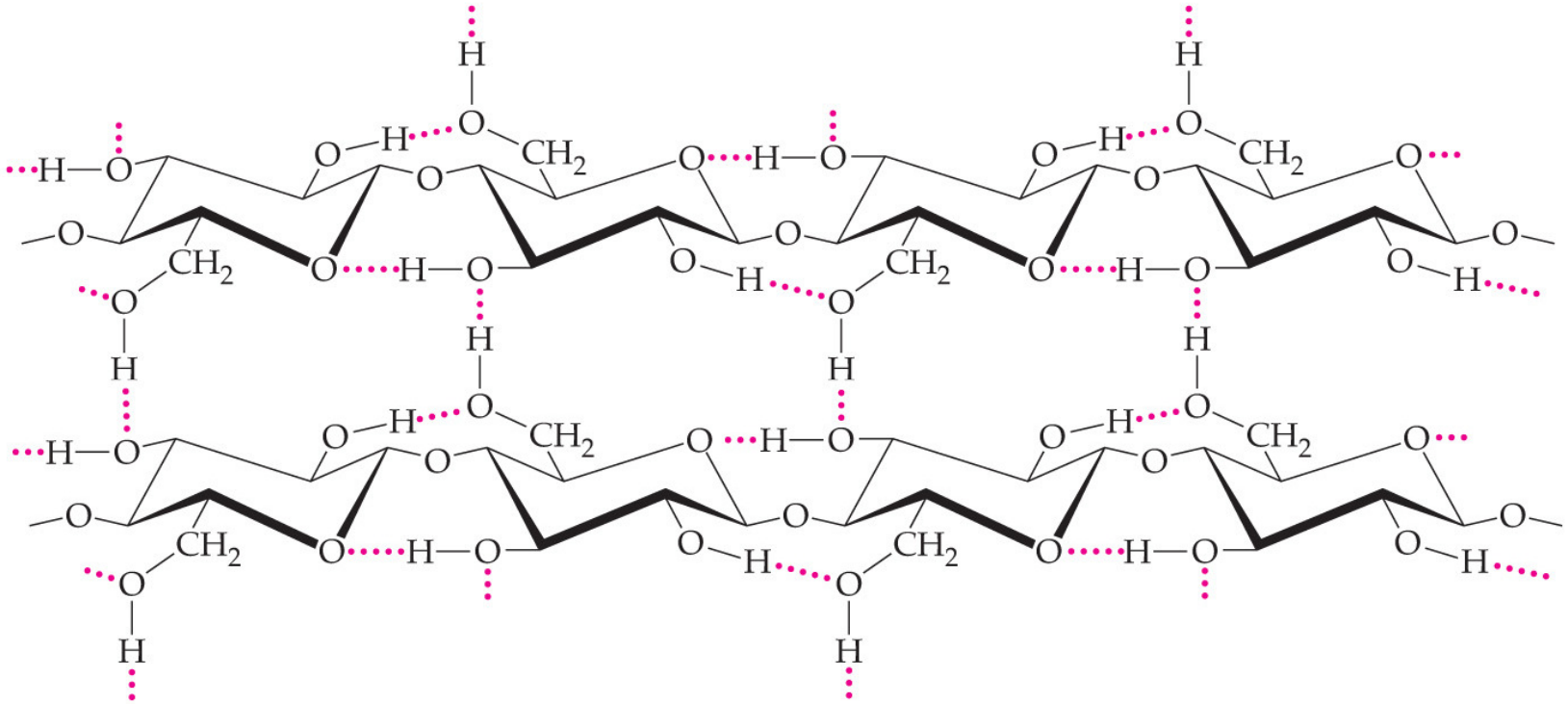
## Cellulose

Cellulose





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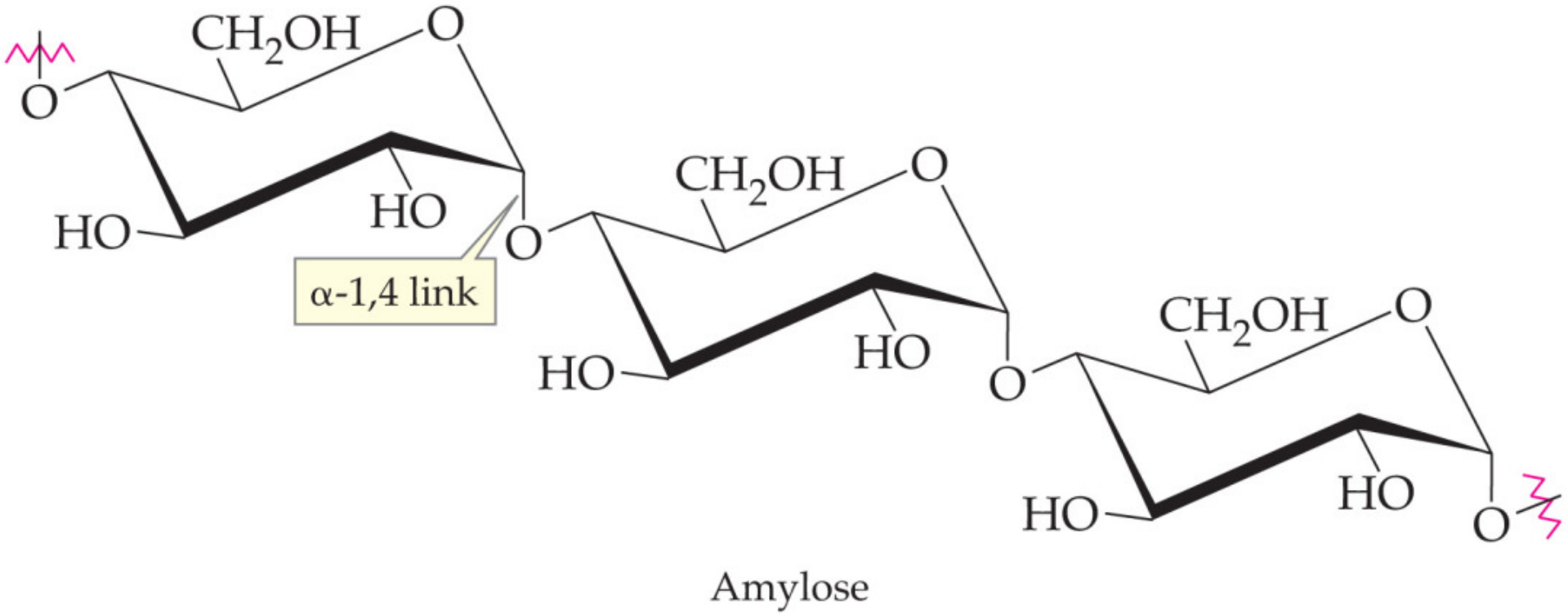
## Zetmeel (amylose en amylopectine)




Amylose



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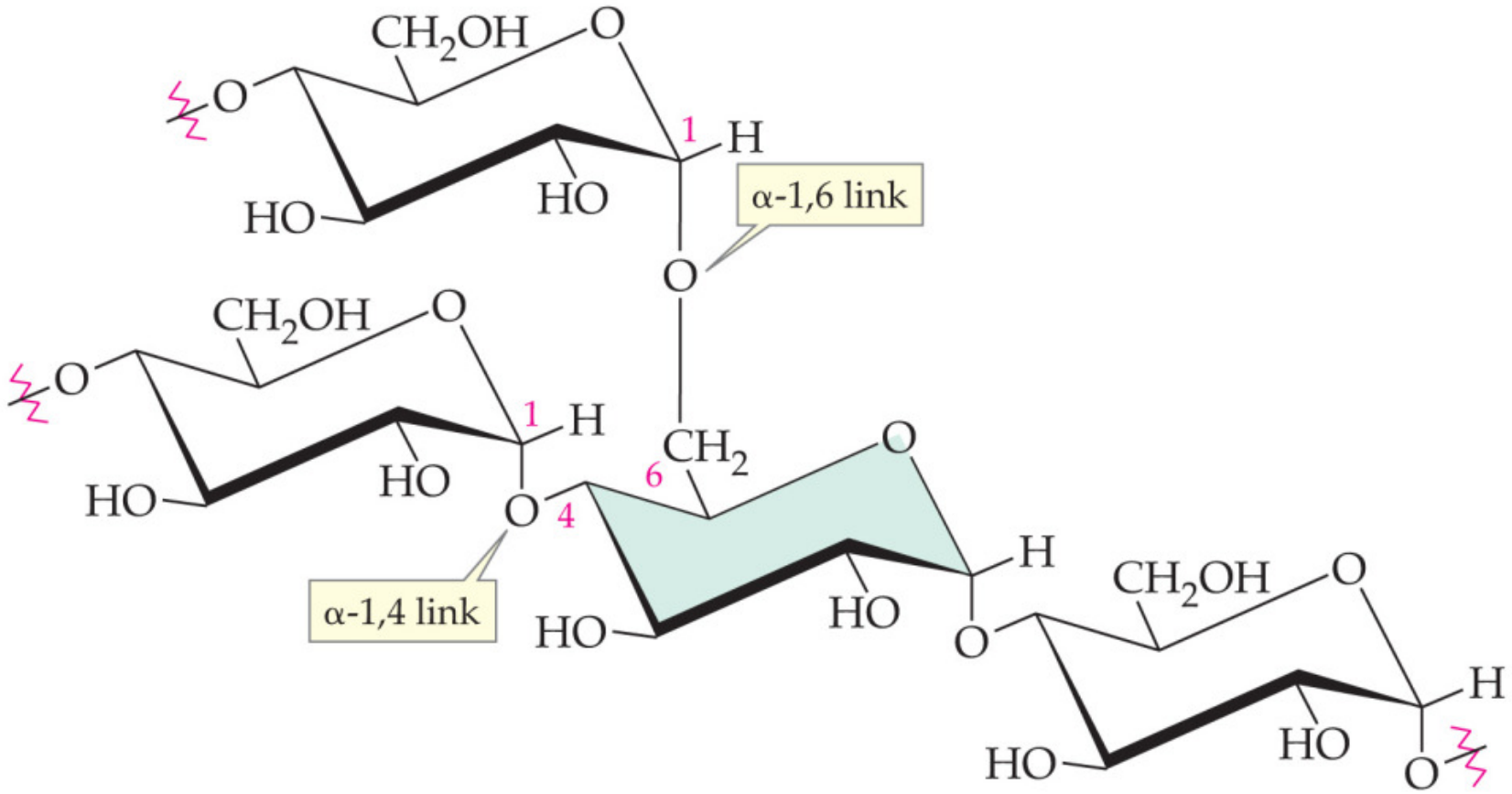
## Zetmeel (amylose en amylopectine)

*Branch point in amylopectin (also glycogen)*



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## Glycogeen

*Comparison of branching in amylopectin and glycogen*