有機化學乙

蔡蘊明 教授

Chapter 22 Carbohydrates

※ Introduction

General formula: $C_x(H_2O)_y$

Simple carbohydrates:
sugars, saccharides (醣類)

例
sucrose
glucose -ose ending
maltose

Viewed from functional groups
polyhydroxy aldehydes or ketones

✓Classification

- monosaccharides 單醣 (無法進一步水解)
- disaccharides
- trisaccharides
- oligosaccharides (2-10 單醣)
- polysaccharides (>10 單醣)

$$1\ \text{maltose} \xrightarrow[H_2O]{H^+} 2\ \text{glucose}$$

disaccharide

$$1\ \text{sucrose} \xrightarrow[H_2O]{H^+} 1\ \text{glucose} + 1\ \text{fructose}$$

starch
cellulose } composed of n glucose

$$\text{monosaccharide} \xrightarrow{H_2O} \text{no hydrolytic cleavage}$$

✓ Biologically

$$xCO_2 + yH_2O + \text{solar E} \xrightarrow{\text{enzyme}} \text{carbohydrates} + xO_2$$

$$\text{carbohydrates} + xO_2 \longrightarrow xCO_2 + yH_2O + E$$

$$ADP \xrightarrow{E} ATP$$

$$ATP \longrightarrow ADP + E$$

※ Monosaccharides

◎ Classification

CH_2OH
|
C=O
|
CHOH
|
CHOH
|
CH_2OH

a ketose

a ketopentose

functional group → "keto"; number of carbons → "pent"

CHO
|
CHOH
|
CHOH
|
CH_2OH

an aldose

an aldotetrose

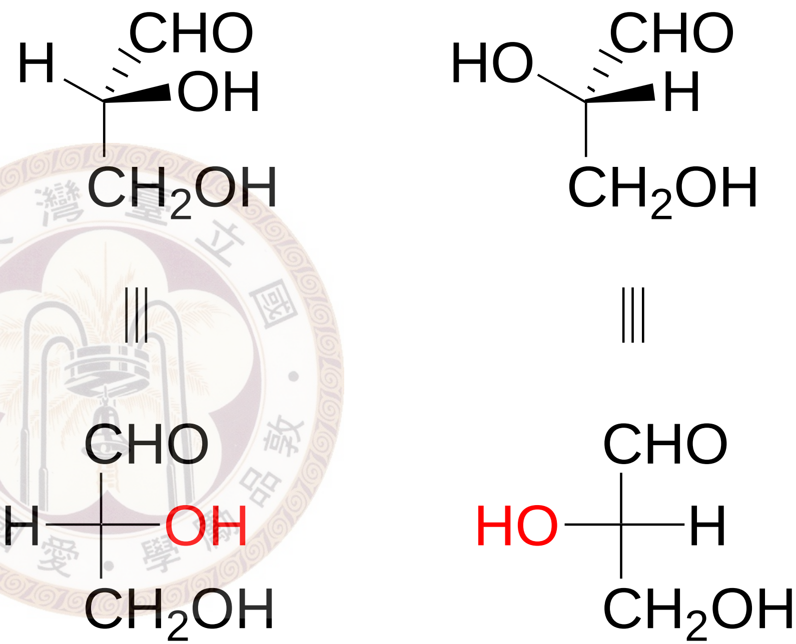
triose
hexose
etc.

◎ D and L designation

glyceraldehyde

CHO
|
*CHOH :
|
CH_2OH

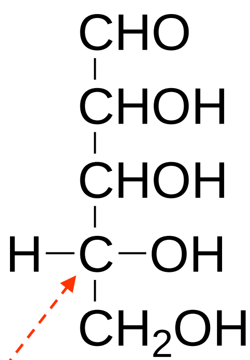
an aldotriose



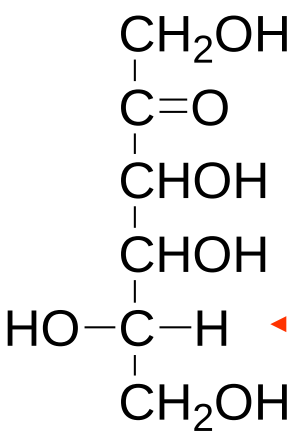
R-(+) *S*-(–)

Designate as: D L

Use D- and L-glyceraldehyde as a reference for other sugars



Highest numbered chiral carbon:
same configuration as D-glyceraldehyde
: an D-aldopentose

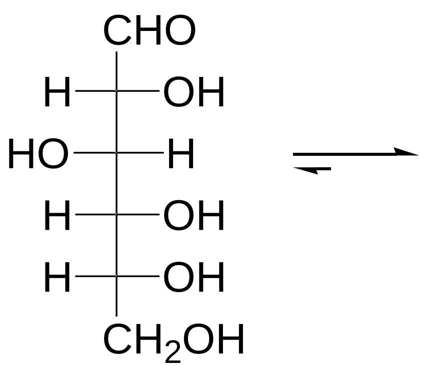


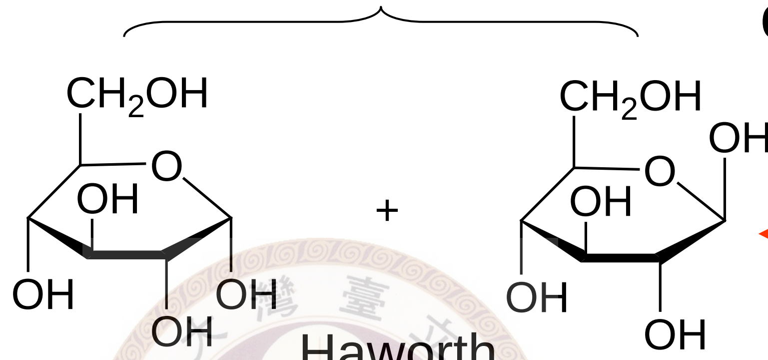
Same configuration as L-glyceraldehyde
: an L-ketohexose

◎ Structure (Emil Fischer)

D-(+)-glucose

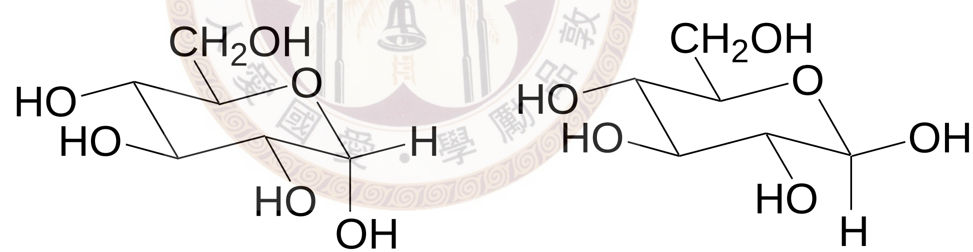
Diastereomers: differed by only one carbon

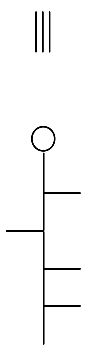




a hemiacetal carbon or anomeric carbon

Haworth projection





α-D-(+)-glucopyranose β-D-(+)-glu-----

C-1 (anomeric) OH and C-6 are trans

C-1 OH and C-6 are cis

A shorthand representation for writing

the two isomers are anomers 變旋異構

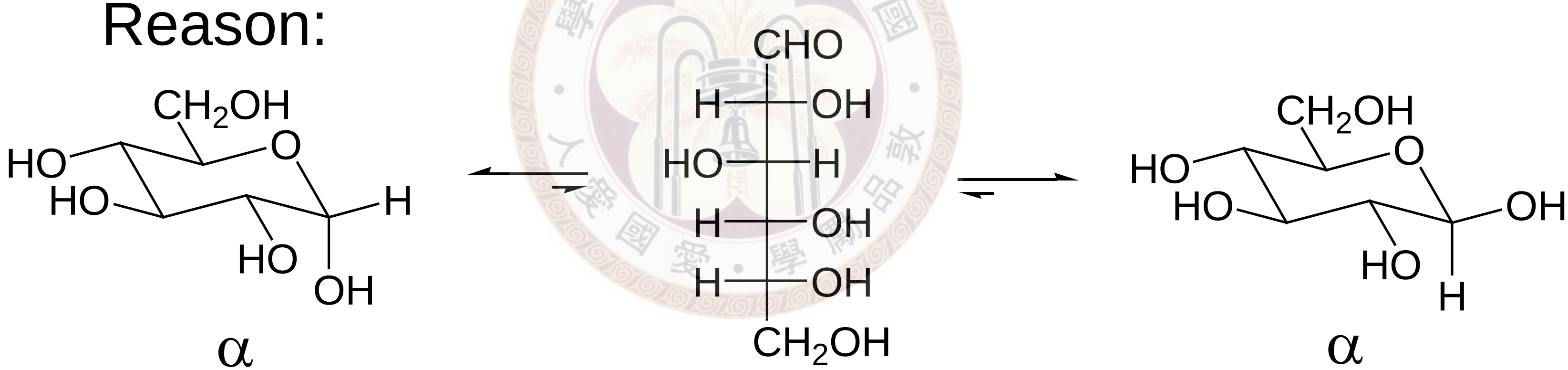
◎ Mutarotation

Ordinary D-(+)-glucose crystallized from water at rt
→ mp 146 °C, [α] = +112°

Crystallized at 98 °C
→ another form: mp 150 °C, [α] = +19 °

In solution: both turn into +52.7 °

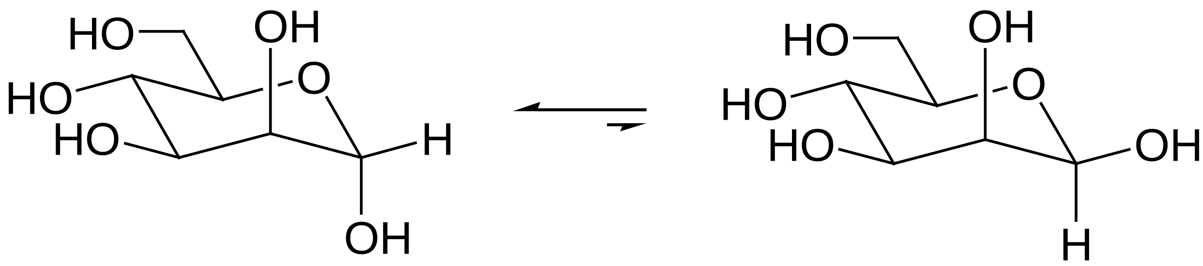
Reason:



α
mp 146 °C
[α] = +112°

at equilibrium
[α] = +52.7°
→ 36% α + 64% β
more stable

α
mp 150 °C
[α] = +19°



α-D-mannopyranose

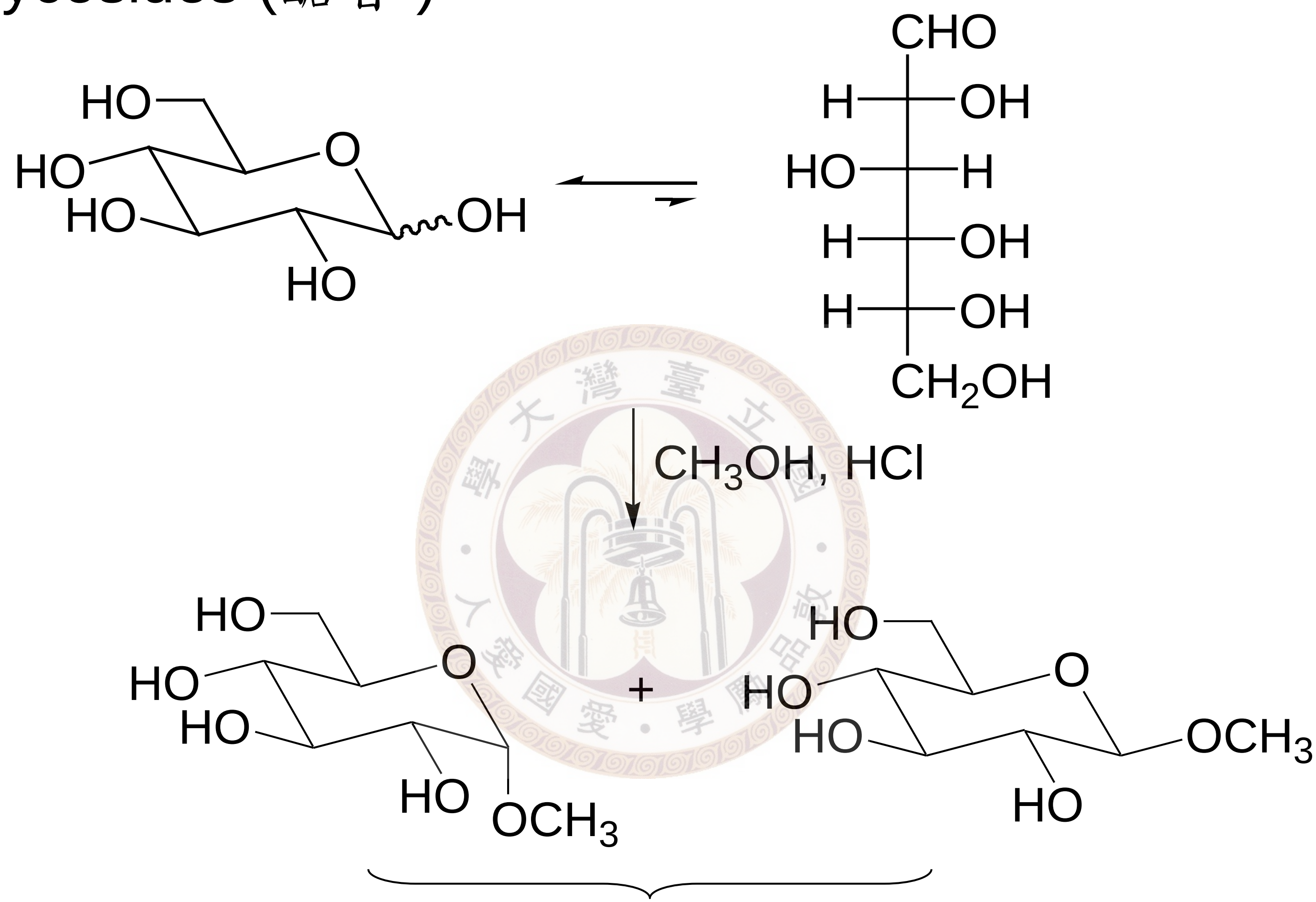
69%

more stable
(anomeric effect)

β-D-mannopyranose

31%

◎ Glycosides (醣苷)



acetals

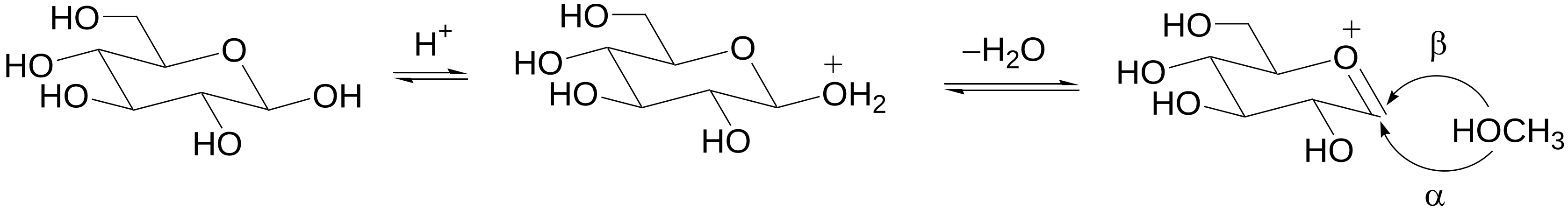
methyl α-D-glucopyranoside

mp 165 ^oC, [α] = +158^o

methyl β-D-glucopyranoside

mp 107 ^oC, [α] = –33^o

Mechanism:

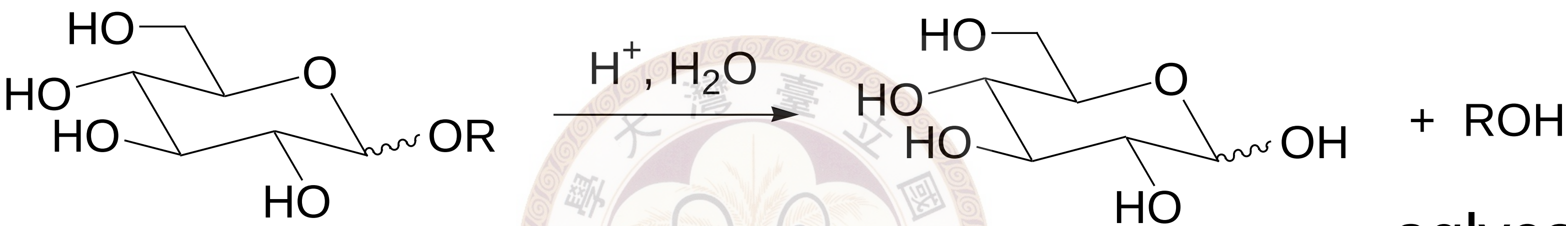


✓ Glycosides:

no mutarotation

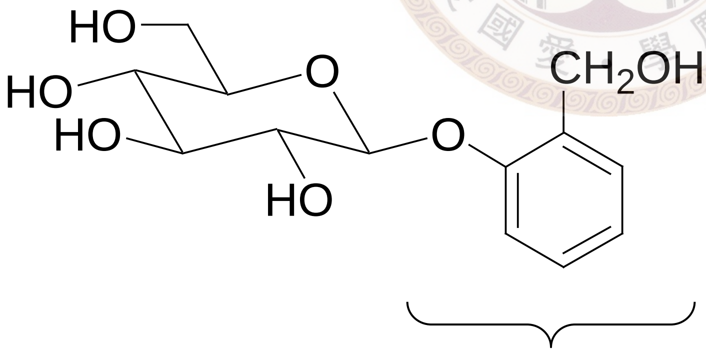
stable in basic condition

hydrolyzes in acidic condition



aglycone

例

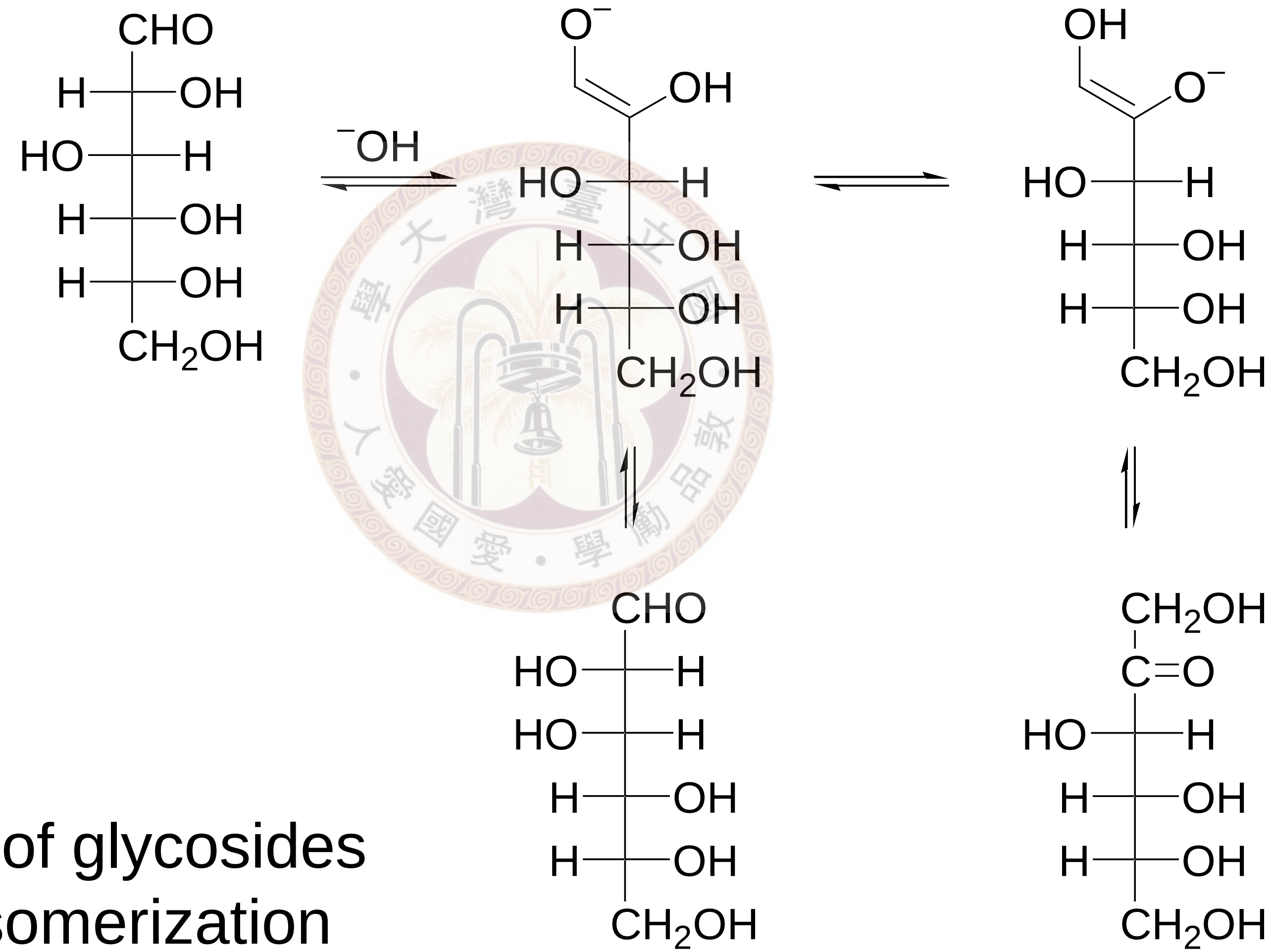


salicin
from willow bark

aglycone

※ Reactions

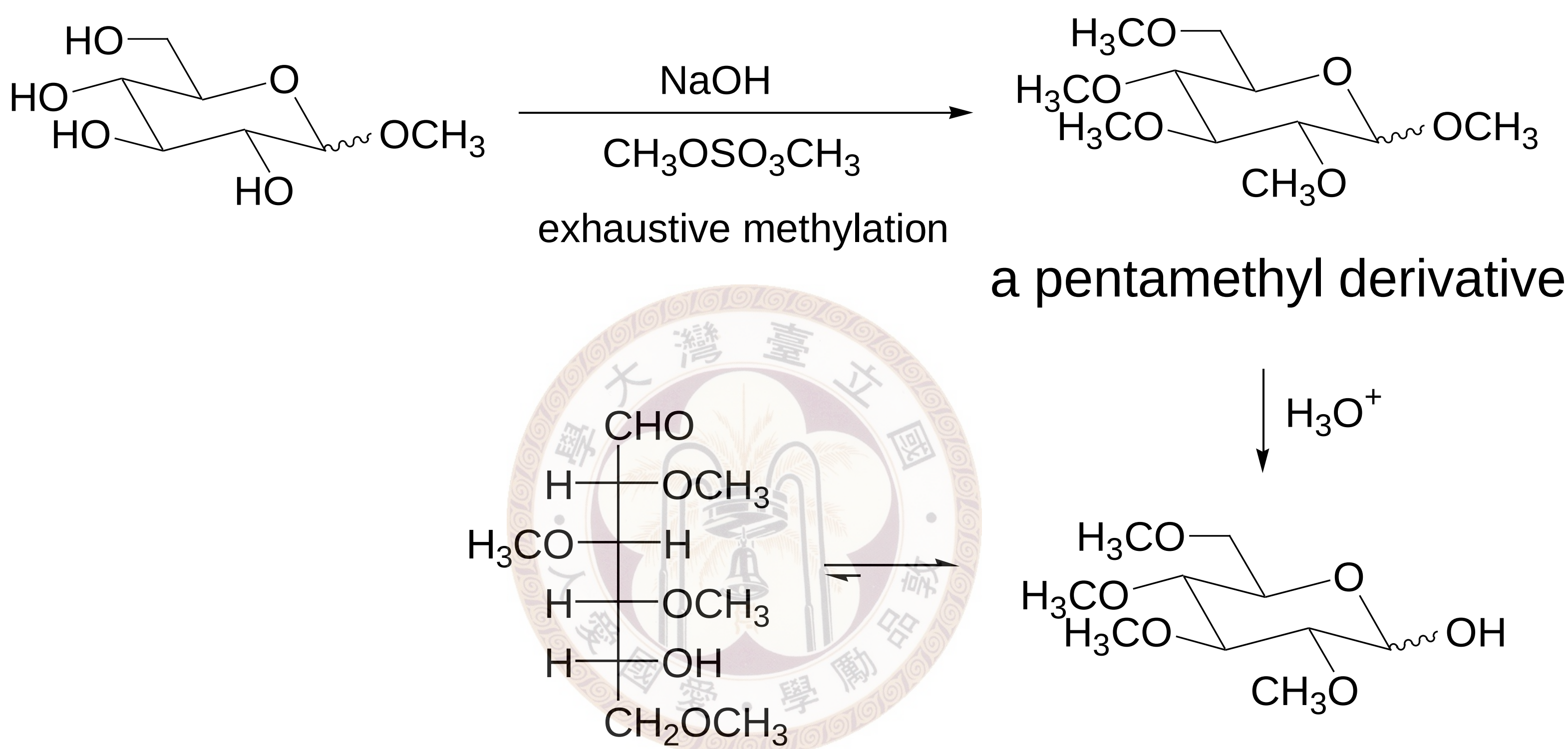
◎ Isomerization of monosaccharides



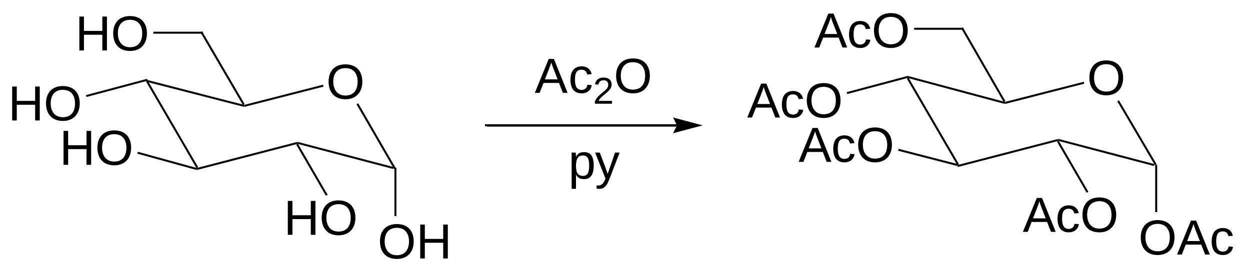
D-mannose D-fructose

*Formation of glycosides stops this isomerization

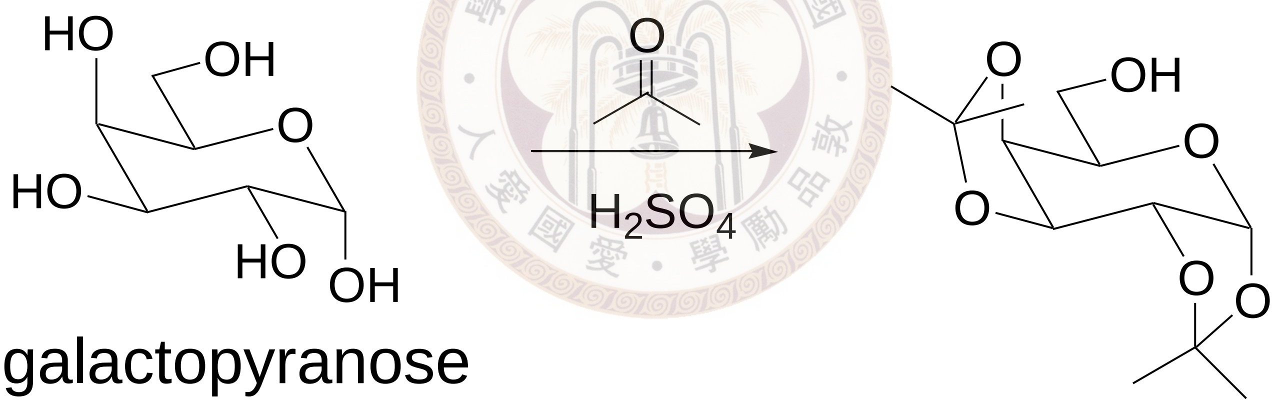
◎ Methylation



◎ Ester formation



◎ Other protection

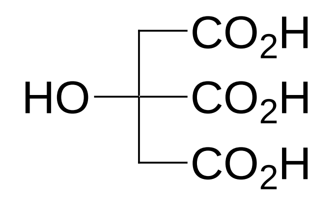


D-galactopyranose

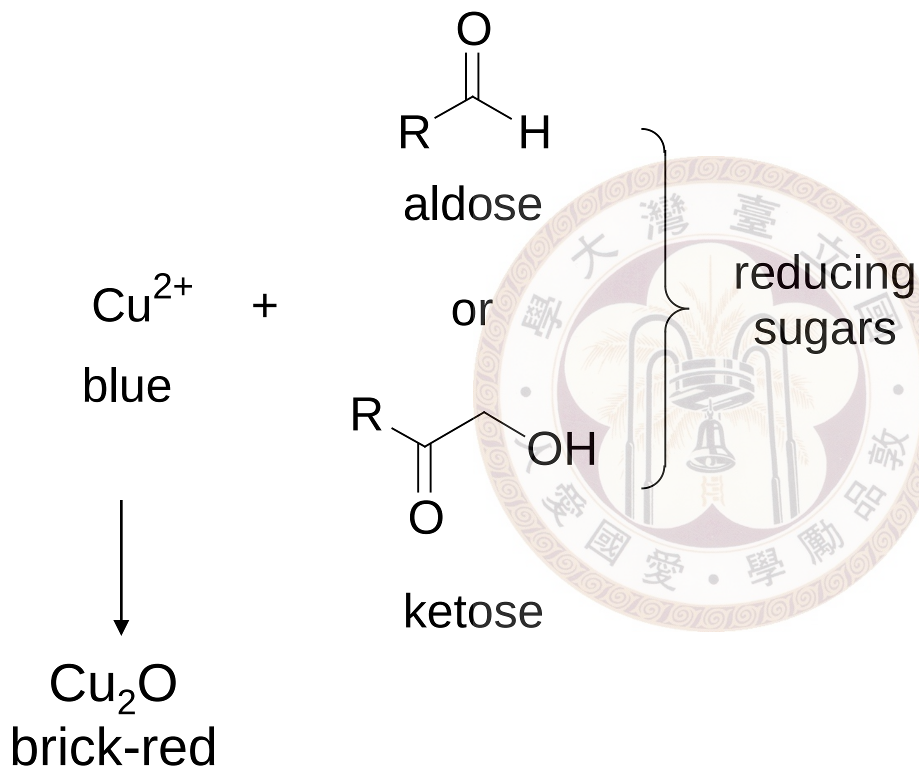
Only the cis diols form cyclic acetals with acetone → acetonides

◎ Oxidation

- ✓ Bendict's reagent: Cu^{2+} complex of citrate
  Fehling's reagent: Cu^{2+} complex of tartrate



citric acid



- ✓ Positive Tollen's test
  → reducing sugars

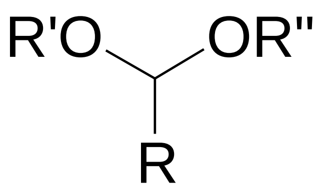
hemiacetals ⇌ the open form

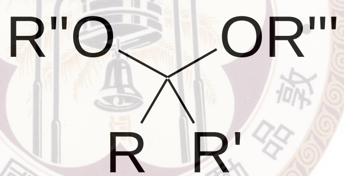
↑

can be oxidized

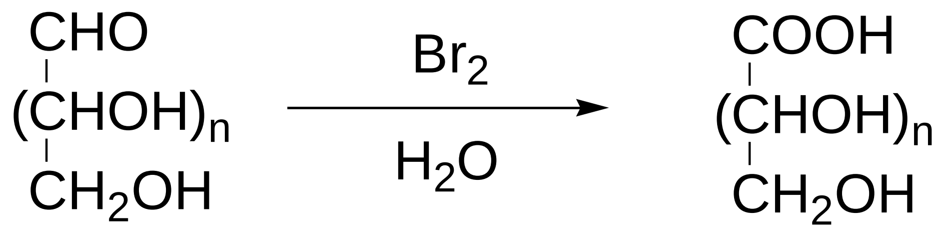
But

acetals are non-reducing sugars



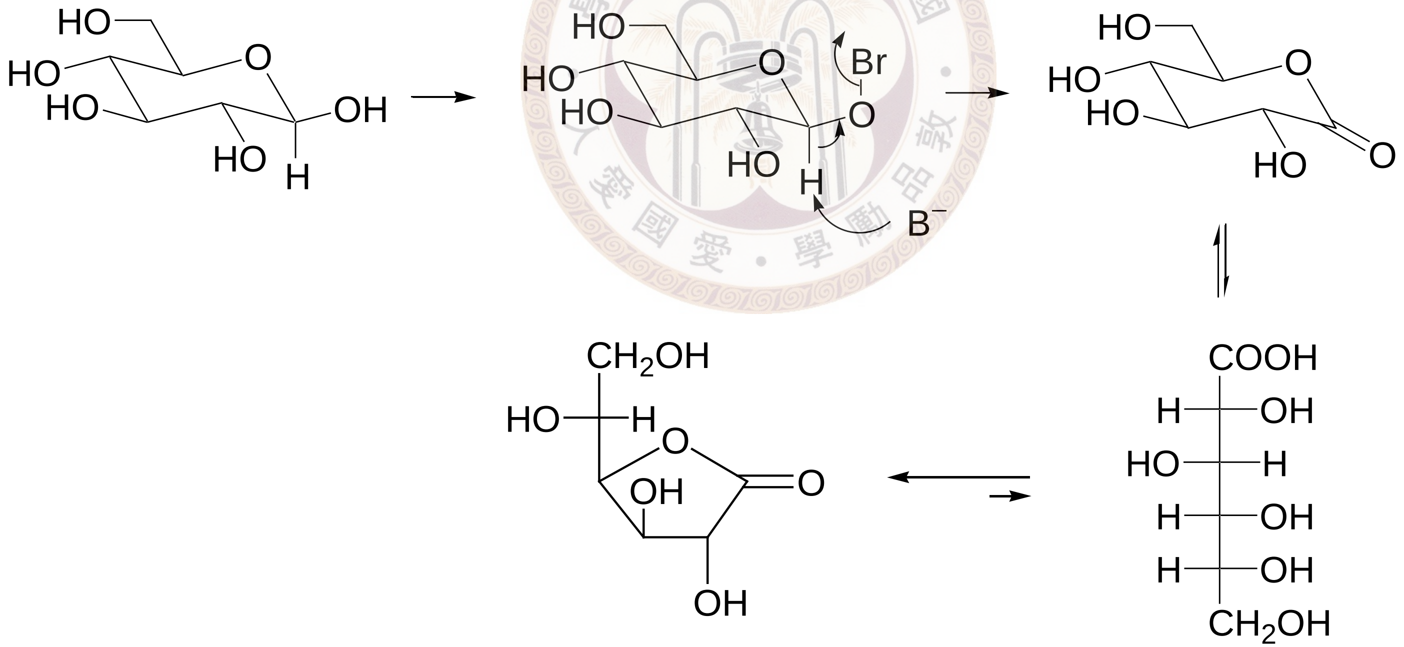


✓ Bromine water oxidation



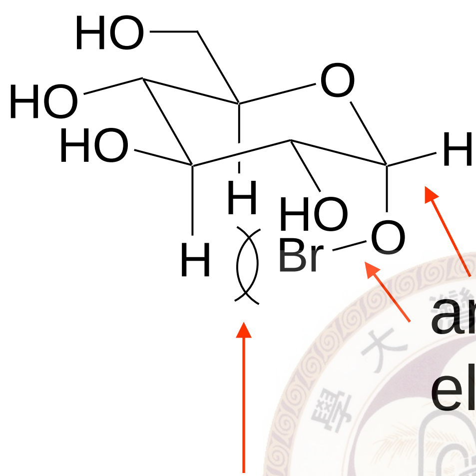
aldose pH = 6.0 aldonic acid

Mechanism:



D-glucono-γ-lactone D-gluconic acid

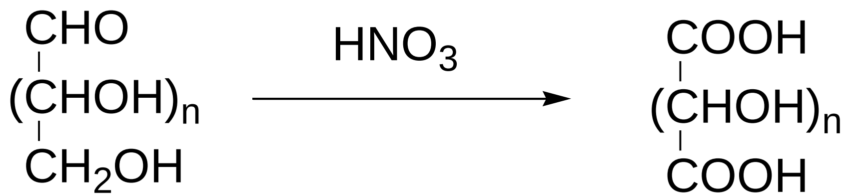
α-form does not react



antiperiplanar requirement for elimination

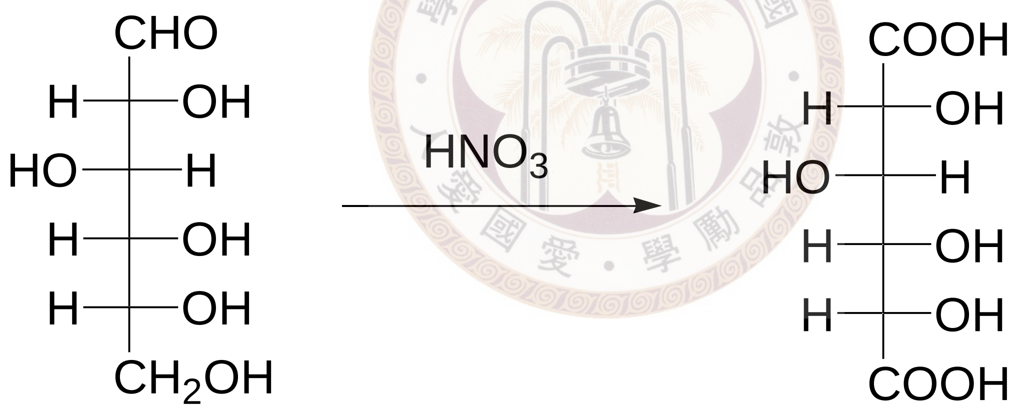
sterically unfavorable

✓ Nitric acid oxidation

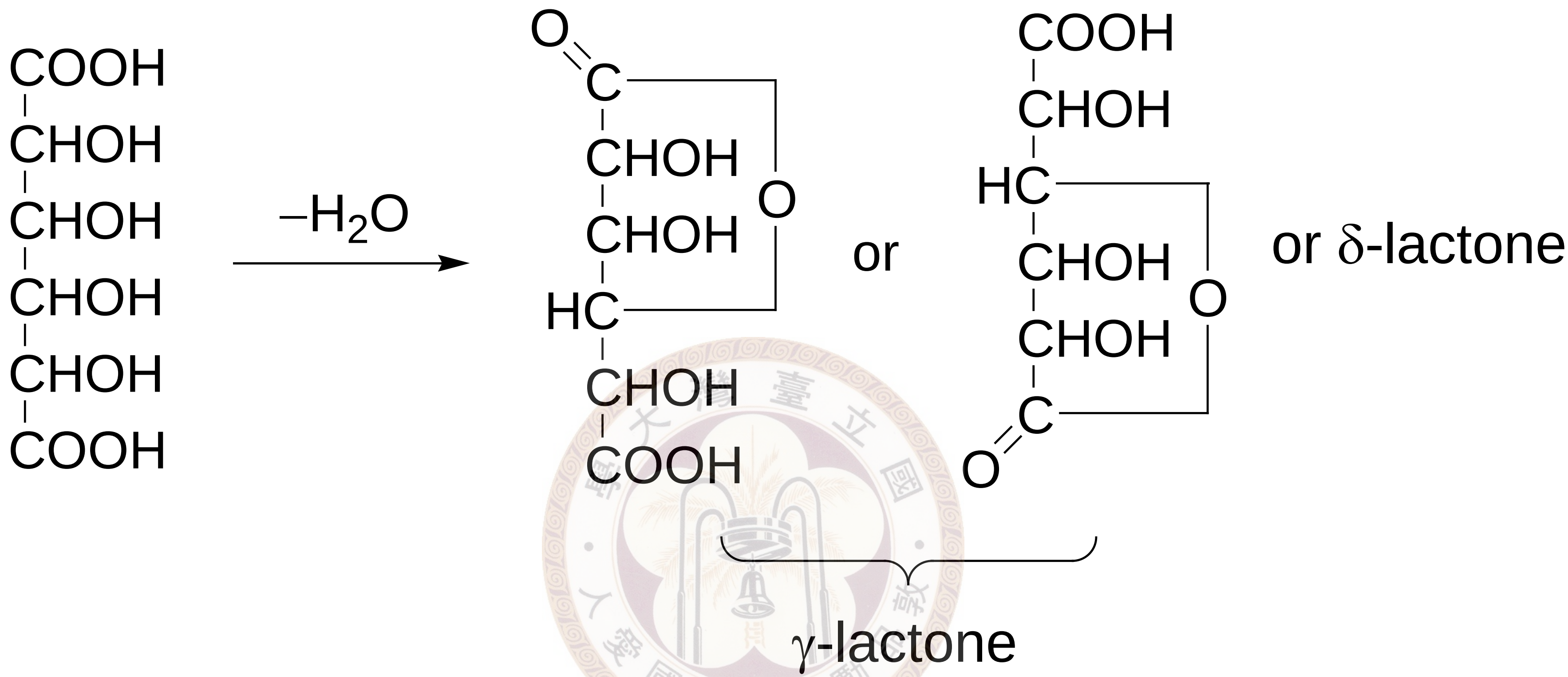


aldose　　aldaric acid

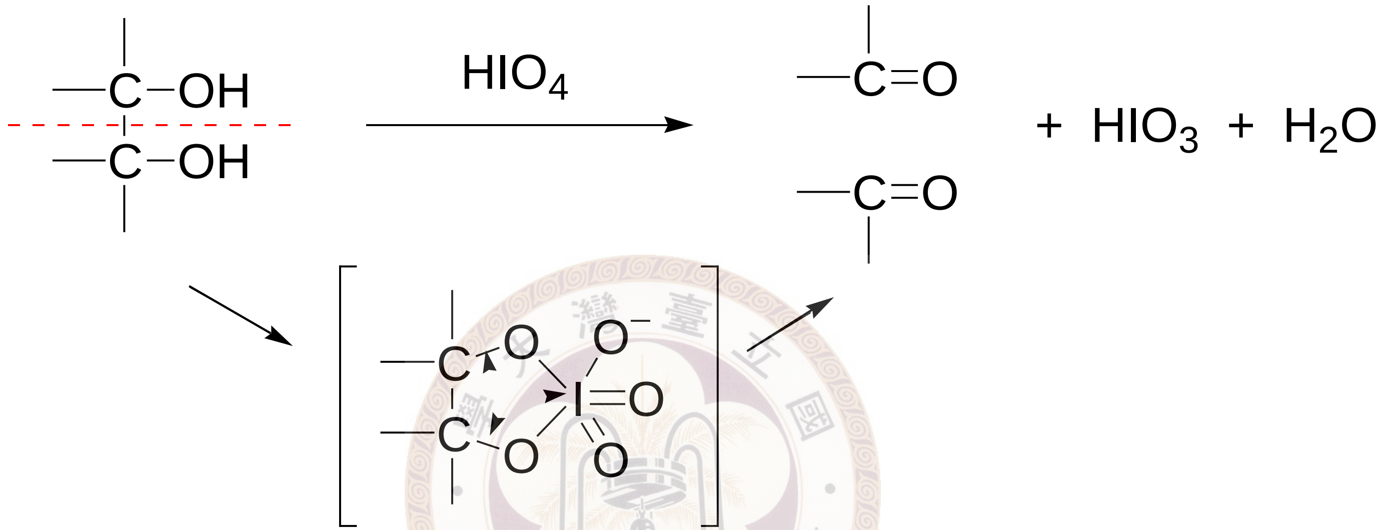
例



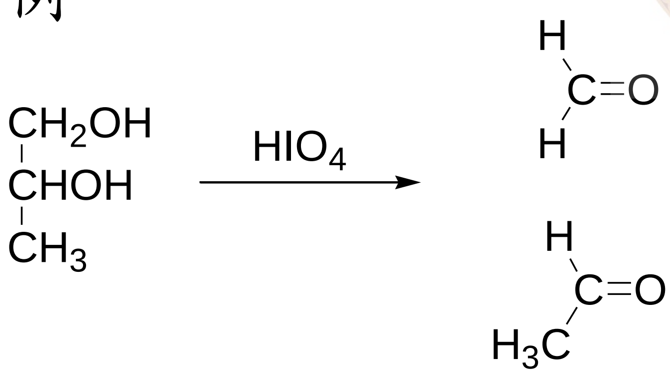
D-glucaric acid

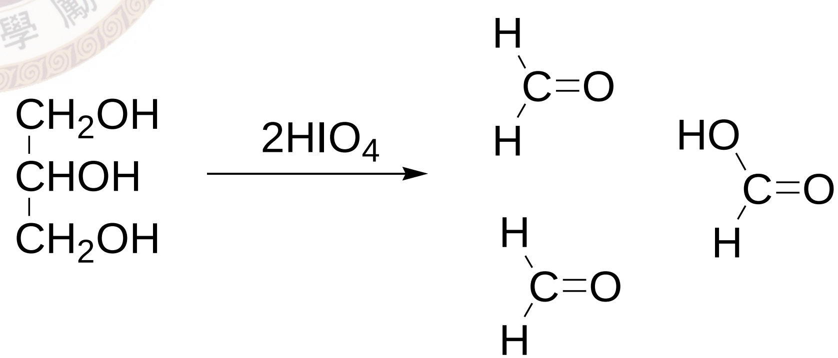

COOH
CHOH
CHOH
CHOH
CHOH
COOH
−H2O
O
C
CHOH
CHOH
HC
CHOH
COOH
O
or
COOH
CHOH
HC
CHOH
CHOH
C
O
O
or δ-lactone
γ-lactone

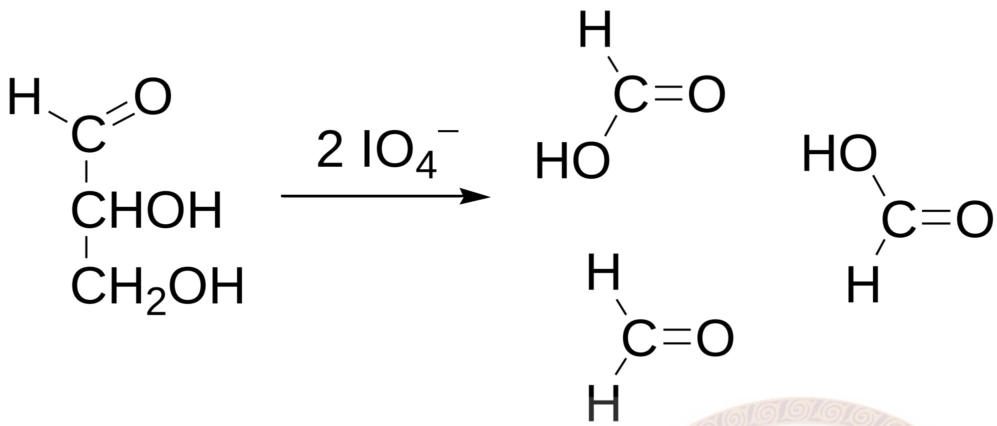
✓ Periodate oxidation

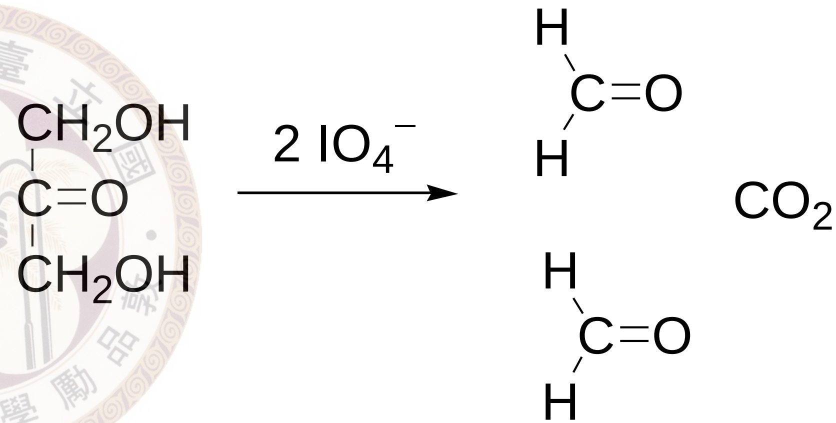


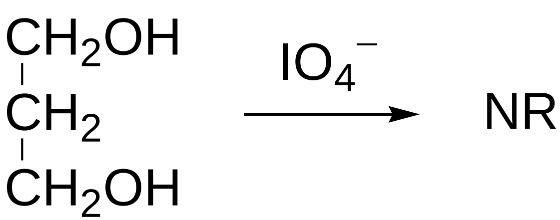
例

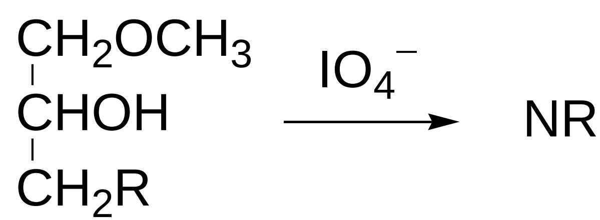


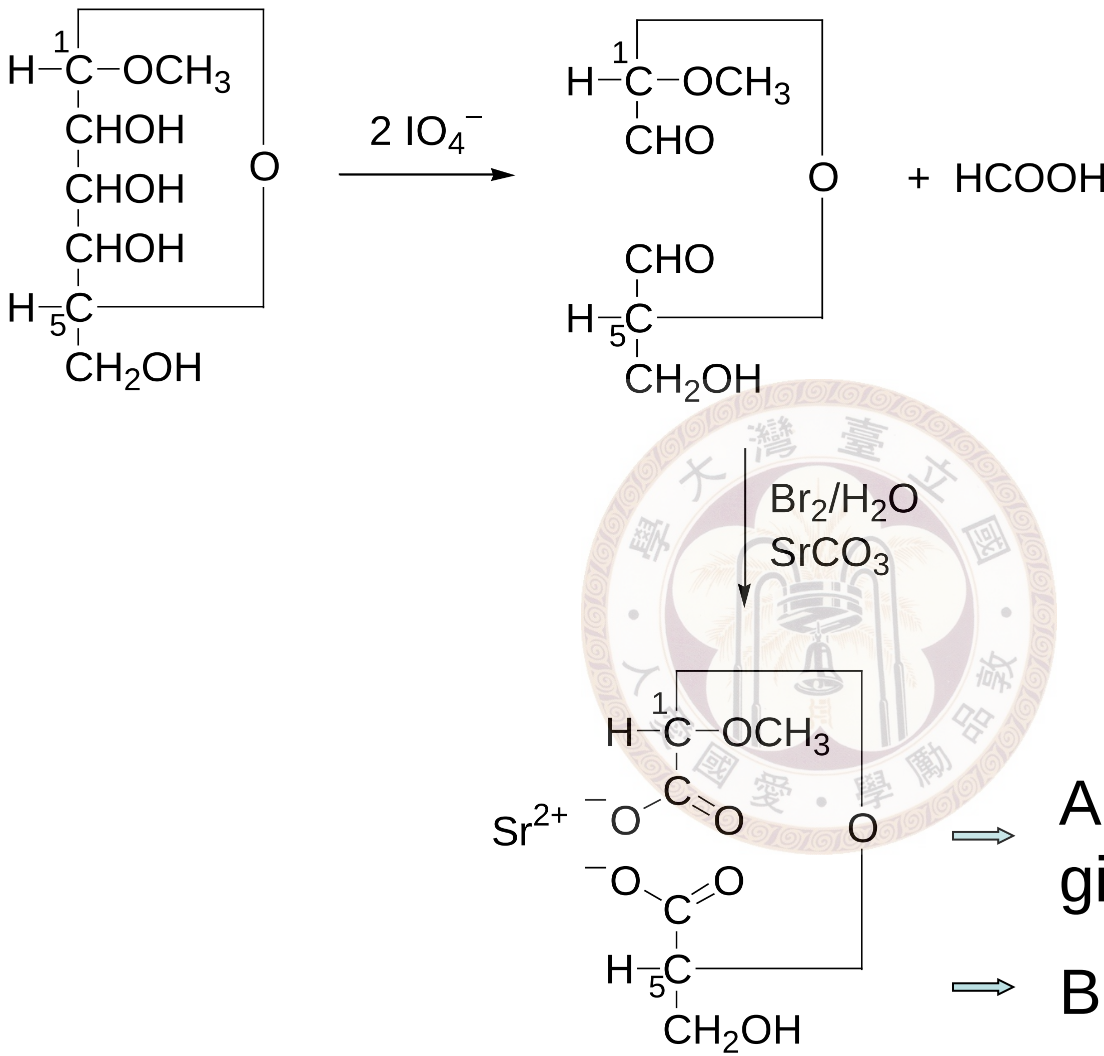








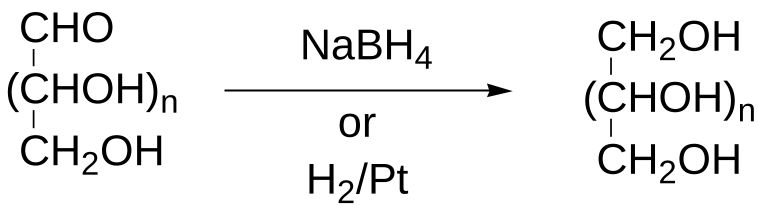




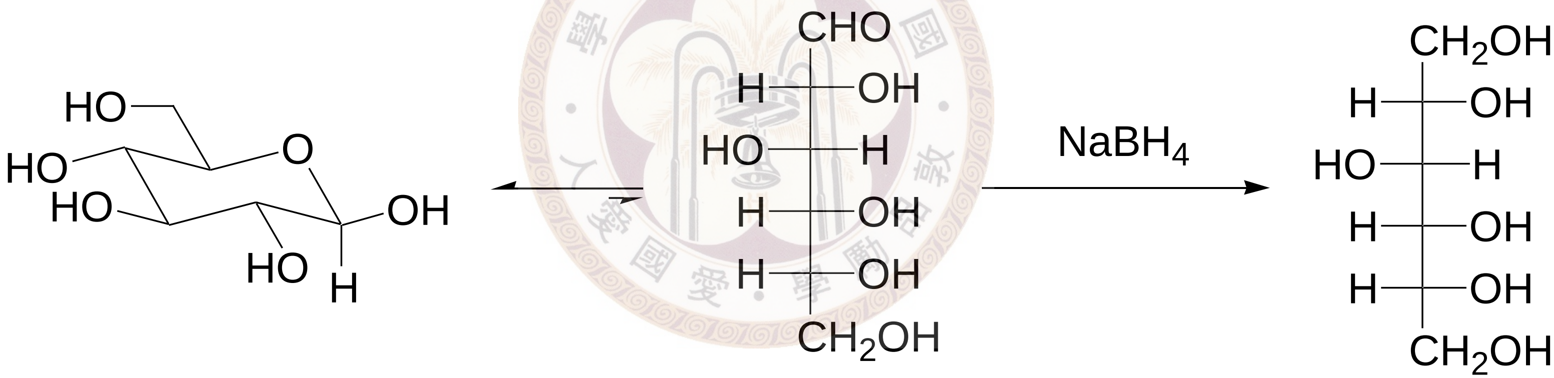
All α-D-hexopyranosides gives the same salt

Because they have the same configuration at C-1 and C-5

◎ Reduction



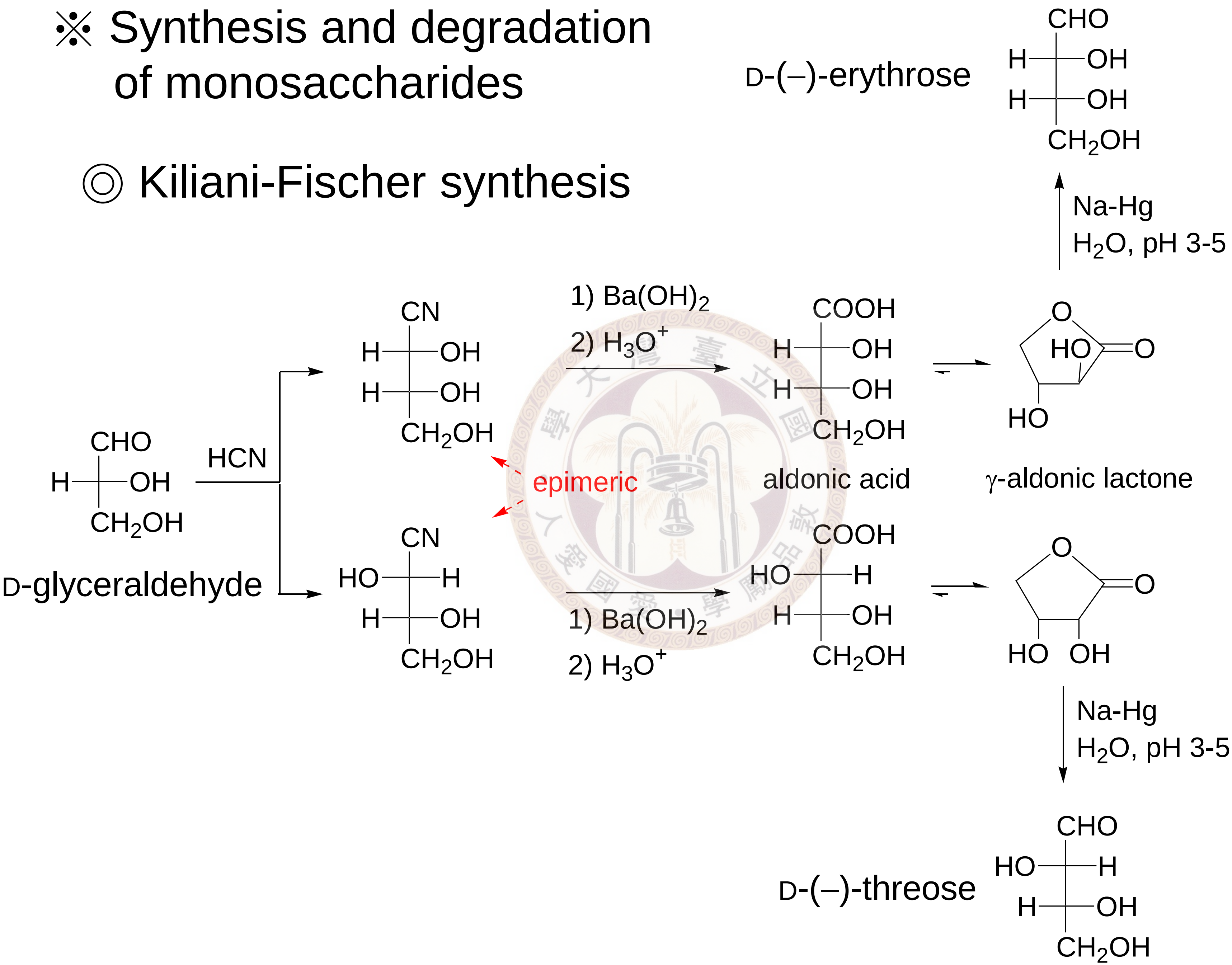
例



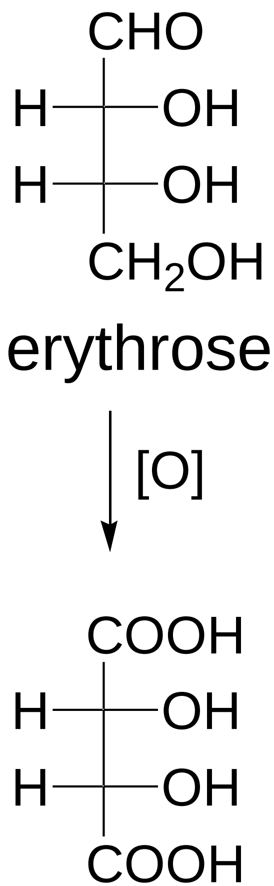
D-glucitol
(or D-sorbitol)

※ Synthesis and degradation of monosaccharides

◎ Kiliani-Fischer synthesis

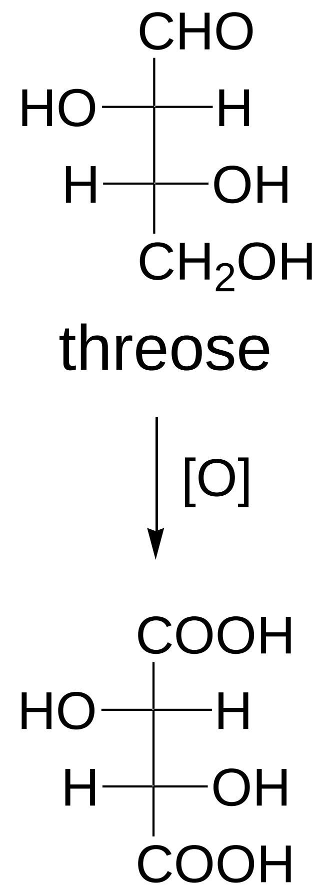


Q: A simple method to determine which is erythrose and which is threose?



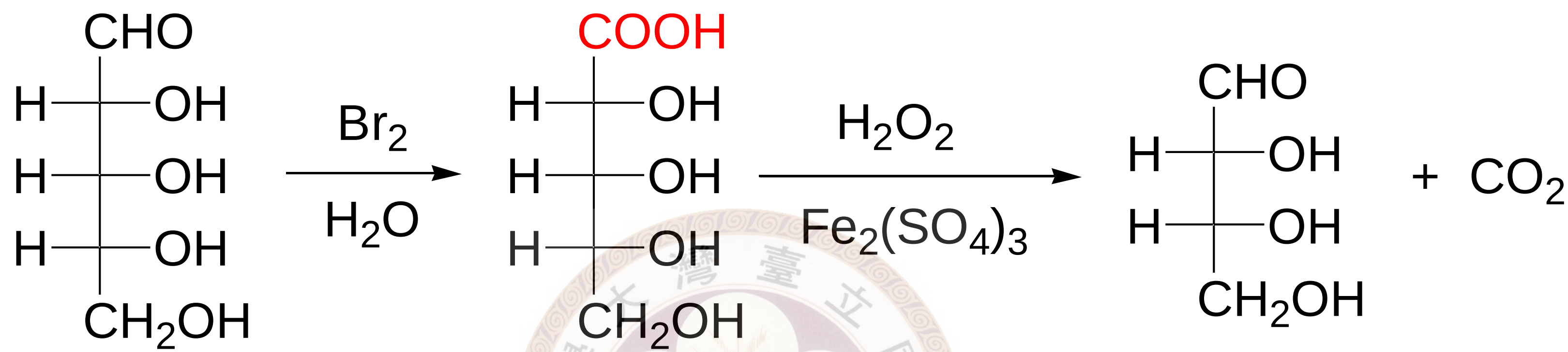
optically inactive (meso)

aldaric acid



optically active

◎ Ruff degradation



D-(–)-ribose D-(–)-erythrose

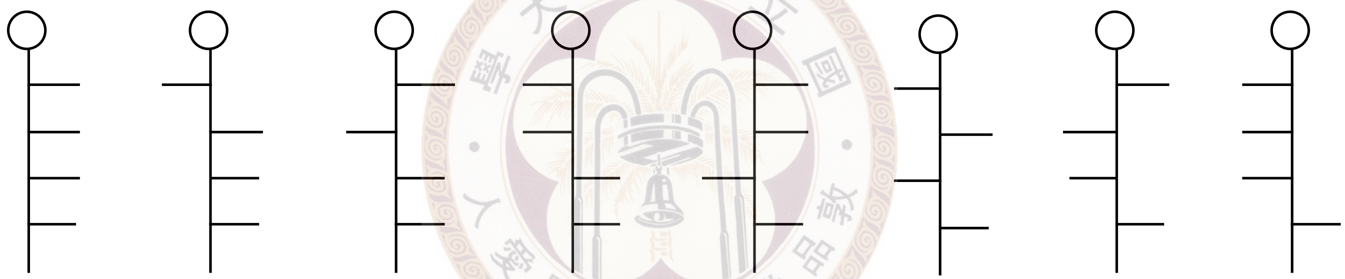
All D-series can be correlated via chemical methods

L-series likewise

※ Fischer's proof of the configuration of D-(+)-glucose

Four chiral centers → $2^4 = 16$ isomers

Arbitrarily consider D only → 8 possibility

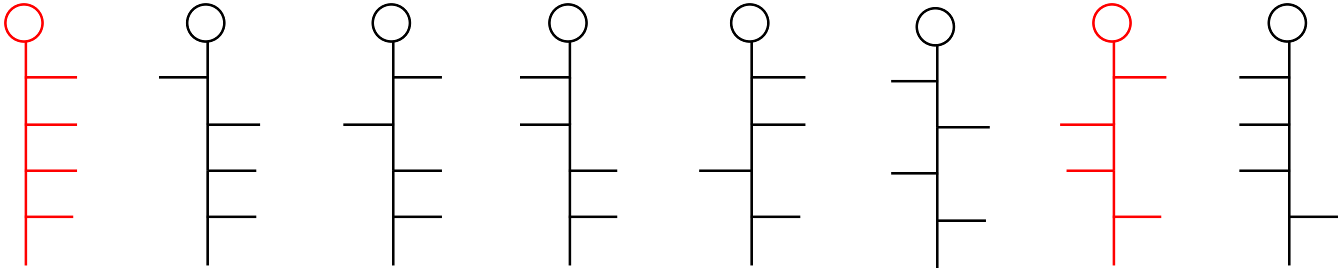


1 2 3 4 5 6 7 8

Experiments:

1) HNO_3 → optically active aldaric acid

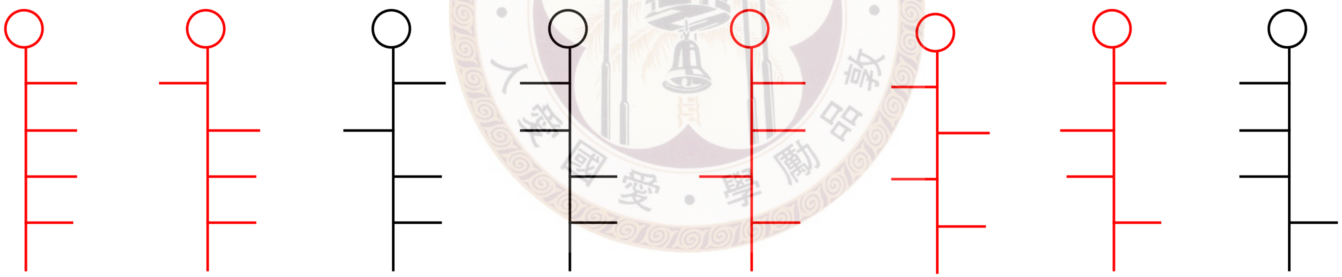
–1, –7



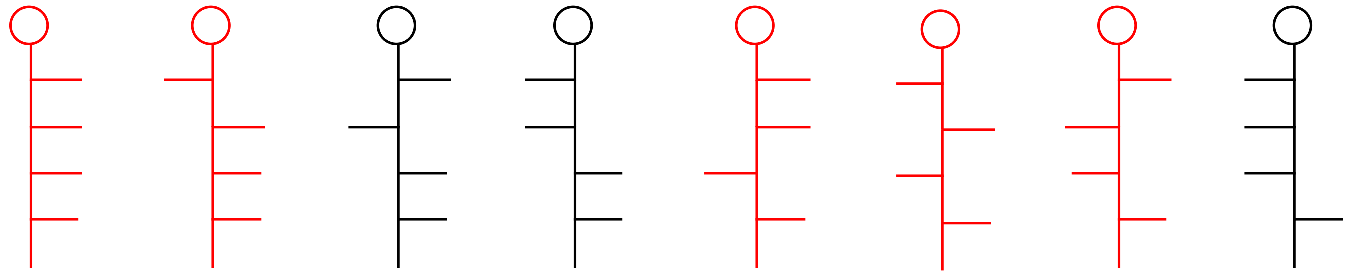
1 2 3 4 5 6 7 8

2) Degradation → HNO_3 → optically active aldaric acid

−2, −5, −6



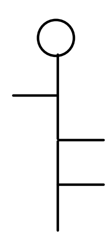
1 2 3 4 5 6 7 8



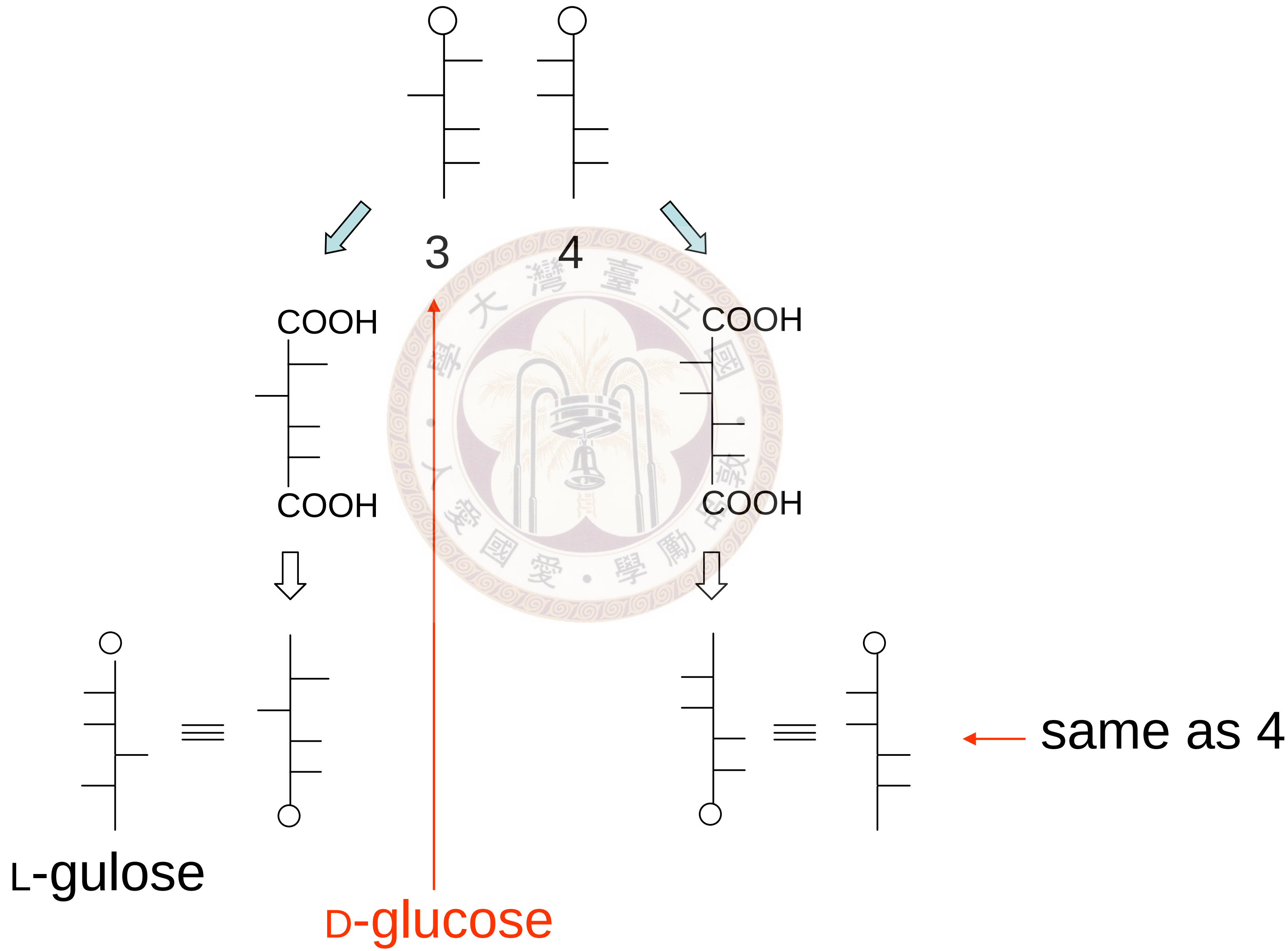
1 2 3 4 5 6 7 8

3) (–)-Arabinose —HCN→ two sugars including glucose plus mannose —HNO_3→ both are optically active

(–7), –8



4) There is an L-sugar → glucaric acid ← D-glucose



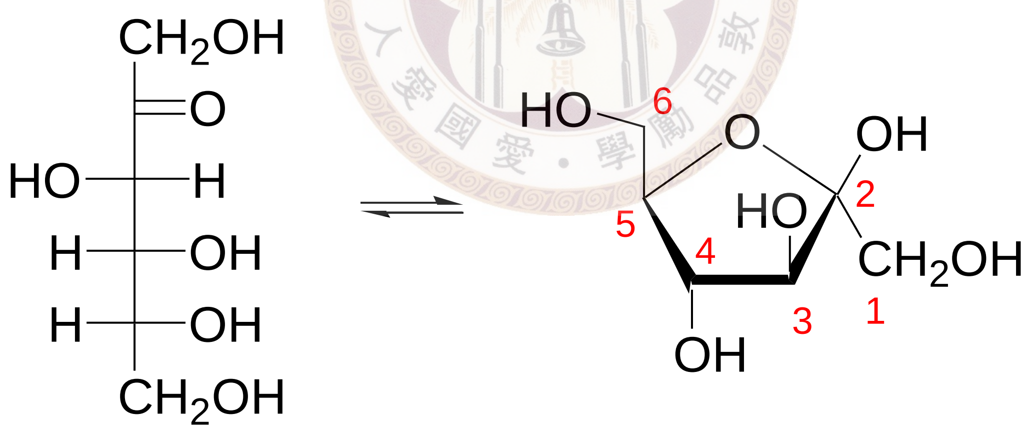
※ Disaccharides

◎ Sucrose

Structure

1) $C_{12}H_{22}O_{11}$ → a disaccharide

2) Acid hydrolysis → D-glucose + D-fructose



← a furanose

D-fructose

β-fructofuranose

3) Negative Bendict's & Tollen's
→ non-reducing sugar
→ no hemiacetal structure
→ must be connection between C-1 of glucose and C-2 of fructose

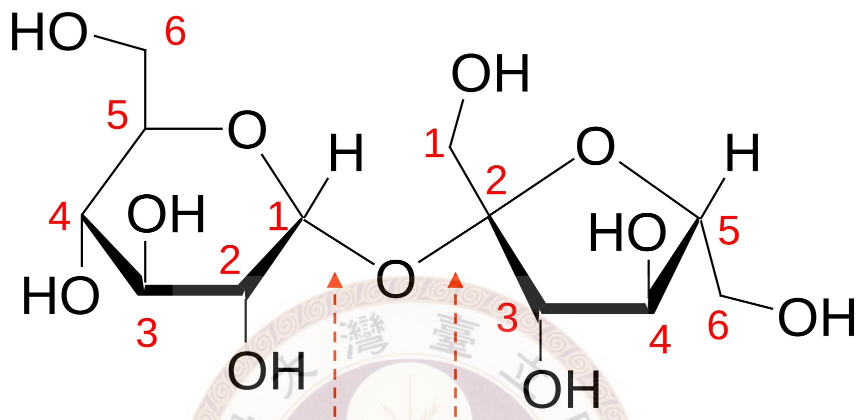
4) Hydrolyzed by α-glucosidase (an enzyme)
→ α-configuration for glucopyranoside
Hydrolyzed by sucrase (hydrolyze β-fructofuranosides)
→ β-configuration for fructofuranoside

- Exhaustive methylation → octamethyl derivatives

$\xrightarrow{\text{hydrolysis}}$ 2,3,4,6-tetra-*O*-methylglucose
+ 1,3,4,6-tetra-*O*-methylfructose

→ Must be pyranoside + furanoside

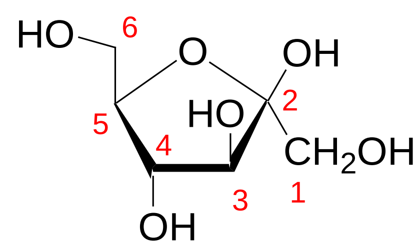
Sucrose:



α-glucosidic linkage β-fructosidic linkage

Proved also by X-ray and synthesis

cf.

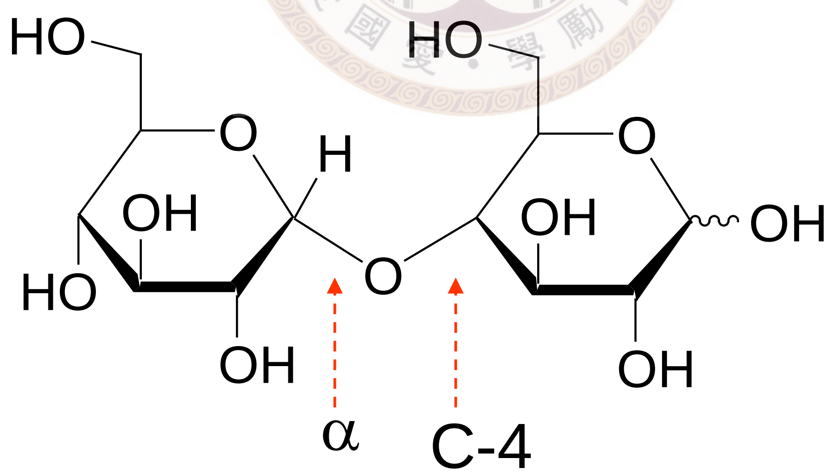


◎ Maltose

1) Hydrolysis → two D-(+)-glucose
2) Positive Fehling's, Bendict's and Tollen's test
→ reducing sugar
3) Two anomeric forms:

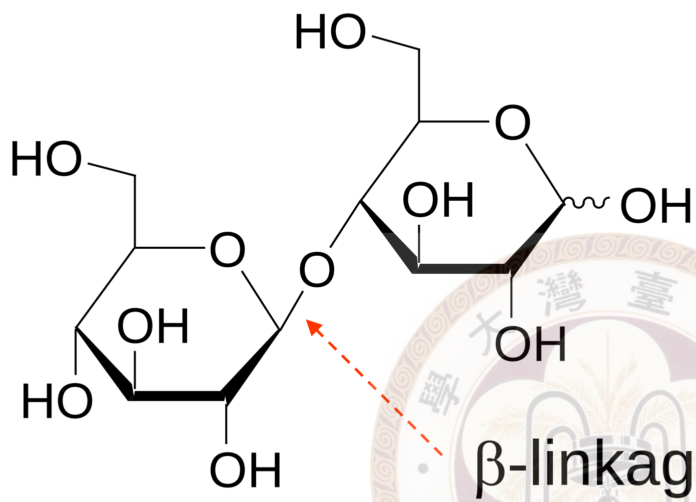
α-maltose [α] = +168° ⎫
β-maltose [α] = +112° ⎭ 136°

→ one glucose must be a hemiacetal
another glucose must be a glucoside



◎ Cellobiose (纖維雙醣)

disaccharides from cellulose



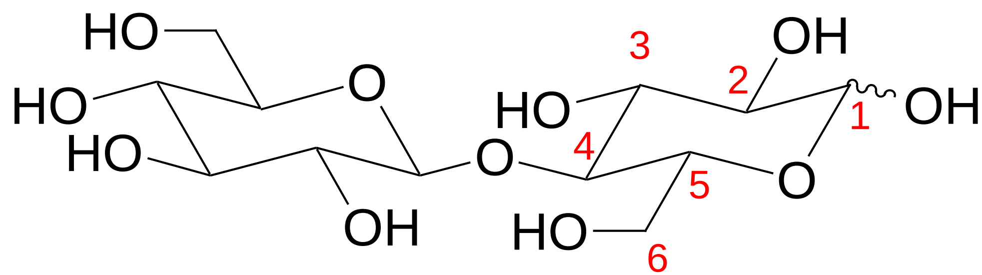
(2 D-(+)-glucose)

β-linkage: the only difference from maltose

4-*O*-(β-D-glucopyranosyl) β-D-glucopyranose

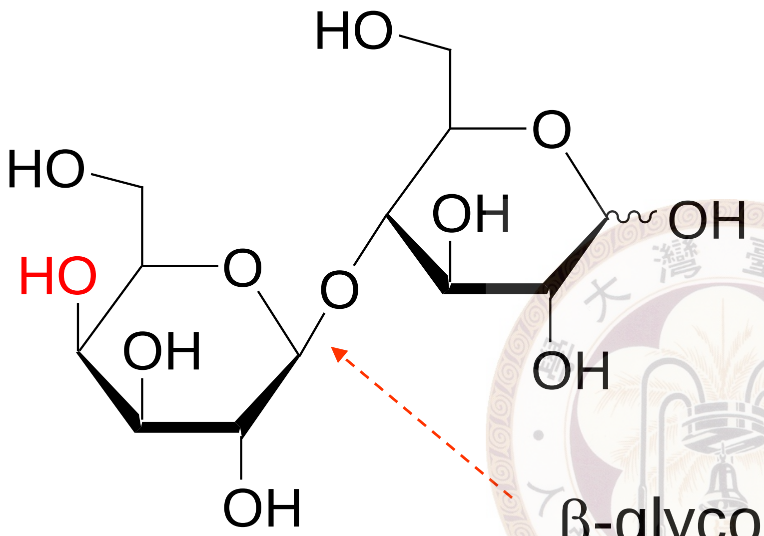
(α)

Conformation:



◎ Lactose (in milk)

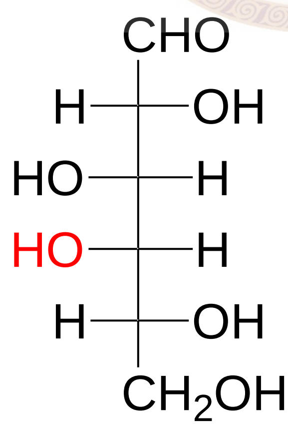
→ D-glucose + D-galactose



A reducing sugar

β-glycosidic linkage

D-galactose:



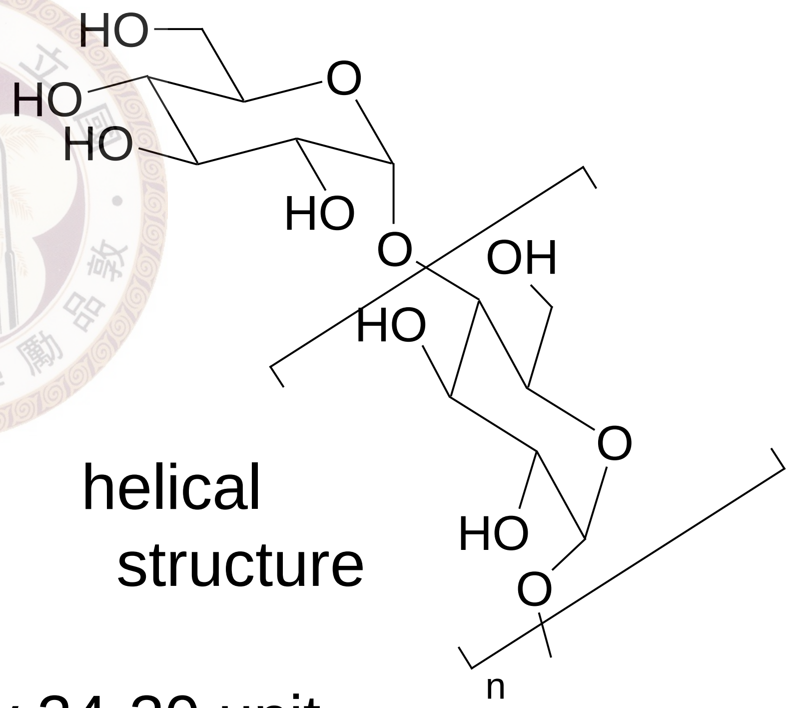
※ Polysaccharides

Starch, glycogen, cellulose
→ Polymers of D-glucose

◎ Starch

- Amylose (10-20%)
- Amylopectine (80-90%)

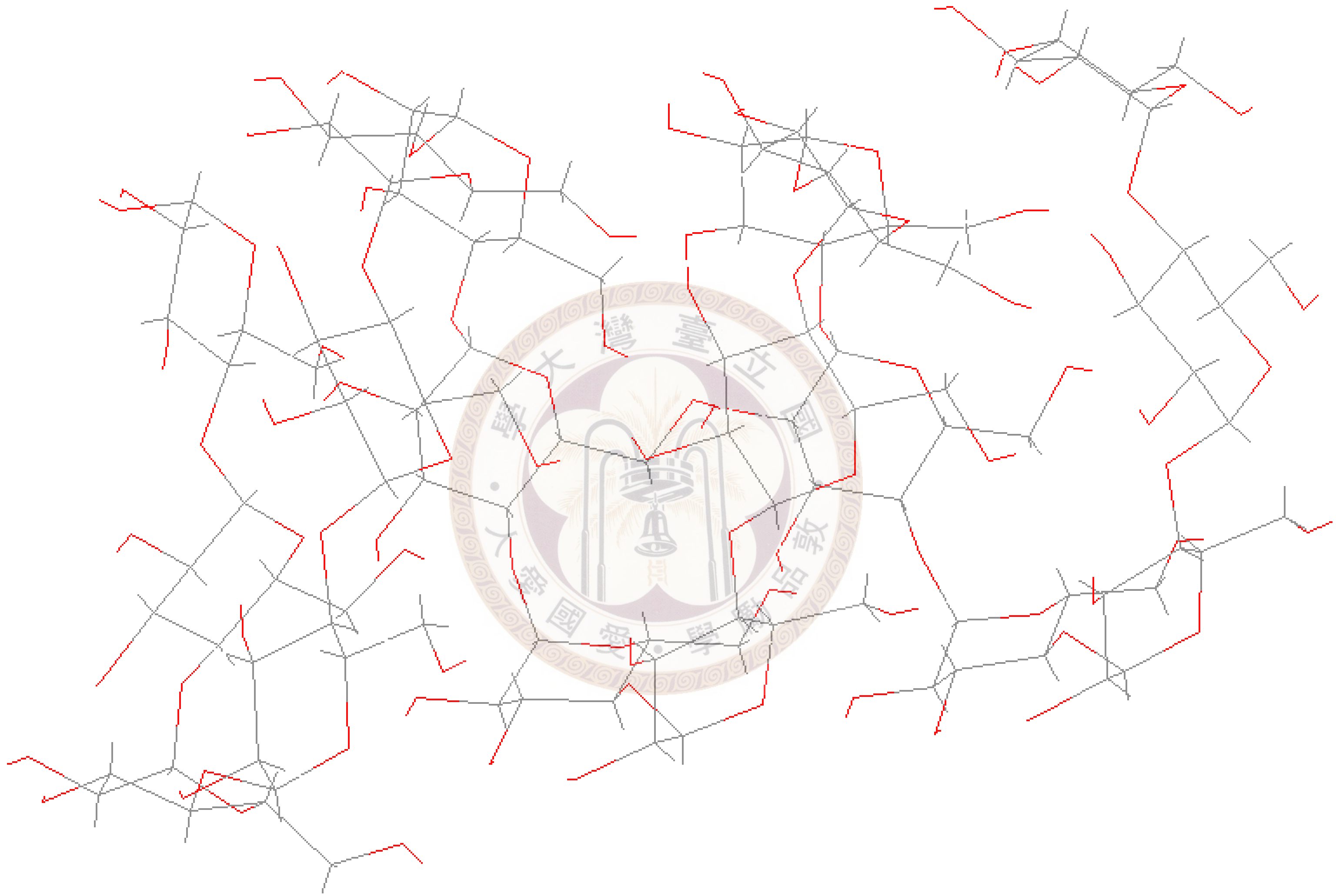
✓Amylose (直鏈澱粉)
C-1 and C-4
α-linkage
100-100,000 units



helical
structure

✓Amylopectin (分枝澱粉)
with branching at C-6 every 24-30 unit
(~400,000 units, larger than amylose)

Helical amylose



◎ Glycogen

similar to amylopectin
with more branching

A rapid source of E

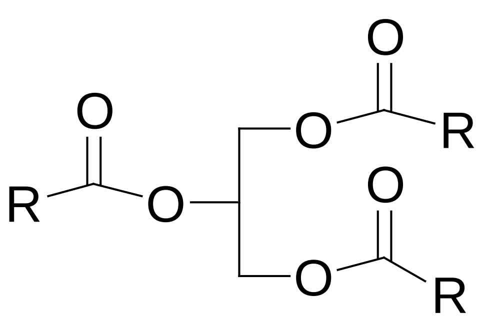
enzyme hydrolyzes from the end group

Stored in the cell

has high MW
→ no osmotic pressure problem

cf. Fats: can store more E

but slow for use: insoluble in water
conc. in cell is low

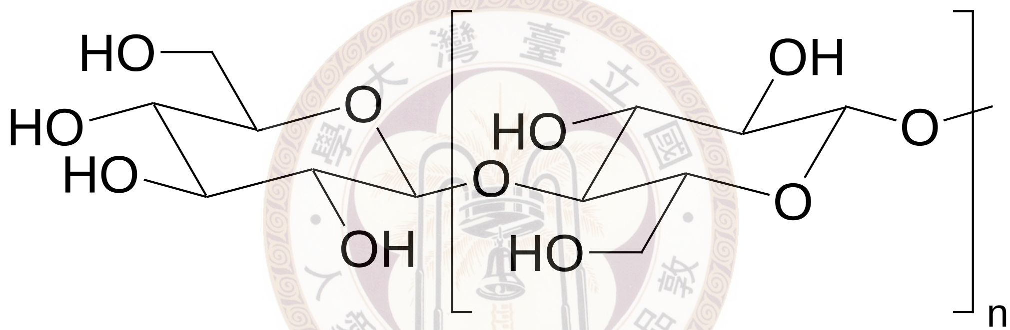


◎ Cellulose

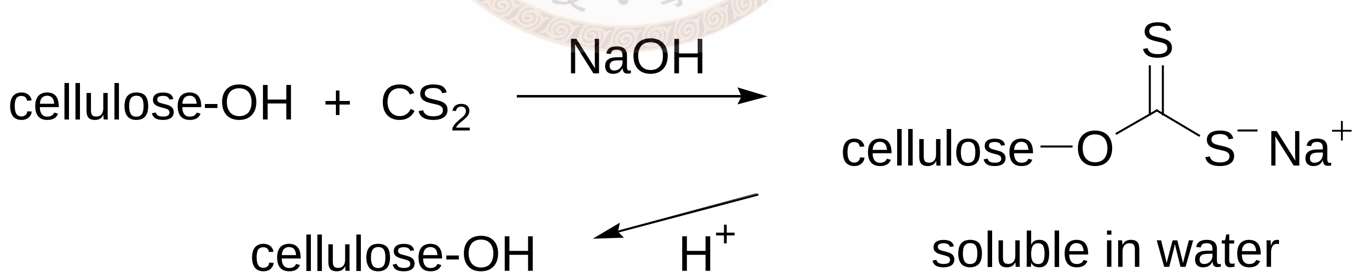
D-glucose linked in 1,4-fashion using β-linkage

Can not be hydrolyzed by human

Linear shape with hydrogen bonding between chain



✓ Cellulose derivatives



formation of a fiber or a sheet
(Rayon or cellophane)

Linear cellulose