생유기화학
(Bioorganic Chemistry)

Carbohydrates-III
(탄수화물-3)

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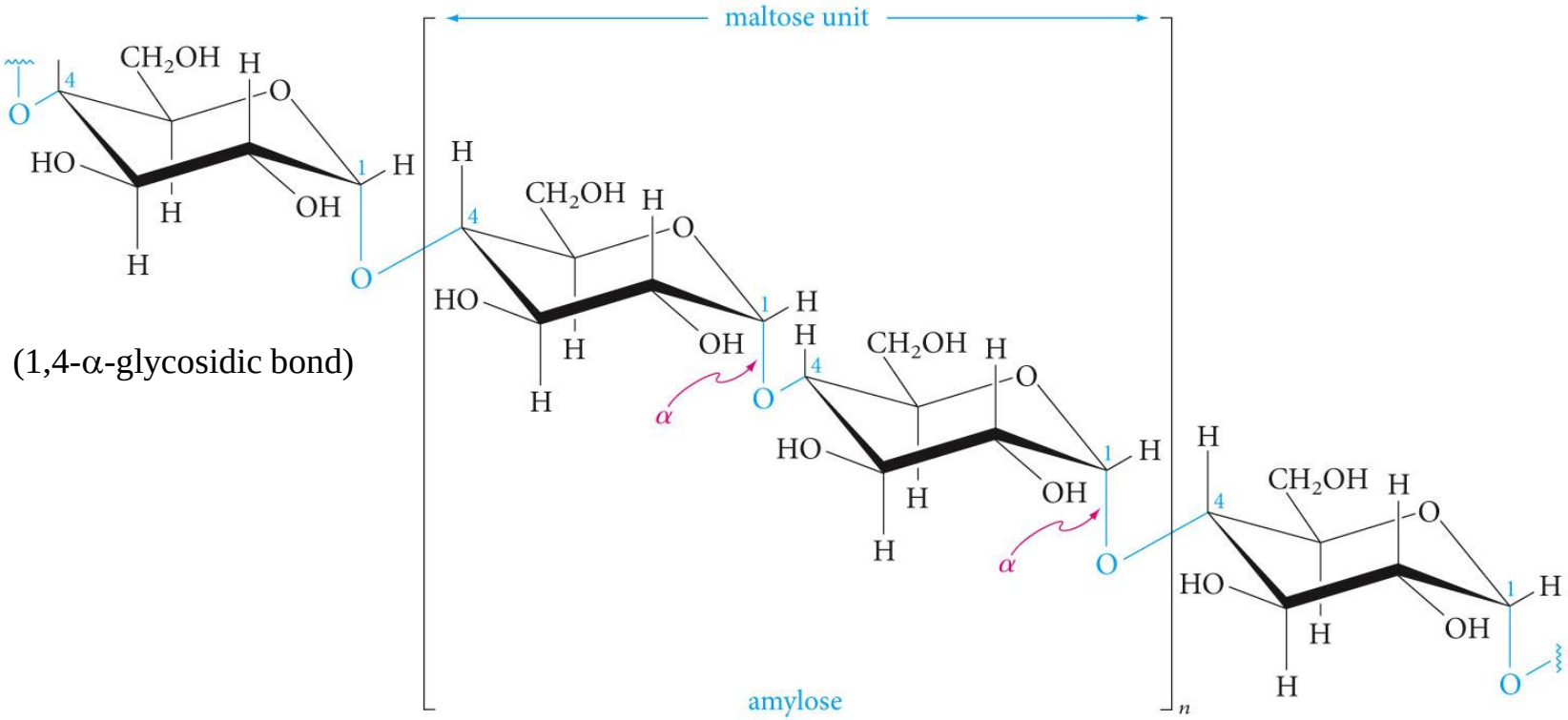
13. Polysaccharides

13.a Starch and Glycogen (녹말과 글리코겐)

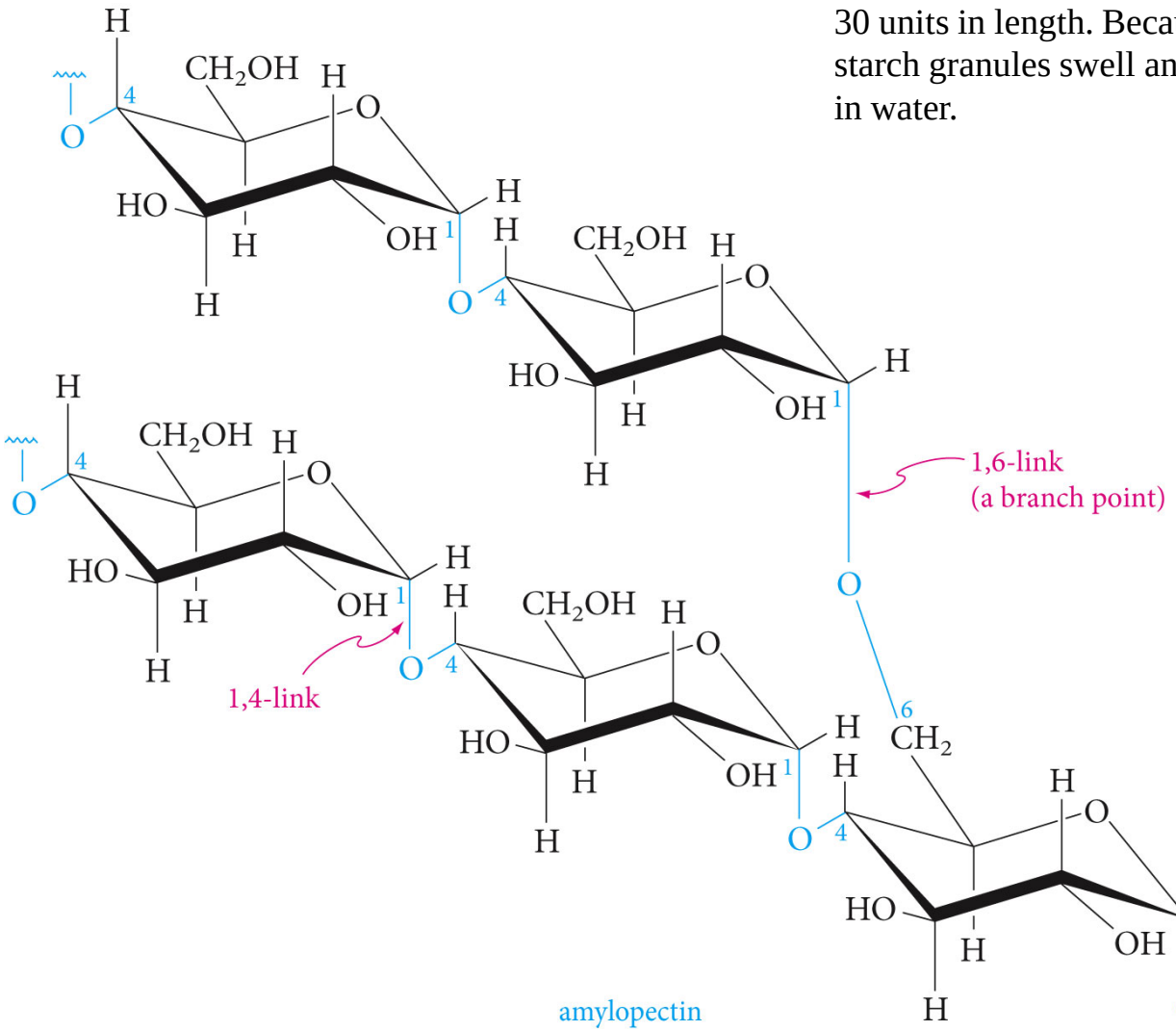
Starch is the energy-storing carbohydrates of plants. It is a major component of cereals, potatoes, corn, and rice. It is the form in which glucose is stored by plants for later use.
수많은 D-글루코스(포도당)가 축합반응을 일으키면서 길게 연결되어 만들어지는 다당류로서 아밀로오스(amylose)와 아밀로펙틴(amylopectin)의 혼합물이다. 녹말의 가수분해는 maltose를 만들고 완전한 가수분해는 glucose를 만든다.
Amlyose: unbranched form of starch

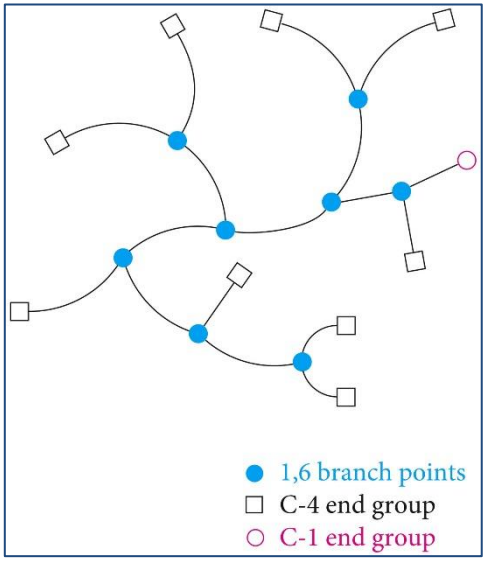


(1,4-α-glycosidic bond)

Amlyopectin: highly branched form of starch

Although each molecule may contain 300 to 5000 glucose units, chains with consecutive 1,4 links average only 25 to 30 units in length. Because of this highly branched structure, starch granules swell and eventually form colloidal systems in water.





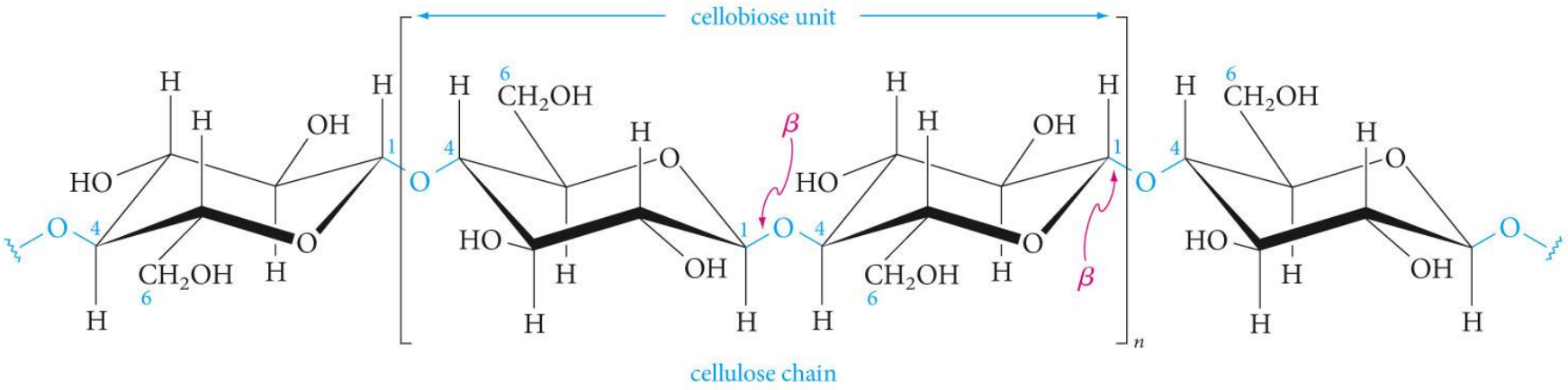
Glycogen: the energy-storing carbohydrate of animals. more branched than amylopectin

13.b Celluose

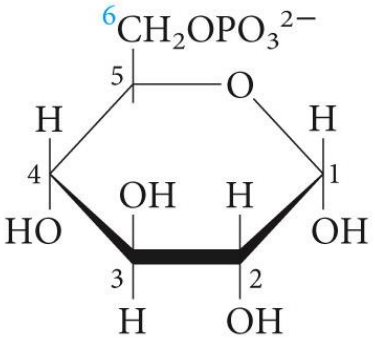
unbranched polymer of glucose joined by 1,4-β-glycosidic bond

these linear molecules aggregate to give fibrils bound together by hydrogen bonds → paper, wood, cotton, straw, etc.

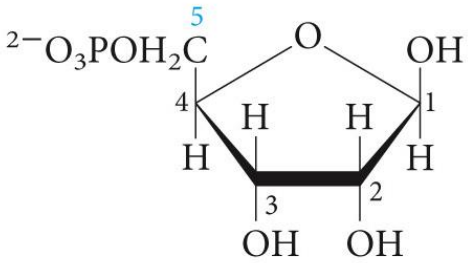
사람은 cellulose를 소화못한다. 사람은 α-glycosidic bond만 소화 가능함



14. Sugar Phosphates



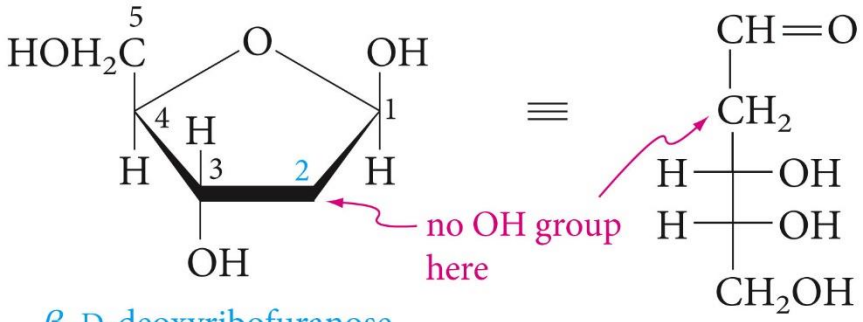
α-D-glucose-6-phosphate



β-D-ribose-5-phosphate

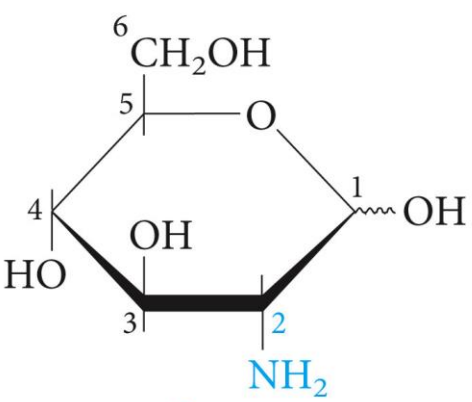
important in biological compounds, such as DNA and RNA

15. Deoxy Sugars

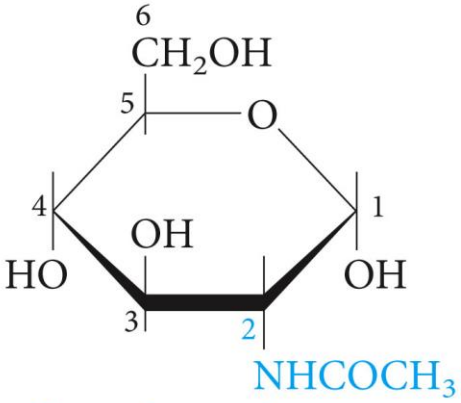


β-D-deoxyribofuranose (the sugar of DNA)

16. Amino Sugars



D-glucosamine
α mp 88°C
β [mp 110°C (decomposes)]

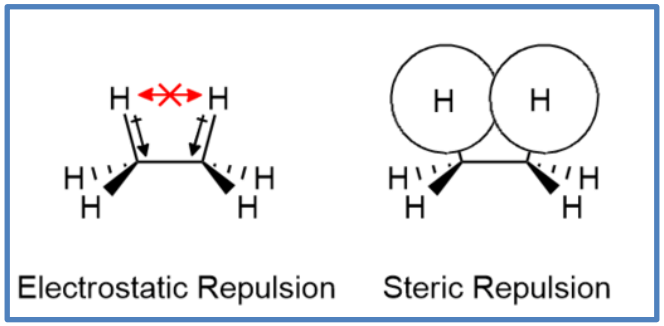


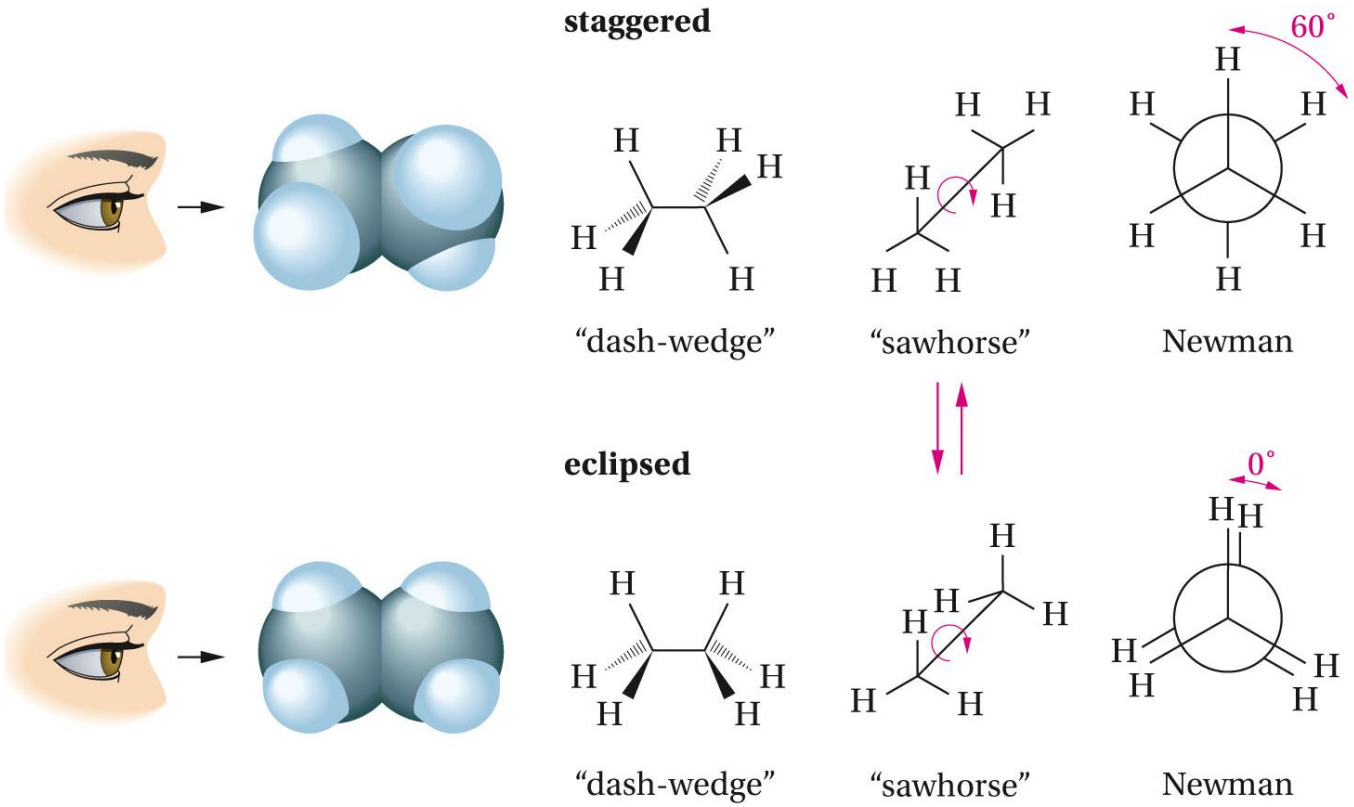
N-acetyl-α-D-glucosamine
[mp 211°C (decomposes)]

In its *N*-acetyl from, β-D-glucosamine is the monosaccharide unit of chitin, which forms the shells of lobsters, crabs, shrimp, and other shellfish.

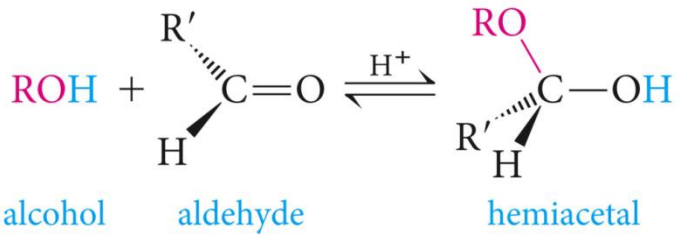
Conformational Isomers : Isomers that differ as a result of the degree of rotation around a carbon-carbon single bond

Conformational isomerism in Ethane



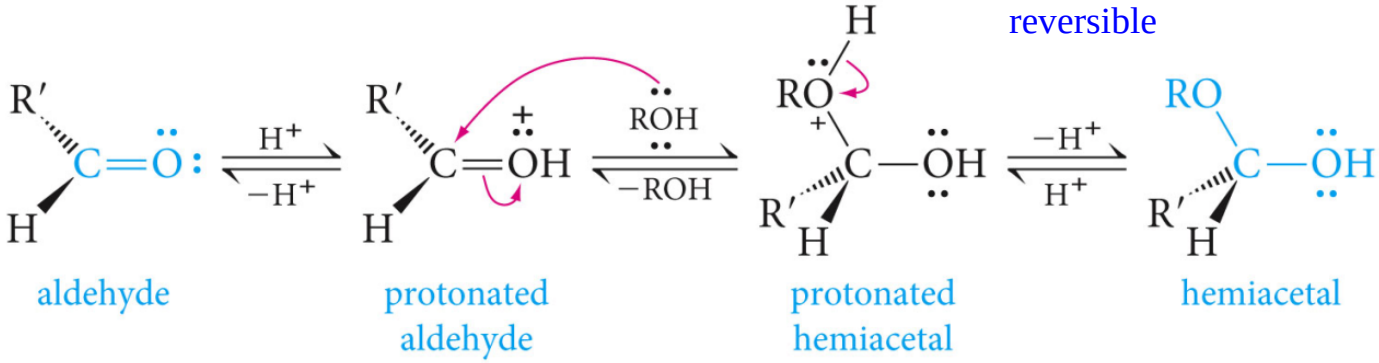


Addition of **Alcohols**: Formation of **Hemiacetals** and Acetals

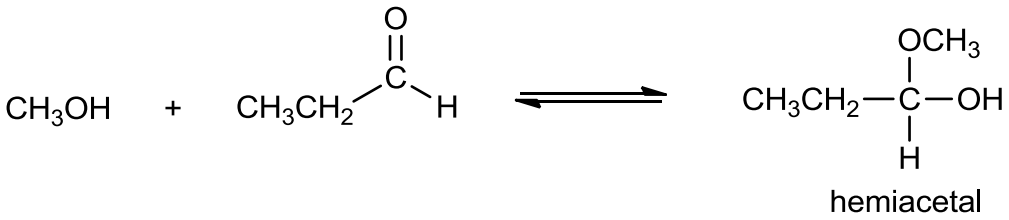


A hemiacetal contains both alcohol and ether functional groups on the same carbon atom.

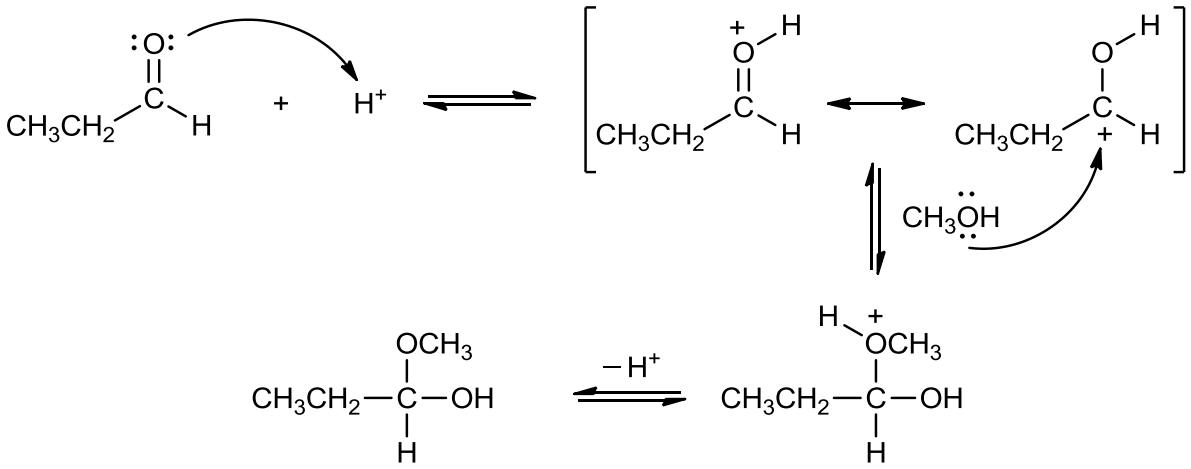
Alcohols are weak nucleophiles. → An acid catalyst is required. (e.g. sulfuric acid)



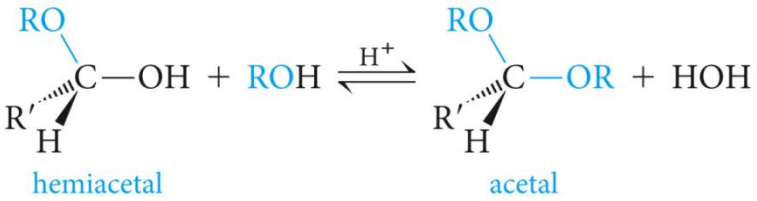
Problem 8. Write an equation for the formation of a hemiacetal from propanal, ethanol, and H^+. Show each step in the reaction mechanism.



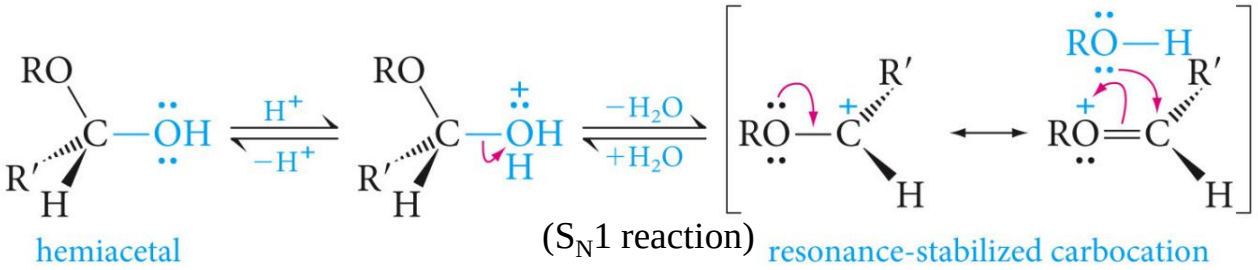
Mechanism



In the presence of excess alcohol, hemiacetals react further to form acetals.

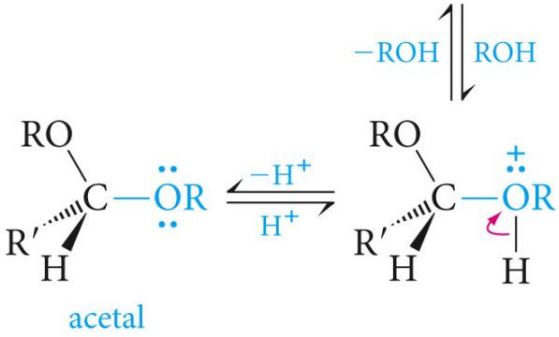


acetal : It has two ether functional groups on the same carbon atom.
That is, the carbon atom has two alkoxyl groups.

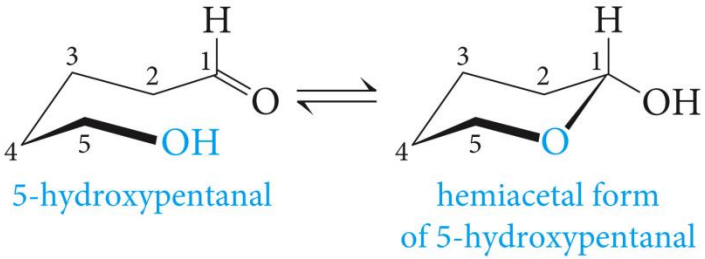


(S_N1 reaction)

Each step is reversible.

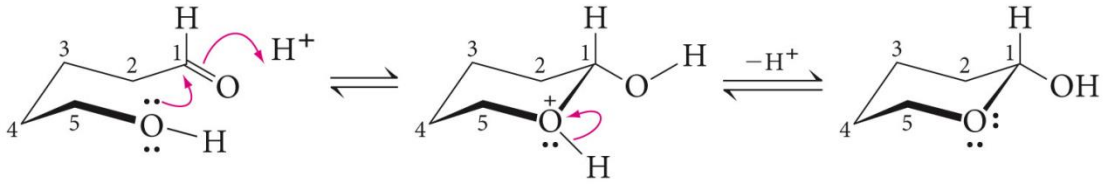


Reaction of this carbocation with alcohol, which is usually the solvent and is present in large excess, give the acetal.

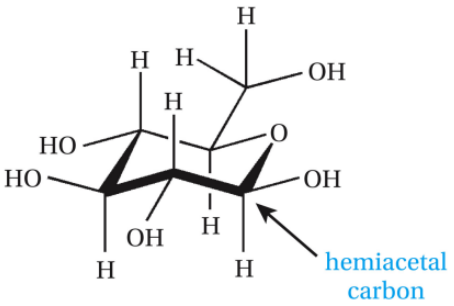


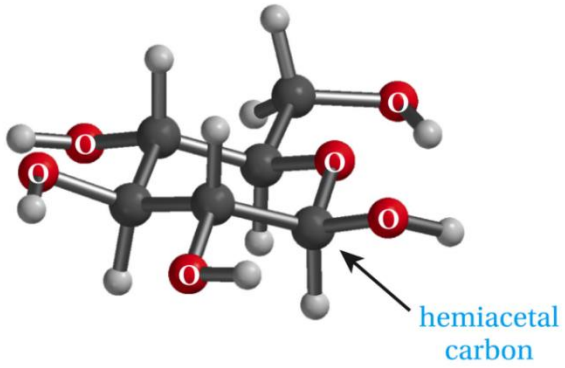
cyclic hemiacetal: the ether group is cyclic

formed by intramolecular nucleophilic addition

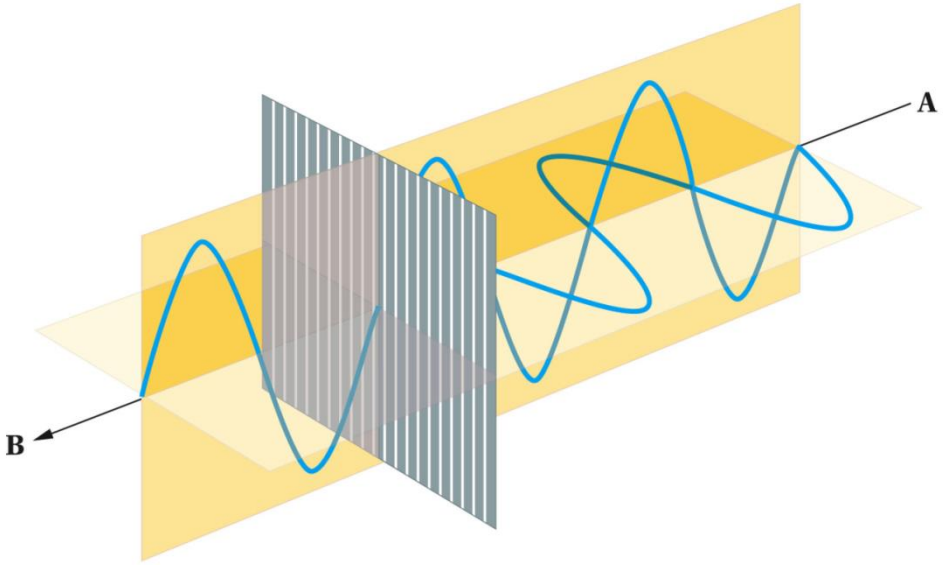


Compounds that is four or five carbons away from the aldehyde group tend to form cyclic hemiacetals, because the ring size is relatively strain free.





Polarized light



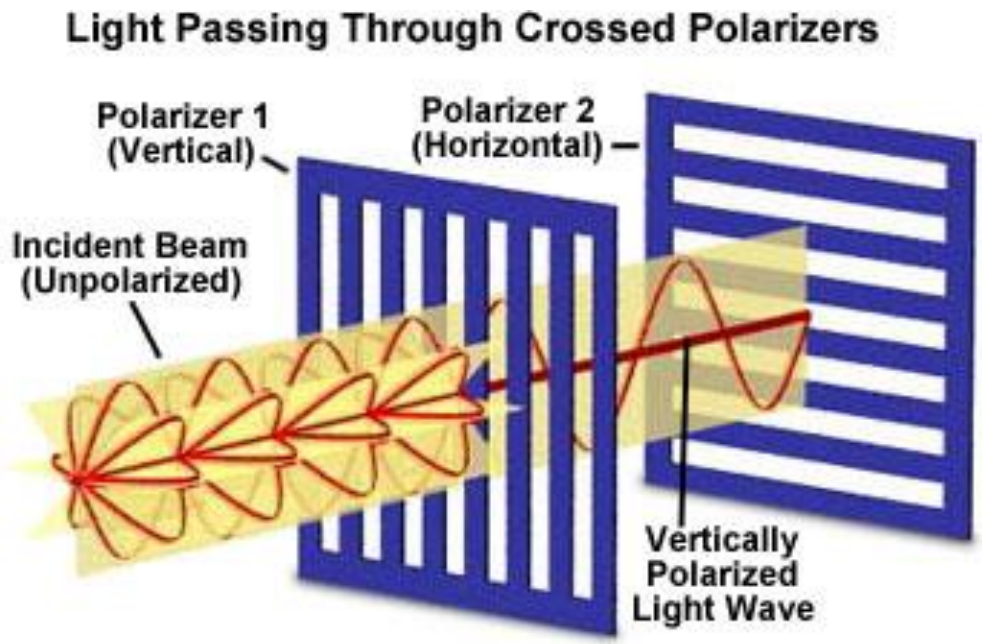
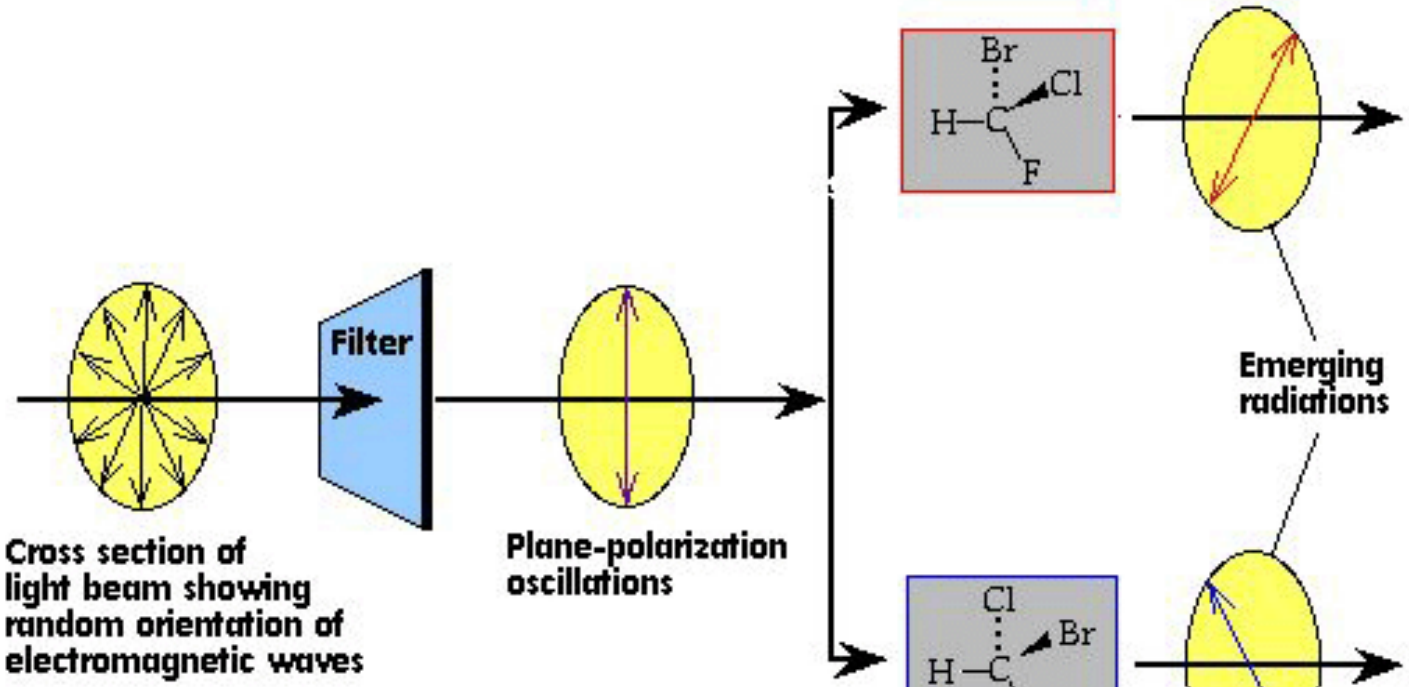


Figure 1



- 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

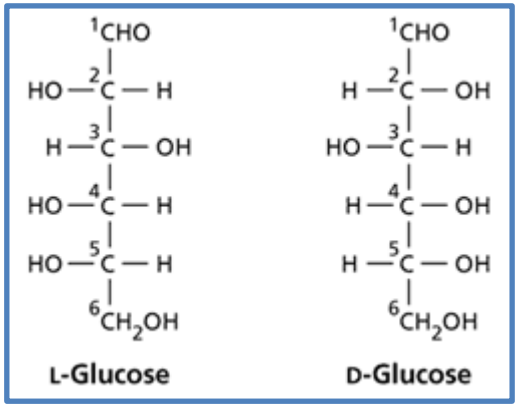
Enantiomers 끼리는 m.p., b.p. density, 용해도등이 모두 같으나 specific rotation만 다르다.

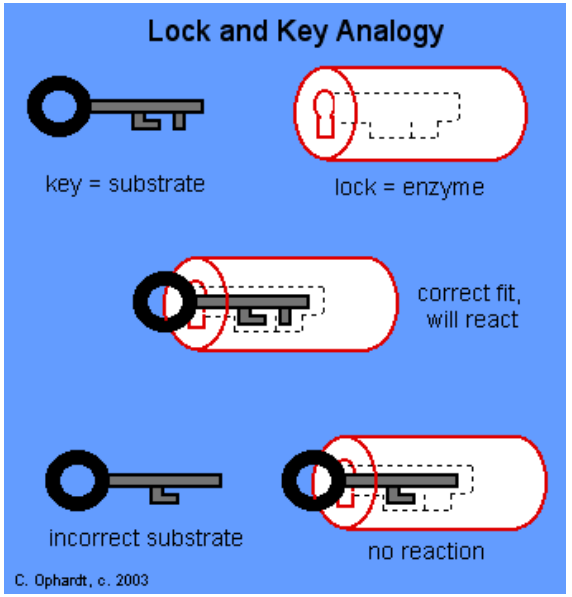
- optically active: enantiomer, chiral molecule, 탄수화물, 단백질, 아미노산, 호르몬 등
- optically inactive: achiral molecule, 물, 소금, 알코올 등

Examples

- (S)-2-Bromobutane +23.1°
- (R)-2-Bromobutane –23.1°
- D-Fructose –92.4°
- D-Glucose +52.5°
- D-Sucrose +66.47°
- D-Lactose +52.3°
- Camphor +44.1°
- Cholesterol –31.5°
- Paclitaxel –49°
- Penicillin V +223°

- (R)-something 이 + x^o 이면 (S)-something – x^o 이다.
- (R)-something이 + x^o or – x^o 인지는 알 수 없다. 측정해야 알 수 있음

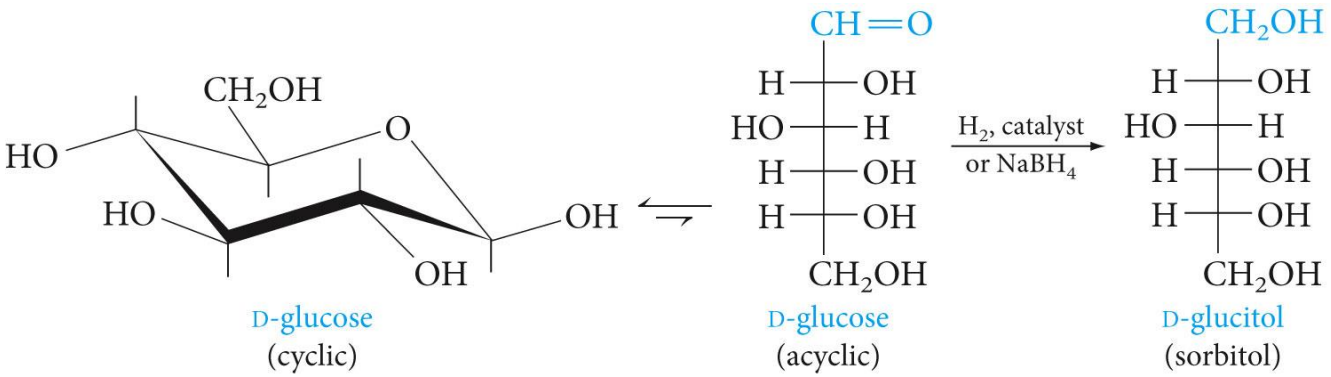




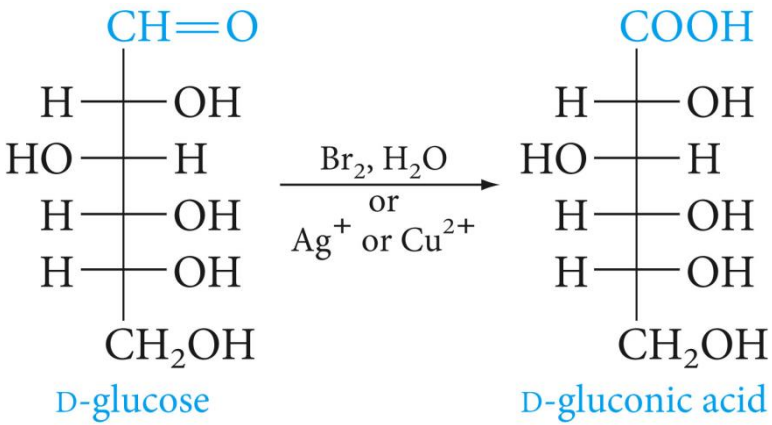
Specific rotation 값이 0으로 나왔다.

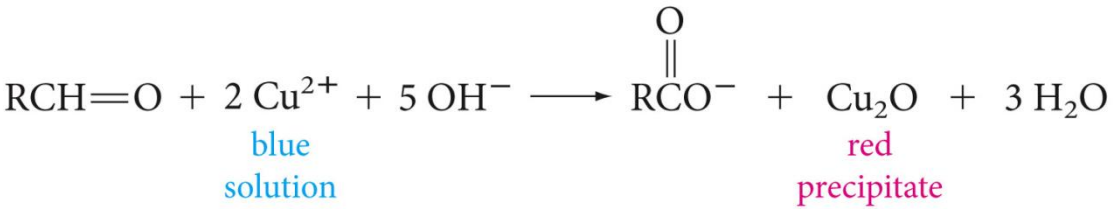
Achiral molecule이다. **or** 50 : 50 의 enantiomers (pair)이다.

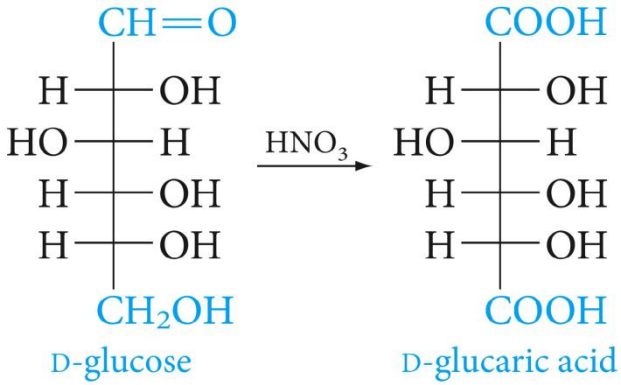
9. Reduction of Monosaccharides



10. Oxidation of Monosaccharides




RCH=O + 2 Cu2+ + 5 OH− → RCO− + Cu2O + 3 H2O
blue solution
red precipitate


CH=O
H—OH
HO—H
H—OH
H—OH
CH2OH
D-glucose
HNO3
COOH
H—OH
HO—H
H—OH
H—OH
COOH
D-glucaric acid