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Bioorganic compounds Carbohydrates

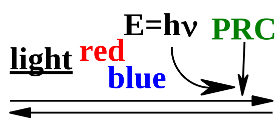
http://aris.gusc.lv/NutritionBioChem/35Ogl45Hidr150211Eng.pdf

Key terms. Bioorganic compounds Glucose, Fructose, classification, building, functional groups. Hexoses pentoses.Aldoses and ketoses. Isomerism: optical isomers, ketone enol tautomerism. Open chain and cyclic hemiacetals. Enzyme class driven reactions E.1 driven oxidation, reduction and E.2 class kinase esterification-phosphorylation.

Glucose and O_{2aqua} green plants **Photosynthesis** with light photons **blue** **red** energy **E=hν**

Photosynthesis => <= Glycolisis + Krebs cycle

Bicarbonate + Hydronium
$6HCO_3^- + 6H_3O^+ + Q + \Delta G_{reaction}$



glucose oxygen water
$C_6H_{12}O_6 + 6O_{2aqua} + 6H_2O$

$\Delta H_{reaction} = (\Delta H°_{C6H12O6} + 6\Delta H°_{O2} + 6\Delta H°_{H2O}) - (6\Delta H°_{H3O+} + 6\Delta H°_{HCO3-}) = +2805{,}3$.................... $^{kJ}/_{mol}$

$= -1263{,}78 - 6*11{,}715 - 6*285{,}85 - (6*-689{,}93 + 6*-285{,}81) = -3049{,}17 + 5854{,}44 = 2805{,}27$ $^{kJ}/_{mol}$...........

$\Delta S_{reaction} = (\Delta S°_{C6H12O6} + 6\Delta S°_{O2} + 6\Delta S°_{H2O}) - (6\Delta S°_{H3O+} + 6\Delta S°_{HCO3-}) = 787{,}6$ .... $^{J}/_{mol/K}$

$= 269{,}45 + 6*110{,}876 + 6*69{,}9565 - (6*98{,}324 + 6*-3{,}854) = 1354{,}45 - 566{,}82 = 787{,}6$................. $^{J}/_{mol/K}$

$\Delta S_{dispersed} = -\Delta H_{reaction} / T = -2805{,}27*1000/298.15 = -9408{,}9$..................... $^{J}/_{mol/K}$

$\Delta S_{total} = \Delta S_r + \Delta S_{dispersed} = 787{,}625 - 9408{,}9217 = -8621{,}3$............................ $^{J}/_{mol/K}$

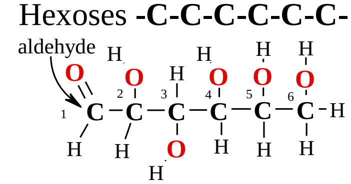
$\Delta G_{reaction} = \Delta H_{reaction} - T \bullet \Delta S_{reaction} = 2805{,}27 - 298{,}15*0{,}787625 = 2805{,}27 - 234{,}83 = 2570{,}4$.............. $^{kJ}/_{mol}$

accumulate in products $C_6H_{12}O_6 + 6O_{2aqua} + 6H_2O$ free energy -2570,4 $^{kJ}/_{mol}$ = $T \bullet \Delta S_{total}$

Bioorganic carbohydrates are carbon-carbon compounds chains C-C-C-C-C-C-C

Bioorganic carbohydrate molecules build chain of atoms combinatoric's 1-7. **C**arbon atoms form the functional groups as are bound to atoms of oxygen **C–O-**, of nitrogen **C-N**< and of sulfur **C–S-**.

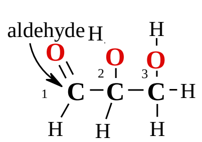
Hexoses **-C-C-C-C-C-C-**

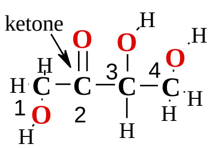


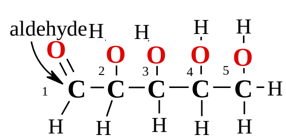
aldohexose D-Glucose

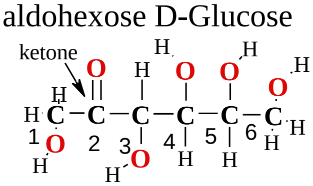
Carbohydrate chain of carbon atoms **:**

Trioses **-C-C-C-**; Tetroses **-C-C-C-C-**; Pentoses **-C-C-C-C-C-**









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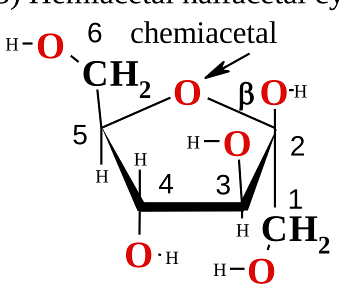
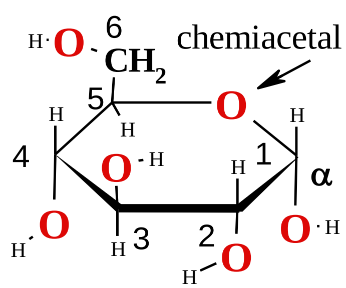
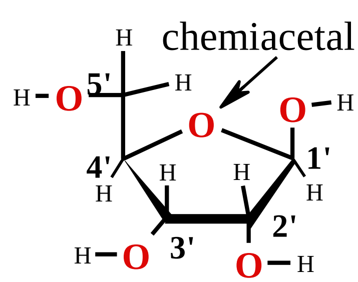
D-gliceraldehīds; ketotetroze D-eritruloze; aldopentoze D-riboze; ketoheksoze D-Fructose

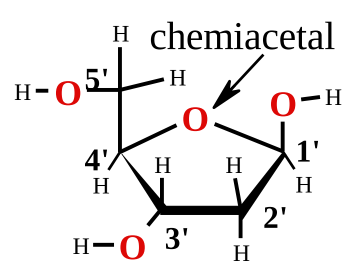
Three functional groups of carbon atom bound with oxygen **C–O-**

1) Aldehyde on top **HC=O** group, Keto group **>C=O** at second **C2**
2) Poly alcohol hydroxyl groups –**CHOH-CHOH-**;
3) Hemiacetal halfacetal cyclic chains of carbon atoms with –**O-**.









β -D-fructose **α** -D-Glucose **β** -D-ribose **β** -D-2-deoxi-ribose

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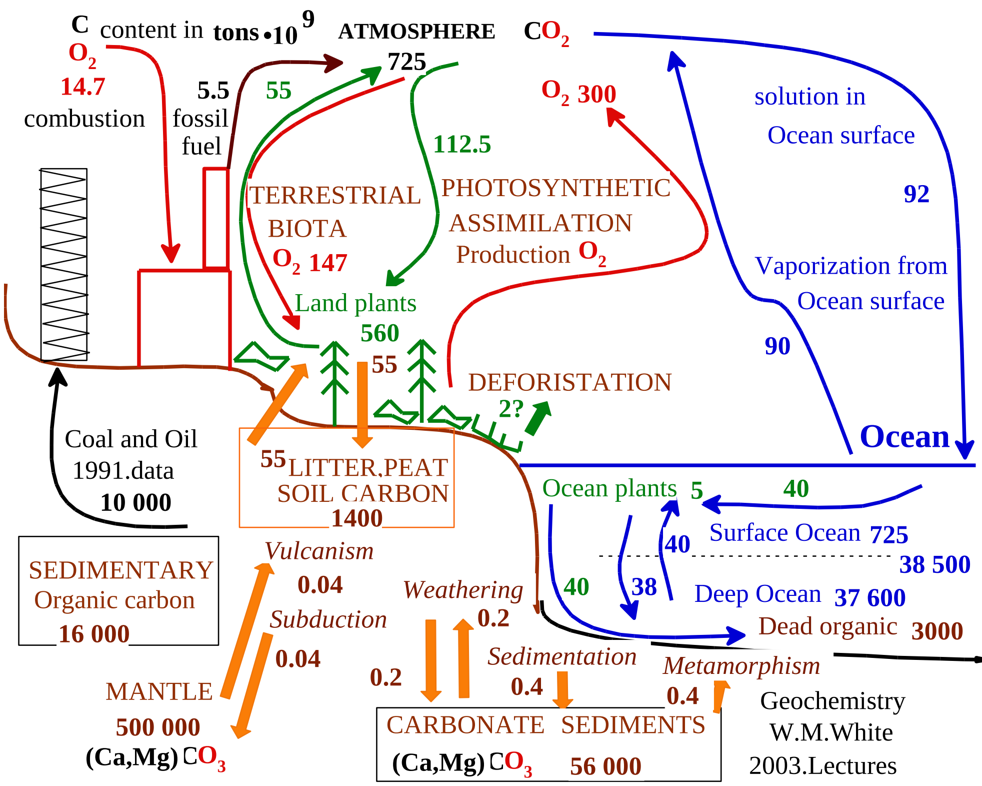
Carbon 6 atoms compound glucose plus 6 water molecules are the biofuel



Fuel for heating coal is solid substance, where carbon atoms are bound between with covalent bonds **C-C-C-C-C-C**. Coal power stations for energy obtaining work in all industrial States, supplying to users electric energy, heat energy. Civilization with combustion pollutions add to atmosphere $\mathbf{CO_2}\uparrow_{gas}$ content 100% about plus 0,76% as well totally global and cosmic processes on Earth 100%. Ocean and in all Earth waters dissolute 53 times greater $\mathbf{CO_2}_{aqua}$ amount as in atmosphere 100%, but carbonate (Ca,Mg)$\mathbf{CO_3}_{ciets}$ sediments in Earth crust contains 77 times more $\mathbf{CO_2}$ as in atmosphere 100%. Green plant photosynthesis each year assimilates $\mathbf{CO_2}$ amount 15,5% from atmosphere 100% and from water total 53*100%, producing glucose $\mathbf{C_6H_{12}O_6}$ with carbon mas 112,5*10^9 tons. Photosynthesis evolved oxygen amount in atmosphere 300*10^9 tons stabilises global $\mathbf{O_2}$ concentration in atmosphere 20,95%.

Six carbon atoms **C-C-C-C-C-C** coal fuel combusts with six oxygen molecules produces six $\mathbf{CO_2}$ molecules.

$$\mathbf{6C_{gr}} + \mathbf{6O_2}\uparrow_{gas} \xrightarrow{\text{Power\_Staition}} \mathbf{6CO_2}\uparrow_{gas} + \Delta G + \mathbf{Q}$$

Reaction is $\Delta \mathbf{G}_{react}$= **-2366,35** $^{kJ}/_{mol}$ exoergic; $\Delta \mathbf{H}_{react}$= **-2361,05** $^{kJ}/_{mol}$ exothermic as heat **Q** evolved.

1. Coal water insoluble therefore insoluble in intracellular and in extracellular space.
2. Gases oxygen and carbon dioxide are deadly for cellular organisms (medical symptom emboly), broken and stuck the transport across cell membranes.

Glucose $\mathbf{C_6H_{12}O_6}$ with six water molecules are biofuel combust by six oxygen molecules.

$$\mathbf{C_6H_{12}O_6} + \mathbf{6H_2O} + \mathbf{6O_2}_{aqua} \xrightarrow{\text{Bio\_oxidation}} \mathbf{6HCO_3^-} + \mathbf{6H_3O^+} + \Delta G + \mathbf{Q}$$

Reaction is $\Delta \mathbf{G}_{react}$= **- 3040,1** $^{kJ}/_{mol}$ exoergic; $\Delta \mathbf{H}_{react}$= **- 2805,27** $^{kJ}/_{mol}$ exothermic as heat **Q** evolved.

1. Glucose is soluble intracellular and in extracellular space.

2. Oxygen and water osmosis through aquaporins entrance cells and mitochondria.

Homeostasis supports the transport of $\mathbf{C_6H_{12}O_6}$, $\mathbf{6H_2O}$ + $\mathbf{6O_2}_{aqua}$ into cells and from cells out $\mathbf{6HCO_3^-}$+$\mathbf{6H_3O^+}$.

Glycolysis and Krebs cycle products generate concentration gradient out of cells $\mathbf{6HCO_3^-}$, $\mathbf{6H_3O^+}$ transported through proton and bicarbonate channels. Oxygen and water osmosis through aquaporins going against osmolar concentration gradient ΔC_{osm} http://aris.gusc.lv/BioThermodynamics/ColigativeProperties.pdf intracellular direction of Bio_oxidation. If glucose blood concentration is normal 5 mM ± 2mM , than maintained transports for glucose established homeostasis in organism.

Note: more profitable is obtain energy from glucose and six water molecules unless from coal.
: Glucose yield similar bioenergy in comparison with gas generator fuel calculated values ~3000 $^{kJ}/_{mol}$.

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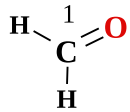
Formula of glucose $\mathbf{C_6H_{12}O_6}$ in carbohydrate form $\mathbf{C_6(H_2O)_6}$ by professor K.Schmit suggestion in 1744. Six $\mathbf{CH_2O}$ group units chain by Aivar Grinberg suggestion forms six C-C-C-C-C-C carbon atom chain $\mathbf{(CH_2O)_6}$. Atoms group unit $\mathbf{CH_2O}$ reflecting combinatorics of atoms counting $\mathbf{CH_2O}$ in life nature 1, 2, 3, 4, 5, 6, 7:

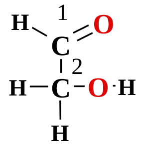
$\mathbf{CH_2O}$,	$\mathbf{(CH_2O)_2}$,	$\mathbf{(CH_2O)_3}$,	$\mathbf{(CH_2O)_4}$,	$\mathbf{(CH_2O)_5}$,	$\mathbf{(CH_2O)_6}$,	$\mathbf{(CH_2O)_7}$:
Formaldehyde	Glycolaldehyde	Glyceraldehyde	Tetrose	Ribose	Glucose	Sedoheptulose

Carbohydrates are polyhydroxyaldehydes, polyhydroxyketones combinatorics 1-7 of atoms group $\mathbf{CH_2O}$

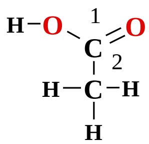
Formaldehyde $\mathbf{CH_2O}$



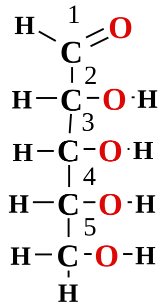
Glycolaldehyde $\mathbf{(CH_2O)_2}$



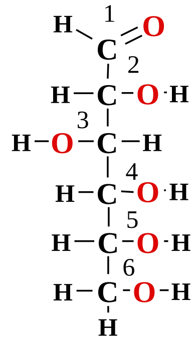
Acetic acid



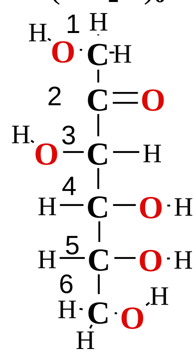
Ribose $\mathbf{(CH_2O)_5}$



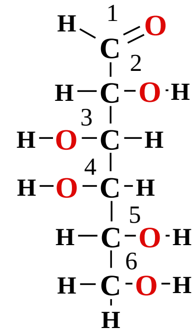
Glucose $\mathbf{(CH_2O)_6}$



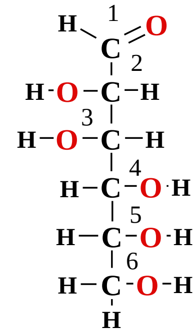
Fructose $\mathbf{(CH_2O)_6}$



Galactose $\mathbf{(CH_2O)_6}$

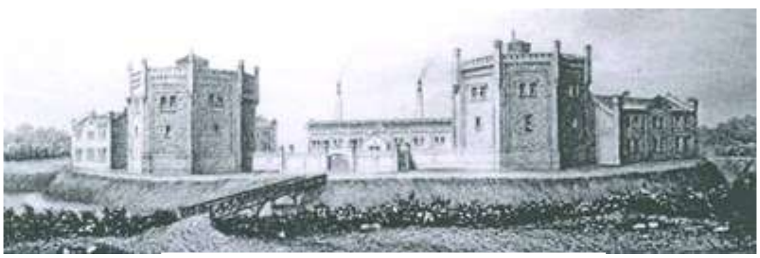


Mannose $\mathbf{(CH_2O)_6}$



Fuel of **glucose** analog **generator gas 6 CO**$\uparrow_{gas}$ **+6 H**$_{2gas}$ for heating and lightning

Generator gas component content ($\mathbf{CO}\uparrow_{gas}$+$\mathbf{H_2}\uparrow_{gas}$) has one atom group $\mathbf{CH_2O}$ but to glucose formula $\mathbf{C_6H_{12}O_6}$ refer six group units $\mathbf{(CH_2O)_6}$ so for generator gas too six 6($\mathbf{CO}\uparrow_{gas}$+$\mathbf{H_2}\uparrow_{gas}$).



City's gas factory at Bastejkalns (1863)

Second gas factory in Riga

Six components of generator gas 6(CO$\uparrow_{gas}$+H$_{2gas}$) are used in 19th and 20th beginning century in Riga for heating and lightning .

Instead former Jakovjevsk ravelin faced to days Bastejkalns one build new factory. Project of Berlin gas factory director Kunnel, but building facade of Riga architect Johan Felsko. Ground stone build on 1861 of 12th july, and 1862 of 6th augus factory opens the doors. The building to days kept the self charm.

In 1874 begins second gas factory building on the place Maskav districts, where prevailing habitants of worker peoples, to days corner of Matis and Bruninieku street. 1903 pipe of gas total longs reaches 89,1 kilometers, but at eve I World War the city had more as 5 thousand of gas lantern. The head (1894–1915) engineer chemists Maksis Rozenkranc.

Six components of generator gas 6(CO$\uparrow_{gas}$+H$_{2gas}$) combusting with 6$O_2\uparrow_{gas}$ produce 6$CO_2\uparrow_{gas}$+6$H_2O\uparrow_{gas}$+Q.

$$\mathbf{6\ CO}\uparrow_{gas} + \mathbf{6\ H}_{2gas} + \mathbf{6\ O_2}\uparrow_{gas} \xrightarrow{\text{generator-gas}} \mathbf{6CO_2}\uparrow_{gas} + 6\ \mathbf{H_2O}\uparrow_{gas} + \Delta G + \mathbf{Q\ exothermic}$$

Reaction is $\Delta \mathbf{G}_{react}$**= -2914,72** $^{kJ}/_{mol}$ exoergic**;** $\Delta \mathbf{H}_{react}$**= -3148,89** $^{kJ}/_{mol}$ exothermic as heat **Q** evolved.

1. Carbon monoxide gas is toxic for chromoproteins active site, as hem poison block such enzyme activity.

2. Gases $\mathbf{6H}_{2gas}$, $\mathbf{6O_2}\uparrow_{gas}$, $\mathbf{6CO_2}\uparrow_{gas}$, 6 $\mathbf{H_2O}\uparrow_{gas}$ are deadly for cellular organisms (medical symptom emboly), broken and stuck the transport across cell membranes.

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Chirality

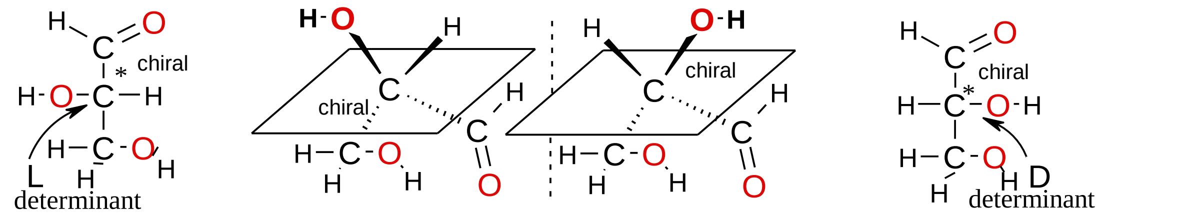
Address: http://aris.gusc.lv/ChemFiles/Saccharides/SSViewe/SSVFrameset.htm.

Molecules that are not identical with their mirror images are said to be **chiral** (**ki-ral** *cheir*, from *Greek* , hands)

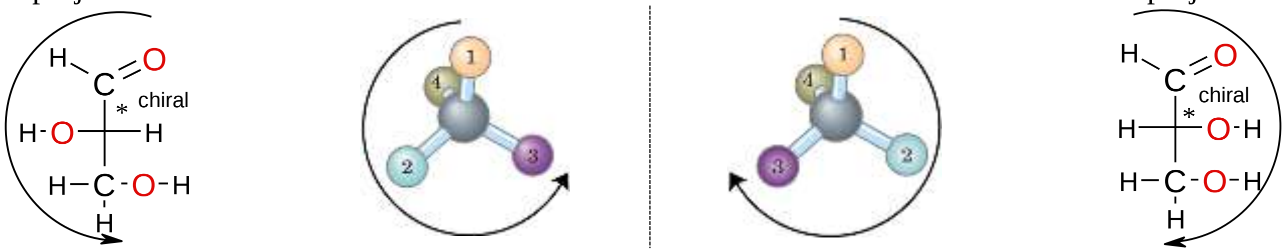
Carbon atoms with four different attachments are **chiral** and show optical isomerism L- and D-

Glyceraldehyde contains one **chiral** carbon and can exist as pair of mirror images - **enantiomers**

L-glyceraldehyde - Levos L | **mirror** | D-glyceraldehyde -Dexter D



Fisher projection | **enantiomers** | Fisher projection



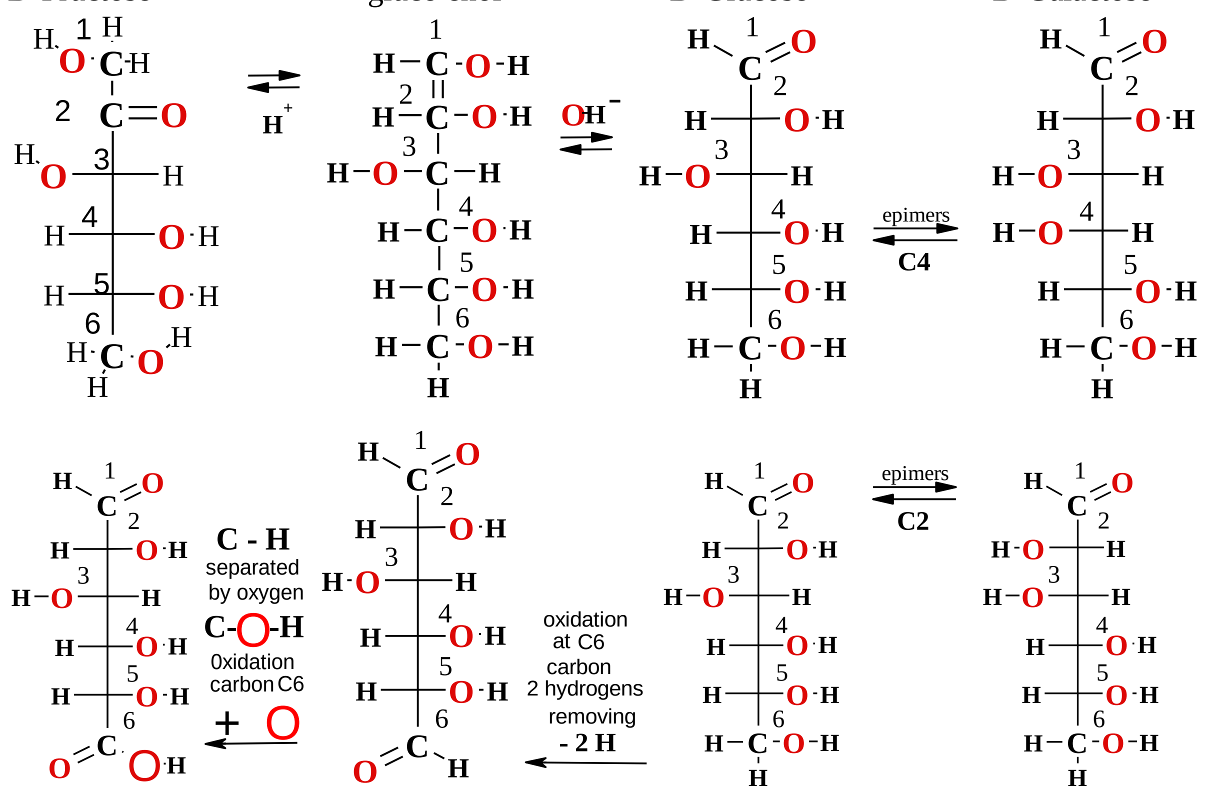
Counter Clockwise rotation CCW | **mirror** | Clockwise rotation CW

Levorotatory (Latin, *laevus*, on the left side) **L -** and

Dextrorotatory (Latin, *dexter*, on the right side) **D -**

Task: complete **Fisher's** projections for given open chain free **monosaccharides**

D-Fructose | gluco enol | D-Glucose | D-Galactose



D-Glucuronic acid | D-Glucuronal | D-Glucose | D-Mannose

5. Carbohydrates and Glucose

http://aris.gusc.lv/NutritionBioChem/35Ogl45Hidr150211Eng.pdf

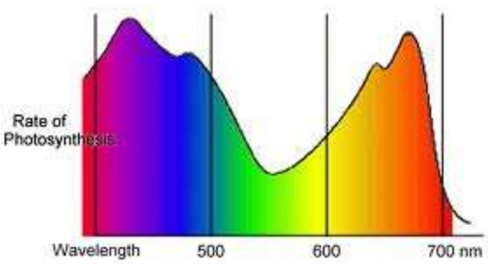
Glucose native origin on planet Earth is green plants photosynthetic reaction, with what green plants global maintain Earth living nature, that also us humans, with glucose and oxygen:

$$6\ \mathbf{CO_2} + 6\ \mathbf{H_2O} + Q_{\text{energy (red \& blue lights)}} \underset{\text{respiration}}{\overset{\text{photosynthes}}{\rightleftarrows}} \mathbf{C_6H_{12}O_6} + 6\ \mathbf{O_2}$$

From glucose in living organisms are forming other carbohydrates, for example, fructose, starch, cellulose, pectin etc., but oxygen living organisms consume breathing in (respiration), that in reverse reaction with glucose and breathed in oxygen get the energy for maintaining of life processes. Such a way from blue lights and red light part of sun lights accumulated energy Q in cells are used for life process maintaining. Scientists are investigate, that respiration in organism, if „burn" 1gram of glucose, stand out 17 kJ or 4 kcal heat Q.

Carbohydrate its name is gained in 1844.year, what suggested professor K.Schmit at Terbat University, because glucose molecules composition can write in two ways $\mathbf{C_6H_{12}O_6}$ and $\mathbf{C_6(H_2O)_6}$, from where visible, as on six carbon atoms are six water molecules, and it means as on each carbon atom in carbohydrate is one water molecule, what can describe with general molecule formula $\mathbf{C_n(H_2O)_n}$.

Such composition carbon and water presence can be experimentally to prove. Into test tube strew a little sugar and under heating sugar melt down, than turns brown as hard candy and finally char black, but on cool test tube neck accumulate water drops. So black carbon burn and water drops describe carbohydrate composition, which general formula is $\mathbf{C_n(H_2O)_m}$ showing molecule composition from **n** carbon **C** atoms and **m** water $\mathbf{H_2O}$ molecules.



8. Fig. Plants garden with different intensity green colors from light green to dark green. White sun light contains three colors red, green and blue. Green plants in photosynthetic reaction use red and blue colors of white sun light, as result we see left one over green color. As darker is plant green color, as more red and blue lights are absorbed for photosynthesis reaction.

Carbohydrates in living cells forms reciprocal compounds and accumulates in polymer molecular forms. Therefore carbohydrates divide into monosaccharides, disaccharides and polysaccharides.

3.1. tab. Monosaccharides, disaccharides and polysaccharides.

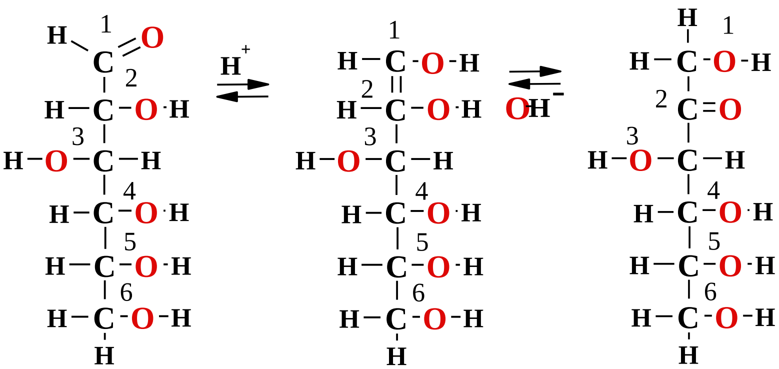
Carbohydrates	Name	Formula
Monosaccharides	glucose	$C_6H_{12}O_6$
	fructose	$C_6H_{12}O_6$
	ribose	$C_5H_{10}O_5$
Disaccharides	sucrose	$C_{12}H_{22}O_{11}$
	lactose	$C_{12}H_{22}O_{11}$
Polysaccharides	starch	$(C_6H_{10}O_5)_n$
	cellulose	$(C_6H_{10}O_5)_n$

Monosaccharides, names and nomenclature

9 Fig. *Pears, grapes, apples, orange, grapefruits, cherries. In fruits du to sour juice present fructose carbohydrate ketohexoses, which is times two sweet as glucose? Therefore ripen fruits and berries taste much sweet.*

Monosaccharides are monomers element links for formation of disaccharides and polysaccharides in living cells. In hydrolyze of disaccharides and polysaccharides obtain free in polymer non bound monosaccharide units.

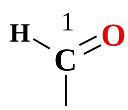
Carbohydrates biological conversion beginning molecules are glucose and fructose. Name fructose comes from Latin word fruktus – fruit. Fructose arises from glucose in acidic water medium. Sweet fruits and berries with acidic taste sweet taste assign fructose. Fructose is two times sweeter as glucose therefore due to sour juice fruits and berries seems sweeter as vegetables.



glucose gluco enol fructose

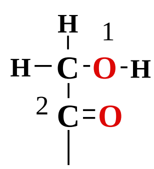
Carbohydrates are organic nature compounds, in which molecules have one carbonyl group >**C=O** . The aldehyde group in basic water medium or the keto group in acidic medium.

Glucose is aldohexose with aldehyde group on top of carbon chan. Cipher word hexos shows number of carbon atoms on chain sixe **6C**.



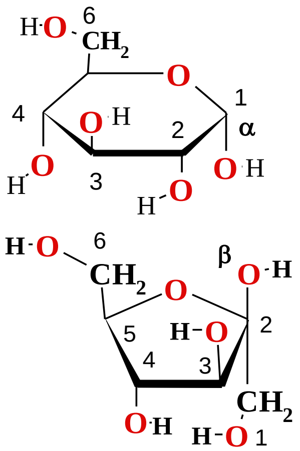
So as aldehyde group lies on carbon chain top, then carbon chain start number from aldehyde carbon top with number 1. Glucose type to be called also as blood sugar, du to weekly basic medium of blood plasma pH=7,36.

Fructose is ketohexose with keto group on beginning of carbon atoms chain at second carbon atom. Fructose is found in fruits and berries therefore it calls also as fruit sugar.



One carbon atom in carbohydrate molecule is carbonyl group >**C=O**, but others carbon atoms are polyvalent spirits, which each have hydroxyl group **-O-H**. Hexose molecules are pentavalent spirit molecules, because fife carbon atoms have fife hydroxyl groups.

Glucose mixture with copper(II) hydroxide in basic medium forms intensively blue solution, because light blue copper(II) hydroxide precipitates dissolves carbohydrate multi-spirit reaction like as glycerol. If intensive blue solution heat, then aldehyde group of glucose oxidizes to gluconic acid and arise yellow univalent copper(I) hydroxide **CuOH** precipitates. To heating in water insoluble base decomposes into copper(I) oxide **Cu_2O** brick red color and water:



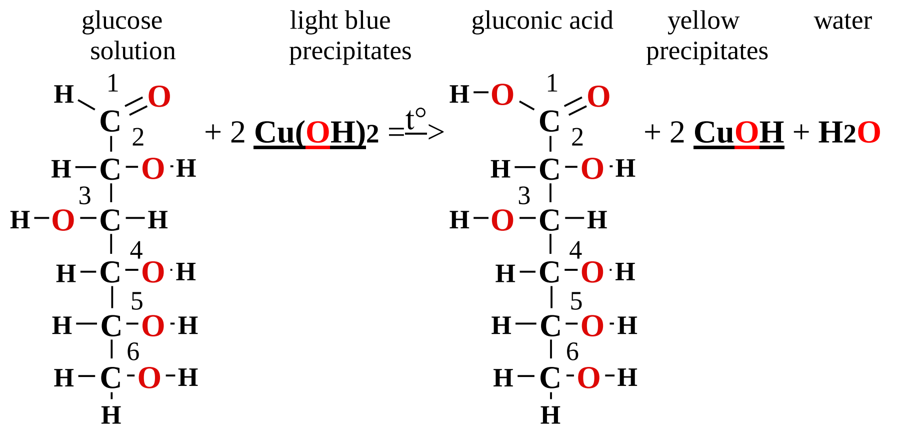
10. Fig. Cyclic glucose type and cyclic fructose type are forming du to water molecule polarity.

0,05%		99,95%
glucose	⇔	**glucose**
opened form	⇔	**cyclic forms**
fructose	⇔	**fructose**
0,01%		99,99%

From only opened and all cyclic glucose forms in water equilibrium are present just 0,05% of open form with free aldehyde group. Fructose opened form ketone amount fraction is else smaller 0,01% from possible forms as cyclic and as open form. Such equilibrium ratio in water medium between only open form and cyclic forms exists for all carbohydrates.

6. Reactions of glucose

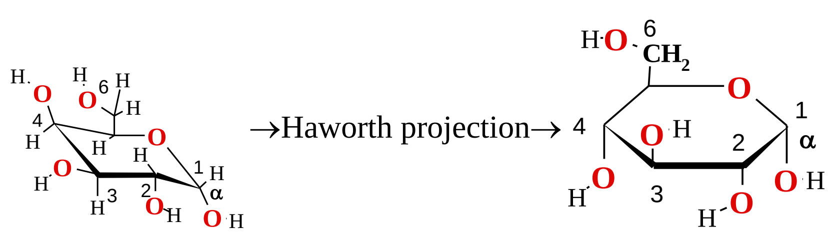
For glucose are known eight characteristic reaction types: aldehyde oxidation reaction, cyclic formation reaction of aldehyde glucose molecules, aldehyde reduction reaction to spirit, multivalent spirit reaction with copper hydroxide, spirit esterification reaction with acids, poly-condensation reactions (forming disaccharides and polysaccharides) fermentation reaction and biologic oxidation reaction cascade up to final combustion products water **H_2O** and carbon(IV) oxide **CO_2** in energy obtaining for maintenance life processes in living organisms, which is reverse reaction green plant photosynthetic reaction forming glucose **$C_6H_{12}O_6$** and oxygen **O_2** (see in former section), and, which, using light red and blue color absorbed energy Q.



$$2\ \underline{CuOH} \xrightarrow{t^\circ} \underline{Cu_2O} + H_2O$$

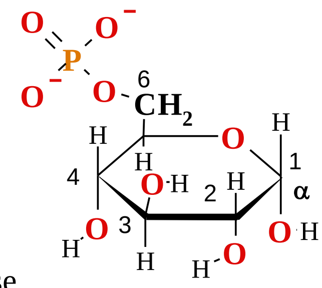
yellow precipitates — red brick precipitates — water

In water medium for all monosaccharides are characteristic cyclic formation reactions. To reproduce cyclic molecule from three dimension image one draw on paper Haworth projection for all carbohydrates. Haworth projection draw planar hexagon or pentagon 45 degree angle versus z axis on front view and in cycle draw the oxygen above right side. On Haworth projection shows vertical direction for hydroxyl group refers against hexagon plane above or below. Carbon atoms in cycle lie on cross points of straight lines: 1,2,3,4,5 and six or last carbon in **$HOCH_2$** group lies above plane of hexagon:



Three dimension image — Haworth projection

Hydroxyl **-O-H** groups of carbohydrates easy form esters with different acids. In cell biology for life sustainable processes essential and important are phosphoric esters with hydroxyl groups. For example, glucose getting inside cell almost momentary esterifies about glucose phosphate ester, which could be able to take a part in many, following gradual oxidation and energy storage processes in glycolysis and Krebs - citrate cycle.

Phosphate esters of glucose  inside cells (pH=7.36) is anion with negative net charge **-2** at phosphate.

Fermentation reactions of glucose

Fermentation processes with glucose takes a place in nature at presence of many microorganisms, because microorganism release ferments which are biocatalysts. Each of ferments performs one self specific reaction. Ferments increase up reaction velocity million times and specialization of ferments reactions do not let forming side products. Fermentation reaction final products form without admixes, fast and with highest efficiency 100%.

Alcoholic fermentation takes a place at presence of yeast fungus in close restricted vessels from air access, what designates with term anaerobic conditions:

$$C_6H_{12}O_6 \xrightarrow{yeast} 2\ C_2H_5OH + 2\ CO_2$$ carbonic acid gas

glucose solution — ethanol — carbon(IV) oxide

If to glucose fermentation mixture reaches air oxygen, then forms the acetic acid:

$$C_6H_{12}O_6 + 2\ O_2 \xrightarrow{yeast} 2\ H_3CCOOH + 2\ CO_2 + 2\ H_2O$$

glucose — oxygen — acetic acid — carbon(IV) oxide — water

Lactic acid bacteria at presence of air oxygen O_2 turns glucose into lactic acid and in household we meet this process each day, because milk turns sour and also cabbage, cucumber, mushrooms and even apples turn sour lactic acid bacteria:

$$C_6H_{12}O_6 \xrightarrow{bacteria} 2\ H_3C\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}COOH$$

glucose — lactic acid

If lactic acid bacteria do not have air oxygen access, than takes place butyric acid fermentation, because arises butanoic acid – butyric acid:

$$C_6H_{12}O_6 \xrightarrow{bacteria} H_3C\text{-}CH_2\text{--}CH_2\text{-}COOH + 2CO_2 + 2\ H_2\uparrow$$

glucose — butyric acid **OH** — carbon(IV) oxide — hydrogen

11 Fig. In sour milk lactic acid bacteria glucose have turn into lactic acid and fresh milk has curdle in sour milk/curdled milk.

Citric acid fermentation of glucose causes mould fungus *Aspergillus niger*:

$$2C_6H_{12}O_6 + 3O_2 \underset{fungus}{\overset{mould}{\rightleftarrows}} 2C_6H_8O_7 + 2H_2O$$

glucose — oxygen — citric acid — water

7. Disaccharides

12. Fig. Sun light shine on Sugar cane green leaves in plantations of Brazil or islands of India ocean and converts $\mathbf{CO_2}$ *and* $\mathbf{H_2O}$ *to sugar and oxygen.*

Carbohydrates polycondensation reactions form disaccharides or polysaccharides and water. Polycondensation of glucose with fructose composes the sucrose – table sugar and water:

$$\mathbf{C_6H_{12}O_6} + \mathbf{C_6H_{12}O_6} \xrightarrow{shugar\_cane} \mathbf{C_{12}H_{22}O_{11}} + \mathbf{H_2O}$$

Glucose fructose sucrose water

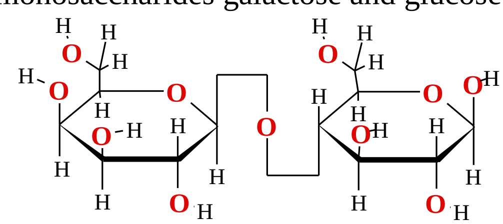
Opposite reaction is hydrolyze reaction, in which sucrose disaccharide decomposes reverse to monosaccharides two glucose molecules in basic medium or two fructose molecules in acidic medium.

$$\mathbf{C_{12}H_{22}O_{11}} + \mathbf{H_2O} \xrightarrow{hydrolize} 2\ \mathbf{C_6H_{12}O_6}$$

disaccharide water two monosaccharides

High sucrose content is I sugar beets 16-20% and sugar canes 14-26%, therefore those crops use for obtaining in manufacture the sugar. Sugar price in stores is strongly dependent on whether circumstances planting the sugar beets or sugar cane. Are enough number of sunny days and or are enough moisture presence in soil, because green plants photosynthesis occurs warm season, on sunlight and water is necessary (see. on beginning of this chapter).

Lactose is second on nature present disaccharides, which consist of two monosaccharides galactose and glucose:



$\mathbf{C_{12}H_{22}O_{11}}$

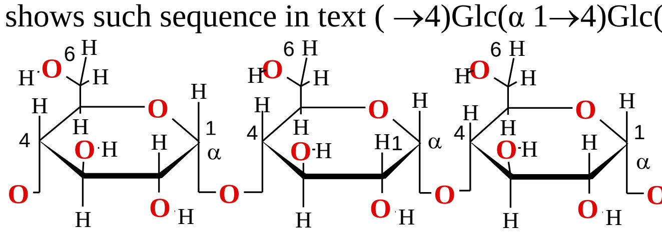
galactose glucose lactose molecule formula

Lactose is in cow milk 5% and in human mother milk 7%

Polysaccharides starch, cellulose

13. Fig. Starch accumulates in potato tubers under green tops of potato, in which photosynthetic reaction from carbon dioxide, water and blue and res light colors forms the glucose, which accumulates in potato tubers at roots as polymer form of starch.

Plants accumulate on photosynthetic reaction obtained glucose molecules in starch polymer form $(\mathbf{C_6H_{10}O_5})_\mathbf{n}$, in which monosaccharide glucose monomers units number **n** can reach **n**=1000000 one million glucose units. As well in microscope can see those molecule aggregates fine, solid grains form, than its call in Latvian "ciete"- solid grains. Glucose is in short cat name designated as Glc and linking together of many α-glucose molecules join it's into long polymer chains. Three structural unit sequence shows Haworth projection structural formula and shows such sequence in text (→4)Glc(α 1→4)Glc(α 1→4)Glc(α 1→)

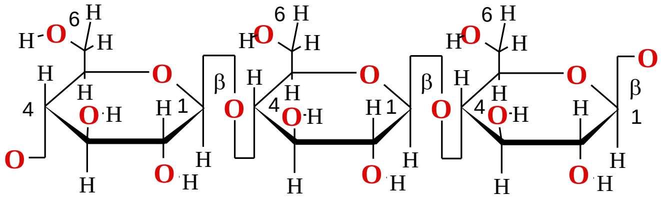


Haworth projection

(→4) Glc (α 1→4) Glc (α 1→4) Glc (α 1→)

The starch water solution with iodine turns intensively blue color, therefore this reaction is used for presence prove of free iodine or starch in water solution using each other against.

Plants in photosynthetic reaction obtained glucose units use for linking together into large cellulose $(C_6H_{10}O_5)_n$ chain fibers. Cellulose serves for plant cells as body frame or matrix, assign for plant stalk structure and mechanical durability for plant organism body.



Haworth projection

(→4) Glc (β 1→4) Glc (β 1→4) Glc (β 1→)

Starch and cellulose polymer molecules have distinguish glucoses linkage structure:

- in starch structure α 1→4 oxygen –**O**- glycoside bridge between glucose monosaccharide molecules, but
- in cellulose structure β 1→4 oxygen –**O**- glycoside bridge between glucose monosaccharide molecules.

In human digestive tract already of mouth saliva is biocatalyst - enzyme amylase, which easy hydrolyses just α 1→4 oxygen –**O**- glycoside bridge between glucose monosaccharide molecules, separating from polymer chain free glucose molecules for maintenance of organism living function:

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + \underset{\text{water}}{H_2O} \xrightarrow{\text{amilaze}} \underset{\text{rest of starch}}{(C_6H_{10}O_5)_{n-1}} + \underset{\text{glucose}}{C_6H_{12}O_6} .$$

Cellulose β 1→4 oxygen –**O**- glycoside bridge between glucose monosaccharide molecules amylase do not able hydrolyze du to different structure. Therefore grass and plant cellulose containing parts in food can not use human. For ruminant animals specific bacteria, which hosts in preliminary stomach, separates free glucose molecules from cellulose polymer. Ruminating free glucose containing mass of food animal delivers food into stomach and in digestive tract glucose absorbs in tissues.

Manufacture of cellulose hydrolyze performs heating cellulose with diluted sulfuric acid:.

$$(C_6H_{10}O_5)_n + n\ H_2O \xrightarrow{H_2SO_4} n\ C_6H_{12}O_6 .$$

Manufacture of starch hydrolyze makes gradually separates into smaller molecules:

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} \xrightarrow{H_2O} \underset{\text{dextrose}}{(C_6H_{10}O_5)_x} \xrightarrow{H_2O} \underset{\text{maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{H_2O} \underset{\text{glucose}}{2\ C_6H_{12}O_6}$$

As catalysts uses diluted sulfuric acid.

14 Fig. To split firewood can easy on fiber direction of cellulose and hardly never perpendicular of cellulose fiber direction.

Diabetes and Glucose Level in Blood, Obesity and Starvation

Glucose (blood sugar) concentration is 5 milimols per one liter of blood (5mM). Glucose (blood sugar) level concentration decreasing or increasing is disease with name **diabetes**.

Name **diabetes** contains preposition **dia** in Greek means <u>between</u> and word **beta** in Latin means <u>sugar beet</u>. **Diabetes** shows to what is both side comprising states. **Diabetes** is state, what comprises two harmful glucose levels in blood:

- hypoglycemia – glucose concentration in blood twice or more times lower as 5 mM un
- hyperglycemia – glucose concentration in blood twice or more times higher as 5 mM.

Normal glucose concentration in human blood is from 4 mM to 8 mM. Uptake nutrition compounds in digestive tract free glucose molecules already in our mouth through mucus skin reach in blood increasing glucose concentration above 5 mM. Increasing of concentration switch on two glucose accumulation mechanisms in liver. On first way forms glucose polymer glycogen, which structure similar to starch in plants, but by size is smaller. On second mechanism liver metabolize glucose to fats, which in form of lipoprotein vesicles (look Obesity and cholesterol) in blood have been transported to all organism cells.

On first way well feed human liver accumulates up to 300 grams glucose in glycogen polymer form, which is similar to starch glucose polymer in potato and in bread grains and also in maize. Accumulated glucose 300 grams is enough amount, which has spent during 8 to 12 hours long sleeping period in human body to night. During the night 300 g accumulated glucose is completely spent maintaining the glucose concentration in blood 5 mM.

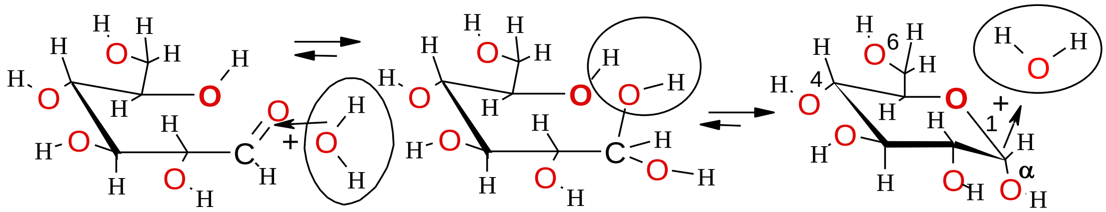
On second way with food uptake energy amount accumulation in liver of glucose is switched to fat production. The liver fatty vesicles of lipoproteins releases in blood (look Obesity and cholesterol) and lipoprotein vesicles transfer to all organism cells and including adipose (fatty) cells, where accumulation and deposition of fats increases and enlarge size of adipose cells.

Excessively usage of carbohydrates in nutrition can leads to **obesity**, but **starvation** take down proteins of muscle cells also in cardio myocytes of hart, what maintains glucose concentration in blood 5 mM. That weakens muscle tissues and hart.

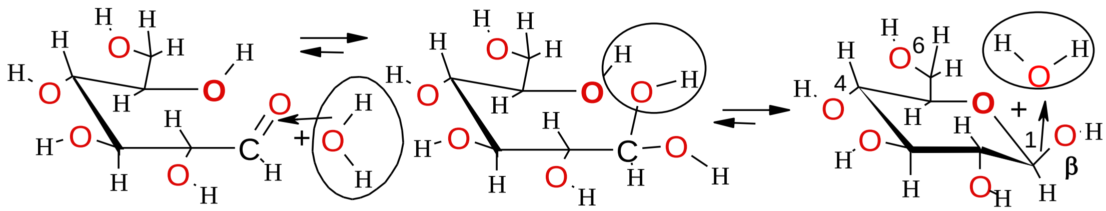
If on weakened muscles applies physical overload, than muscle cells have got injury and die, and this disease designates with word myocardial infarction or simple hart strike. In all occurrences reason is insufficient glucose concentration supply below 4 mM to hart muscle cells or also if blood vessels of hart dam up with cholesterin plaques or du to starvation of organism. We must memorize, that **starvation** prevent brain development, action and weaken ability of human mind, what especially unfavorably influences children growth and development.

15. Fig. Glucose in nutrition we uptake with sweet fruits, with potato, with sugar beet or sugar cane sugar, what we call as table sugar, with bread and meal meals, for example, grits, manna, macaroni etc. meals.

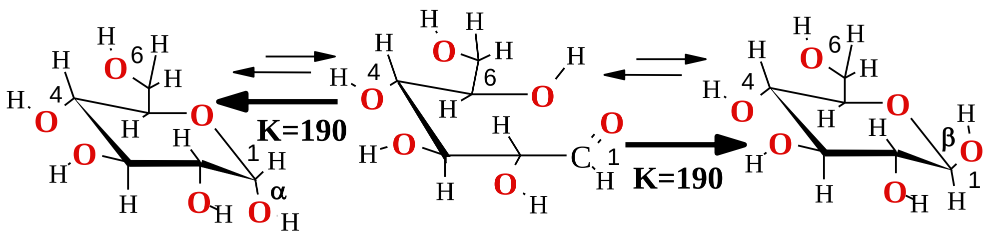
Water concentration 55.3 M driven **cyclic glucose and fructose** formation



Water oxygen attacks carbonyl carbon atom and after cycle formation water return



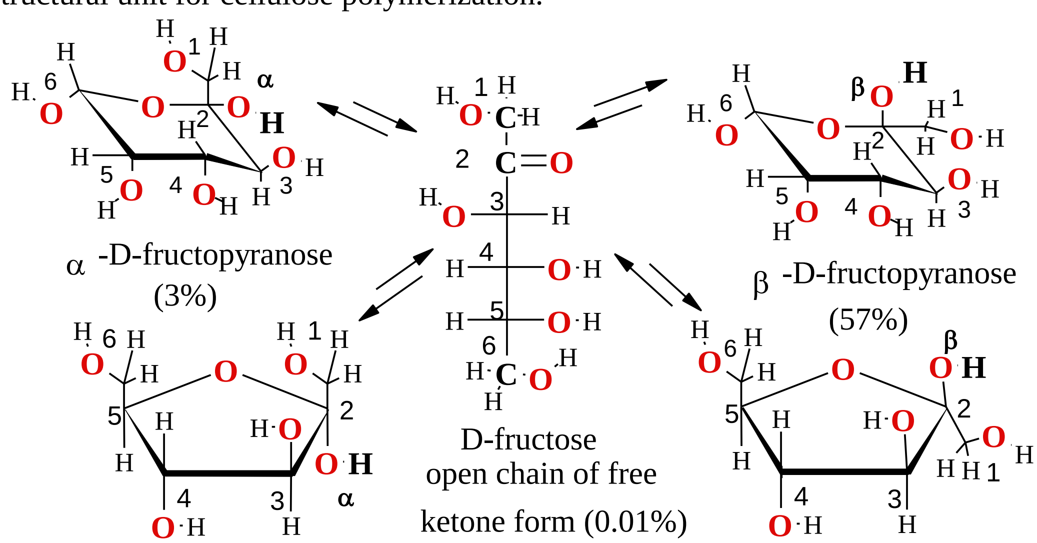
open chain **K ≥ 190** $\mathbf{K_{eq}}=\frac{[cyclic\_]}{[open\_]}$=**190 fraction w%**=1/191*100%=**0.05%**



α -D-glucose mp 146°C [α]=+112° free aldehyde, β-D-glucose mp 190°C [α]=+19°

Hemiacetal alpha **α**- and beta **β**- forms cyclic.

Biochemical and Physiological different are alpha and beta glucose forms.
Alpha glucose is structural unit for starch amylose polymerization.
Beta glucose is structural unit for cellulose polymerization.



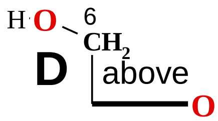
α-D-fructose (9%) **β**-D-fructose (31%)

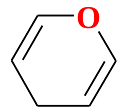
The only Biochemical and Physiological important cyclic form in metabolism equilibrium is **β**-D-fructose (31%) into aqueous solution with open chain D-fructose.

$\mathbf{K_{eq}}=\frac{[cyclic\_]}{[open\_]}$=**9999 Open chain mass fraction w%**=1/10000*100%=.........**0.01**.**%**

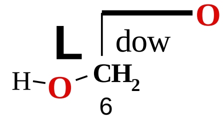
Aris Kaksis 2018.year Riga Stradin's University credit: by Aivar Grinberg permission !

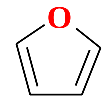
Cyclic hemiacetal or hemiketal **D-** (but only for fucose **L-**) **Haworth's** projections





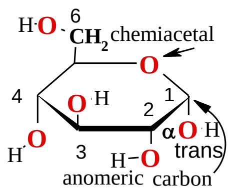
Pyranose cycles

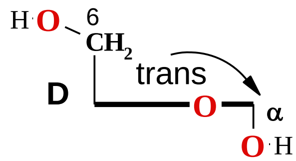


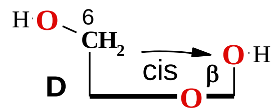


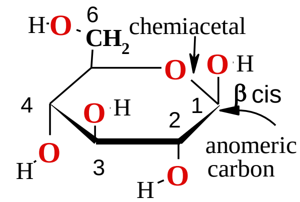
Furanose cycles like

Furanoses and pyranoses, **α** - and β - (*trans* - and *cis* - isomers) monosaccharides.

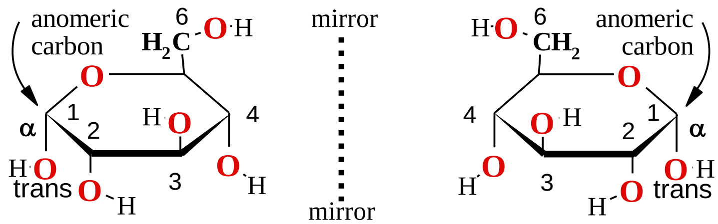


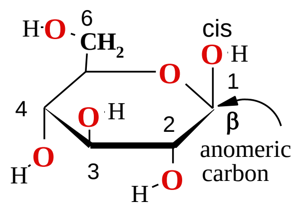






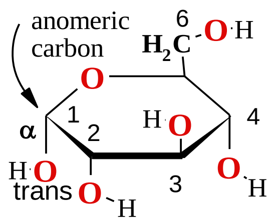
← Enantiomers → **← Epimers at C1→**

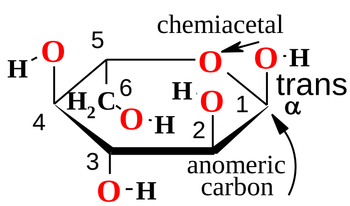


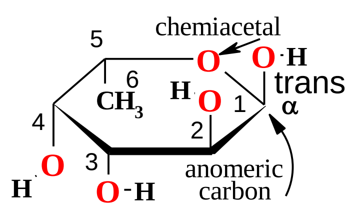


mirror image **α**-L-Glucose from **α** -D-Glucose **β**-D-Glucose

←C4 epimer α-L-6deoxy-Galactose -→



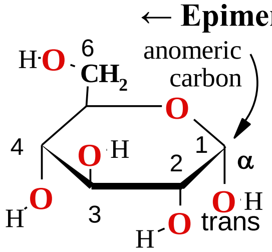


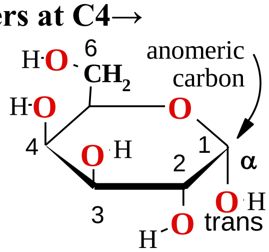


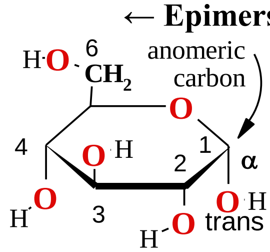
mirror **α**-L-Glucose **α**-L- Glucose **α**-L-Fucose

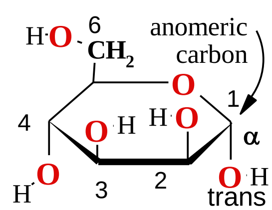
α-L-Fucose unit is linked **(α1→)** as side group on oligosaccharide chains in extra cellular space of human organism as **Immunological marker** for host molecular bodies recognition soon as non-host bodies - anti-genes binding and removing.

← Epimers at C4→ **← Epimers at C2→**

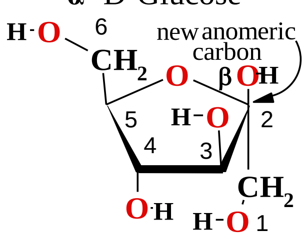




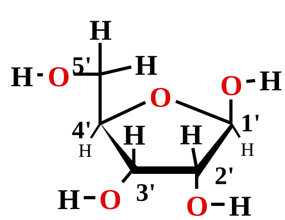




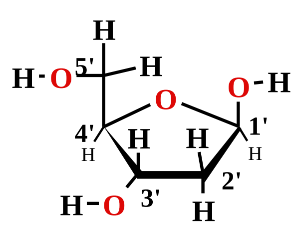
α -D-Glucose **α**-D-Galactose **α** -D-Glucose **α**-D-Mannose



β -D-fructose (31%)



β -D-ribose in **RNA**
ribose phosphate polymer
backbone component



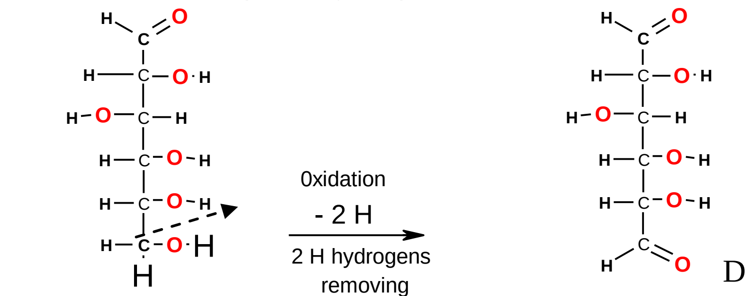
β -D-2-deoxy-ribose in **DNA**
deoxy ribose phosphate polymer
backbone component

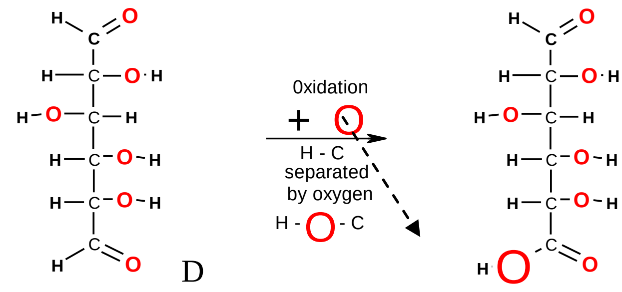
Aris Kaksis 2018.year Riga Stradin's University credit: by Aivar Grinberg permission !

Reactions products for carbohydrate opened chains !

Glucose sixth carbon **C6** hydroxyl two step **oxidation** reactions:

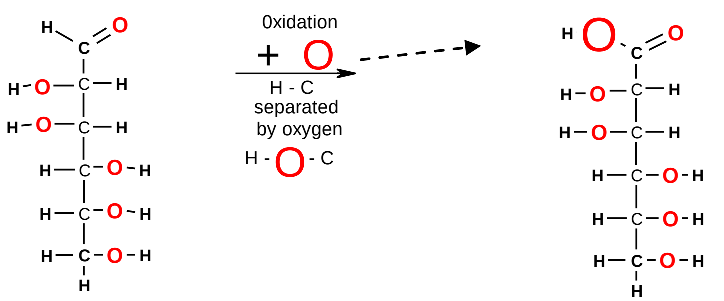
Oxidation C6 removing two hydrogens. Next oxidation step forms –COOH acid.

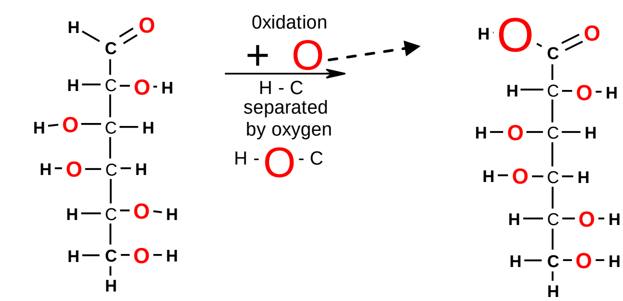




D Glucose Glucural D Glucural D D Glucuronic acid

Aldehyde oxidation by oxygen O separates H – C hydrogen from carbon H – O – C

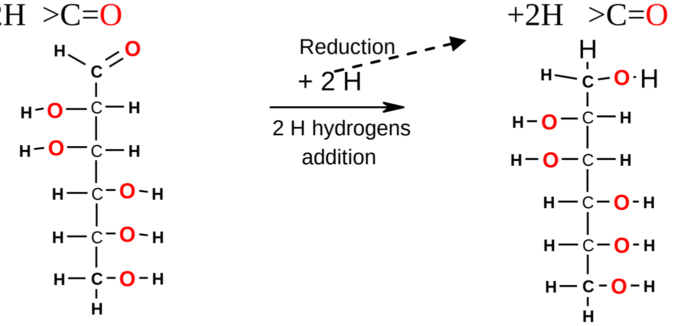


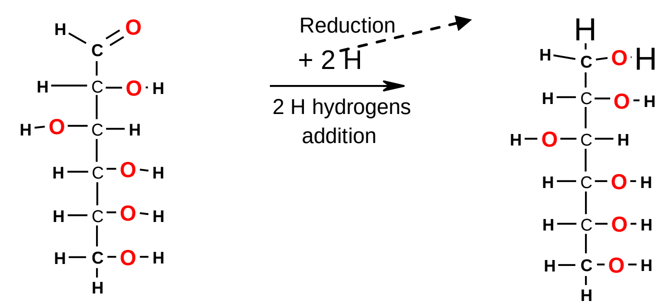


D Mannose D Mannoic acid D Galactose D galctonic acid

Reduction is two hydrogens addition + 2 H to mannose and to glucose carbonyl group

+2H >C=O +2H >C=O

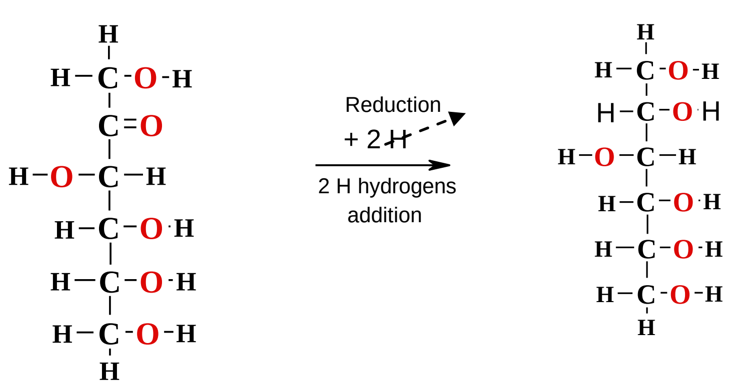


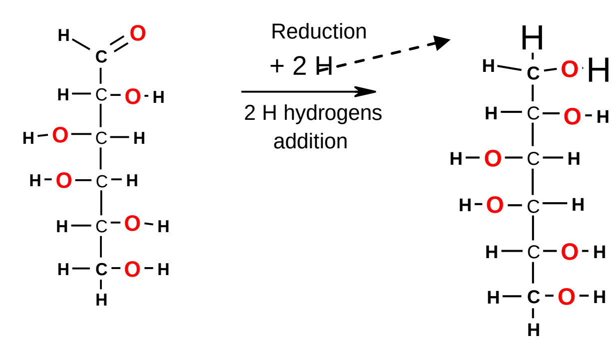


D Mannose D Mannositol D Glucose D Sorbitol

Fructose & galactose reduction is two hydrogens addition +2H to carbonyl group

+2H >**C**=**O** +2H >C=O

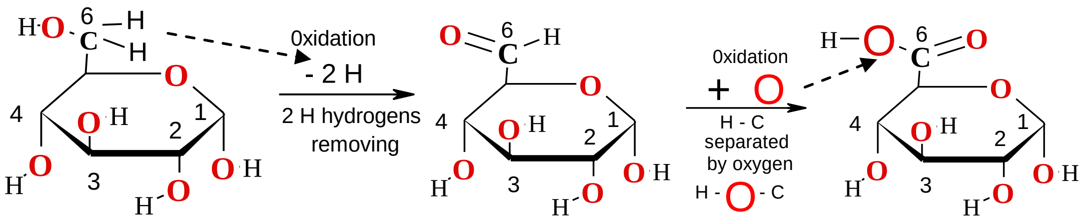




D Fructose D Sorbitol D Galactose D Galactosol

Reactions products for oxidation, acid + base and esterification !

1 Removing two hydrogens from glucose; 2 glucural oxidation forms glucuronic acid

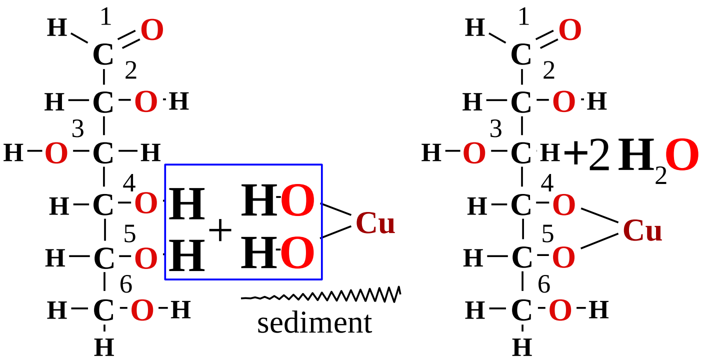


α-D-glucose α-D-glucural α-D-glucuronic acid

The prove of hydroxyl groups in glucose ($C_6H_{12}O_6$) copper glycolate and phosphate esters

The presence two or more adjacent carbon atoms hydroxyl groups **-CHOH-CHOH** assign to aldo-& ketohexoses the properties of multiple alcohol that may solute the **copper (II)** hydroxide precipitates **$Cu(OH)_2$**↓. The formed **copper** glycolate-like compound is the complex compound and therefore good soluble in water with bright blue color: **$CuSO_4$** + **2 NaOH** → **$Cu(OH)_2$**↓ + **Na_2SO_4**

copper sulfate sodium hydroxide **cooper** hydroxide precipitates sodium sulfate solution



Describe observations!

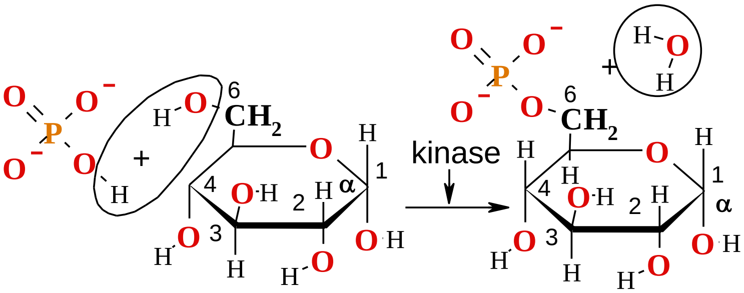
Why colour changes?

Explain the changes?
What causes this converting of compounds?

D-Glucose **cooper(II)** hydroxide **copper** glycolate blue colored solution in water

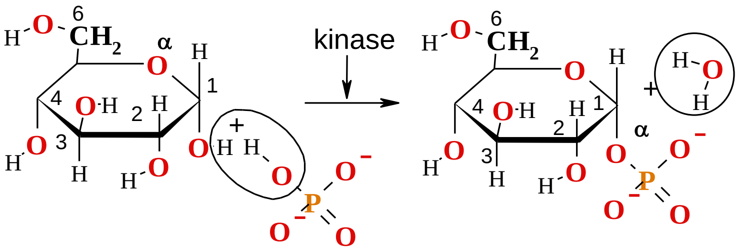
<u>Way of practical work.</u> In the test tube you have to mix one 1 drop of **copper(II)** sulfate **$CuSO_4$** solution by six 6 drops of sodium hydroxide **NaOH** solution. To **copper(II)** hydroxide precipitates **$Cu(OH)_2$**↓ to add one-two 1-2 drops of glucose **$C_6H_{12}O_6$** solution (glikoze). You have to mix prepared solution!
Have your observations described features? Mark what fit and what doesn't?

Hydrolase E.2 class enzymes **Kinases** phosphorylate-esterificate Hydroxyl group >**HC-OH**



Physiologic pH=7.36 protolytic balance determines charge -2 at phosphate of Glc6P^{2-} Neutral glucose D-Glc obtaines negative charge -2 with phosphate group.

HPO_4^{2-} phosphate α-D-glucose α-D-glucose-6-phosphate^{2-}



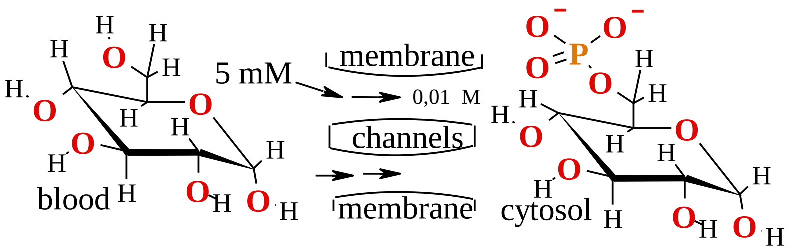
Write the esterification by Kinase-Hydrolases E.2 class enzyme products

α-D-glucose-1-phosphate^{2-} Glc1P^{2-} and water!

α-D-glucose HPO_4^{2-} hydrogen phosphate α-D-glucose-1-phosphate^{2-}

Describe phosphorylation importance for concentration gradient maintenance on cell membrane!

Glucose transporters via <u>cell membranes</u> from blood into cell glucose uptake drives by concentration gradient $[Glc_{blood}]$=5 mM>$[Glc_{cytosol}]$= 0.01 μM.
↓ External $[Glc_{blood}]$=5 mM glucose incoming cytosole phosphorylated hexokinases so



decreases concentration $[Glc_{cytosol}]$=0.01 μM because phosphorylated glucose concentration $[Glc6P^{2-}]$ doesn't affect gradient of glucose across the cell membrane.

Polymer glycogen store in liver cell cytosole [Glc]=0.4 M glucose units.
The total amount of glycogen in the body of a well-nourished adult is about 350 g, divided almost equally between liver and muscle. In Human body muscle and liver cells stored 350g glucose to night sleeping. Hydrolyse of glycogen glucose molecules consume human organism during 8 hours sleeping that to maintain blood glucose normal concentration [Glc]=5 mM. Glycogen is the reserve carbohydrate for animals.

Like amylopectin in plants, glycogen is a nonlinear-branched polymer of D-glucose joined by α-1,4- and α -1,6-glycoside bonds, but it has a lower molecular weight and an even more highly branched structure (Figure).

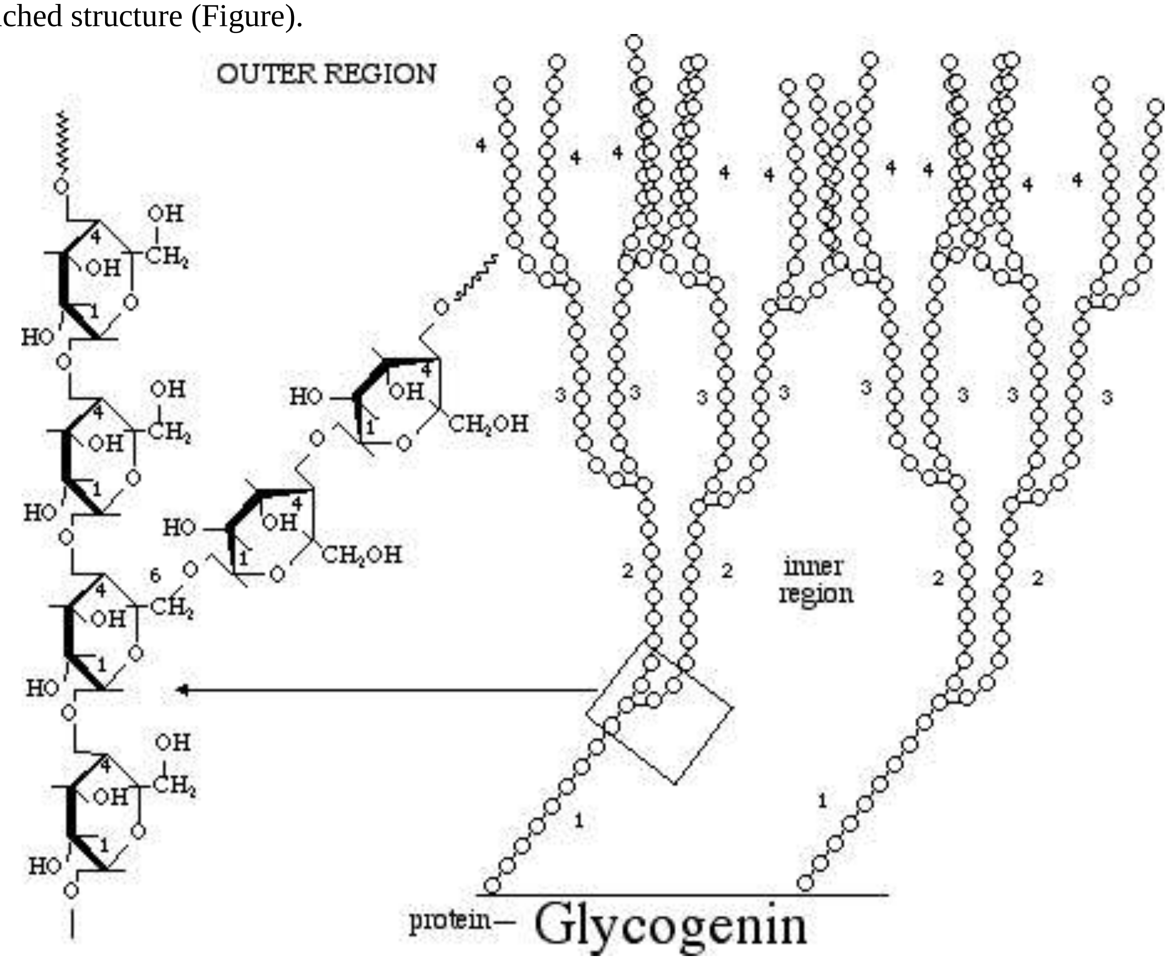


Figure Glycogen is a highly branched polymer of D-glucose joined by α-1,4-glycoside bond.
Branch points created by α -1,6-glycoside bonds contain 10-18 units of glucose.

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Theoretical concepts and key terms. Description and classification of composite-carbohydrates. The structural types of di-saccharides glycoside bonds **C-O-C** in : maltose, lactose and sucrose. The different features in glycoside bonding **-O-** can be observed in **Maltose, Lactose, Cellobiose, Sucrose, Lactose, Starch, Glycogen** and **Cellulose** structures of molecules. Distinctions in di-saccharides those type bindings 1-4 and 1-1 or 1-2 relate to chemical properties, classified as **reducing carbohydrates** and as **non reducing carbohydrates**.

The hydrolyse of composite carbohydrates. Inversion of Fructose. The gradual hydrolyse of the starch and cellulose and its products. The products proof for composite carbohydrates hydrolysis.

Address:http://aris.gusc.lv/ChemFiles/Saccharides/SSViewer/SSVFrameset.htm

Synthesis (polycondensation) and **hydrolyze** by E.2 class Hydrolase enzymes driven reactions

Write the carbohydrates **polycondensation-synthesis** reactions to form disaccharides with glycoside bond **-O-**............ (acetal formation) releasing the water molecule.

Write the polycondensation molecular expression of glucose with fructose composes the sucrose – table sugar and water!

$$\mathbf{C_6H_{12}O_6} + \mathbf{C_6H_{12}O_6} \xrightarrow{\text{cane\_sugar}} \mathbf{C_{12}H_{22}O_{11}} \text{.............} + \mathbf{H_2O}\text{............}$$

glucose fructose sucrose water

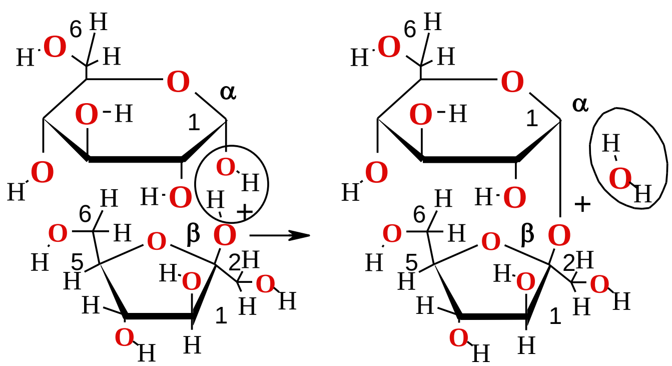
Write the polycondensation expression with glucose and fructose structures composes the structure of sucrose – table sugar and water!

Write disaccharide structure in Haworth projection!

α-D-Glucose

\+

β -D-Fructose



Sucrose

Glc(**α**1→2**β**)Fruc

Disaccharide with

-O-..........

glycoside bond

(acetal)

releasing +

water molecule

H_2O...........

Hydrolyze reaction is reverse to **synthesis** (**polycondensation**) reaction.

Write the formula expression sucrose (disaccharide) for decomposition hydrolyze within the water , the glucose and the fructose!

$$\mathbf{C_{12}H_{22}O_{11}} + \mathbf{H_2O} \xrightarrow{\text{hydrolyse}} 2\ \mathbf{C_6H_{12}O_6}\text{..........}+\text{.............}$$

disaccharide two mono saccharides glucose and fructose

Write the Haworth projection sucrose (disaccharide) decomposition hydrolyze with water to structures of the glucose and the fructose in products!

Sucrose

Glc(**α**1→2**β**)Fruc

-O-

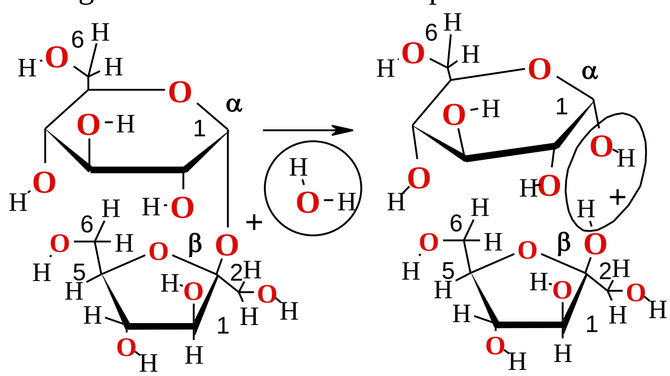
glycoside bond

(acetal)

\+

Water

H_2O



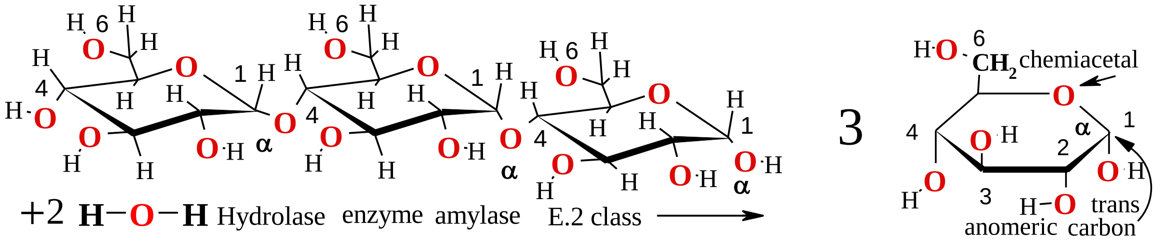
α-D-Glucose

\+

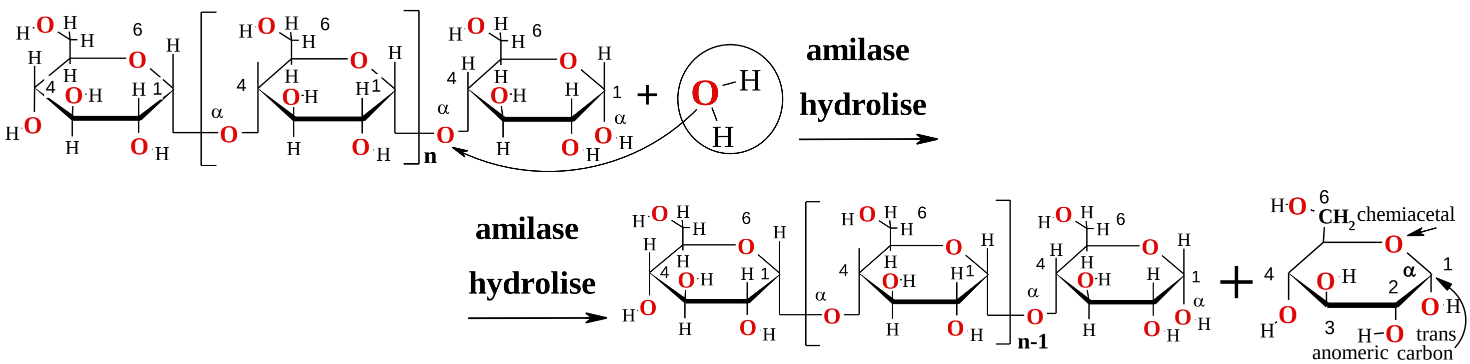
β -D-Fructose

Plants accumulate on photosynthetic reaction obtained **starch** polymer $(C_6H_{10}O_5)_n$, where number **n** can reach **n=**1000000 one million glucose units. In microscope can see those molecule aggregates fine, solid grains form, than its call in Latvian "ciete"- solid grains. Glucose is in short cat name designated as Glc and linking together α-glucose molecules join it's into polymer chains.

Write the starch triose α1—4 two glycoside **-O-** bonds hydrolyse by Hydrolase E.2 class enzyme and to show on the paper Haworth projections of 3 α-D-glucose unit $C_6H_{12}O_6$ after hydrolyse into water solution!



Three structural unit sequence shows Haworth projection structural formula sequence of **starch**. Write the **Starch** sequence Glc[(α1→4)Glc]$_n$(α1→4)Glc hydrolyze α1→4 glycoside **-O-** bridge between glucose structural units separating from polymer chain free glucose molecule



Starch hydrolyze products of human digestive tract already of mouth saliva has biocatalyst - enzyme amylase.

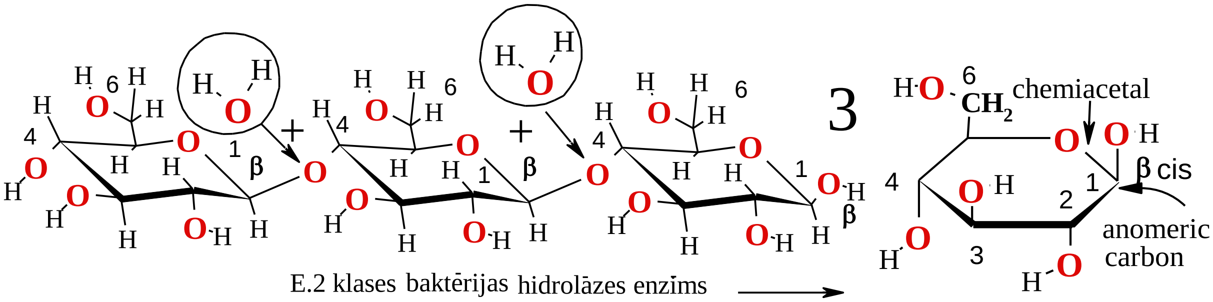
$(C_6H_{10}O_5)_n + H_2O => (C_6H_{10}O_5)_{n-1} + C_6H_{12}O_6$.................
starch water rest of starch glucose

Plants in photosynthetic reaction obtained glucose units use for linking together into framing structure in cross linked chain fibers of **cellulose** $(C_6H_{10}O_5)_n$. **Cellulose** serves for plant cells as body frame or matrix, assign for plant stalk structure and mechanical durability for plant organism body.

Human digestive tract can not hydrolyses **cellulose** polymer β1→4 and β1→6 glycoside **-O-** bridge between glucose monosaccharide structural units.

Amylase do not able hydrolyze **Cellulose** β1→4 and β1→6 oxygen **-O-** glycoside bridge du to different structure of α1→4 and α1→6 oxygen **-O-** glycoside bridge. Therefore grass and plant cellulose containing parts in food can not be used in human digestive system.

For ruminant animals specific bacteria, which hosts in preliminary stomach, separates free glucose molecules from cellulose polymer as triose β1—4 two glycoside **-O-** bonds hydrolyze by bacterial Hydrolase enzyme



Free glucose containing mass of food animal delivers into stomach and digestive tract absorbs glucose in tissues.

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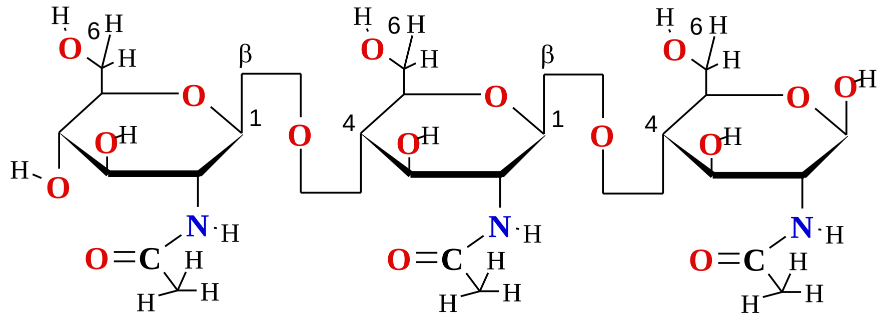
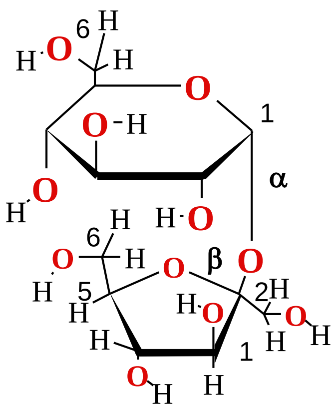
Address:http://aris.gusc.lv/ChemFiles/Saccharides/SSViewer/SSVFrameset.htm
http://aris.gusc.lv/ChemFiles/Saccharides/PolySaccharides/HyalurChondroitHeparKeratMucHTM/0GlycoProteinComponents.html

Chitin triose Complete Haworth projections of two glycoside **-O-** connections
lcNA(**β**1→4) GlcNA(**β**1→4)GlcNA-**β** !



β -NAcetyl-D-glucosamine **β** -NAcetyl-D-glucosamine **β**-NAcetyl-D-glucosamine



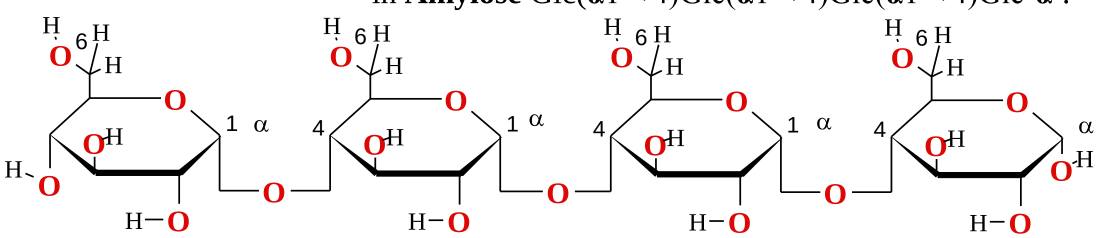
Complete Haworth projections for glucose and fructose units with glycoside **-O-** connection in **sucrose** Glc(**α**1→2**β**)Fruc !

α-D-Glucose unit

(**α**1→2**β**) **–O-** glycoside bond (acetal)

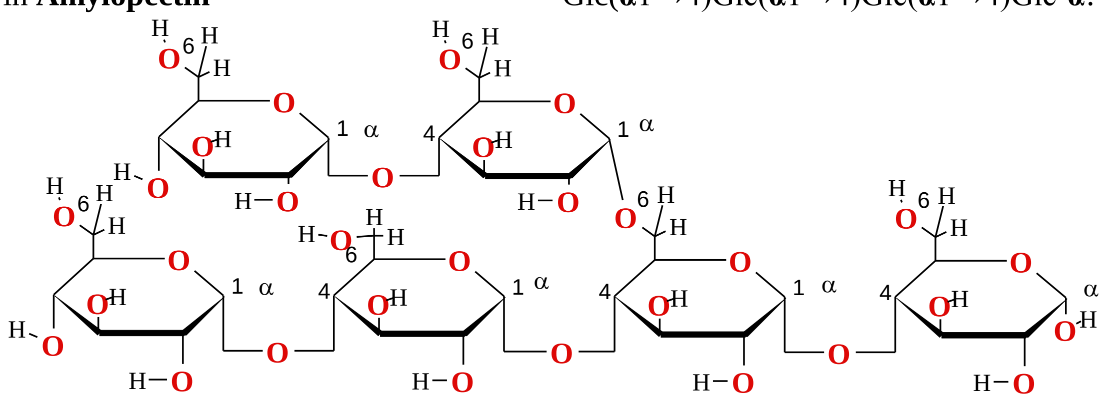
β –D-Fructose unit

Complete Haworth projections for glycoside **-O-** bonds connection
in **Amylose** Glc(**α**1→4)Glc(**α**1→4)Glc(**α**1→4)Glc-**α** !



α-D-Glucose unit **α**-D-
Glucose unit **α**-D-Glucose unit **α**-D-Glucose unit

Complete Haworth projections for connection **–O-** Glc(**α**1→4)Glc(**α**1→6)↓
in **Amylopectin** Glc(**α**1→4)Glc(**α**1→4)Glc(**α**1→4)Glc-**α**!



α -D-Glucose unit **α** -D-Glucose unit **α** -D-Glucose unit **α** -D-Glucose unit

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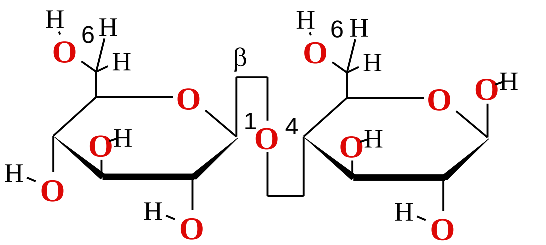
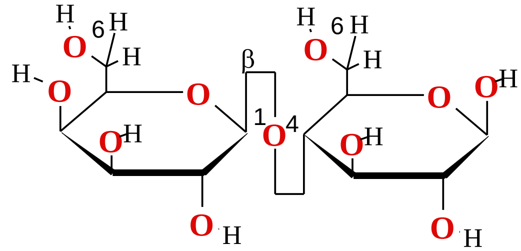
Complete Haworth projections for glycoside **-O-** bond connection

in **Cellobiose** **Lactose** !

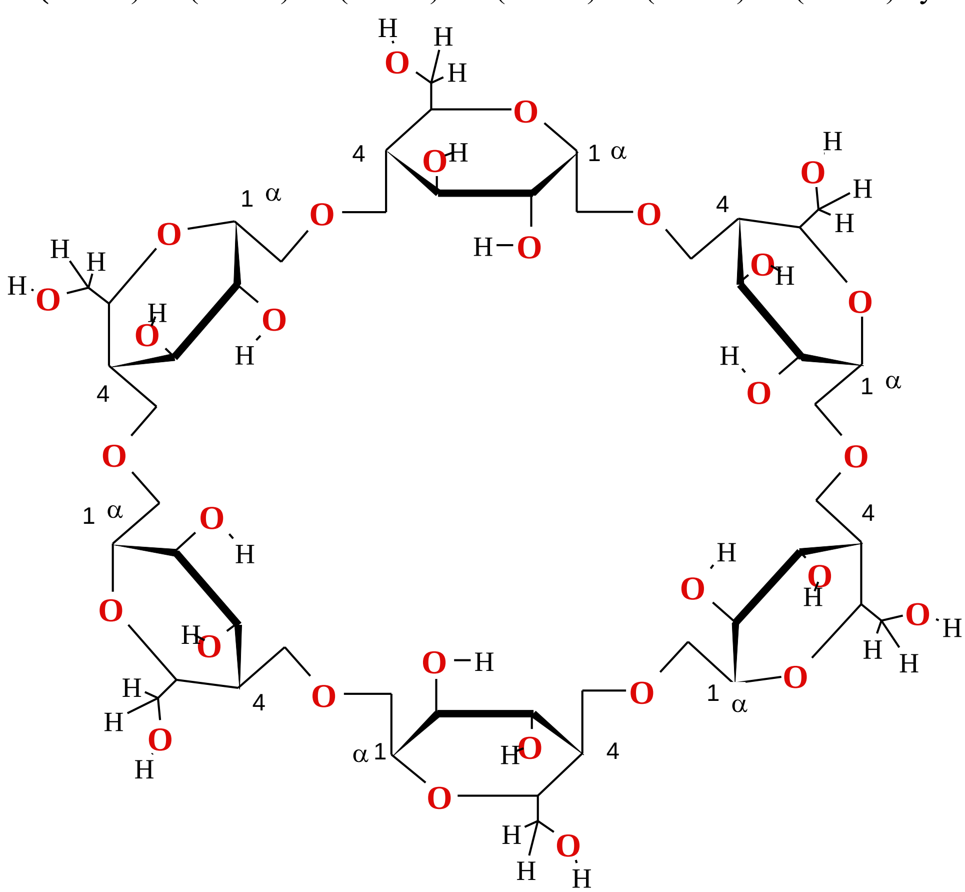
Glc(**β**1→4)Glc-**β** Gal(**β**1→4)Glc-**β**





Complete Haworth projections for glycoside **-O-** connection in **Cyclo Hexa Amylose**!

Glc(**α**1→4)Glc(**α**1→4)Glc(**α**1→4) Glc(**α**1→4)Glc(**α**1→4)Glc(**α**1→4) cyclic



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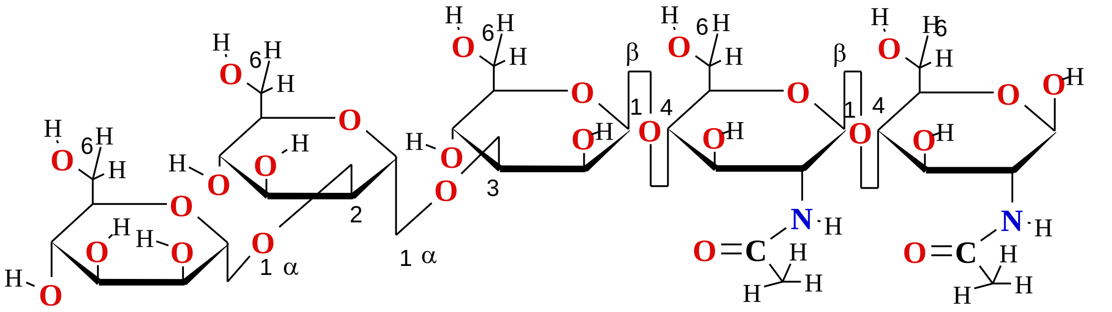
Complete Haworth projections for glycoside **-O-** connection

in **Mucin linear** !

Man(**α**1→2)Man(**α**1→3)Man(**β**1→4)GlcNAc(**β**1→4)GlcNAc-**β**



β-NAcetyl-D-Glucosamine **β**-NAcetyl-D-Glucosamine

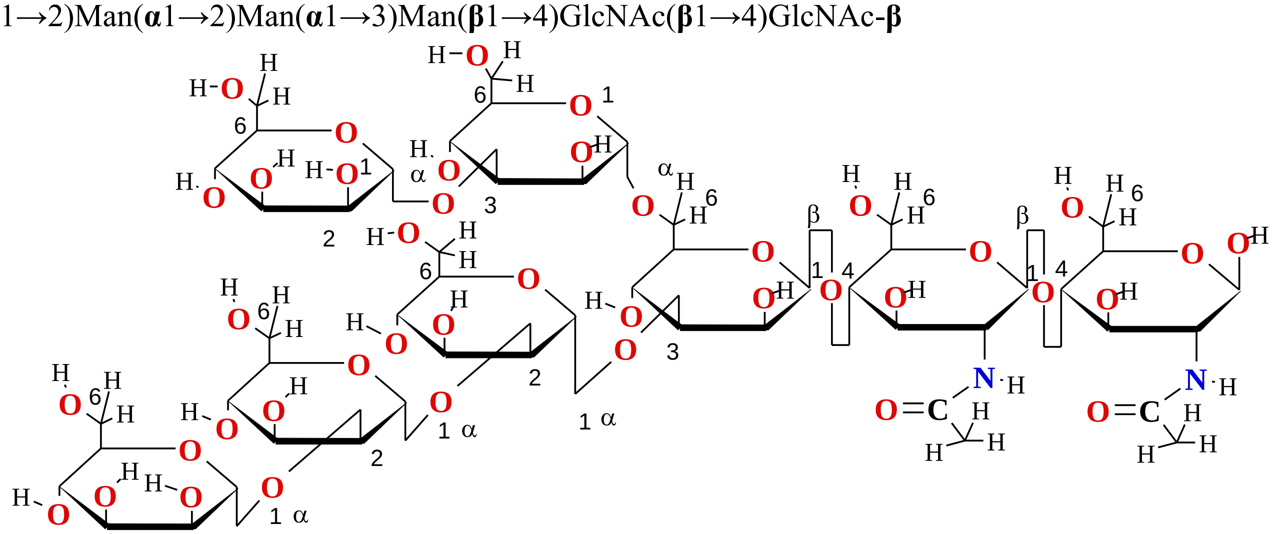
α-D-Mannose **α**-D-Mannose **α**-D-Mannose

Complete Haworth projections for glycoside **-O-** connection

in **Mucin branched (forked)** !

Man(**α**1→3)Man(**α**1→6)↓

Man(**α**1→2)Man(**α**1→2)Man(**α**1→3)Man(**β**1→4)GlcNAc(**β**1→4)GlcNAc-**β**



α-D-Mannose **α**-D-Mannose ↓

α-D-Mannose **α**-D-Mannose **α**-D-Mannose **α**-D-Mannose **β**-N-Acetyl-D-Glucosamine

β-N-Acetyl-D-Glucosamine

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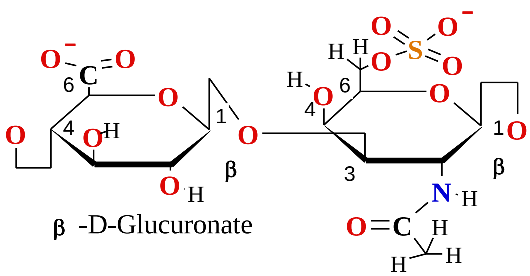
Complete eight disaccharide units of Proteoglycan components in Haworth projections!

Chondroitin 6-sulfate

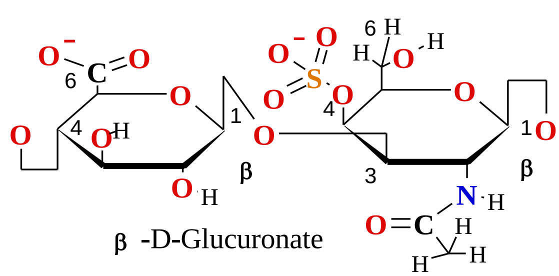
GlcUA(**β**1→3)GalNAc(**β**1→4)
∟6-O-Sulfate



β -N-Acetyl-D-Galactosamine-6-sulfate

Chondroitin 4-sulfate

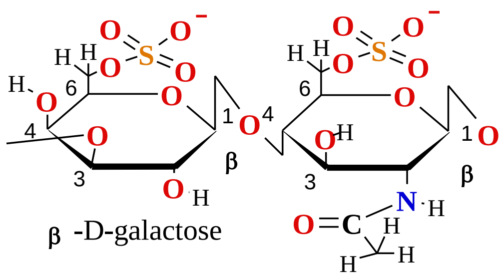
GlcUA(**β**1→3)GalNAc(**β**1→4)
∟4-O-Sulfate



β-N-Acetyl-D-Galactosamine-4-Sulfate

Keratan (6-Sulfate)

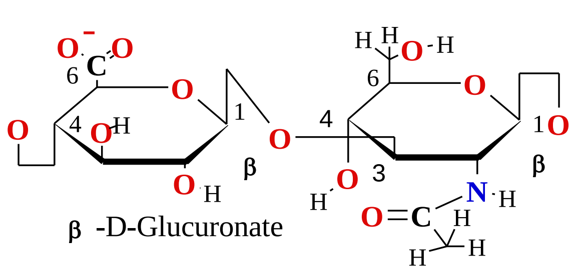
Gal(**β**1→4)GlcNAc(**β**1→3)
∟6-O-Sulfate∟6-O-Sulfate



β-N-Acetyl-D-Glucosamine (-6-Sulfate)

Hyaluronate

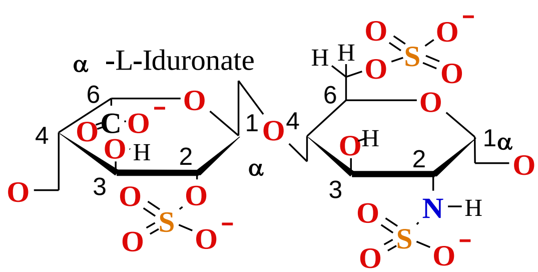
GlcUA(**β**1→3)GlcNAc(**β**1→4)
50000 units polysaccharide



β-N-Acetyl-D-Glucosamine

Heparin

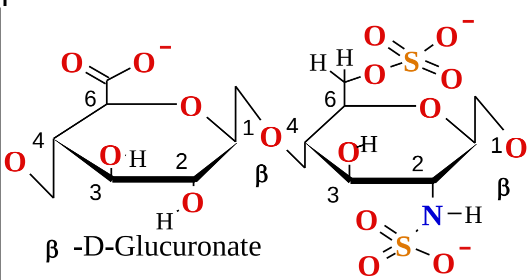
(**α**1→4)IdUA(**α**1→4)GlcNSO$_3^-$(**α**1→4)
∟2-O-Sulfate ∟6-O-Sulfate



α-N-Acetyl or N-sulfo-D-Glucosamine

Heparan sulfate

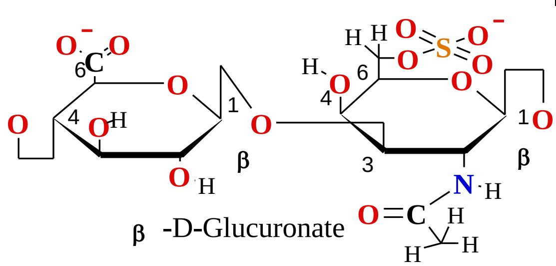
(**α**1→4)GlcUA(**β**1→4)GlcNSO$_3^-$(**β**1→4)
∟6-O-Sulfate



β-N-Acetyl or N-sulfo-D-Glucosamine

Dermatan sulfate 6-O-Sulfate

GlcUA(**β**1→3)GalNAc(**β**1→4)
∟6-O-Sulfate



Dermatan sulfate 4-O-Sulfate

IdUA(**α**1→3)GalNAc(**β**1→4)
∟4-O-Sulfate