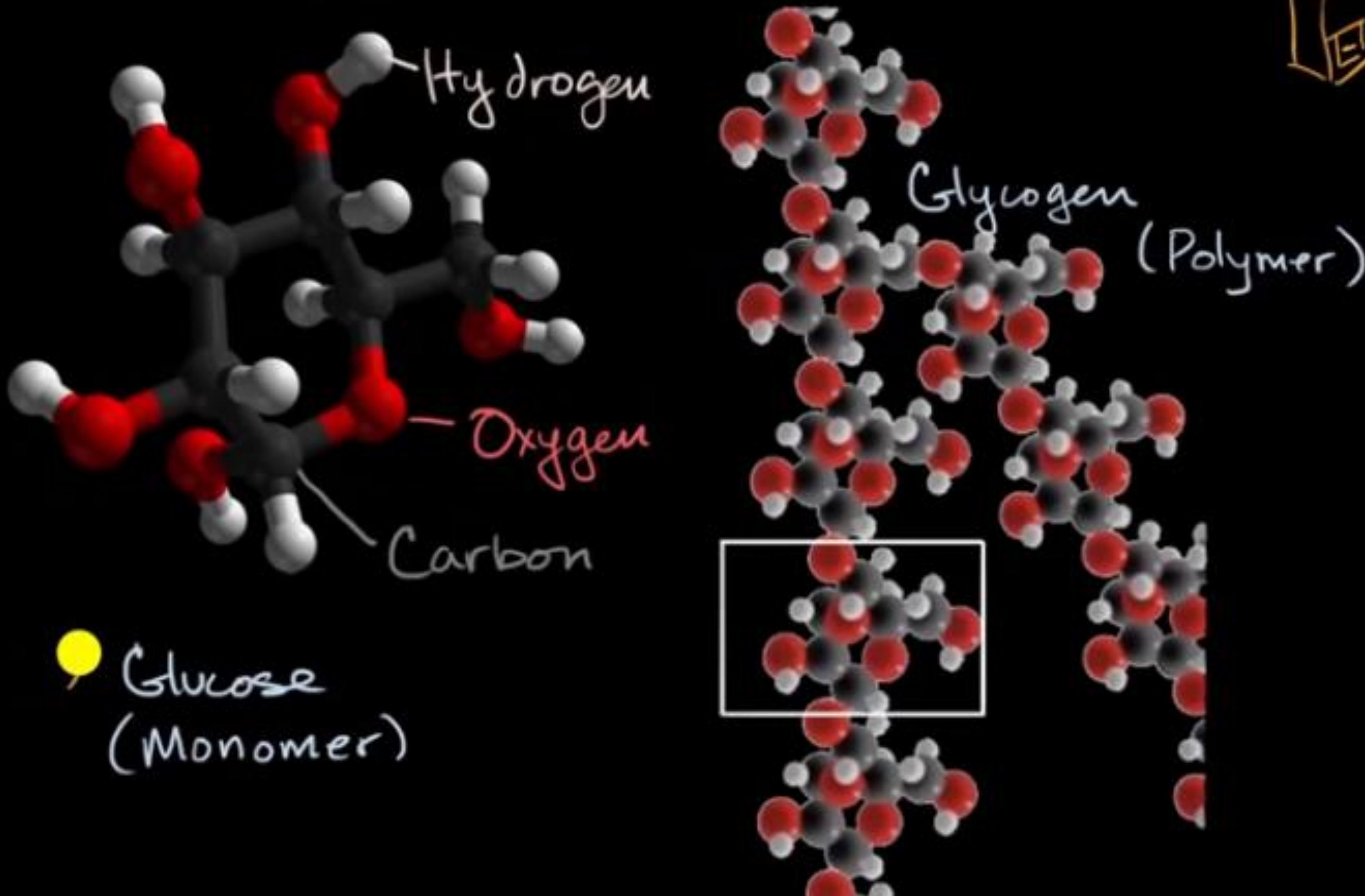
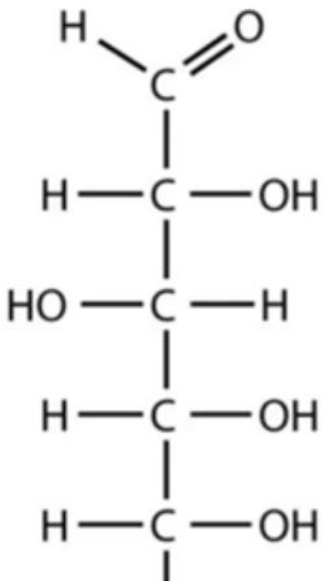
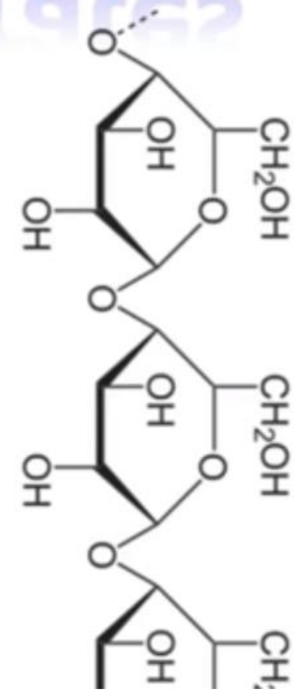
Carbohydrates



Classification of carbohydrates



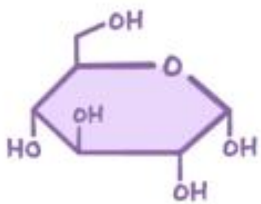
- Monosaccharides
- Oligosaccharides
- Polysaccharides



SUGAR ~ SACCHARIDES

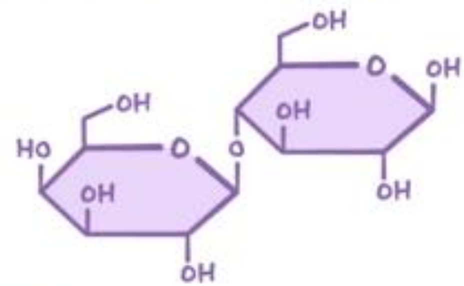
ONE

MONOSACCHARIDE



TWO

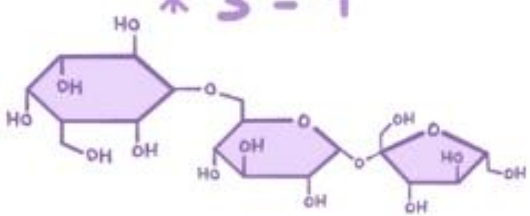
DISACCHARIDE



A FEW

OLIGOSACCHARIDE

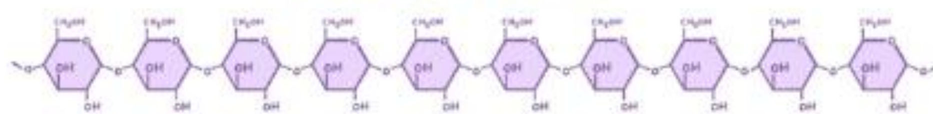
* 3 - 9



MANY

POLYSACCHARIDE

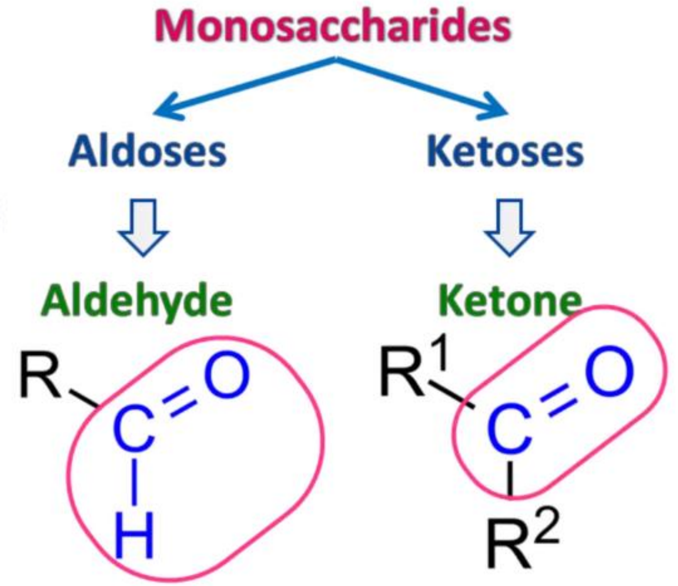
* 10 OR MORE



Monosaccharides

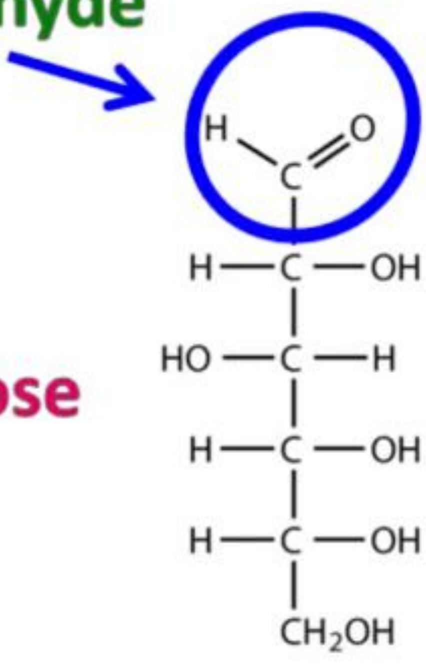
Simplest carbohydrates found in the nature

$C_n(H_2O)_n$

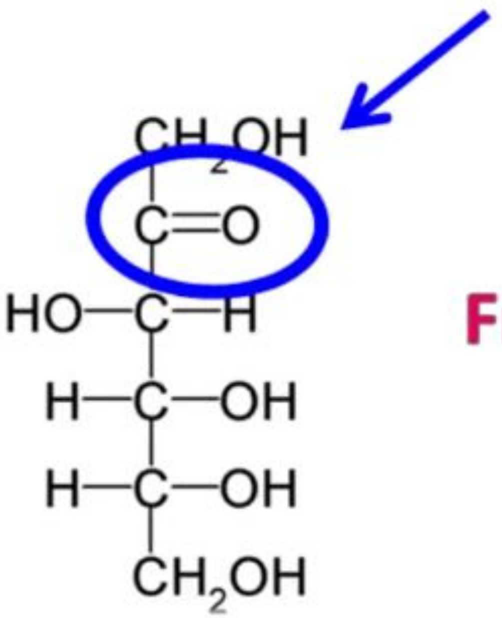


Aldehyde

Glucose



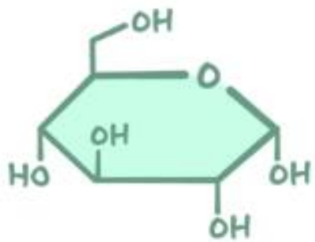
Ketone



Fructose

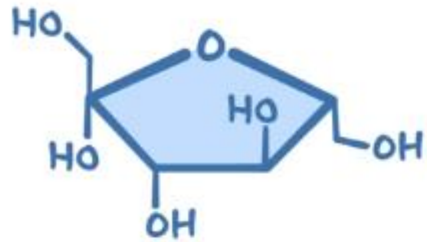
GLUCOSE

* MOST IMPORTANT *



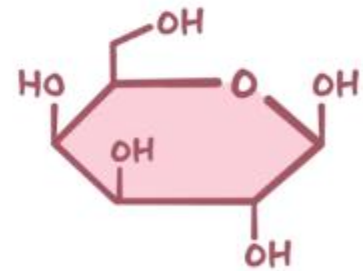
* ONE OF THE MAIN SOURCES OF CALORIES
* CAN CROSS BLOOD-BRAIN BARRIER
  → NOURISHES THE BRAIN

FRUCTOSE

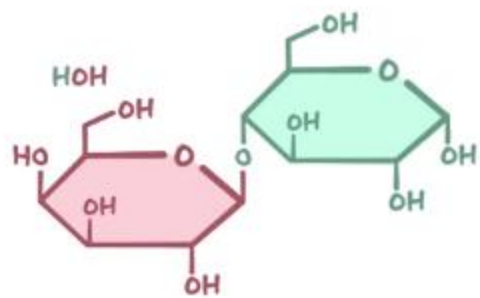


* COMMONY FOUND IN HONEY, FRUITS, & ROOT VEGETABLES

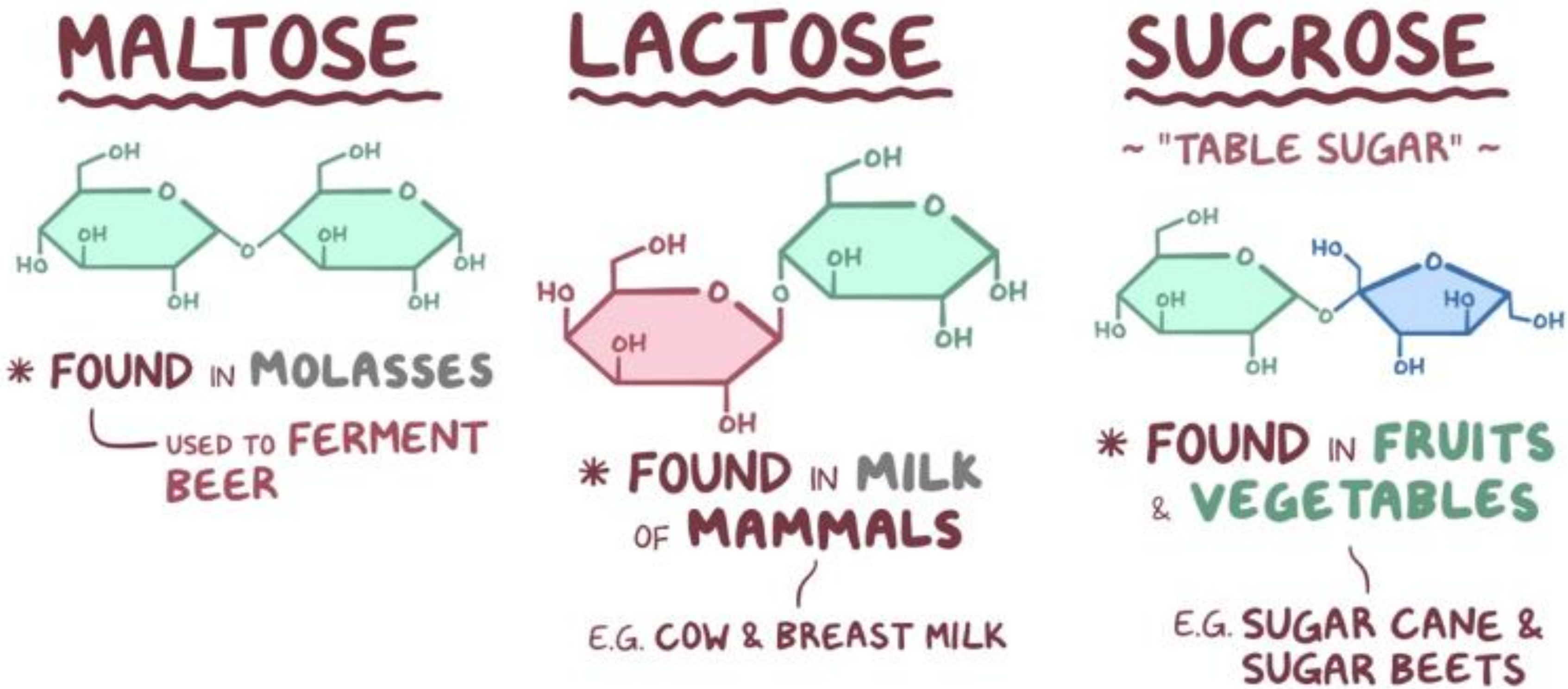
GALACTOSE



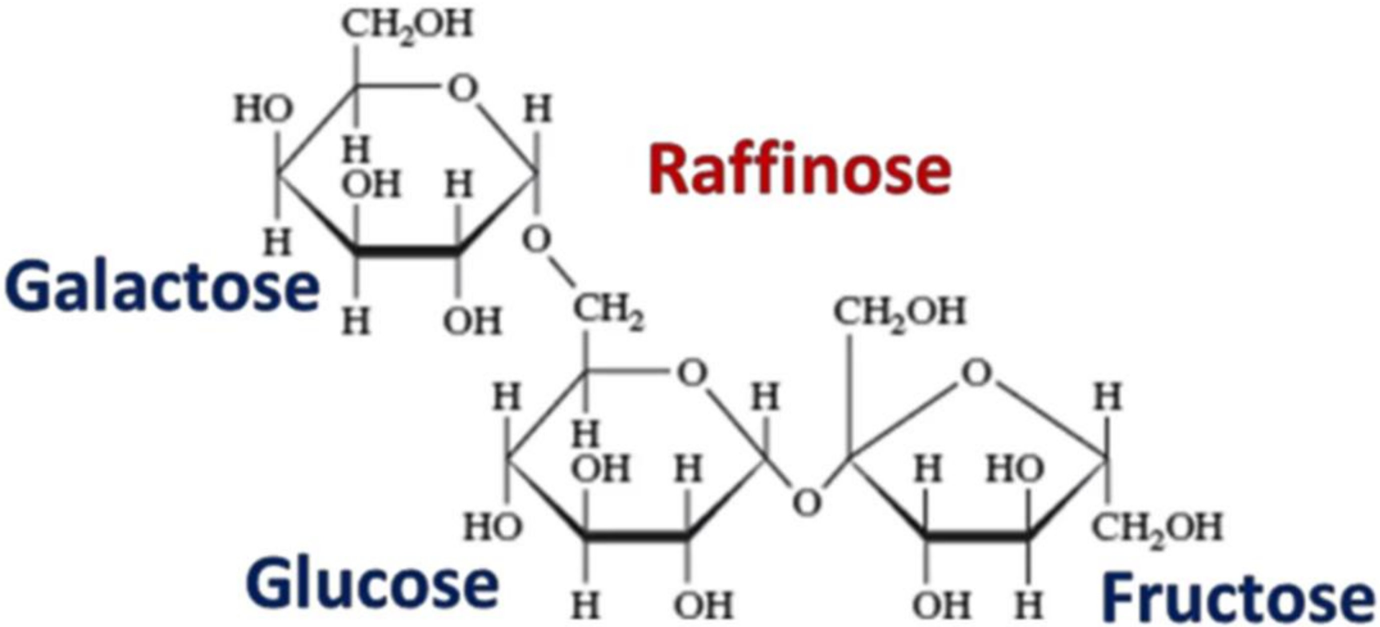
* "MILK SUGAR"



Glucose	Glucose	Glucose
+	+	+
Glucose	Galactose	Fructose

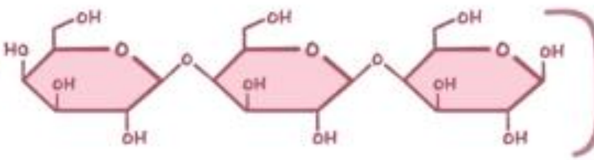


Trisaccharide



COMPLEX CARBOHYDRATES

OLIGOSACCHARIDES ~

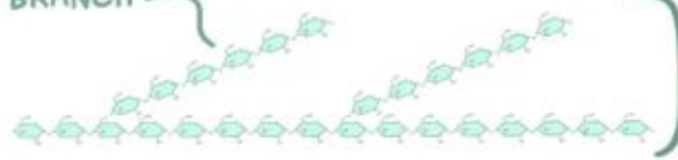


GALACTO-OLIGOSACCHARIDE

* IN **SOYBEANS**

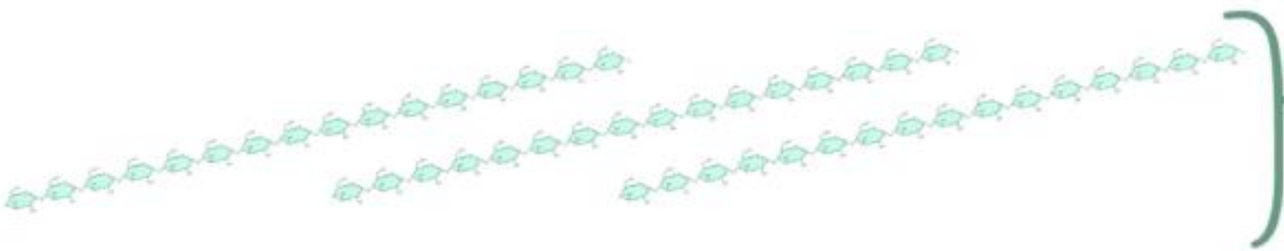
POLYSACCHARIDES ~

* MOST ABUNDANT CARBOHYDRATE IN FOOD



STARCHES

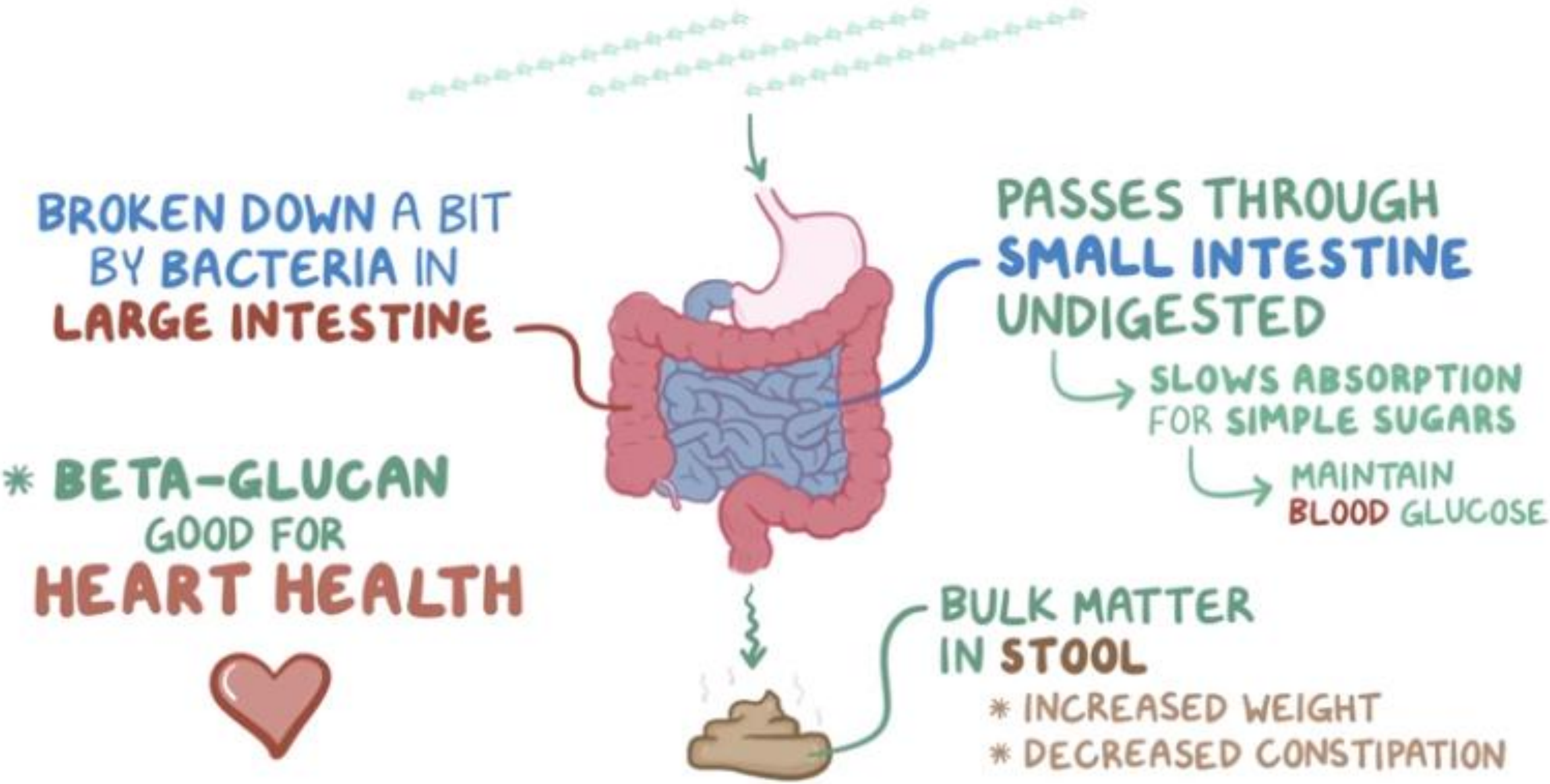
* INTESTINAL ENZYMES **CAN** BREAK DOWN
* IN RICE, POTATOES WHEAT & MAIZE
* **NOT** SWEET



DIETARY FIBERS

* INTESTINAL ENZYMES **CANNOT** BREAK DOWN

DIETARY FIBERS



Polysaccharides

Homo polysaccharide	Hetero polysaccharide
Polymer of same monosaccharide units	Polymer of different monosaccharide units

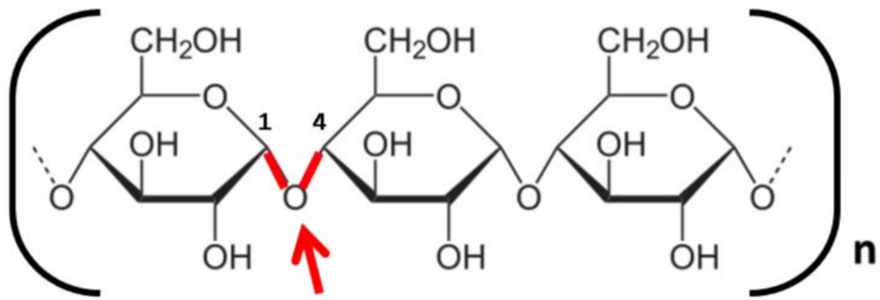
Homo polysaccharide

α (1-4) linkage

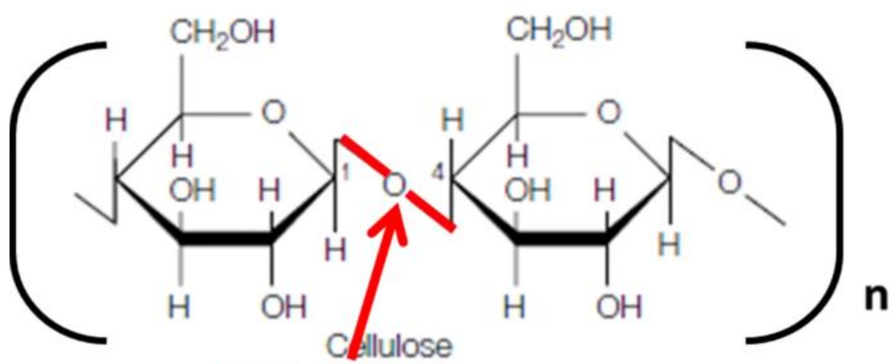
Starch

β (1-4) linkage

Cellulose

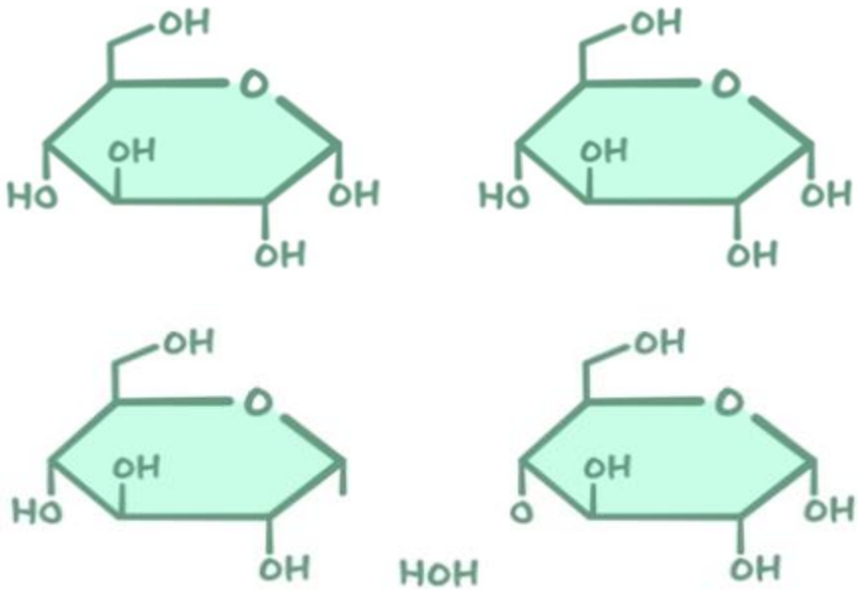


α (1-4) linkage

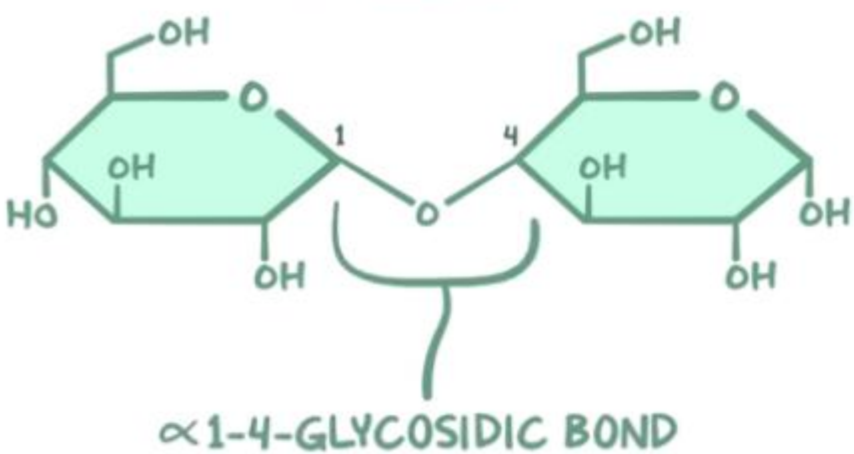


β (1-4) linkage

GLYCOSIDIC BONDING

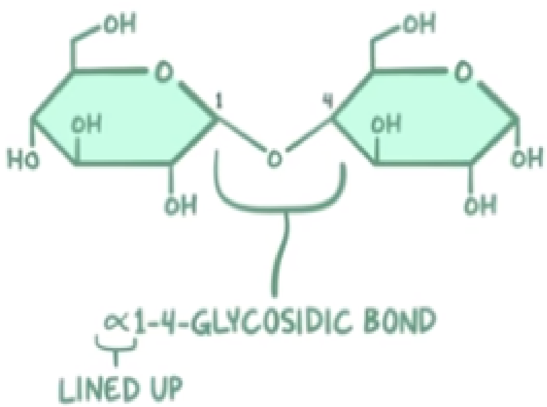


~ MALTOSE ~

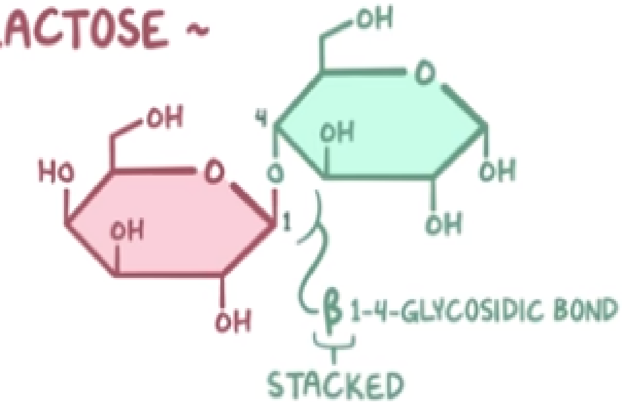


GLYCOSIDIC BONDING

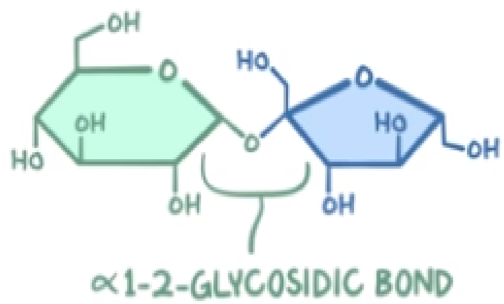
~ MALTOSE ~



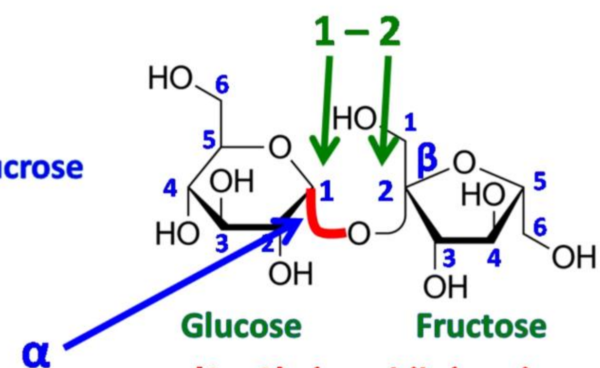
~ LACTOSE ~



~ SUCROSE ~

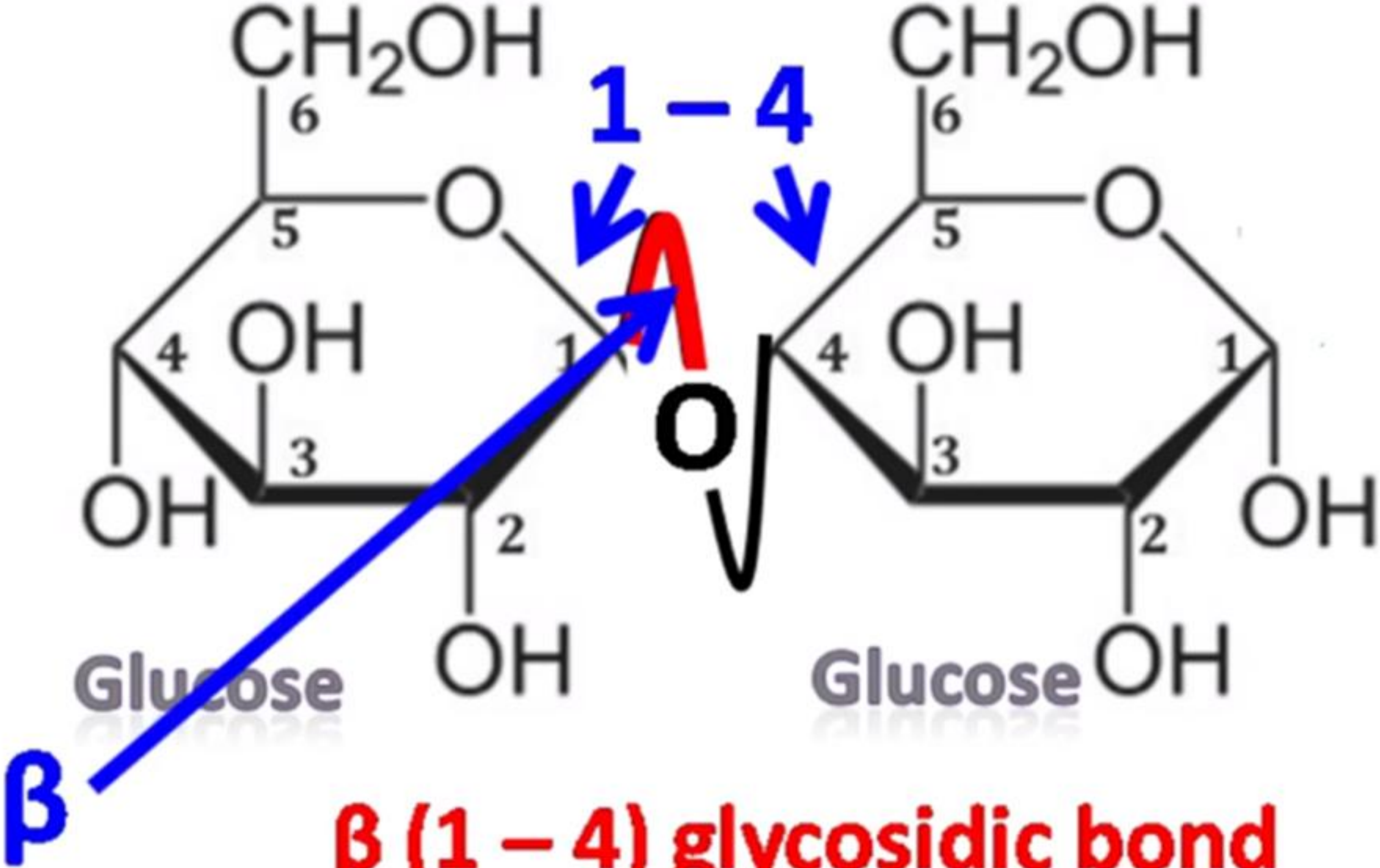


Sucrose



α (1 – 2) glycosidic bond

Cellobiose

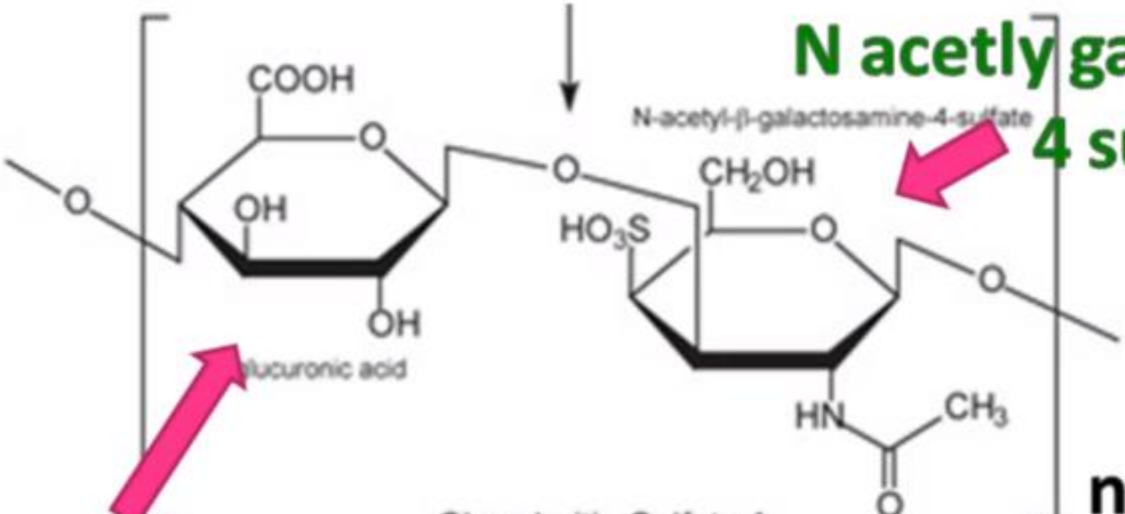


β (1 – 4) glycosidic bond

Hetero polysaccharide

Chondrotin 4 sulfate

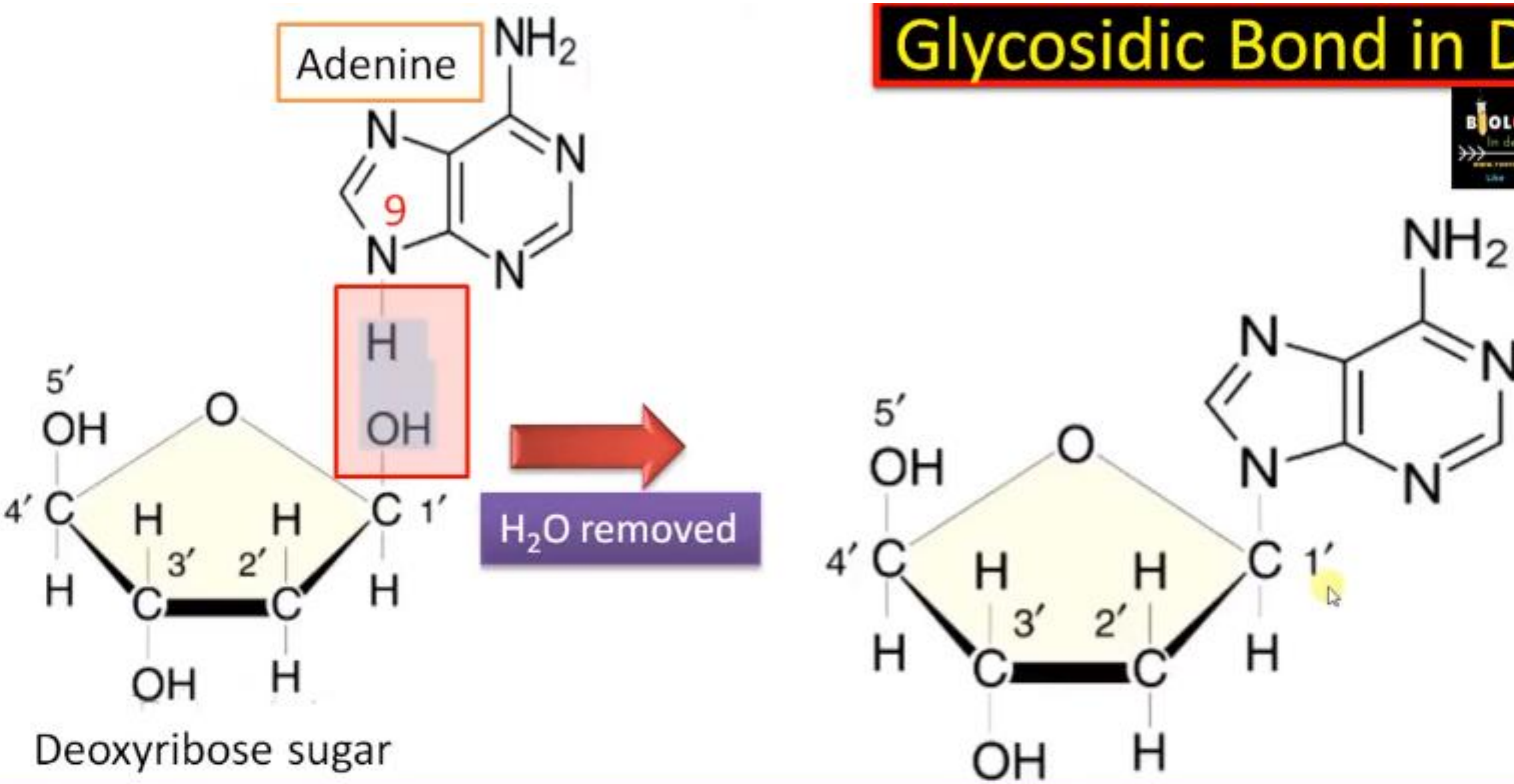
N acetly galactosamine 4 sulfate



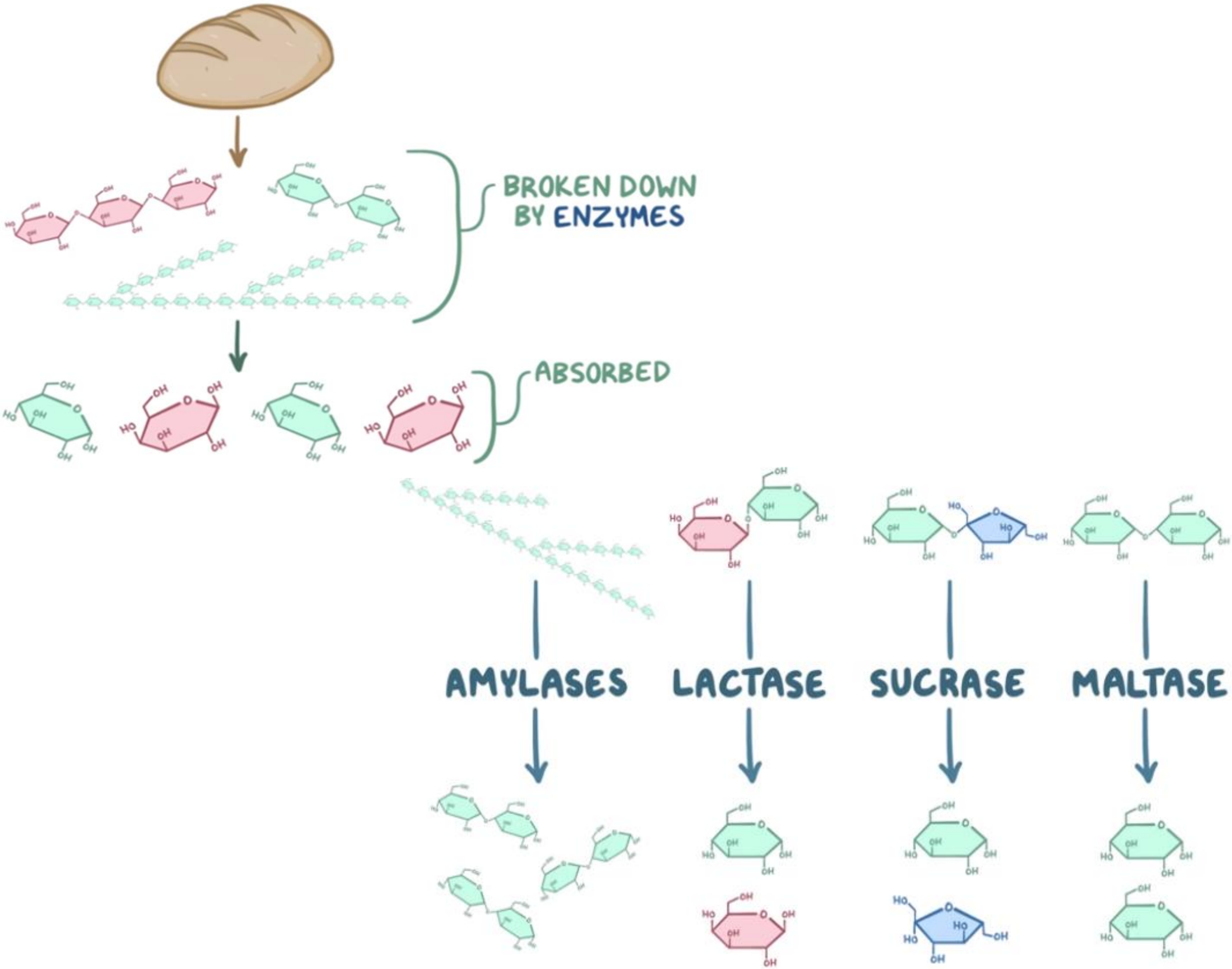
Chondroitin Sulfate A

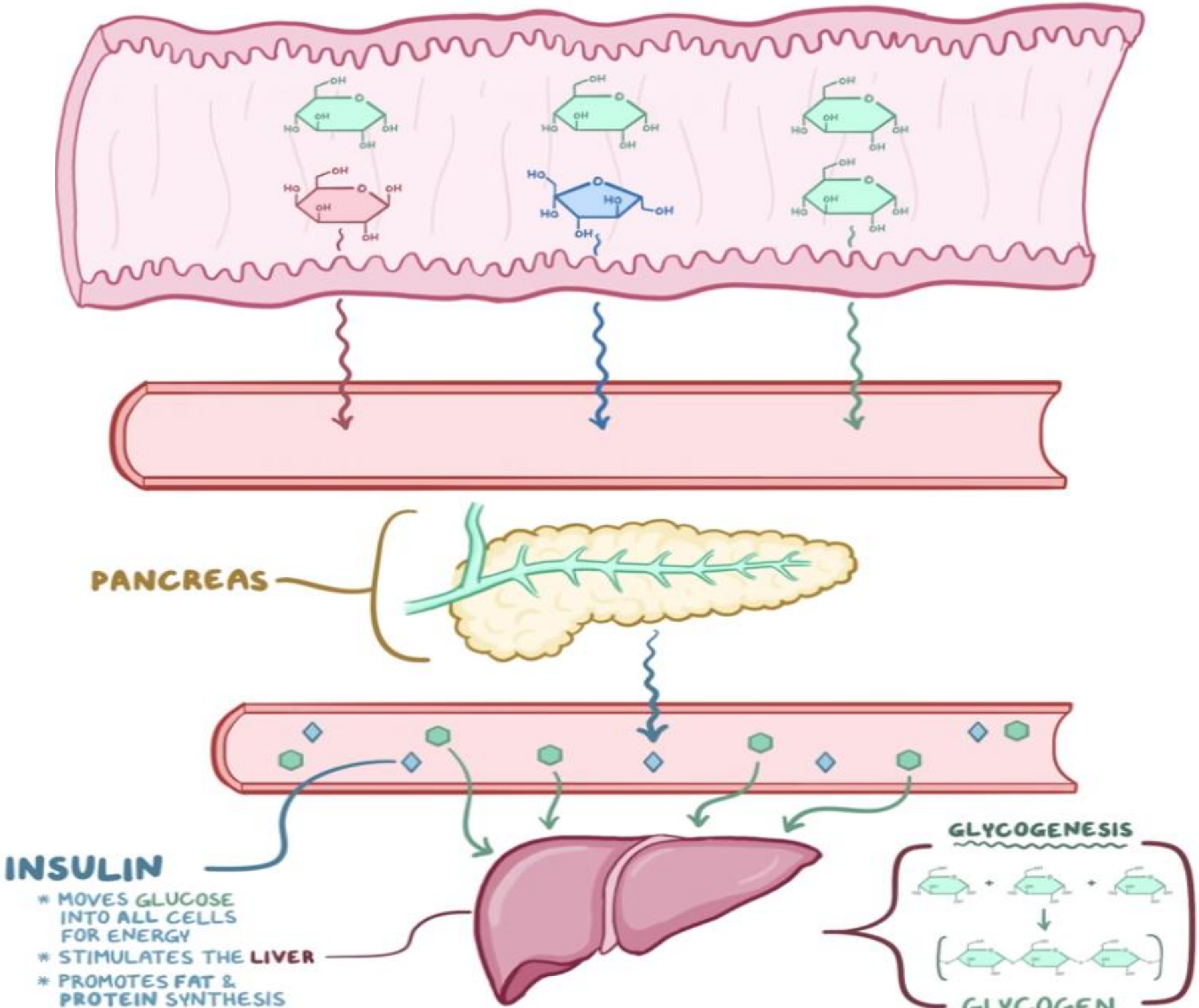
Glucuronic acid

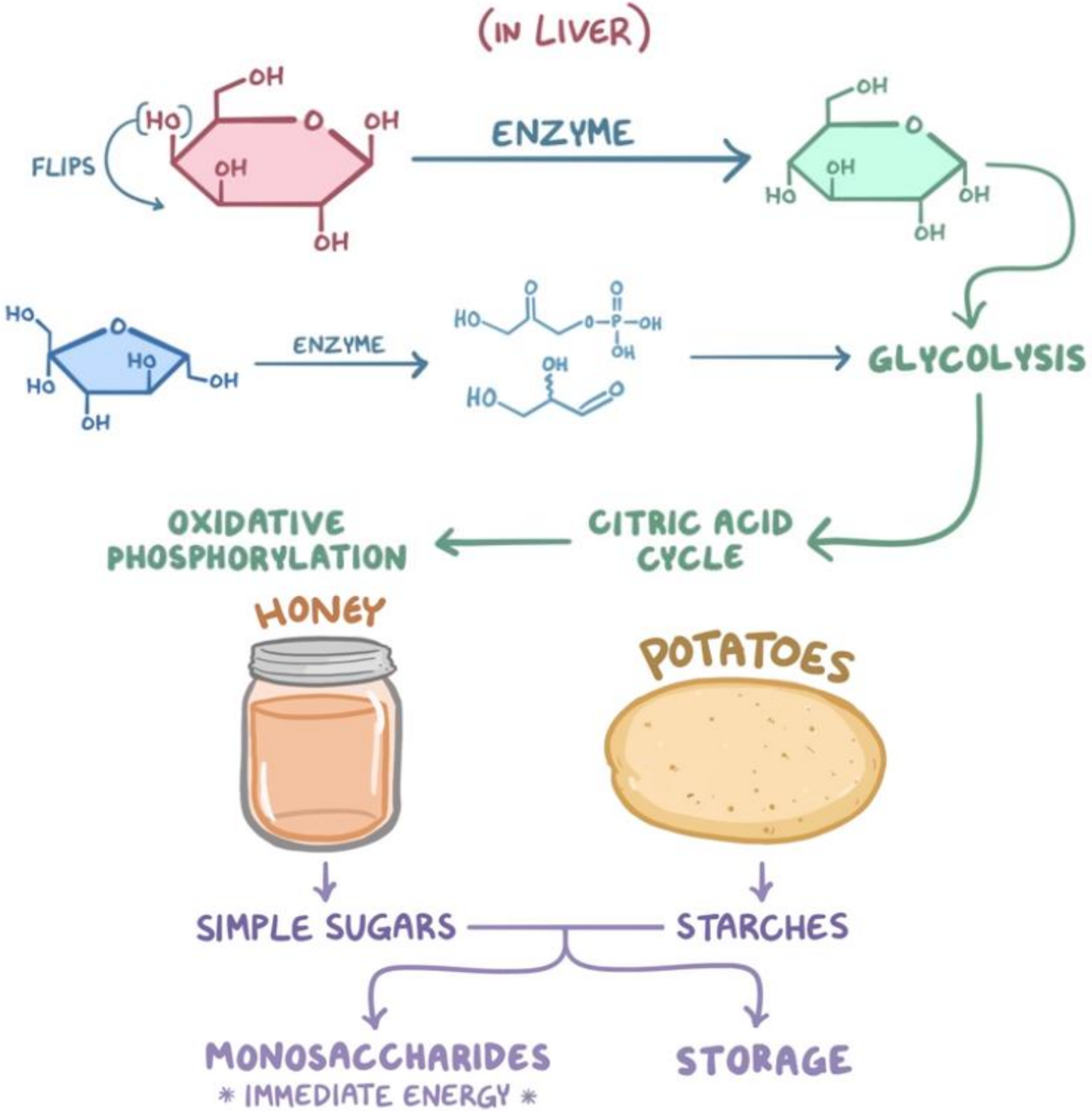
Glycosidic Bond in DNA



In DNA, Glycosidic Bond, N-C linkage connects Sugar with Nitrogenous base.
The C1 of deoxyribose forms **β-N-Glycosidic bond**


BROKEN DOWN BY ENZYMES
ABSORBED
AMYLASES
LACTASE
SUCRASE
MALTASE


PANCREAS
INSULIN
* MOVES GLUCOSE INTO ALL CELLS FOR ENERGY
* STIMULATES THE LIVER
* PROMOTES FAT & PROTEIN SYNTHESIS
GLYCOGENESIS
GLYCOGEN

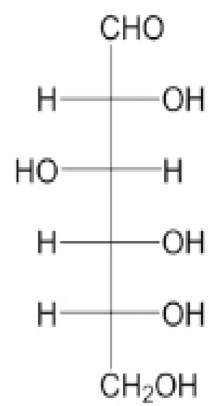


(IN LIVER)
FLIPS
ENZYME
ENZYME
GLYCOLYSIS
CITRIC ACID CYCLE
OXIDATIVE PHOSPHORYLATION
HONEY
POTATOES
SIMPLE SUGARS
STARCHES
MONOSACCHARIDES
* IMMEDIATE ENERGY *
STORAGE

Carbohydrate Structure

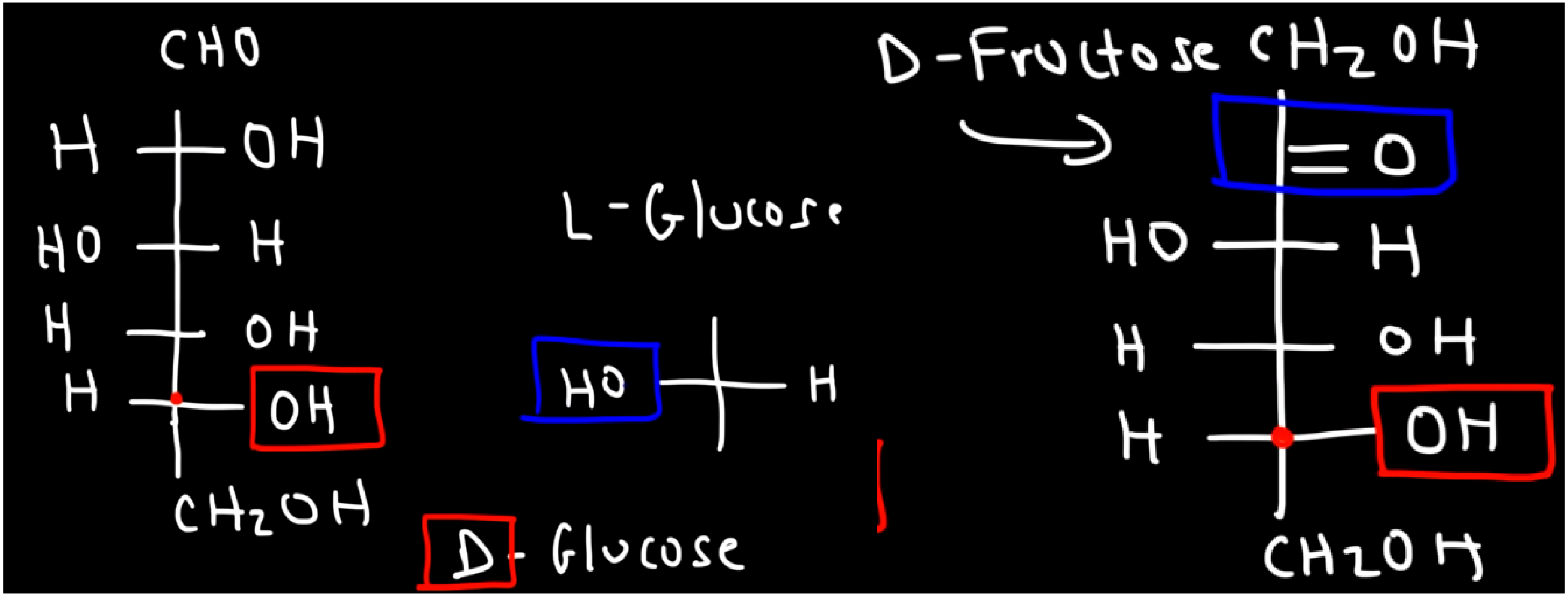
- Polyhydroxylated carbonyl compounds (usually aldehydes or ketones)

- General formula: $C_n(H_2O)_n$ (one unsaturation)

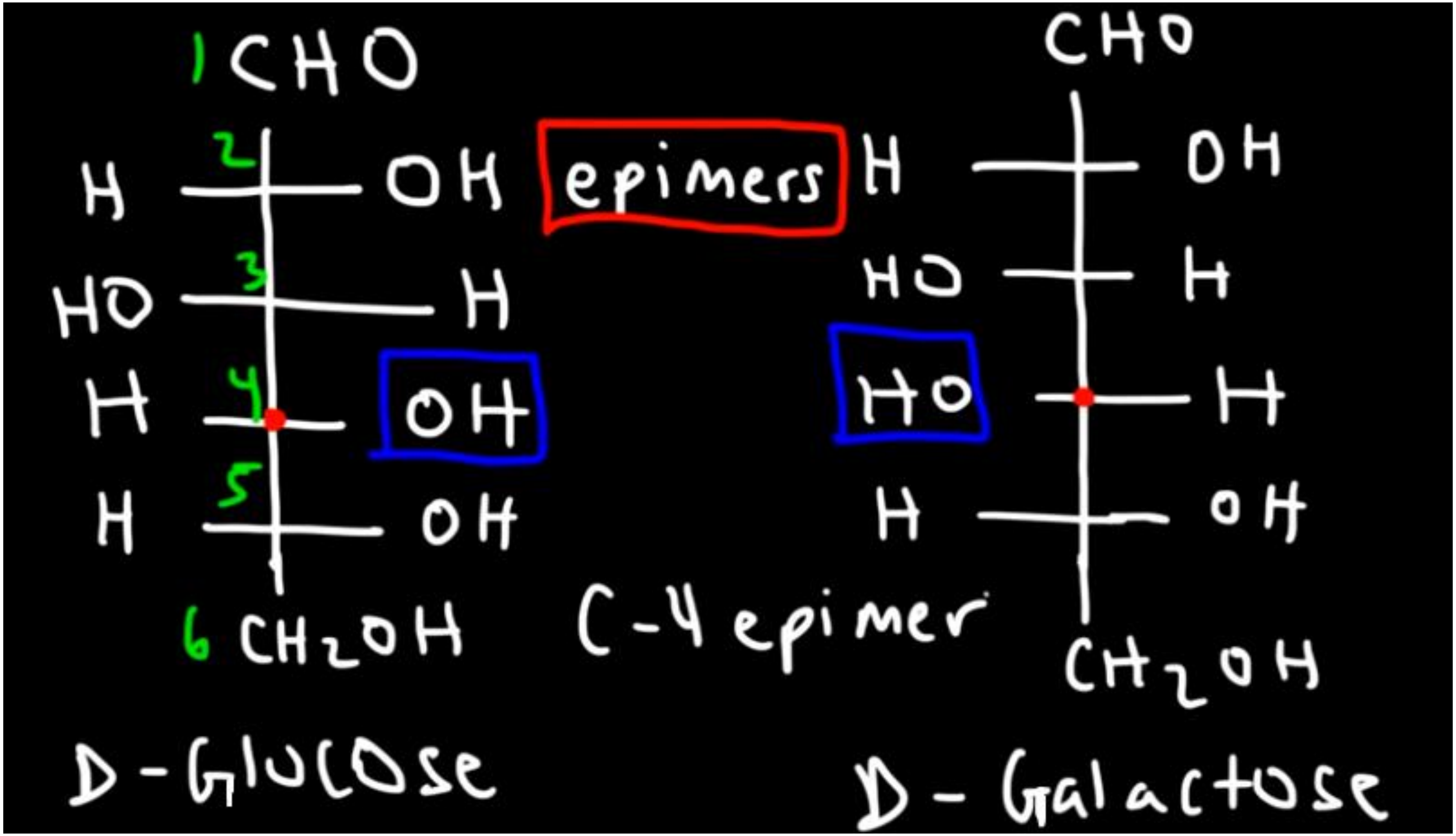


Fischer projection
(open chain view)

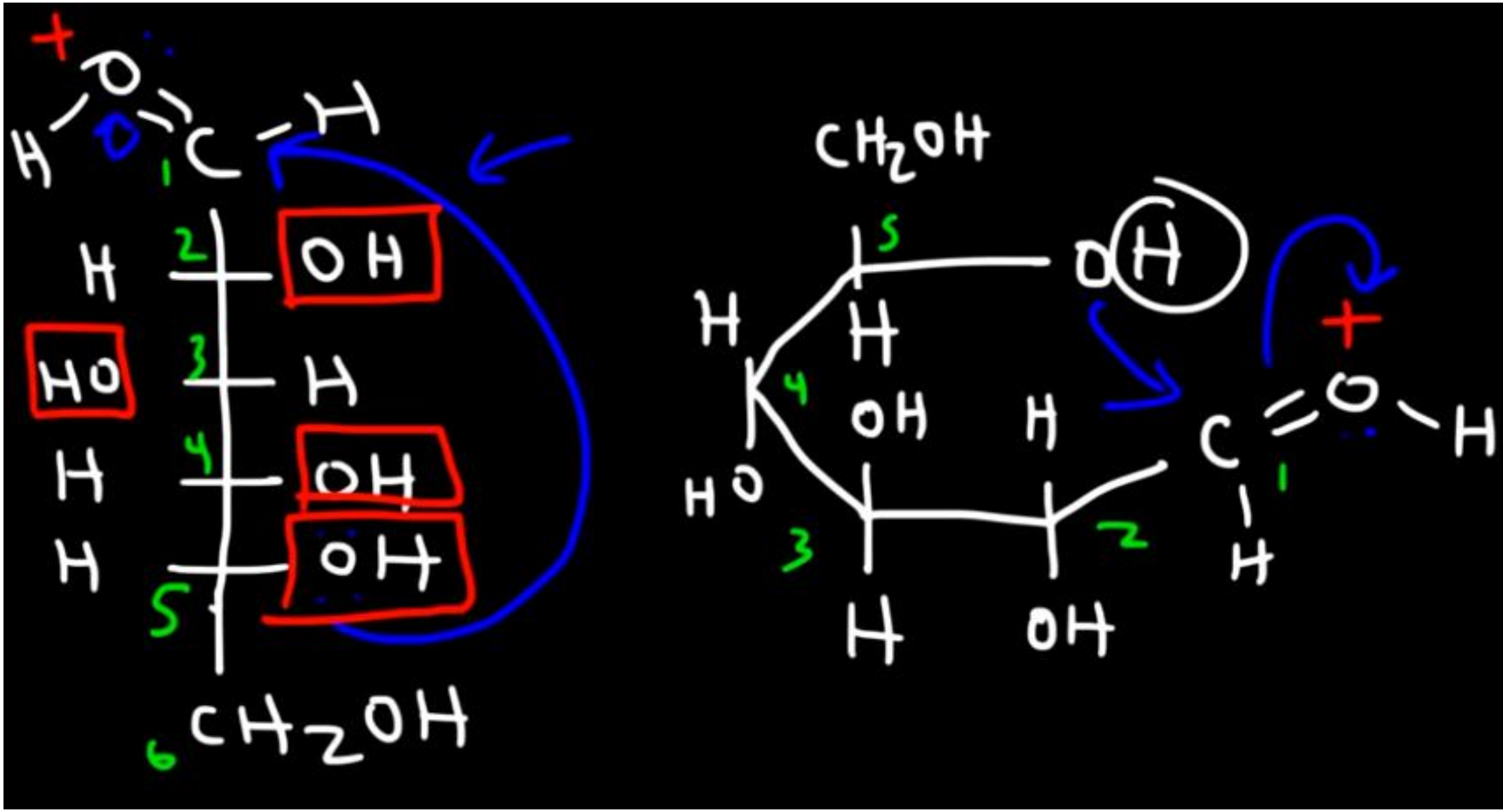
GlycoNet



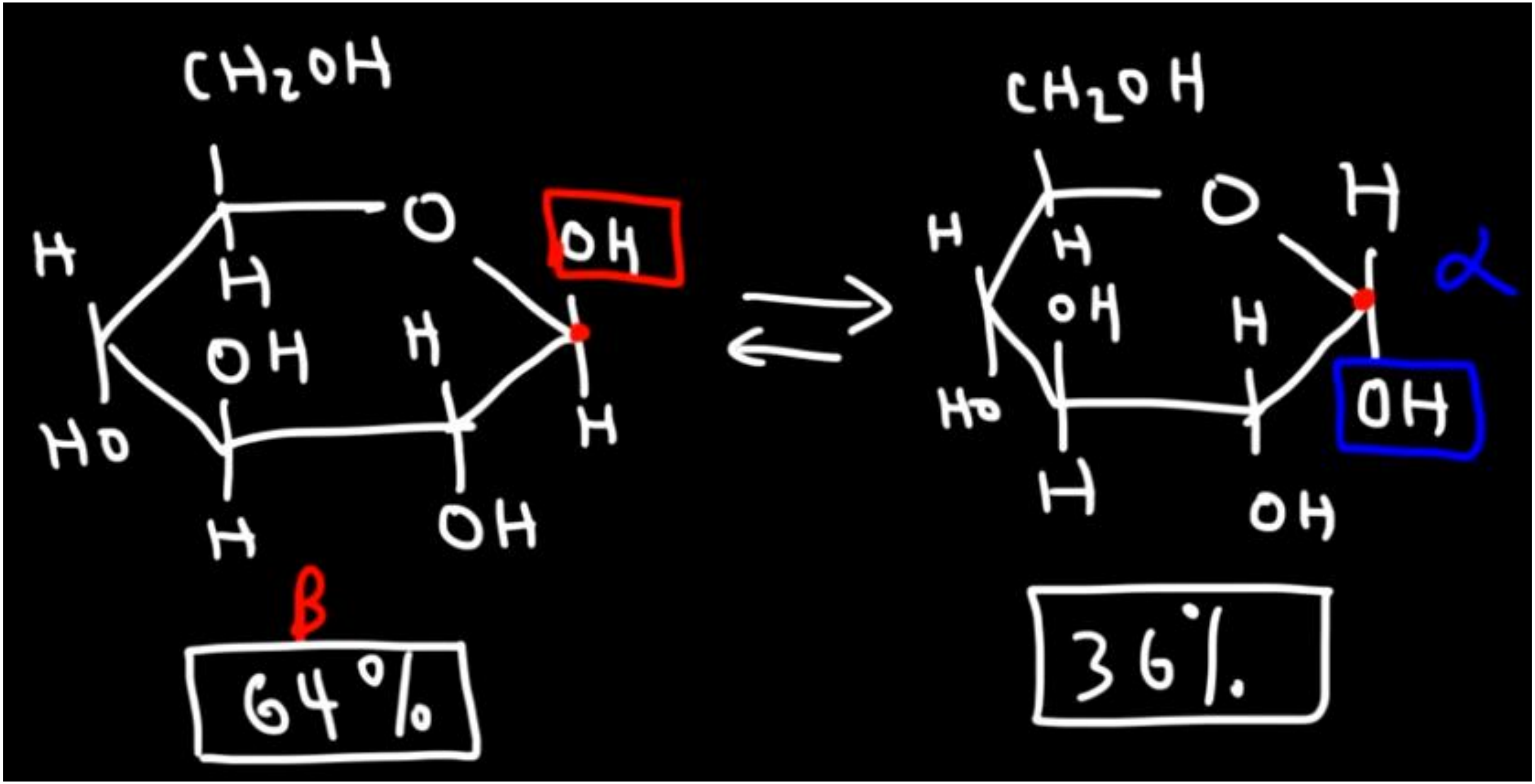
CHO
H OH
HO H
H OH
H OH
CH2OH
D-Glucose
L-Glucose
HO H
D-Fructose CH2OH
=O
HO H
H OH
H OH
CH2OH



1 CHO
2
H OH
3
HO H
4
H OH
5
H OH
6 CH2OH
D-Glucose
epimers
C-4 epimer
CHO
H OH
HO H
HO H
H OH
CH2OH
D-Galactose



CH2OH
OH
HO
OH
OH
CH2OH
OH
HO
OH
OH



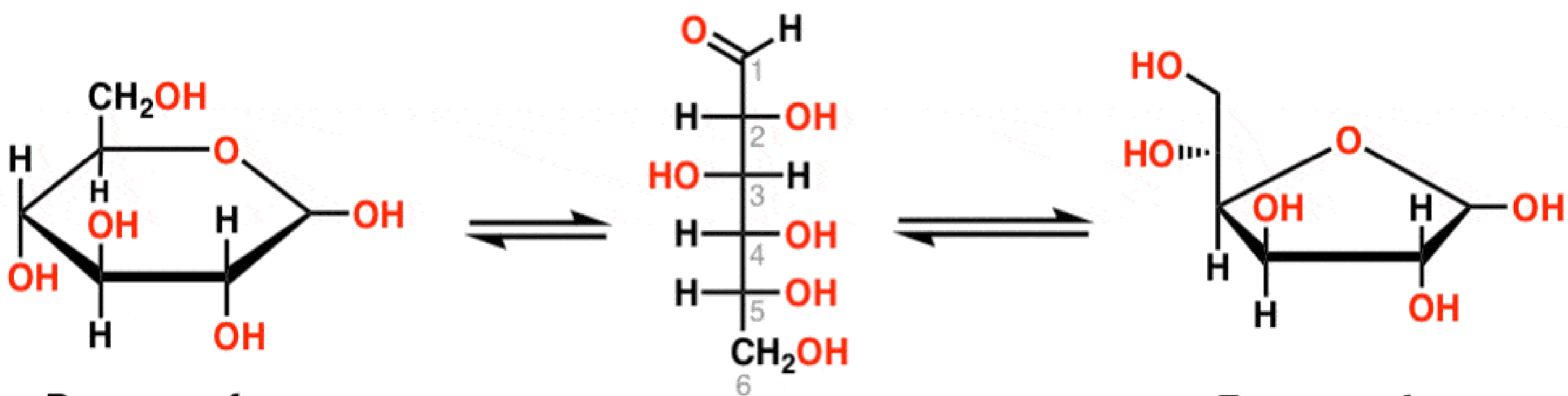
CH2OH
O
OH
H
OH
HO
H
OH
H
H
H
β
64%
CH2OH
O
H
α
H
H
OH
H
HO
OH
H
OH
36%

Summary: Pyranoses, Furanoses, and Ring-Chain Tautomerism

Sugars exist in equilibrium between their open-chain and various closed-chain forms. (This is called "ring-chain tautomerism")

Particularly important for hexoses (e.g. glucose) and pentoses (e.g. ribose)

e.g. D-glucose (below)



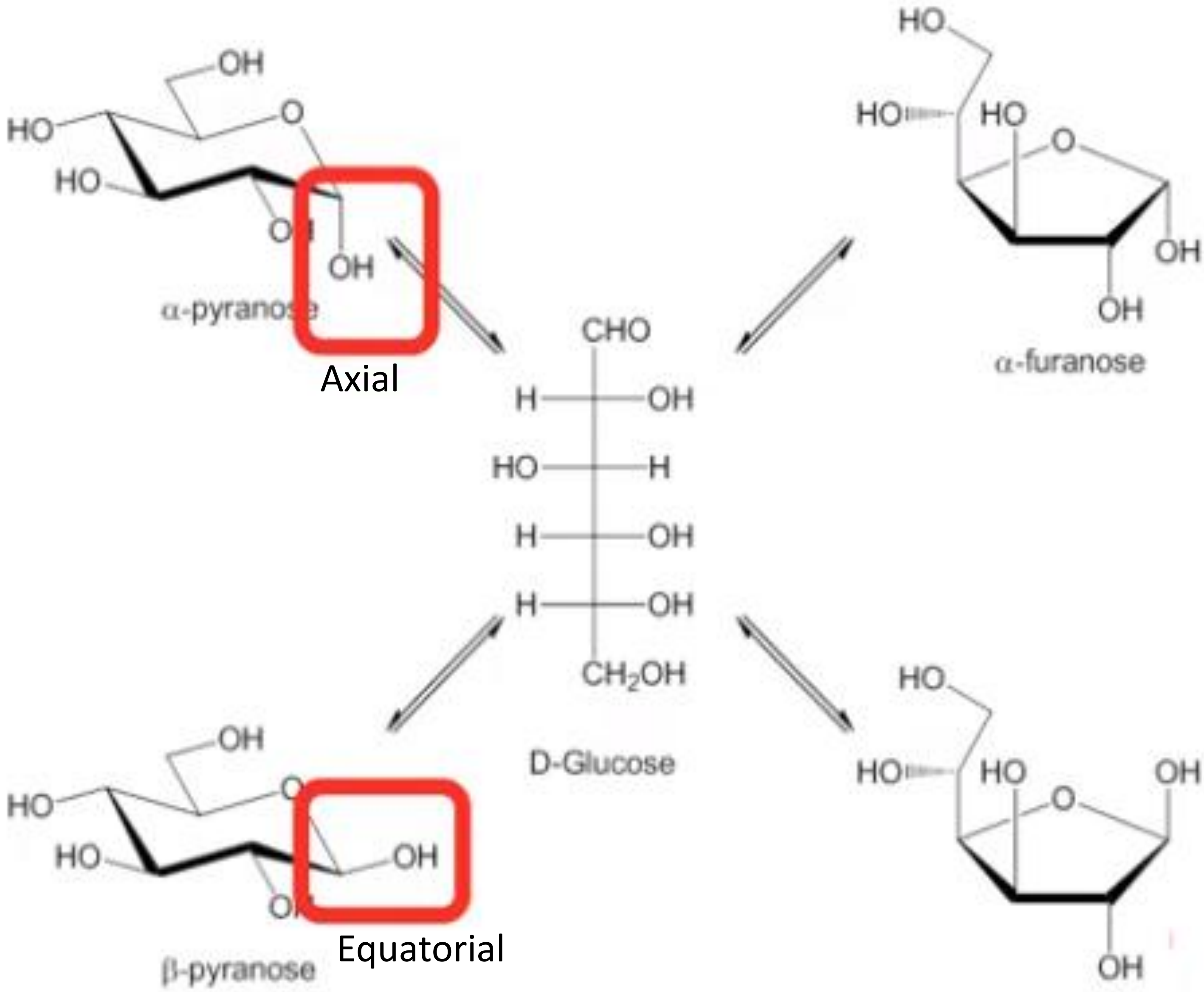
Pyranose forms (α + β) — **99%**

Open-chain form — **0.25%**

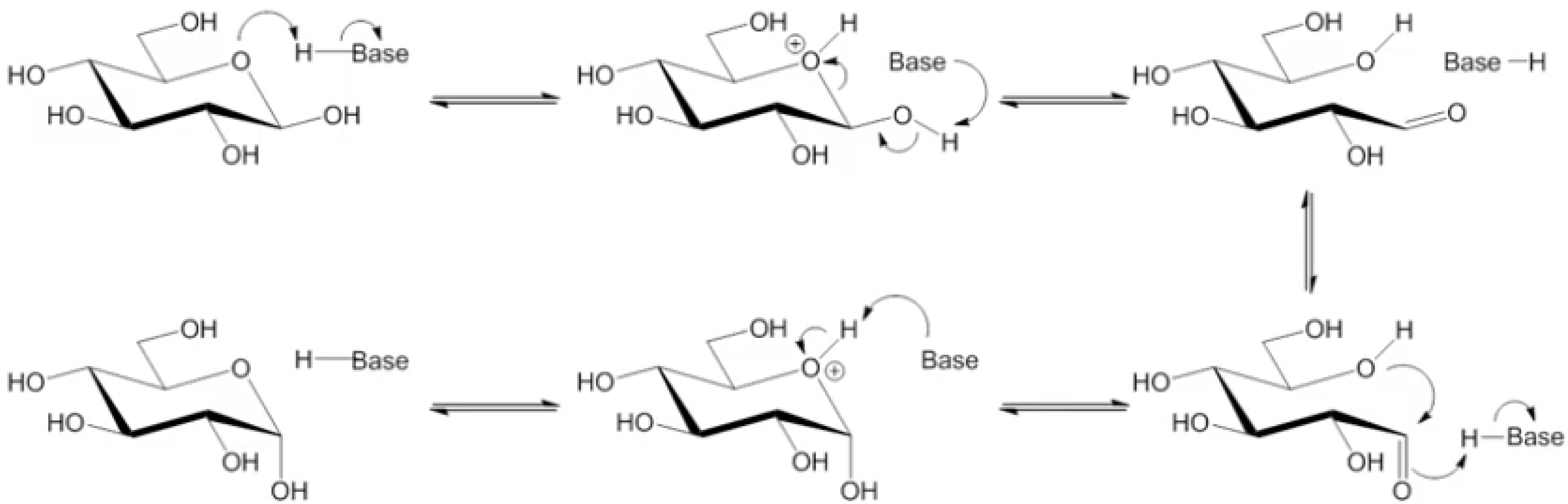
Furanose forms (α + β) — **< 1%**

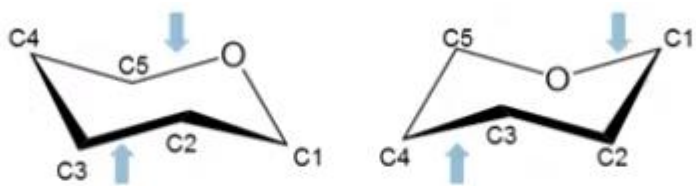
The six-membered cyclic form is generally referred to as the "pyranose" form, and the five-membered cyclic form is called the "furanose" form

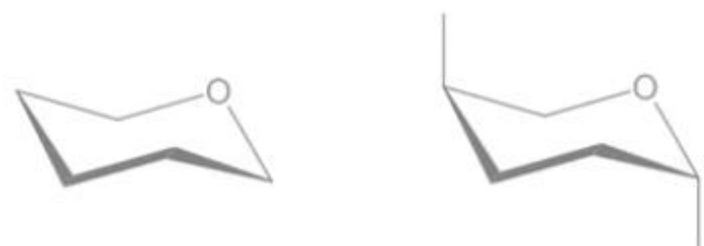
Closure of the ring creates a chiral center at C-1, resulting in two diastereomers (sometimes called "anomers") - the alpha (α) and beta (β) forms

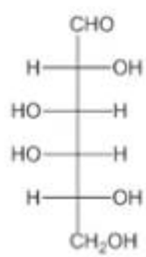

α-pyranose
Axial
CHO
H OH
HO H
H OH
H OH
CH2OH
D-Glucose
α-furanose
β-pyranose
Equatorial
β-furanose

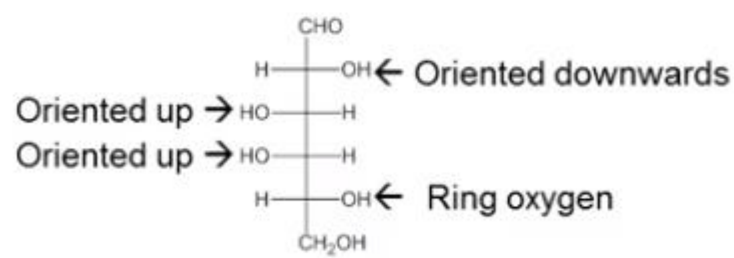
Mutarotation



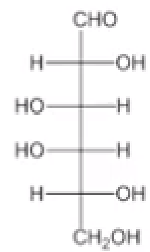


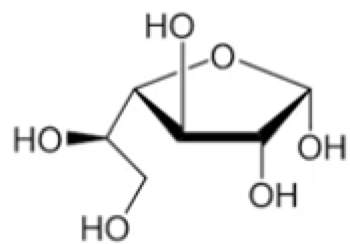




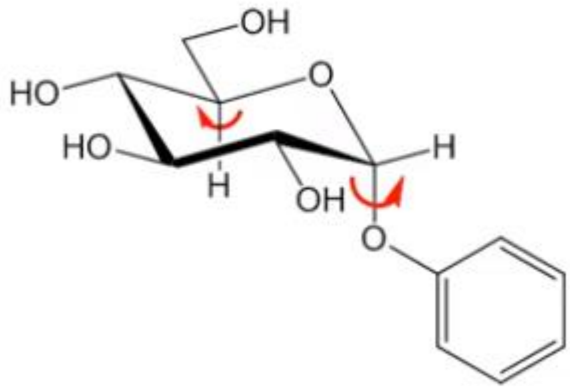


Ring oxygen →

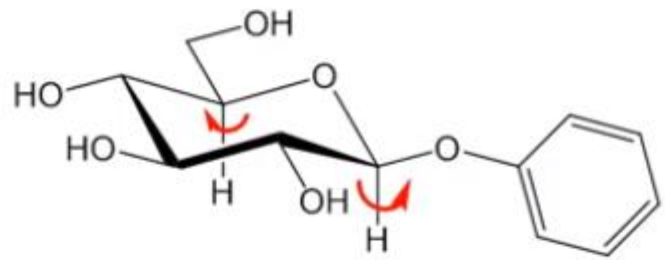




Glycosides



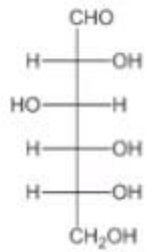
Oxygen @ C-5 is on the right
Oxygen @ C-1 is on the right
Configuration is α

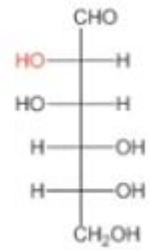


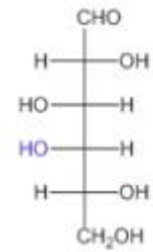
Oxygen @ C-5 is on the right
Oxygen @ C-1 is on the left
Configuration is β

Common Sugars

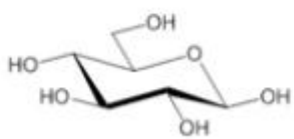
Fischer projection:

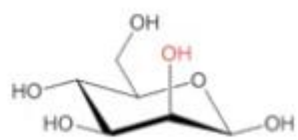


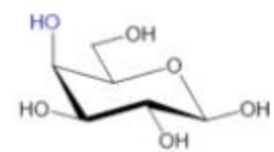




Line drawing:





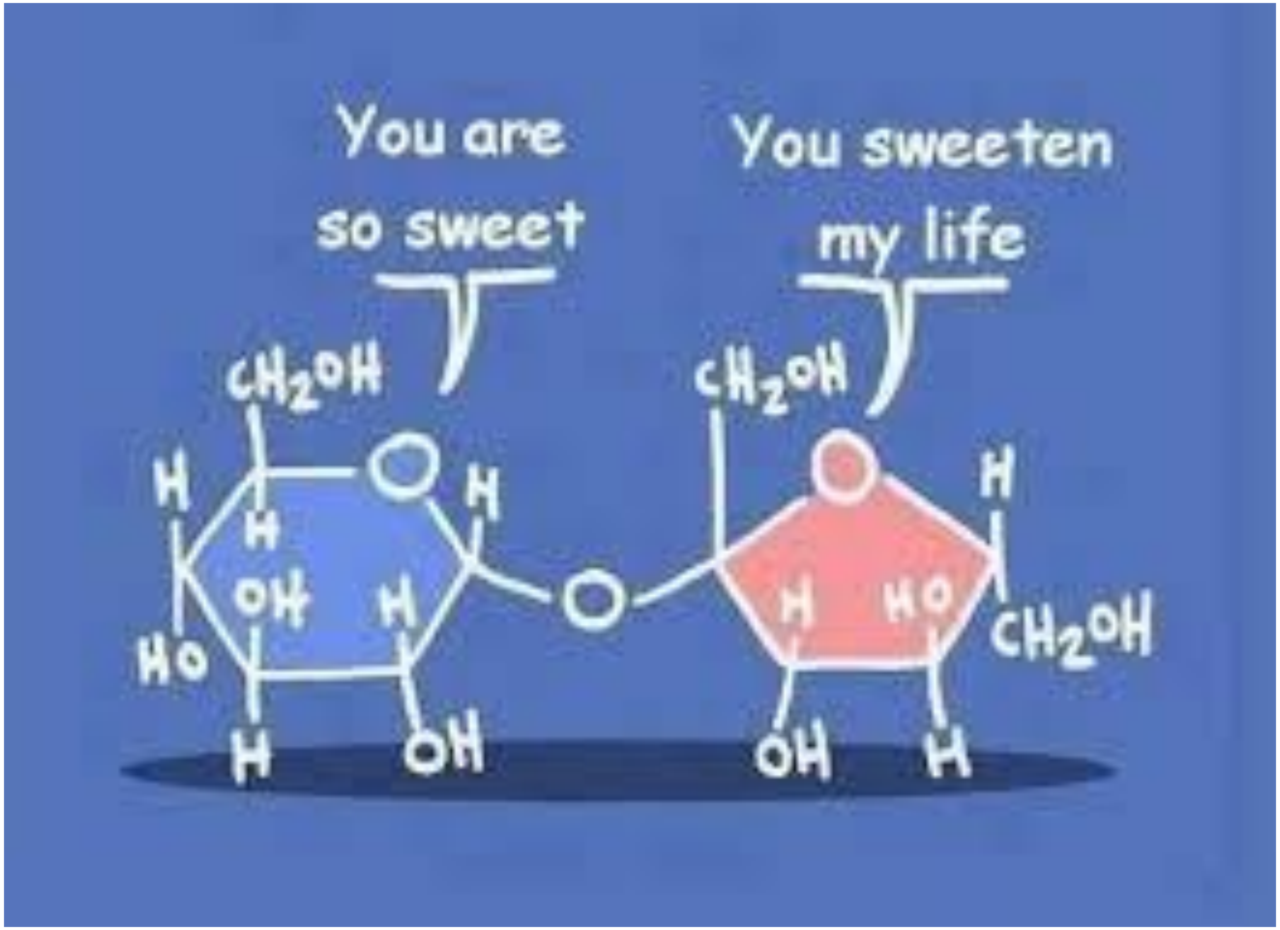


Name:
(Abbreviation)

β-D-glucose (Glc)

β-D-mannose (Man)

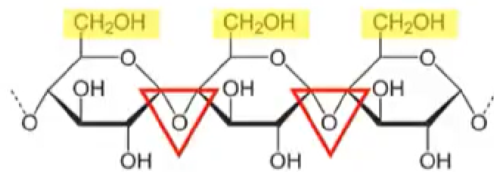
β-D-galactose (Gal)


You are so sweet
You sweeten my life
CH2OH
H
H
OH
H
HO
H
OH
H
O
O
CH2OH
H
H
HO
CH2OH
OH
H
O

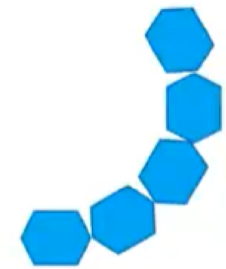
1. Which polysaccharide makes up plant cell walls?
2. Which monosaccharide makes up this polysaccharide?
3. Is this polysaccharide branched or unbranched?

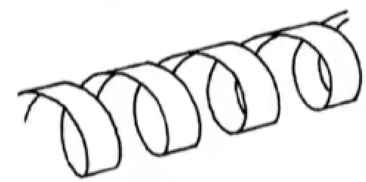
Alpha (α) vs. Beta (β) glycosidic linkages

- Alpha (α)
  - Create **HELICAL** shaped polysaccharide
  - Humans CAN digest/break them apart
    - Our guts (digestive systems) make enzymes that hydrolyze α linkages



https://upload.wikimedia.org/wikipedia/commons/thumb/e/ec/Amylose3.svg/800px-Amylose3.svg.png

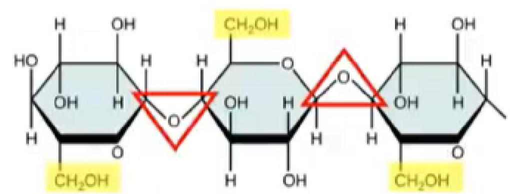




https://commons.wikimedia.org/wiki/File:Hand-drawn_helix_ribbons_at_various_angles.jpg

Helical shape

- Beta (β)
  - Create straight chain shaped polysaccharides
  - Humans CANNOT digest/break them apart
    - Our guts do NOT make any enzymes that can hydrolyze β linkages



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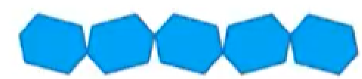


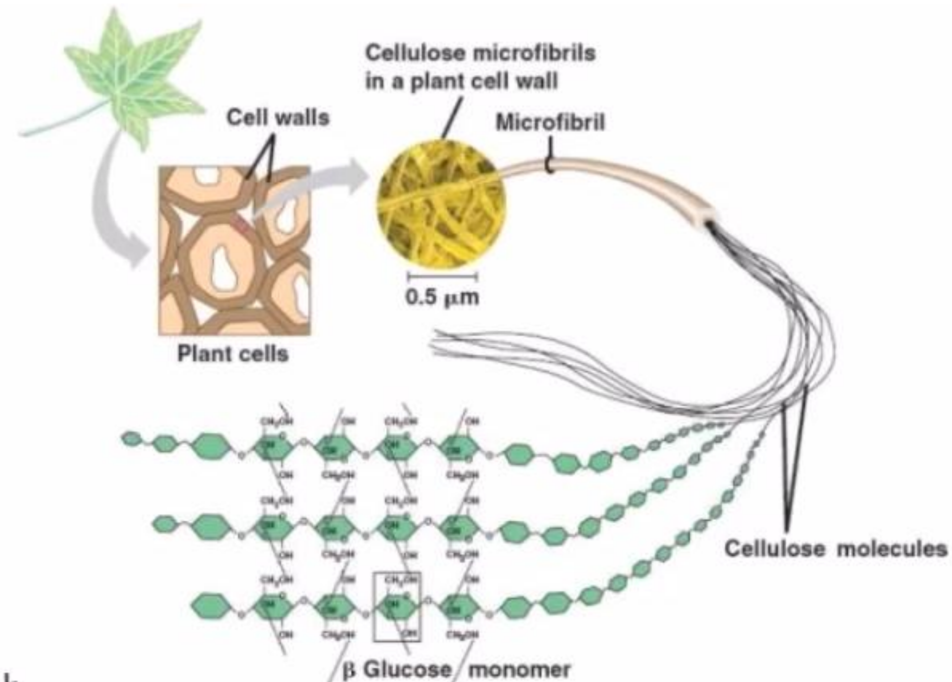
Straight chain shape

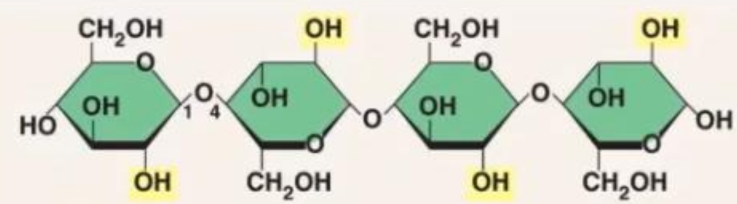
Cellulose - *structure*

Cellulose is made up of β-glucose monomers linked by β 1-4 glycosidic bonds.

Cellulose does not branch.

The monomers are packed tightly as extended long chains held adjacent to each other by hydrogen bonding. This gives cellulose its rigidity and strength.





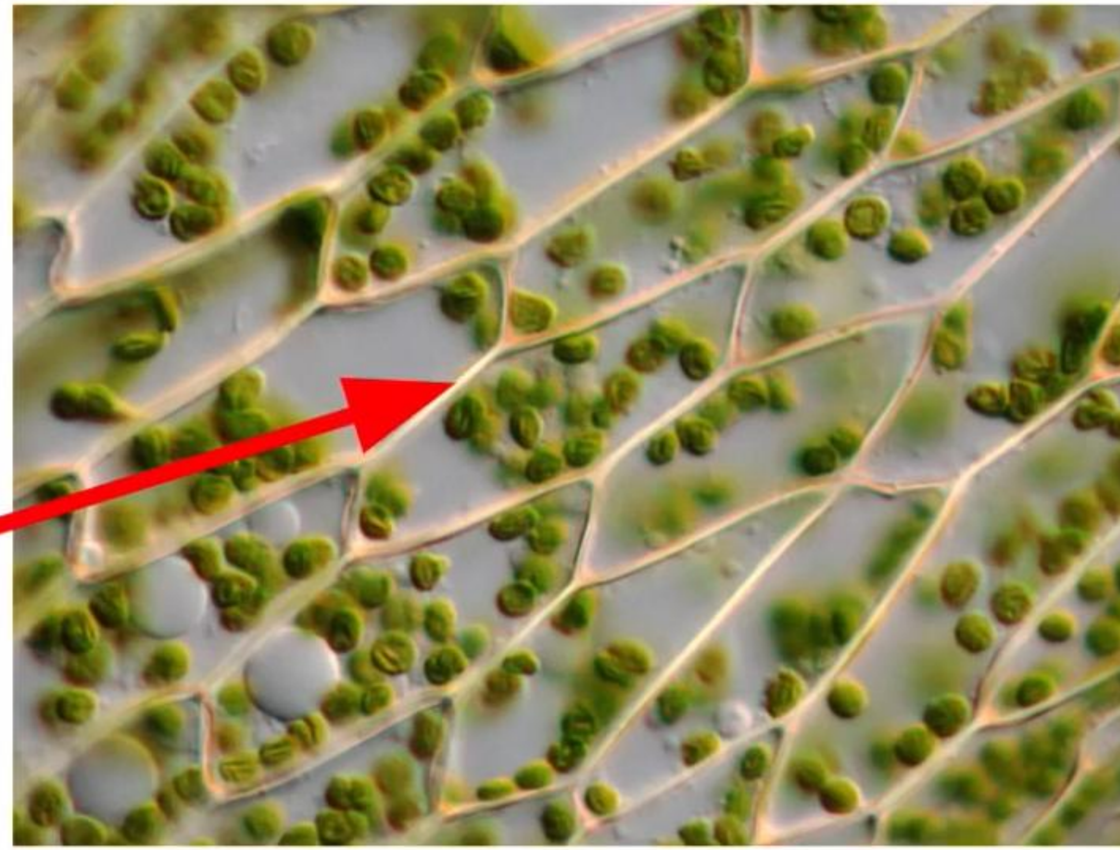
(c) Cellulose: 1–4 linkage of β glucose monomers

In cellulose, every β-glucose monomer is "upside down" with respect to its neighbors.

Cellulose - *function*

The cell wall of plants is mostly made of cellulose; this provides structural support to the cell.

Fun fact: wood and paper are mostly cellulose!



Cellulose!

Cellulose - *function (just read)*

The β 1-4 linkage found in cellulose cannot be broken down by human digestive enzymes.

The cellulose we eat is called "fiber" in every day lingo.

Fiber moves through the digestive tract undigested and then is egested from the body (poop).

Fiber has an important function of maintaining health of the digestive tract.

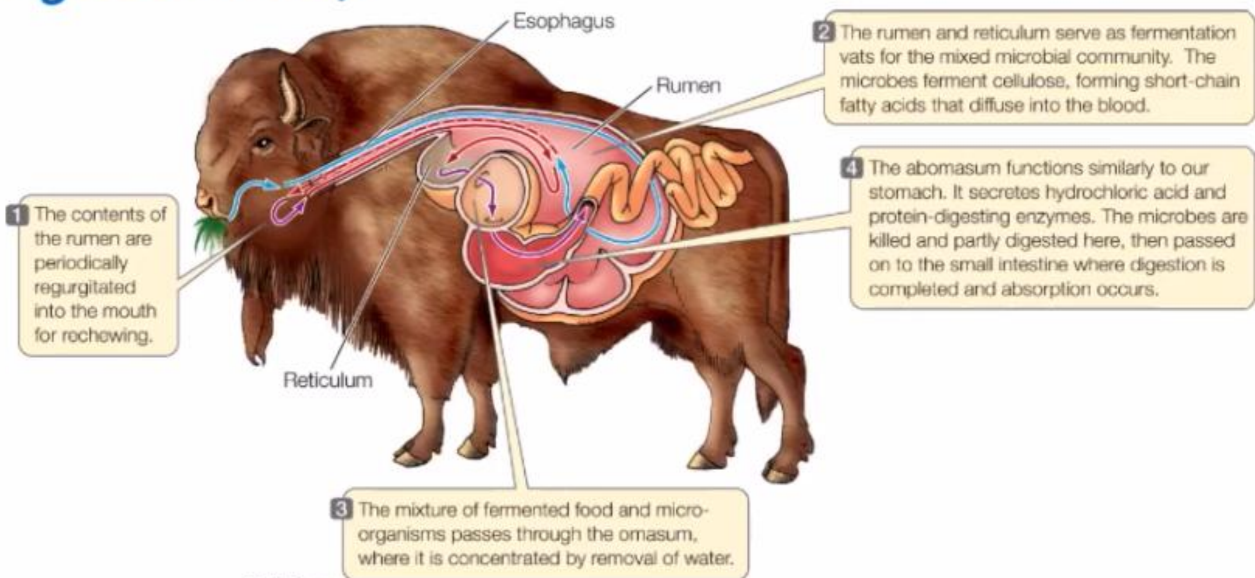
Why can't humans digest cellulose?

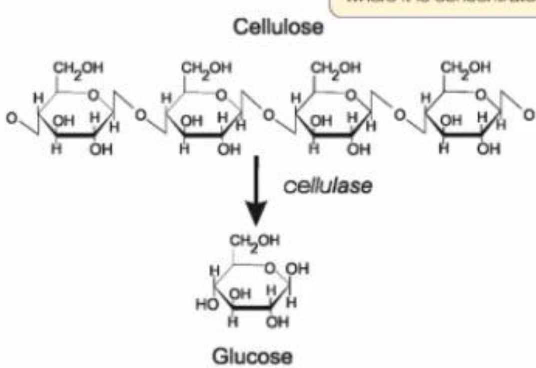
- We don't produce
  Cellulase
- Ruminants, like cows, have symbiotic bacteria in their stomachs

Cellulose - *function (just read)*

Herbivores (such as cows, koalas, buffalos, and horses) have specialized bacteria in their digestive tracts that digest cellulose and use it as a food source.

In these animals, bacteria in the rumen secrete the enzyme cellulase. Cellulase breaks down cellulose into glucose monomers that can be used as an energy source by the animal.





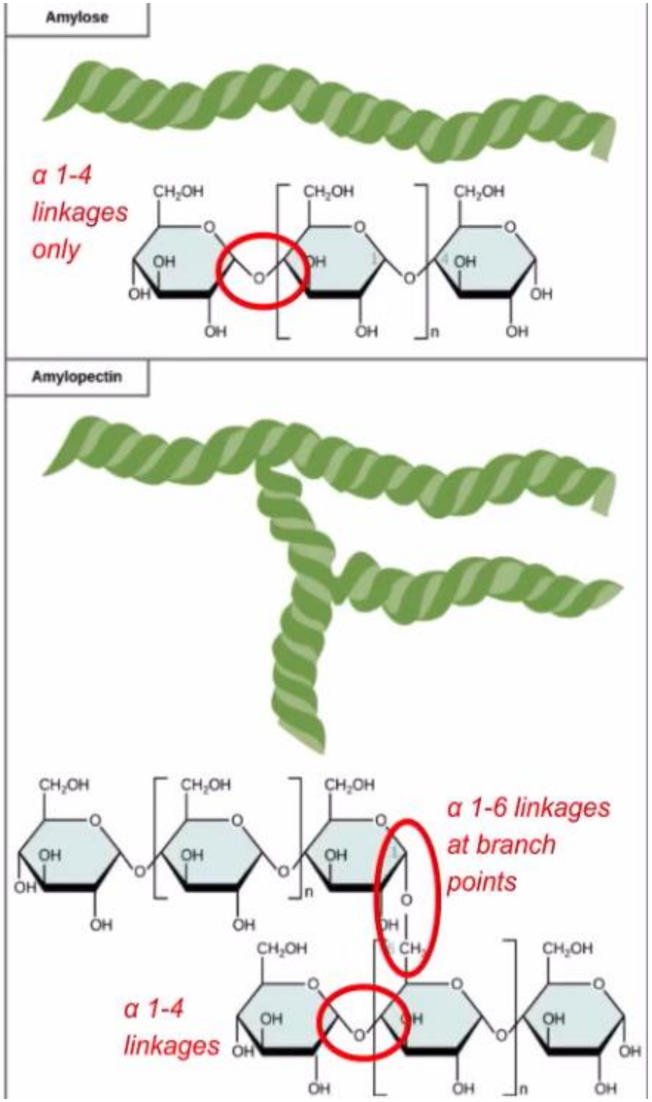
Starch - *structure*

Starch is made up of α-glucose monomers.

There are two types of starch: amylose and amylopectin (both polymers of α-glucose).

Amylose is starch formed by **unbranched** chains of glucose monomers (only α **1-4*** linkages)

Amylopectin is a **branched** polysaccharide (α **1-4*** linkages and α **1-6** linkages at the branch points).



**The numbers 1-4 and 1-6 refer to the carbon number of the two monosaccharides that have joined to form the bond.*

- α-glucose molecules joined by α1-4 glycosidic bonds with α1-6 branches every 20-30 monomers

Starch - *function*

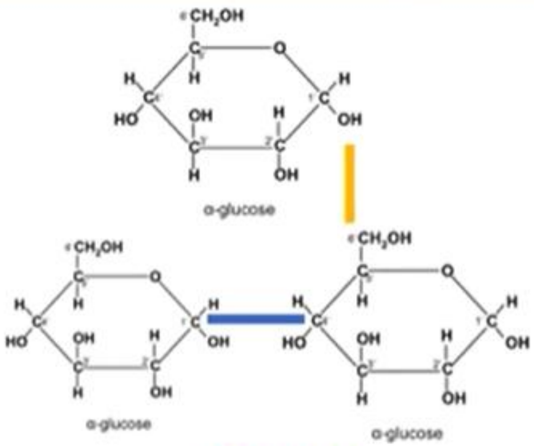
Starch* is the storage form of carbohydrates in plants.

Plants are able to synthesize glucose in photosynthesis, and the excess glucose, beyond the plant's immediate energy needs, is stored as starch in different plant parts, including roots and seeds.

The plants form the basis of the food chain. Animals eat the plants as a source of carbohydrates.

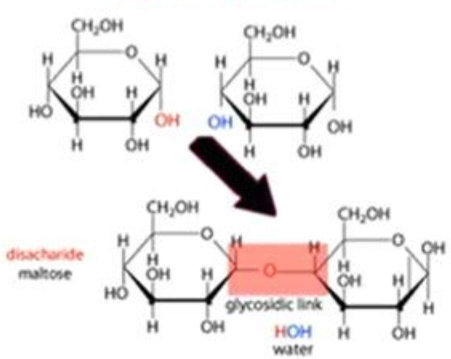
**Both amylose and amylopectin forms of starch have the same function*

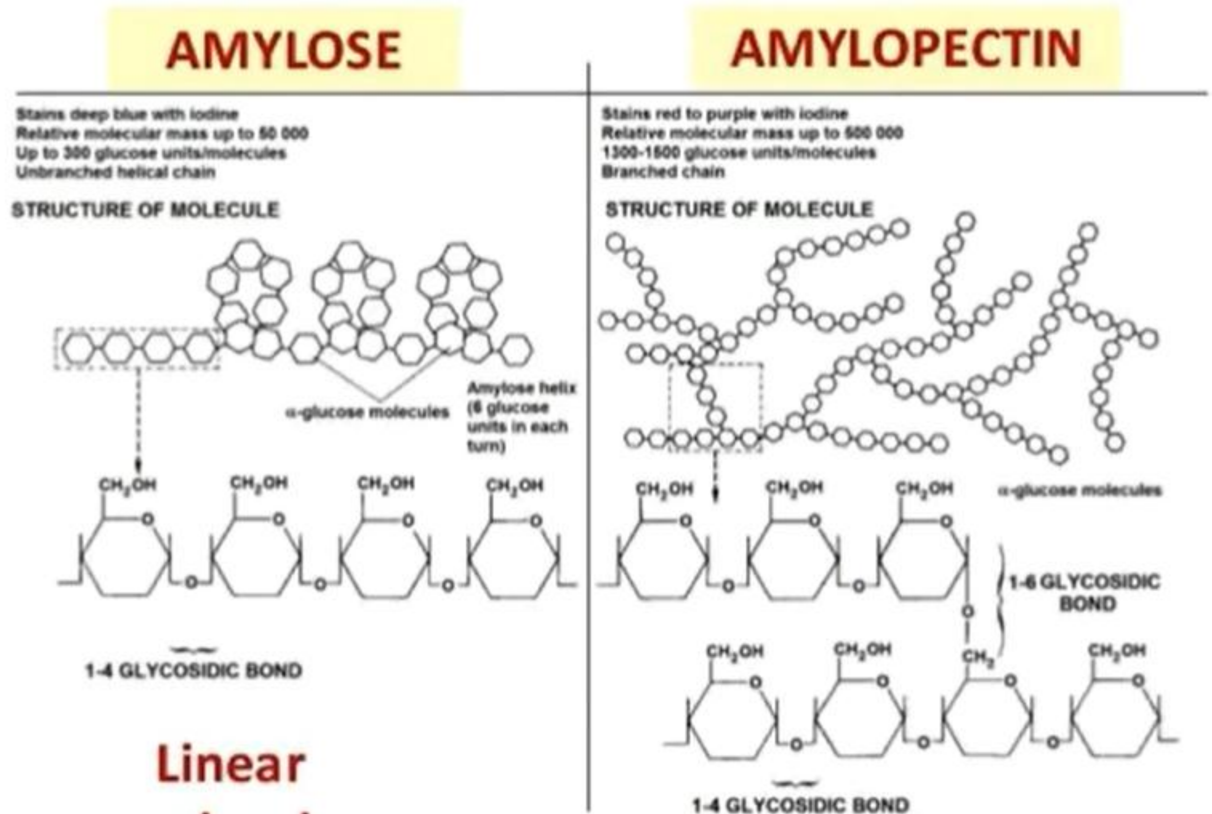
Starch: Amylose and Amylopectin



Picture 1

Condensation reaction

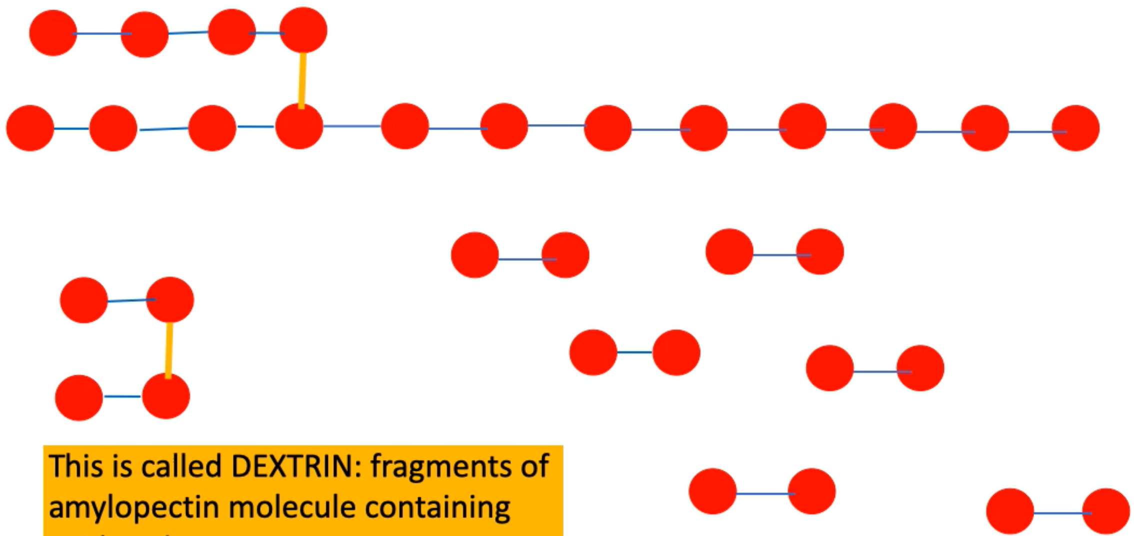




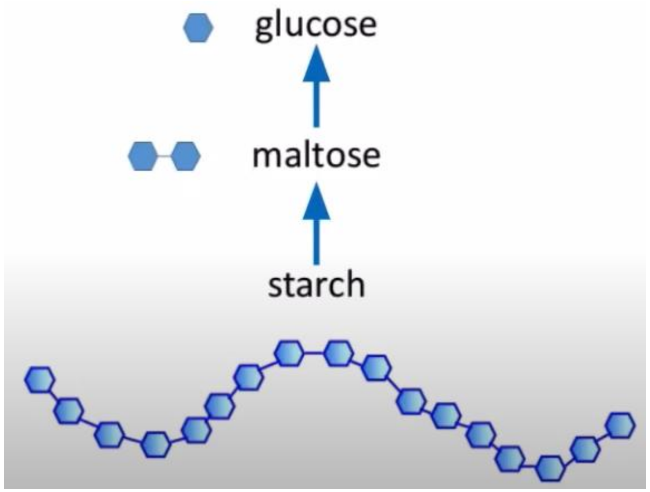
Linear molecule

Branched molecule

Therefore, amylase cannot fully digest amylopectin



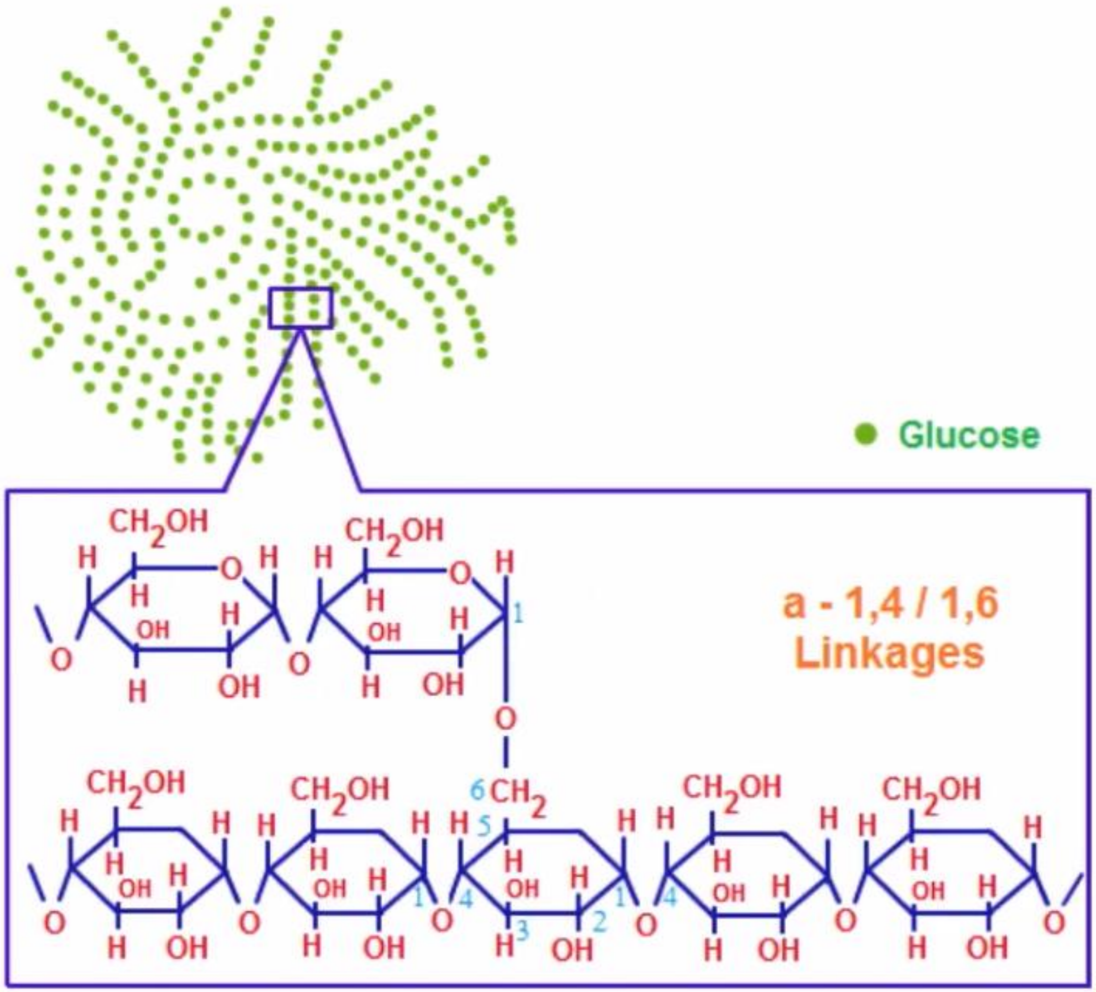
This is called DEXTRIN: fragments of amylopectin molecule containing 1,6 bond



Glycogen - *structure*

Glycogen is made up of α-glucose monomers.

Glycogen is a **highly branched** molecule, with α **1-4** linkages and α **1-6** linkage at the branch points.

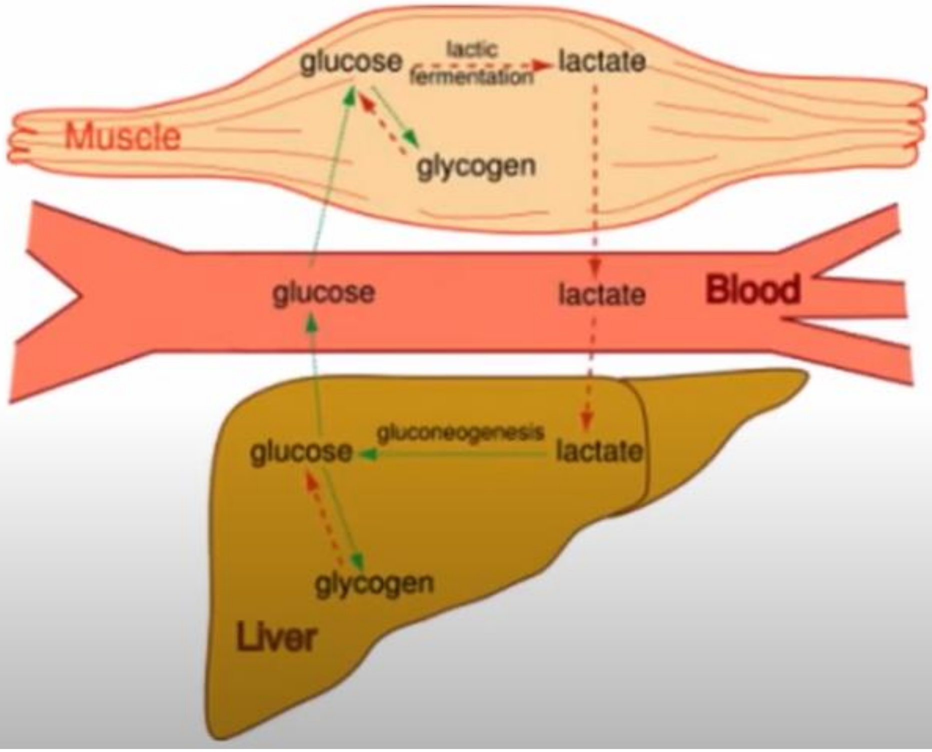


Glycogen - *function*

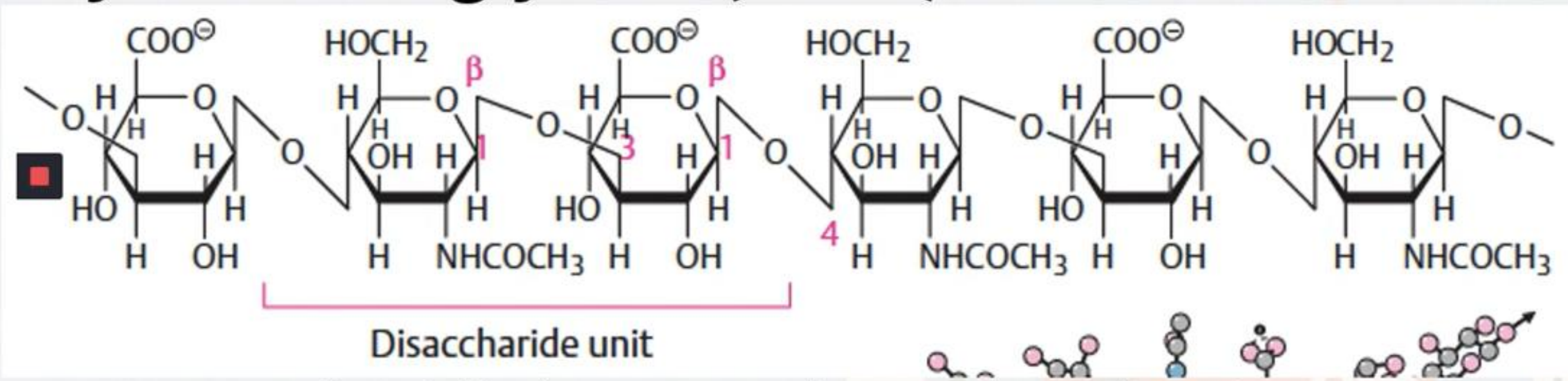
Glycogen is the storage form of carbohydrates in humans and other vertebrates.

When blood glucose levels *increase* (i.e. after eating), glucose is stored as glycogen in liver and muscle cells.

When blood glucose levels *decrease*, glycogen is broken down to release glucose into the blood so the cells can continue doing cellular respiration.



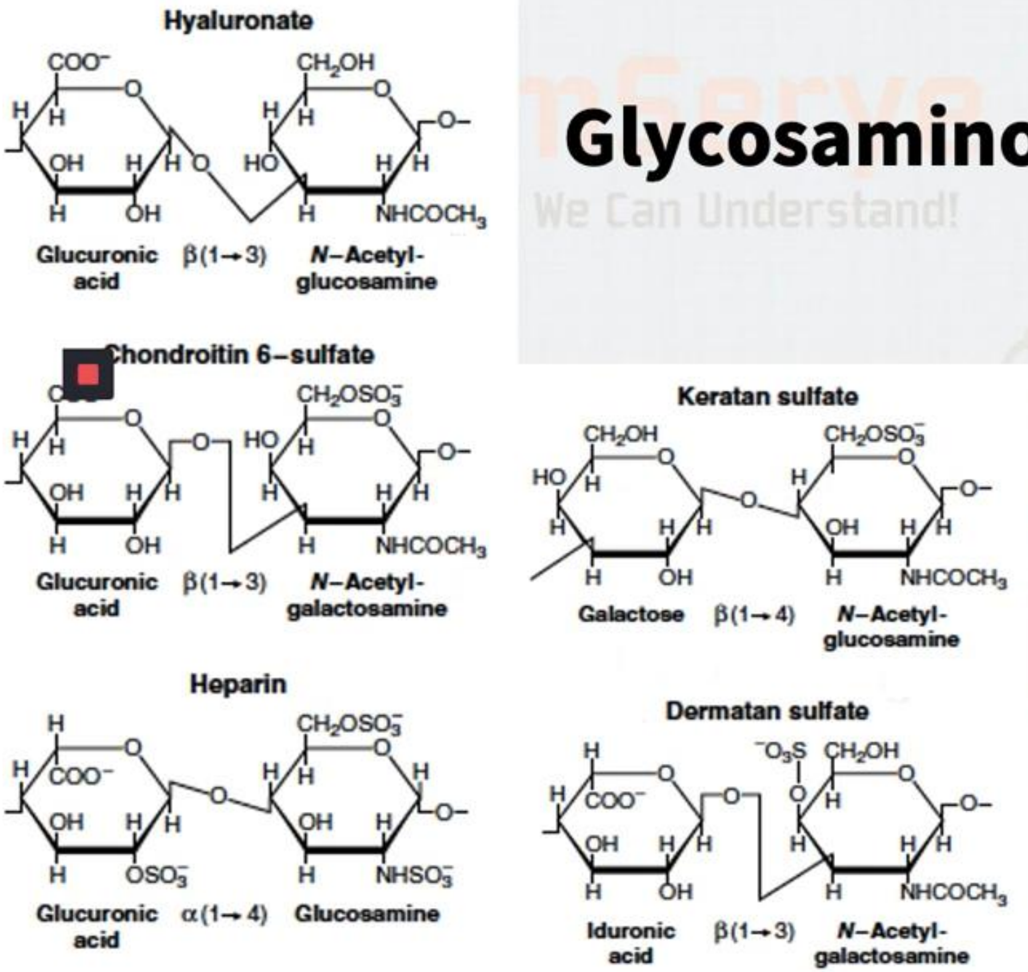
Glycosaminoglycans (GAGs)



- a group of acidic heteropolysaccharides; important structural elements of the ECM
- made up of repeating disaccharide units, each of which consists of one uronic acid and one amino sugar

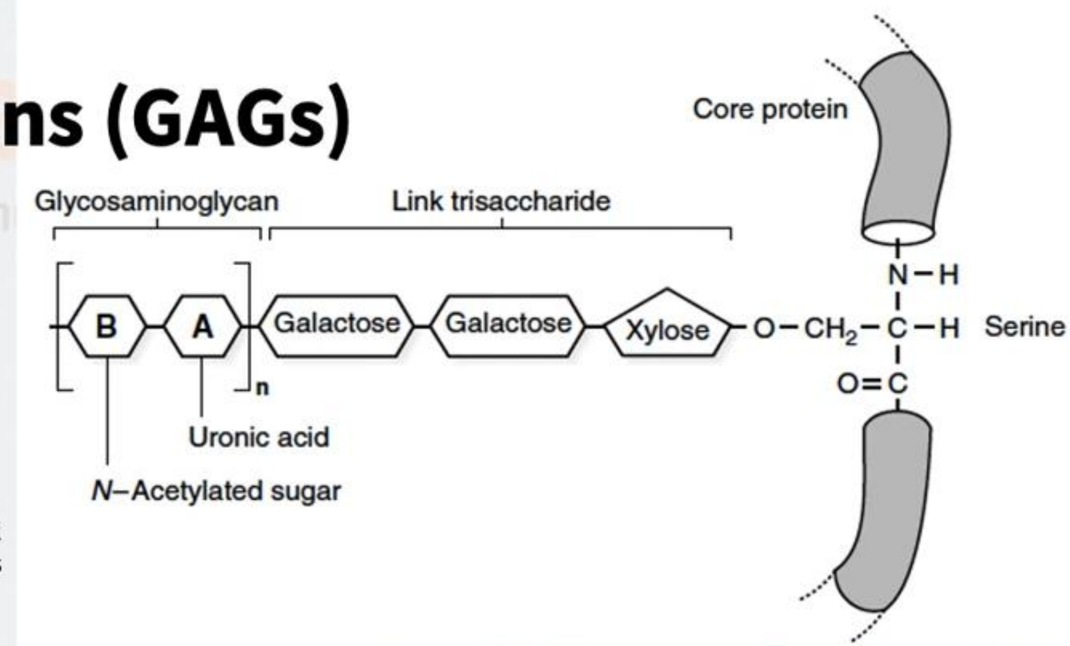
Glycosaminoglycans (GAGs)

- has repeating disaccharide units
  - uronic acid (glucuronic acid or iduronic acid)
  - amino sugar (N-acetylglucosamine or N-acetylgalactosamine)
- hyaluronic acid, chondroitin sulfate, heparin, keratan sulfate and dermatan sulfate



Mark's Basic Medical Biochemistry A Clinical Approach, 5th ed Liberman and Marks

Glycosaminoglycans (GAGs)



Mark's Basic Medical Biochemistry A Clinical Approach, 5th ed Liberman and Marks

- least 6 types of GAGs
- except for hyaluronic acid, the GAGs are linked to proteins, usually attached covalently to serine or threonine residues
- keratan sulfate I is attached to asparagine
- attachment of GAGs to core proteins give rise to **proteoglycans**

Glycosaminoglycans and Proteoglycans

Glycosaminoglycan	Function
Hyaluronic acid	Cell migration in: Embryogenesis Morphogenesis Wound healing
Chondroitin sulfate proteoglycans	Formation of bone, cartilage, cornea
Keratan sulfate proteoglycans	Transparency of cornea
Dermatan sulfate proteoglycans	Transparency of cornea Binds LDL to plasma walls
Heparin	Anticoagulant (binds antithrombin III) Causes release of lipoprotein lipase from capillary walls
Heparan sulfate (syndecan)	Component of skin fibroblasts and aortic wall; commonly found on cell surfaces

Glycoproteins and Proteoglycans

- **Glycoproteins**
  - compounds containing carbohydrate, or glycan, covalently linked to protein
  - carbohydrate may be in the form of a monosaccharide, disaccharides, oligosaccharides, polysaccharides, or their derivatives
- **Proteoglycans**
  - subclass of glycoproteins in which the carbohydrate units are polysaccharides that contain amino sugars (glycosaminoglycans or GAGs)

Glycoproteins (mucoproteins)

Hexoses	Mannose (Man) Galactose (Gal)
Acetyl hexosamines	*N*-Acetylglucosamine (GlcNAc) *N*-Acetylgalactosamine (GalNAc)
Pentoses	Arabinose (Ara) Xylose (Xyl)
M[redacted]yl pentose	L-Fucose (Fuc; see Figure 13–15)
Sialic acids	N-Acyl derivatives of neuraminic acid, eg, *N*-acetylneuraminic acid (NeuAc; see Figure 13–16), the predominant sialic acid.

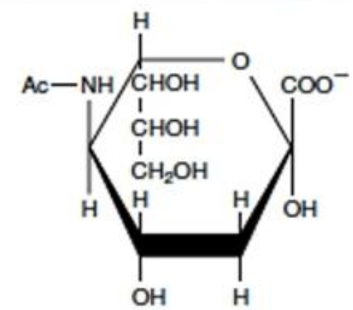
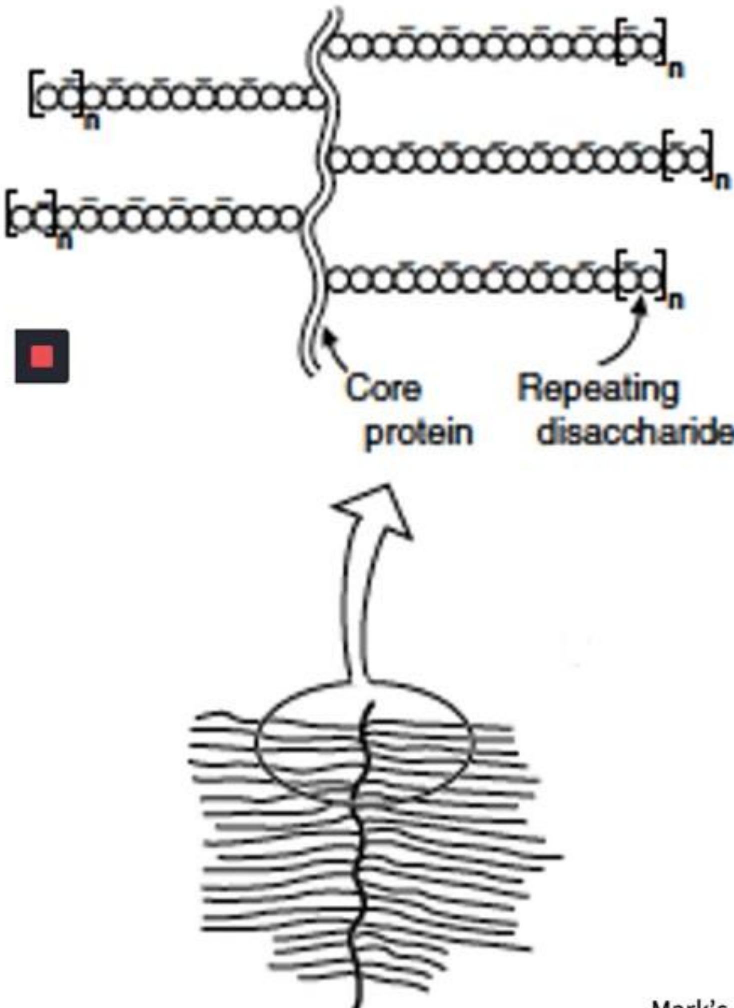


Figure 13–16. Structure of *N*-acetylneuraminic acid, a sialic acid (Ac = CH_3—CO—).

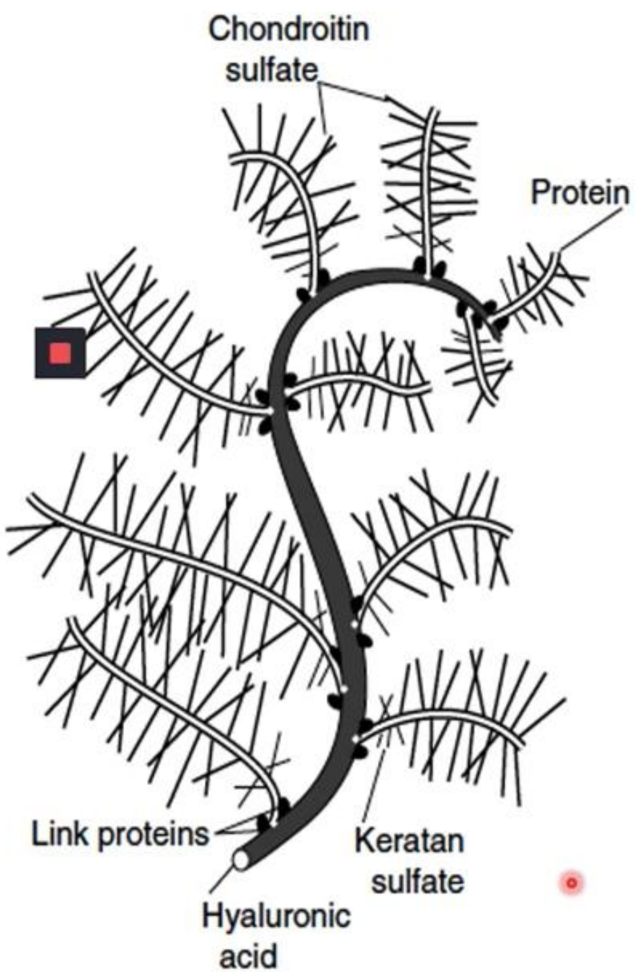
- in fluids and tissues, including the cell membranes
- proteins containing branched or unbranched oligosaccharide chains
- **sialic acids**
  - N- or O-acyl derivatives of neuraminic acid, a nine-carbon sugar derived from mannosamine (an epimer of glucosamine) and pyruvate
  - constituents of both glycoproteins and gangliosides

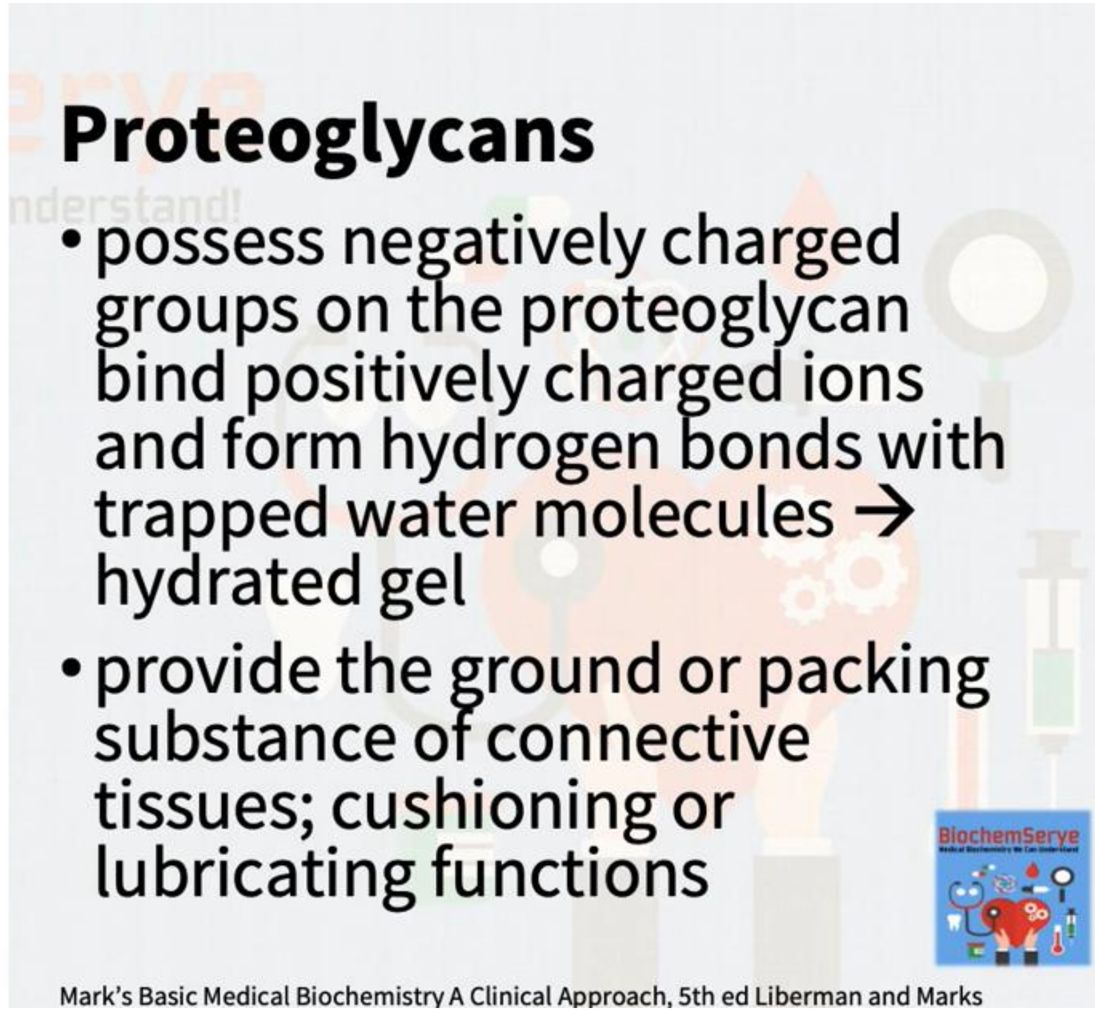


Proteoglycans

- contain many long unbranched GAGs attached to a core protein
- essential parts of the extracellular matrix, the aqueous humor of the eye, secretions of mucus-producing cells, and cartilage
- most GAGs have sulfated sugars contributing to negative charges → GAGs chains radiate out from the protein leading to overall "bottlebrush" structure
- may contain more than 100 GAG chains
- up to 95% oligosaccharide by weight

Mark's Basic Medical Biochemistry A Clinical Approach, 5th ed Liberman and Marks





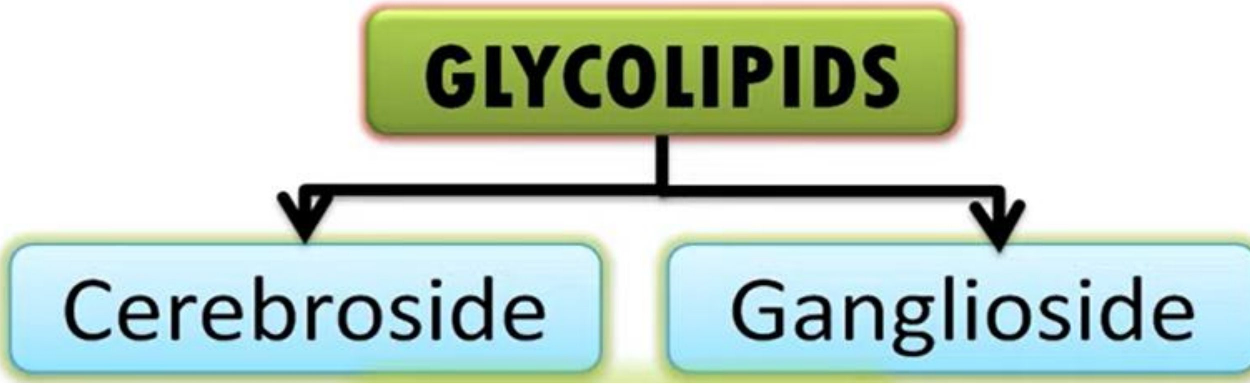
Hyaluronic acid, also called hyaluronan, is an anionic, nonsulfated glycosaminoglycan distributed widely throughout connective, epithelial, and neural tissues.

Mucopolysaccharidoses

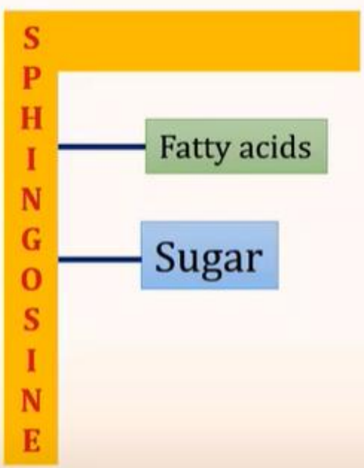
Disease	Enzyme Deficiency	Accumulated Products
Hunter	Iduronate sulfatase	Heparan sulfate, Dermatan sulfate
Hurler + Scheie	α-L-Iduronidase	Heparan sulfate, Dermatan sulfate
Maroteaux-Lamy	*N*-Acetylgalactosamine sulfatase	Dermatan sulfate
Mucolipidosis VII	β-Glucuronidase	Heparan sulfate, Dermatan sulfate
Sanfilippo A	Heparan sulfamidase	Heparan sulfate
Sanfilippo B	*N*-Acetylglucosaminidase	Heparan sulfate
Sanfilippo D	*N*-Acetylglucosamine 6-sulfatase	Heparin sulfate

- caused by deficiencies of lysosomal glycosidases → partially degraded carbohydrates from proteoglycans, glycoproteins, glycolipids to accumulate within membrane-enclosed vesicles inside cells
- residual bodies can cause marked enlargement of the organ with impairment of its function
- affect multiple organ systems, with **bone** and **cartilage** being a primary target; significant neuronal involvement, leading to **mental retardation**

What are Glycolipids? Cerebroside vs Ganglioside



GLYCOLIPIDS



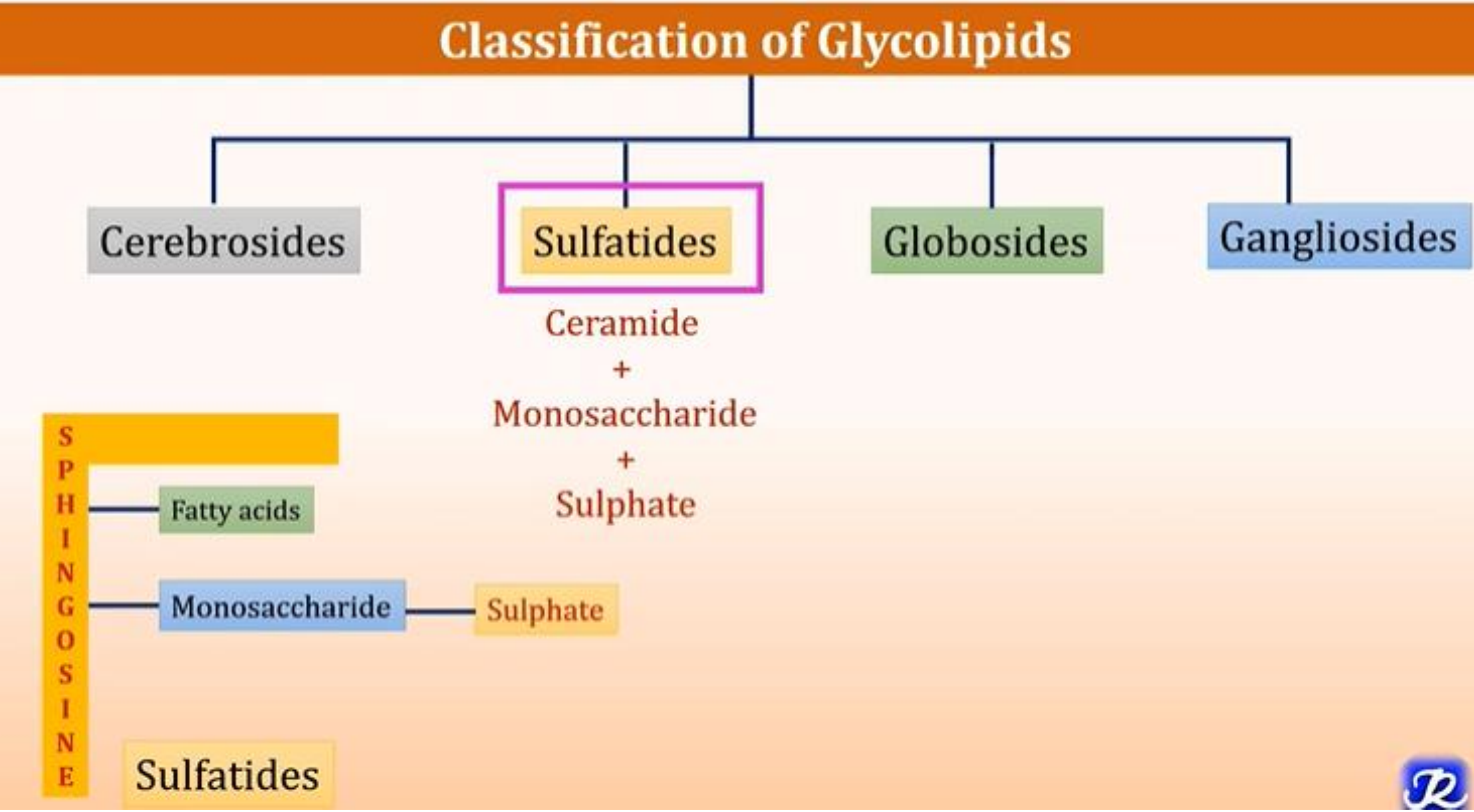
- Glycosphingolipids
- Important constituent of cell membrane and nervous tissues(brain)

- No glycerol
- No phosphate

Classification of Glycolipids

- Cerebrosides
- Sulfatides
- Globosides
- Gangliosides

Ceramide + Monosaccharide

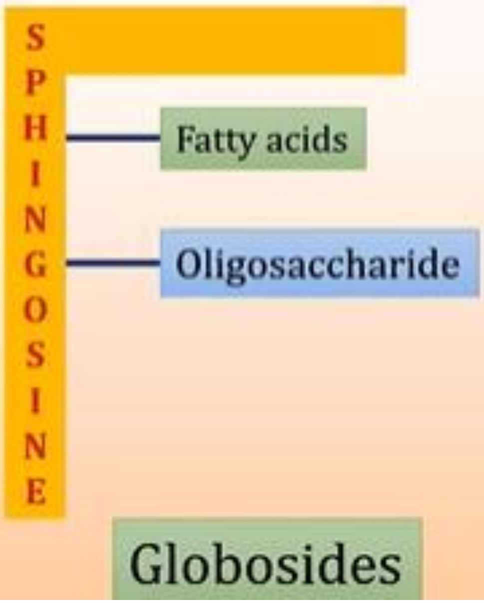

Classification of Glycolipids
Cerebrosides
Sulfatides
Globosides
Gangliosides
Ceramide
+
Monosaccharide
+
Sulphate
SPHINGOSINE
Fatty acids
Monosaccharide
Sulphate
Sulfatides

Classification of Glycolipid

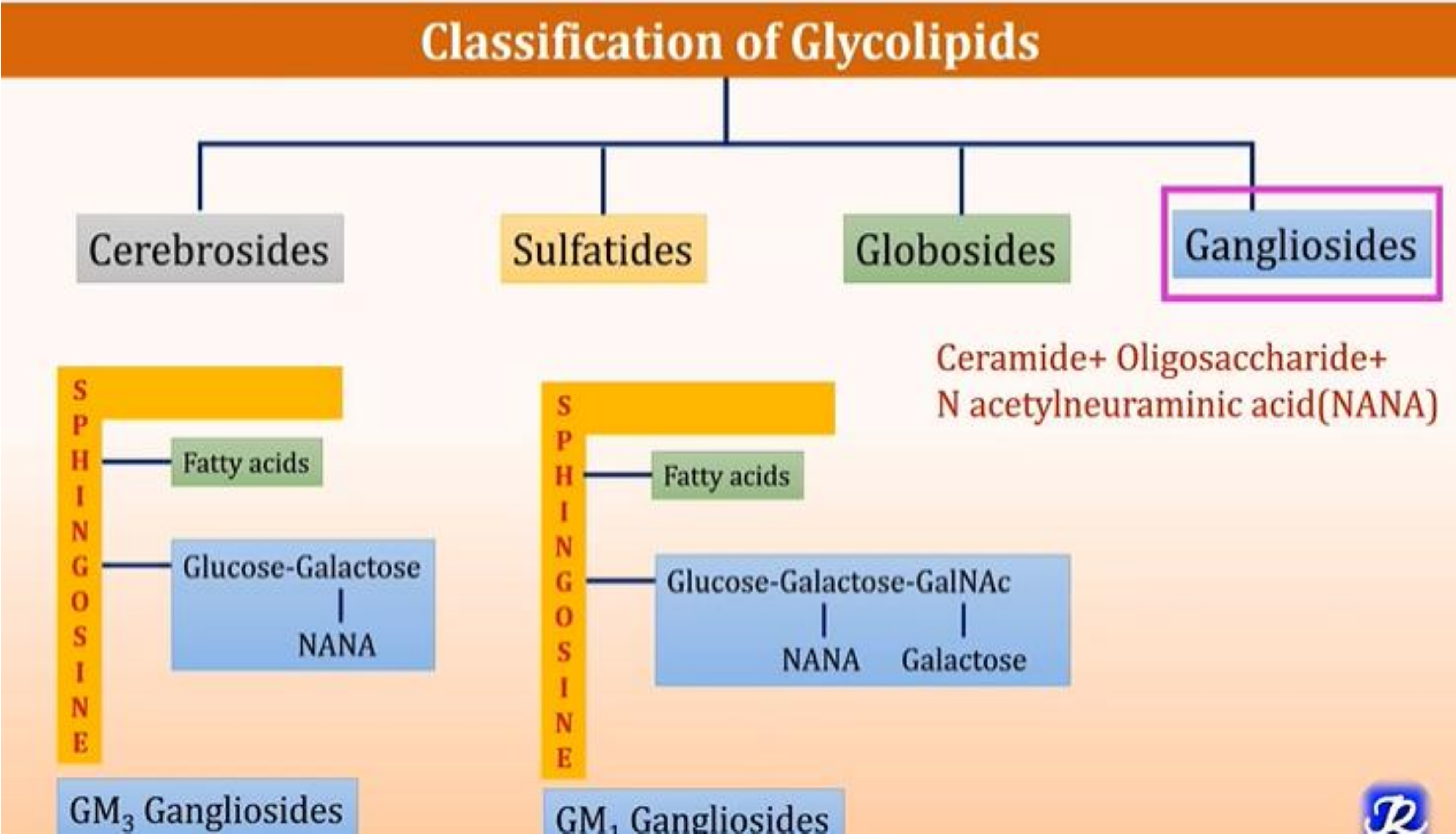
- Cerebrosides
- Sulfatides
- Globosides
- Gangliosides

Globosides

Ceramide
+
Oligosaccharide

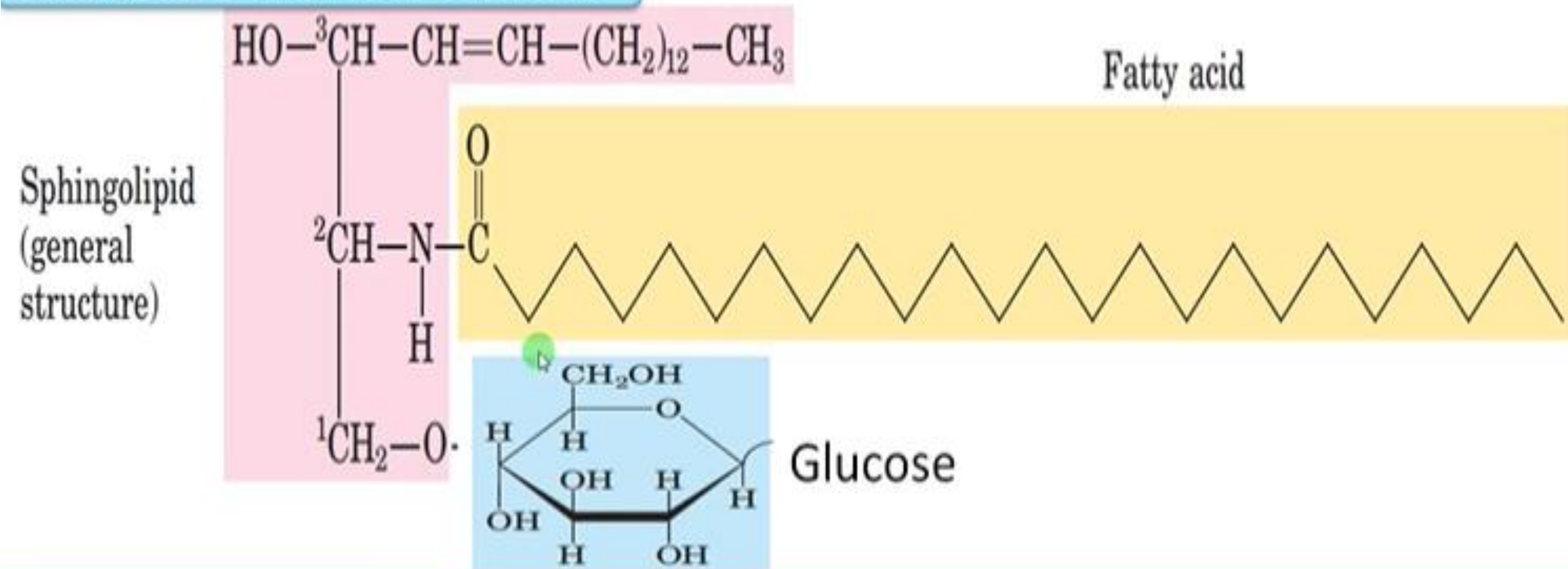


- Constituents of the RBC-membrane


Classification of Glycolipids
Cerebrosides
Sulfatides
Globosides
Gangliosides
Ceramide+ Oligosaccharide+
N acetylneuraminic acid(NANA)
SPHINGOSINE
Fatty acids
Glucose-Galactose
NANA
GM3 Gangliosides
SPHINGOSINE
Fatty acids
Glucose-Galactose-GalNAc
NANA
Galactose
GM1 Gangliosides

Glycolipid (Glycosphingolipids) 1. Cerebroside

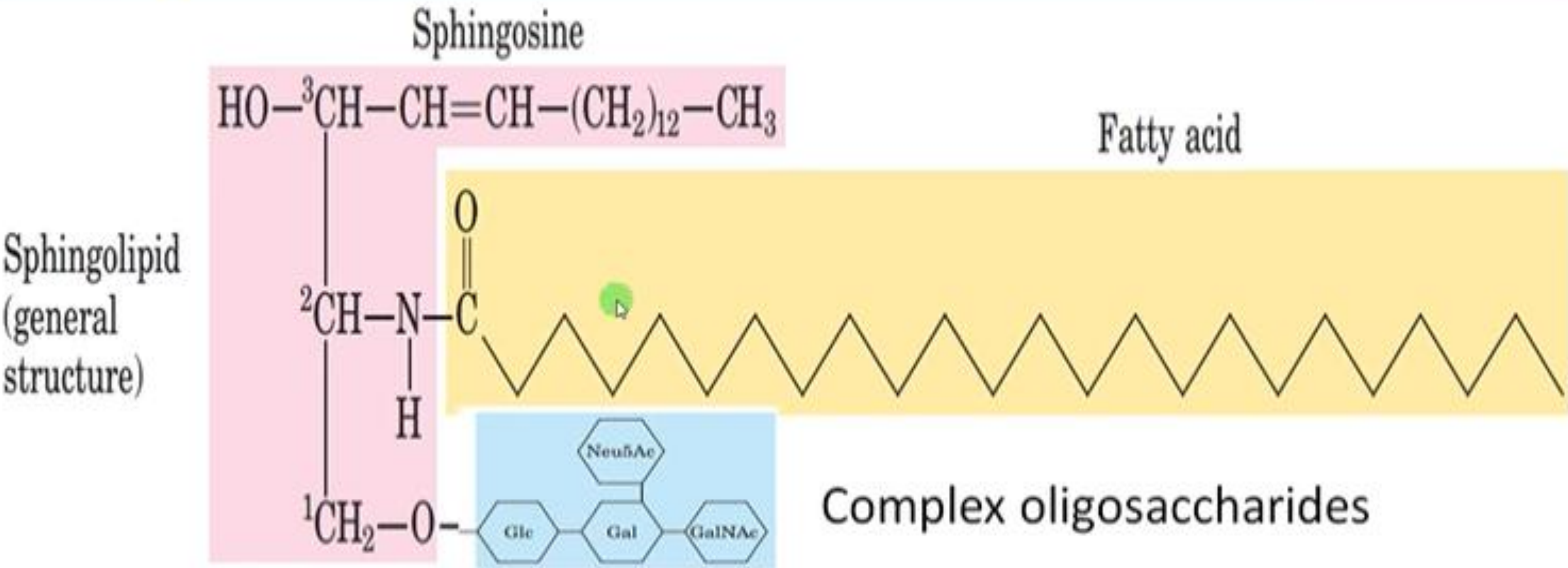
Sphingosine+fatty acid=Ceramide



Glyco: Sugar- lipid complexes

Formed by the joining of 1 or more monosaccharides connected directly to the –OH at C-1 of the ceramide moiety by glycosidic bond

2. Ganglioside- Sialic acid-containing glycosphingolipids



Formed by the joining of complex oligosaccharides at C1 head group, (D-glucose , D- galactose, n-acetyl D galactosamine and N-acetyl neuraminic acid (NANA) (sialic acid)

Robert K, Y., Tsai, Y. T., Ariga, T., & Yanagisawa, M. (2011). Structures, biosynthesis, and functions of gangliosides: an overview. Journal of oleo science, 60(10), 537-544.