생유기화학
(Bioorganic Chemistry)

Carbohydrates-I
(탄수화물-1)

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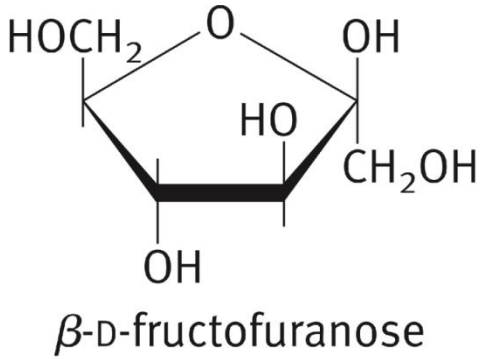
Carbohydrates



β-D-fructofuranose

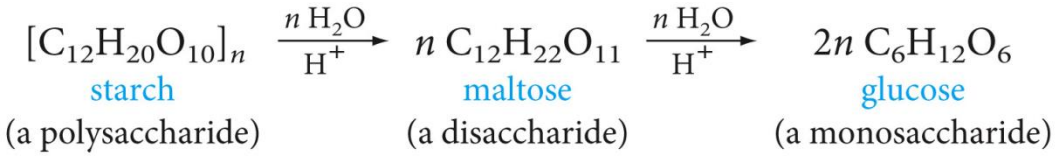
Fructose (fruit sugar)는 sucrose (table sugar)보다 50% 이상 sweeter하다. 꿀의 주성분이다.

Through photosynthesis, plants convert atmospheric carbon dioxide to carbohydrates, mainly cellulose, starch, and sugars.

어렵고 중요한 chapter

1. Definitions and Classification

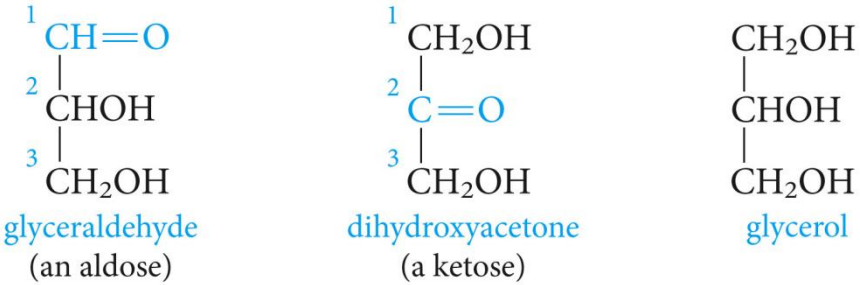
(hydrolysis)



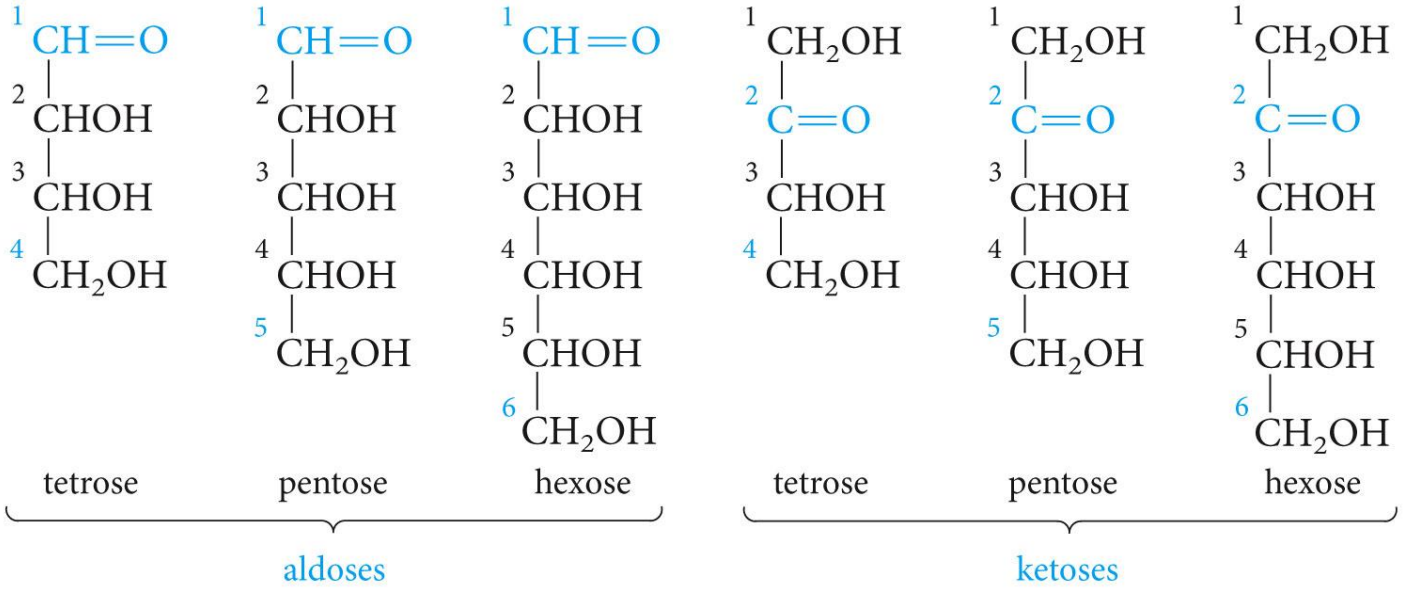
monosaccharide = (simple) sugar

2. Monosaccharides

only two trioses
(simplest aldose and ketose)



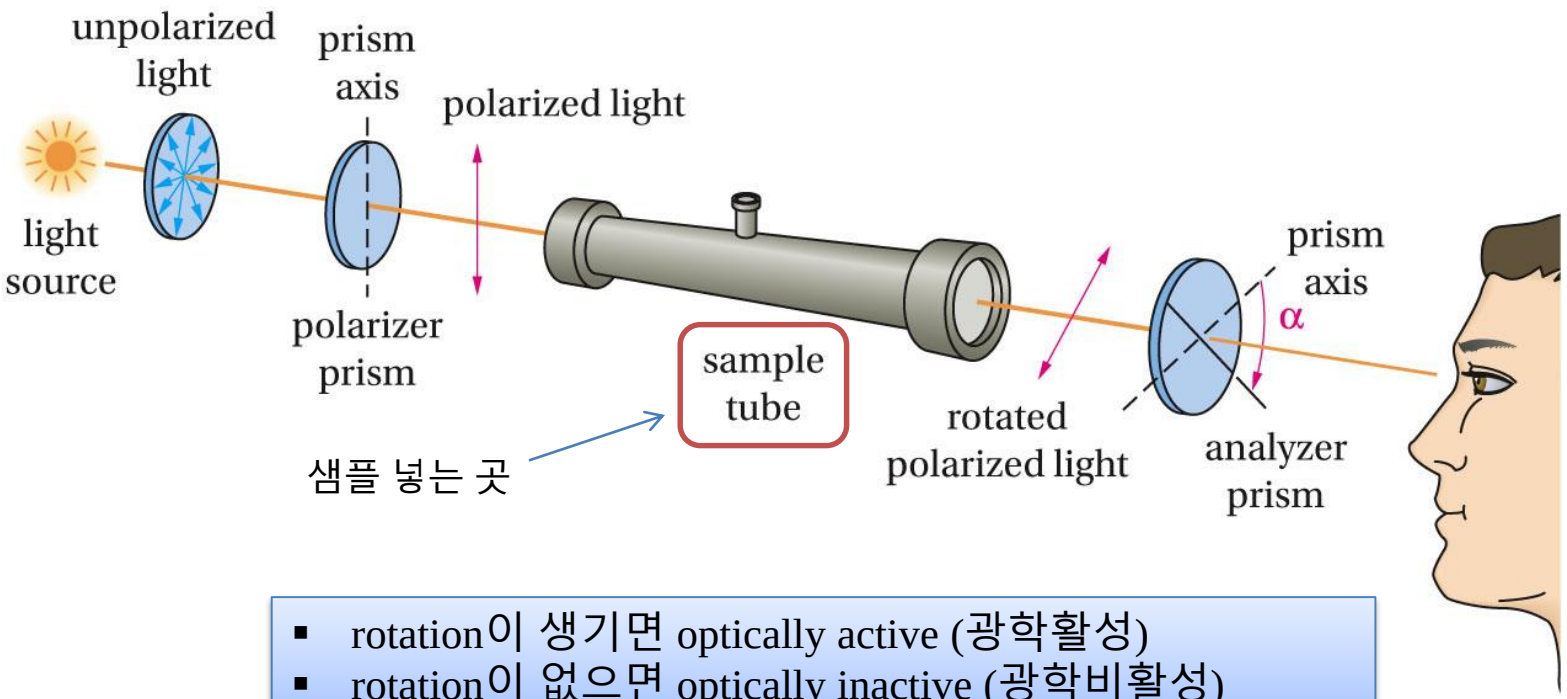
(aldehyde을 포함하면 aldose, ketone을 포함하면 ketose)



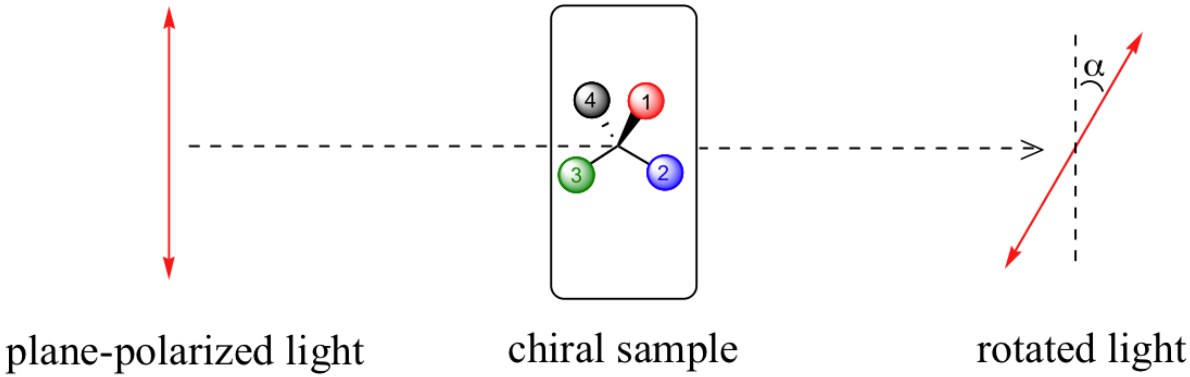
In most ketoses, the carbonyl group is located at C-2.

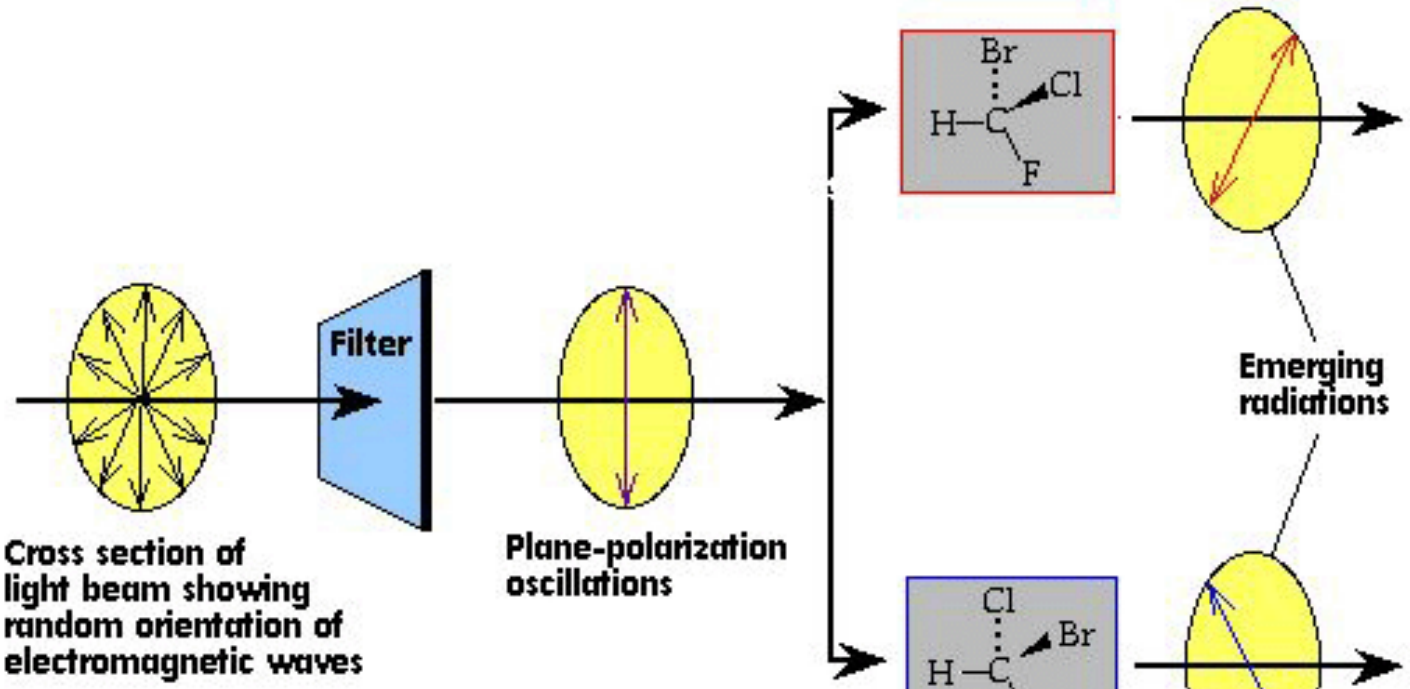
Polarimeter

spectropolarimeter



- rotation이 생기면 optically active (광학활성)
- rotation이 없으면 optically inactive (광학비활성)





- dextrorotatory
- (+)
- d
- right
- clockwise
- (R)- or (S)-

- levorotatory
- (-)
- l
- left
- counterclockwise
- (R)- or (S)-

$$\text{Specific rotation} = [\alpha]_{\lambda}^{t} = \frac{\alpha}{l \times c}\,(\text{solvent})$$

$$[\alpha]_{D}^{25} = \frac{\alpha}{lc}$$

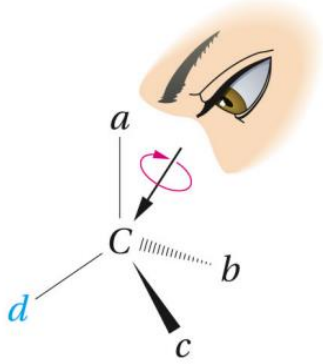
α : rotation degree, l : sample tube length (dm)
c : concentration (g / ml), t : 온도, λ : 파장

Enantiomers 끼리는 m.p., b.p. density, 용해도등이 모두 같으나 specific rotation만 다르다.

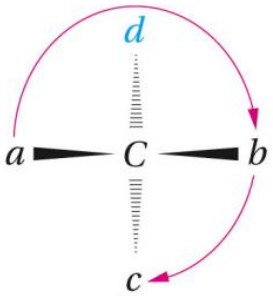
Configuration

The arrangement of groups is called the configuration of the stereogenic center.

a > b > c > d



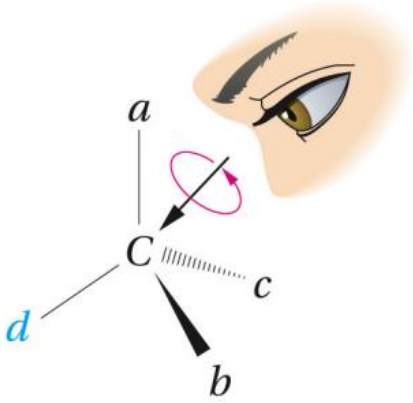
or



clockwise → R

a → *b* → *c* clockwise
R

a → *b* → *c* clockwise
R



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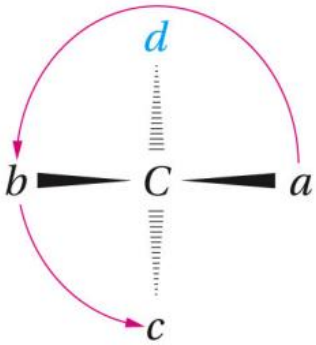


counterclockwise, anticlockwise → S

a → *b* → *c* counterclockwise
S

a → *b* → *c* counterclockwise
S

Priority 정하는 법

Rule 1

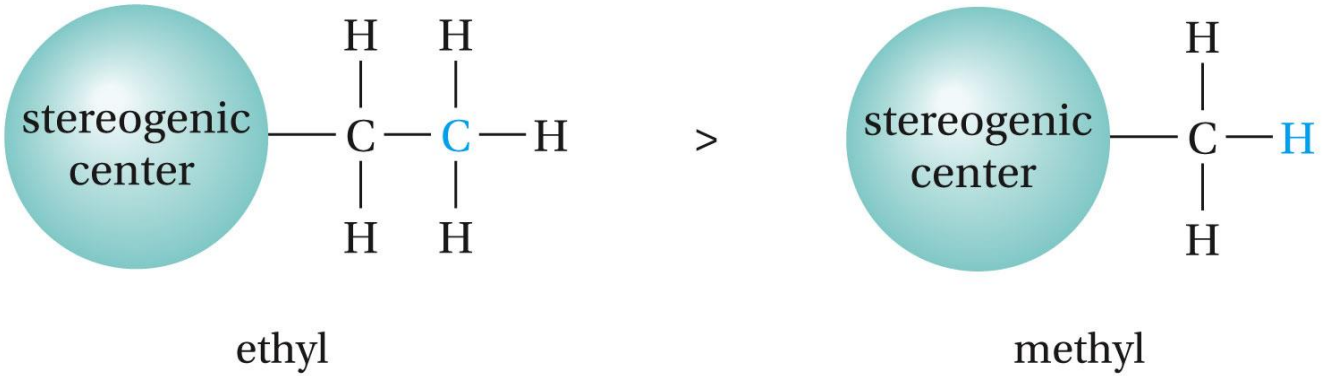
Cl > O > C > H

high priority — low priority

atomic number order

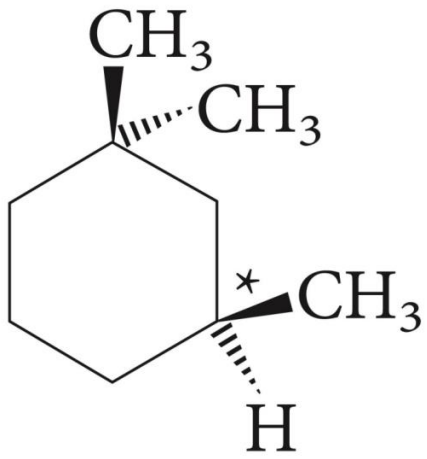
Rule 2

rule 1이 적용 안될 때



ethyl > methyl

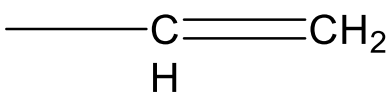
문제: Find the stereogenic center of the following compound, and assign the priorities.

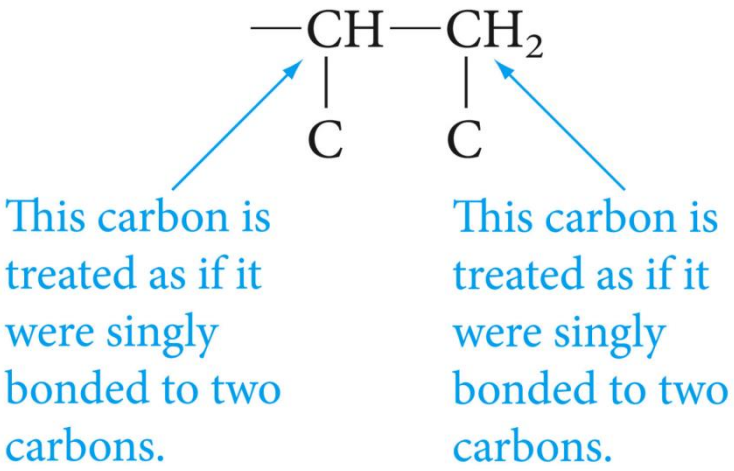


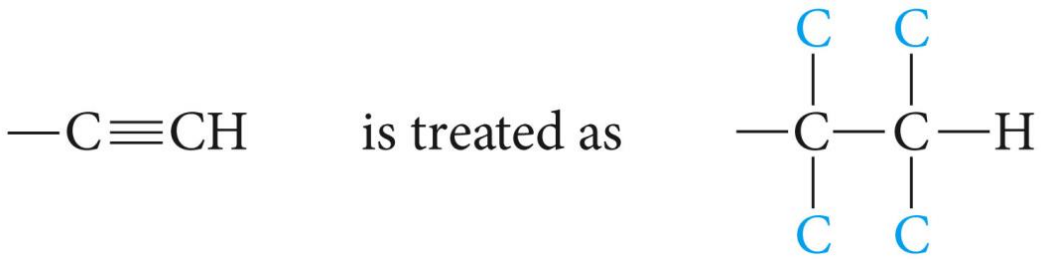
1,1,3-trimethylcyclohexane

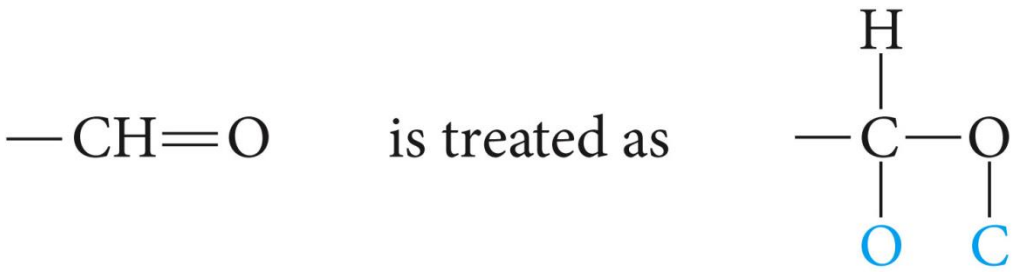
Rule 3

double bond, triple bond 가 존재할 때

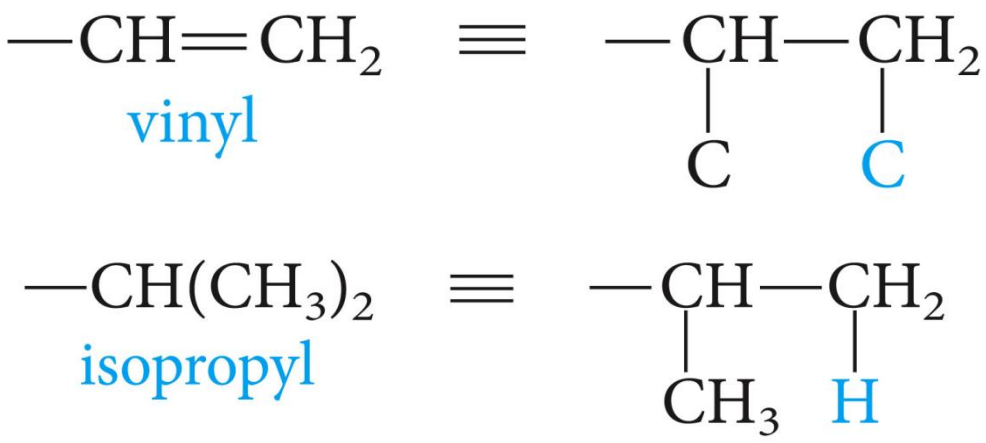






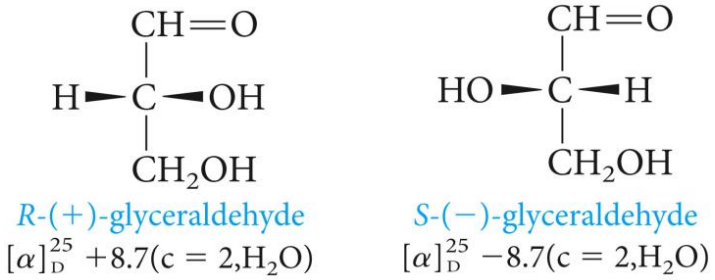


문제: Which group has the higher priority, isopropyl or vinyl ?

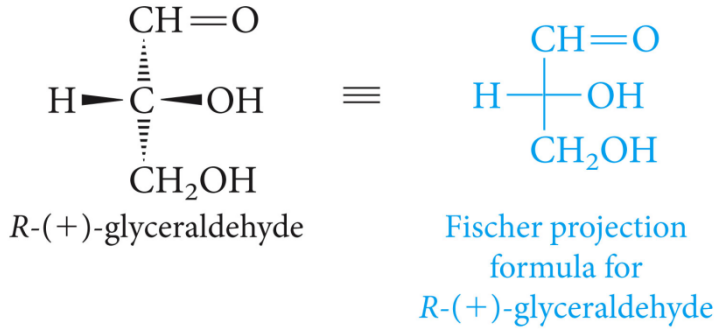


3. Chirality in Monosaccharides; Fischer Projection Formulas and D,L-Sugars

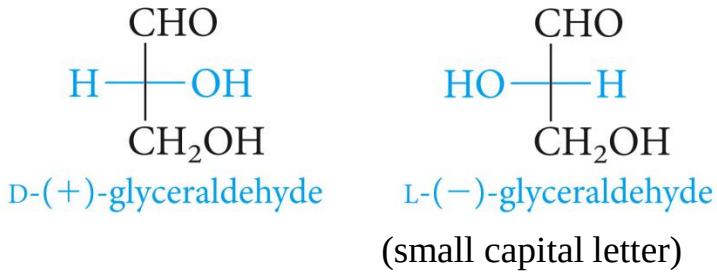
two enantiomers



Configuration과 optical rotation sign간에 상관관계는 전혀 없다.

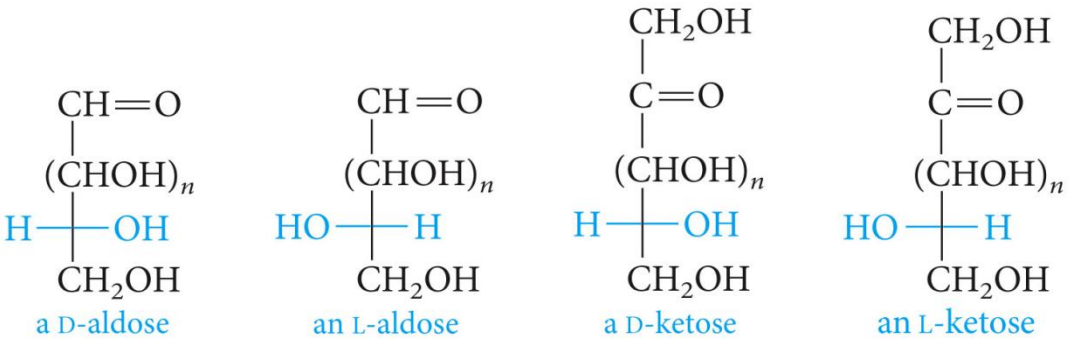


D represents R configuration.



(small capital letter)

The most oxidized carbon (CHO) was placed at the top.



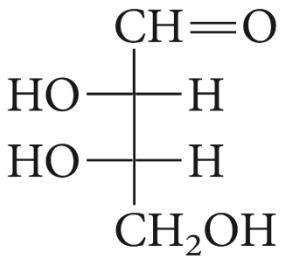
다른 monosaccharide들의 경우...

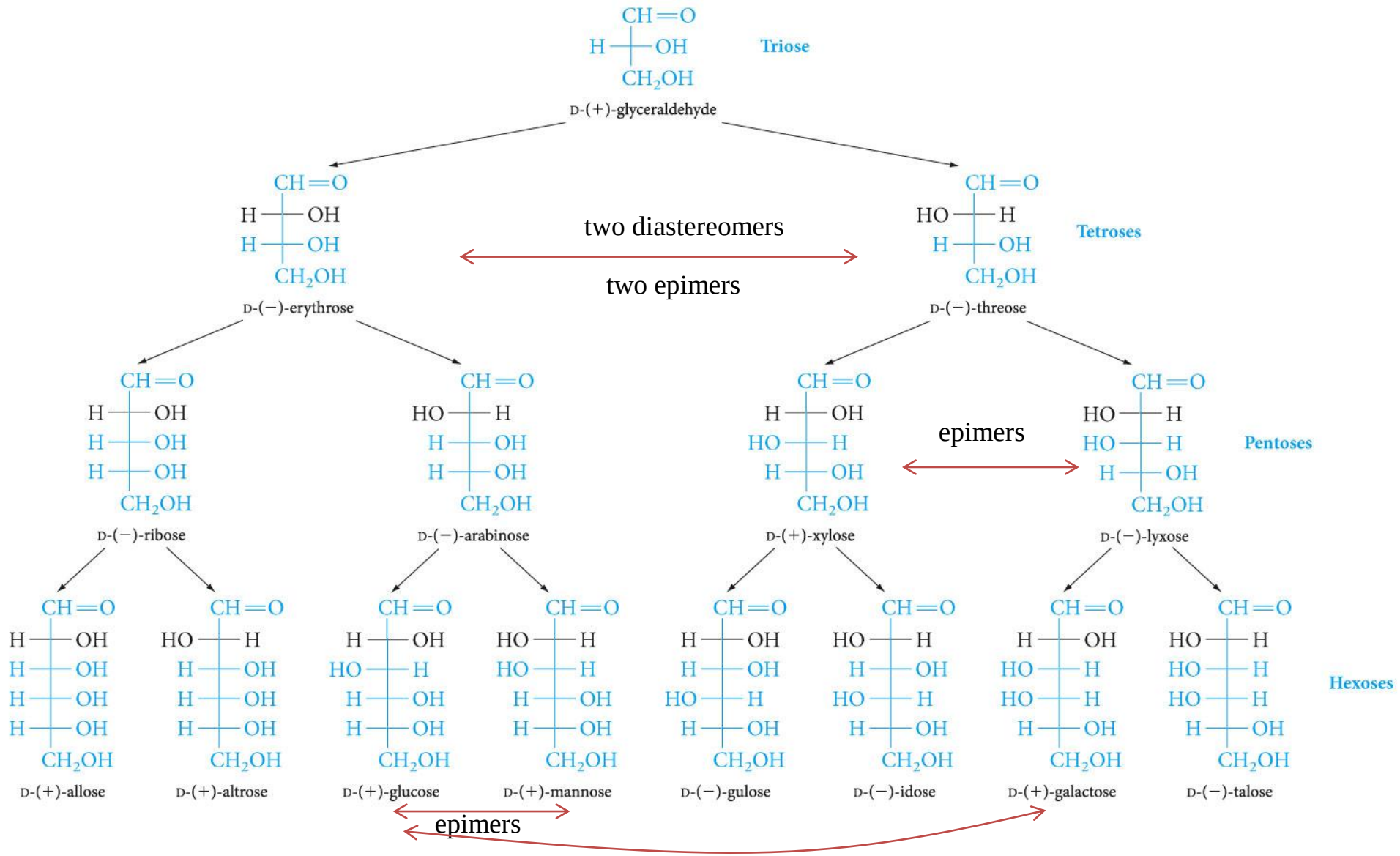
Stereogenic carbon이 CH=O(aldehyde)나 C=O(ketone)로부터 가장 멀고, D configuration을 가질 때 D-sugar라고 불리었다. L configuration을 가지면 L-sugar라고 불리었다.

D represents R configuration. (= stereogenic carbon의 OH가 오른쪽에 있을때)

이 때, CH=O or C=O는 윗쪽에 그린다.

Example 16.1 L-erythrose의 Fischer projection을 그려라.

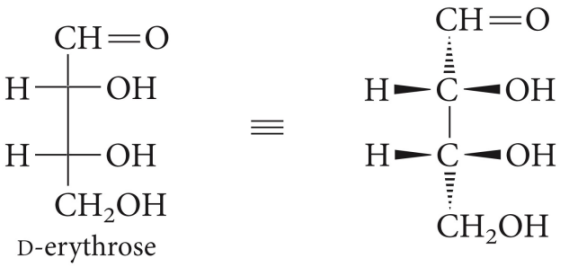


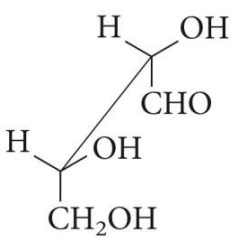


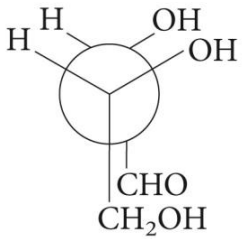
CH-OH unit 하나씩 새로 insertion

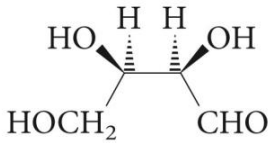
epimer: diatereomers that differ in configuration at only one stereogenic center

Example 2. D-erythrose의 three-dimensional structural formula를 그려라.

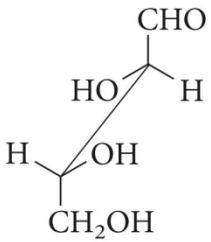


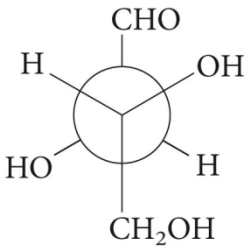


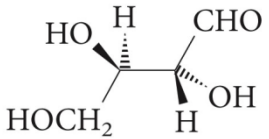


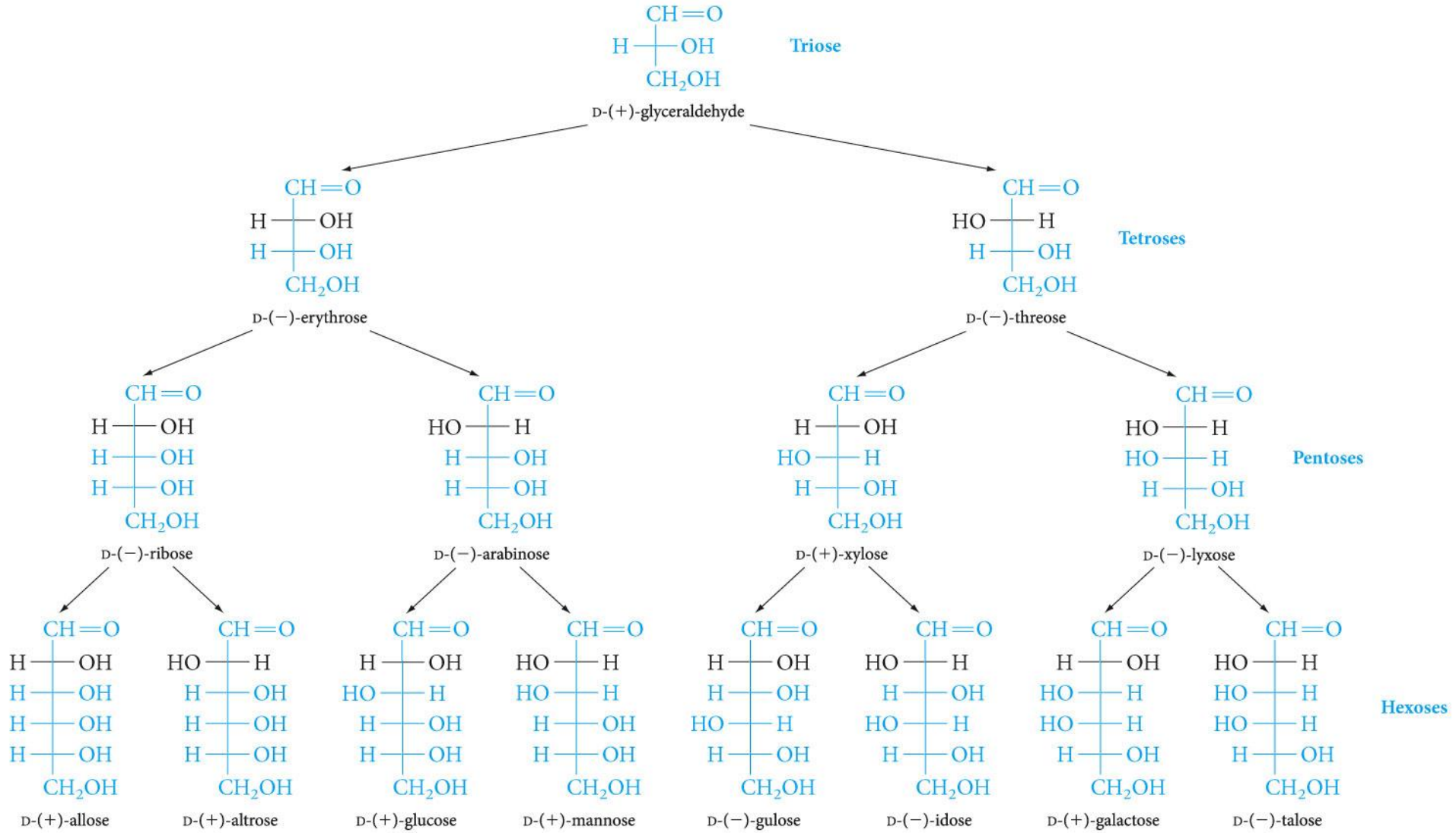


C-C bond의 rotation









Notice that there is no direct relationship between configuration and the sign of optical rotation. Although all of the sugars in above are D-sugars, some are dextrorotatory (+) and others are levorotatory (-).