FOOD CHEMISTRY

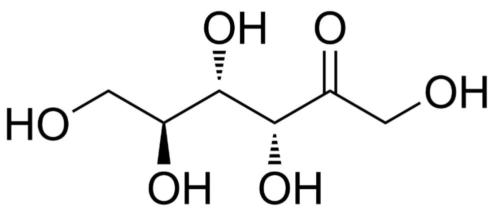
Chapter 4 : Carbohydrates

4.1 DEFINITIONS AND CLASSIFICATION
Carbohydrates and monosaccharides

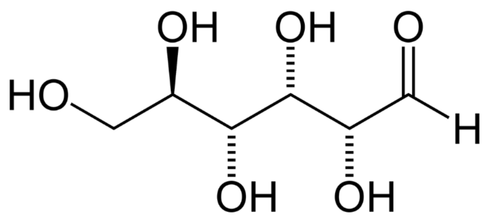
- Carbohydrates are mainly polyhydroxy aldehydes and ketones of general formula $C_n(H_2O)_n$.

- Simple monosaccharides are named generically according to their number of carbon atoms : trioses, tetroses, pentoses, hexoses,etc.

- If the carbonyl is an aldehyde at the beginning of the chain, the monosaccharide is said to be an aldose, otherwise it is a ketose.



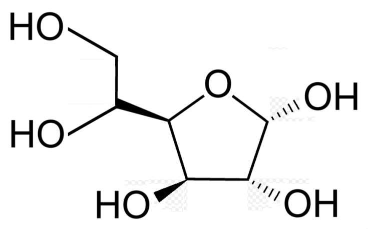
Fructose, a ketohexose



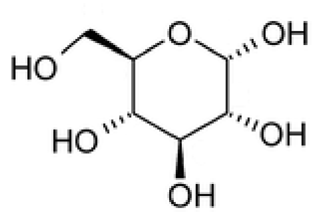
Glucose, an aldohexose

4.1 DEFINITIONS AND CLASSIFICATION
Cyclic monosaccharides, di-, oligo and polysaccharides

Ring closure creates hemiacetals, giving rise to five or six member rings (pyranoses and furanoses).

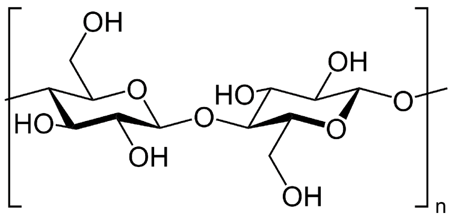


α – D – glucofuranose

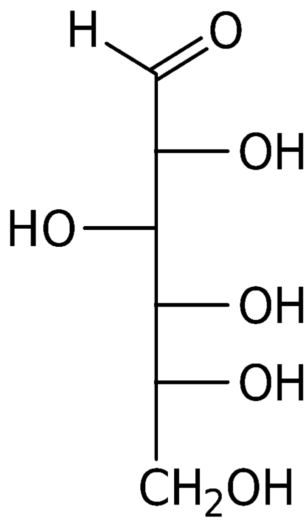


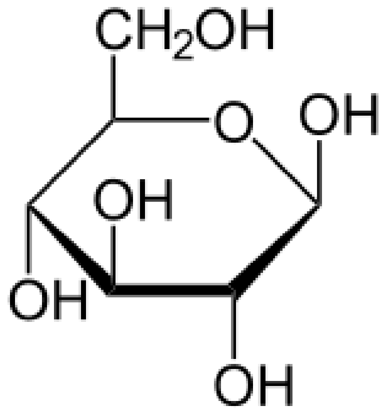
α – D – glucopyranose

Monosaccharides can react with water elimination to form di-, oligo- or polysaccharides.



4.2 STRUCTURAL REPRESENTATIONS
Fisher and Haworth projections



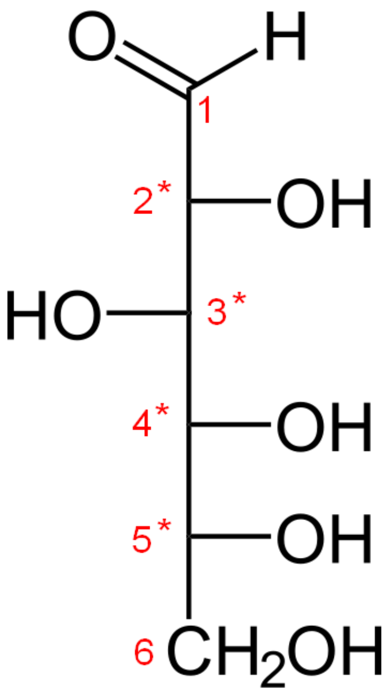


In a Fischer projection, all horizontal bonds project toward the viewer, while vertical bonds project away from the viewer. The carbon chain is depicted vertically, with carbon atoms represented by the center of crossing lines. The orientation of the carbon chain is so that carbon 1 is at the top.

In a Haworth projection, carbon is the implicit type of atom. The ring is depicted by a hexagon or pentagon, with carbon 1 at the right. Hydrogen atoms on carbon are implicit. A thicker line indicates atoms that are closer to the observer.

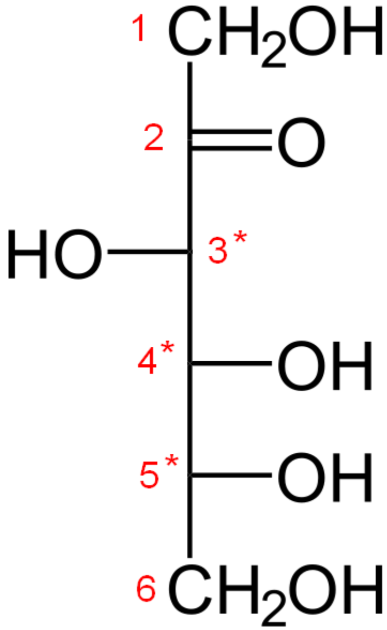
4.2 STRUCTURAL REPRESENTATIONS

Optical isomers of mono-saccharides



Haldohexoses

2^4 = 16 isomers

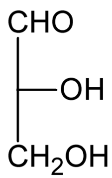


Ketohexoses

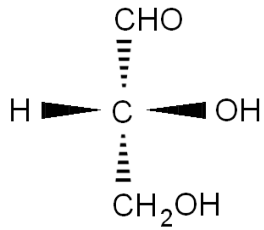
2^3 = 8 isomers

4.2 STRUCTURAL REPRESENTATIONS

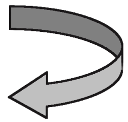
Sugars stereochemical notation



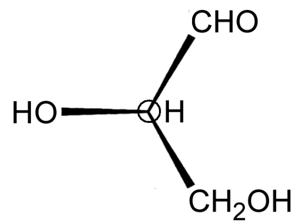
Fisher projection of D-glyceraldehyde



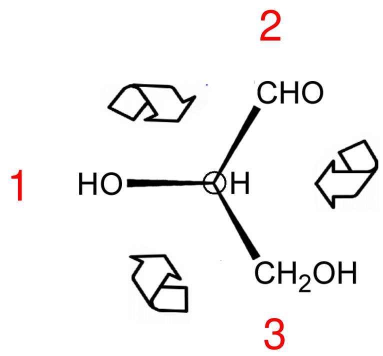
Wedge and dash projection



120° rotation



Newman projection



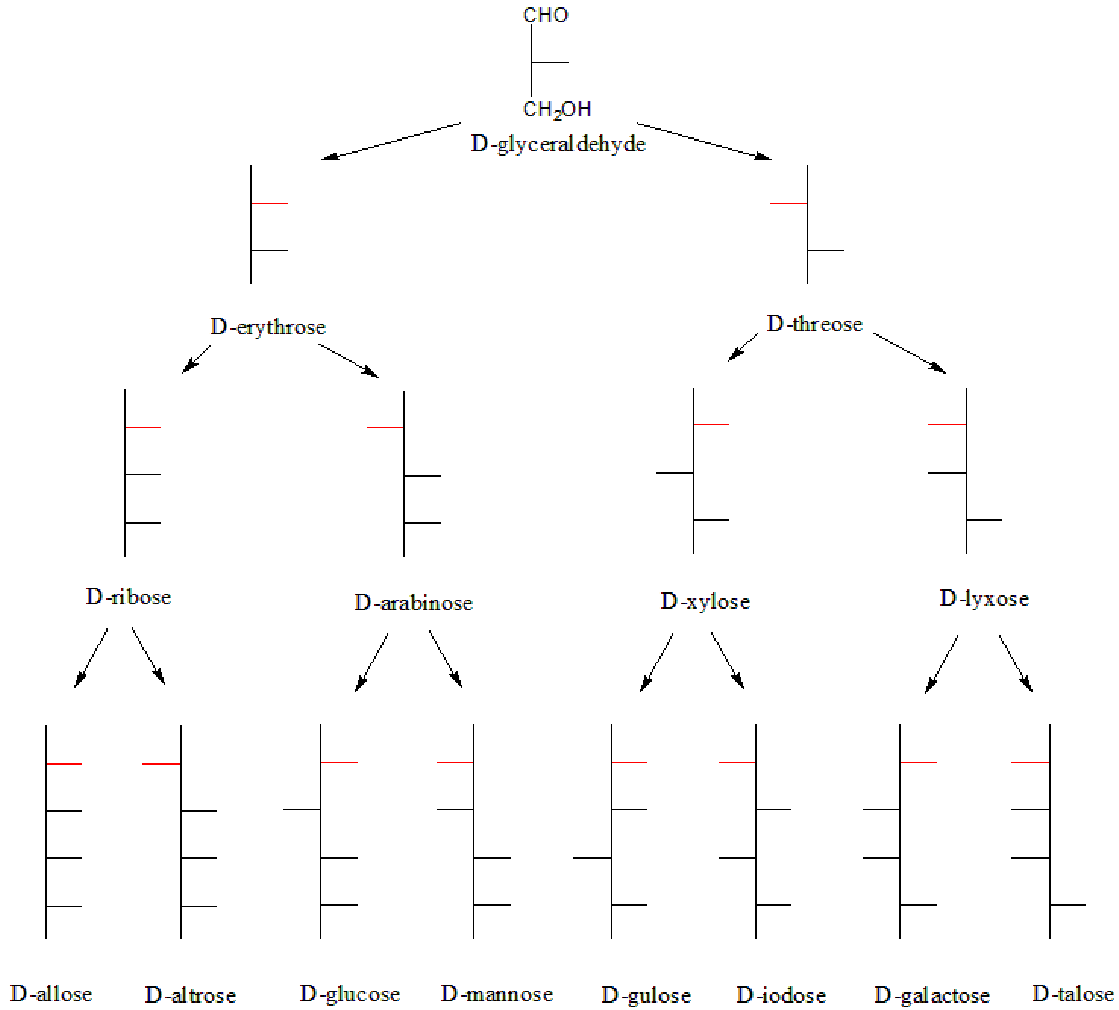
D-glyceraldehyde bears the R-conformation according to Cahn, Ingold & Prelog

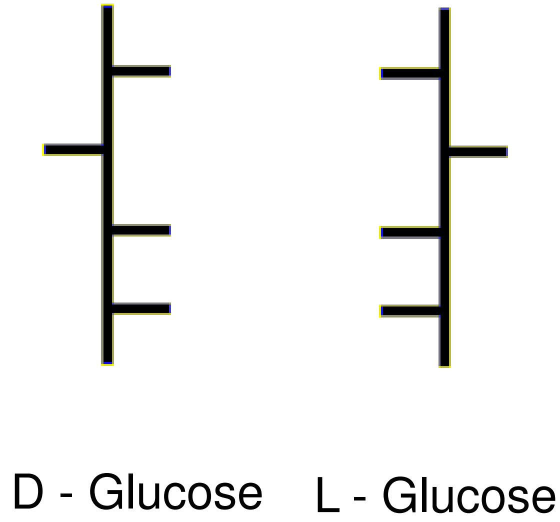
rules used in organic chemistry to name the stereoisomers of a molecule

1966 Bürgenstock Conference

4.2 STRUCTURAL REPRESENTATIONS

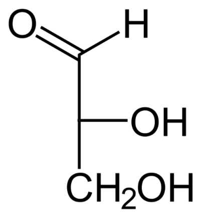
Stereochemistry of natural aldoses



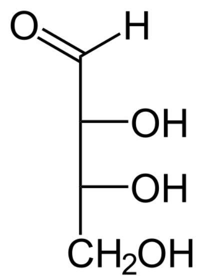


4.3 ALDOSES AND KETOSES

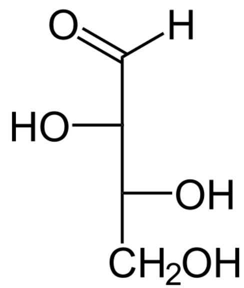
Some important D-aldoses



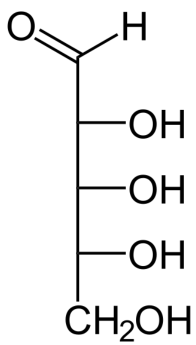
Glyceraldehyde
glycolyse



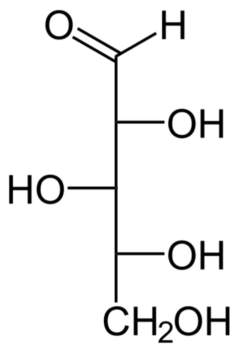
Erythrose
Précursor of a.a



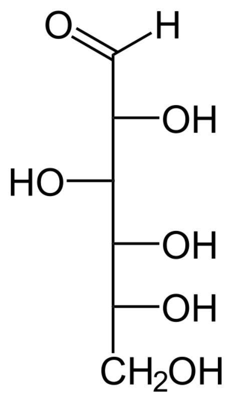
Threose
Oxydation→ malic acid



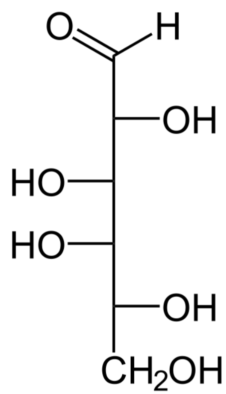
Ribose
DNA sugar



Xylose
From wood



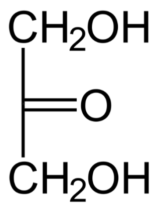
Glucose

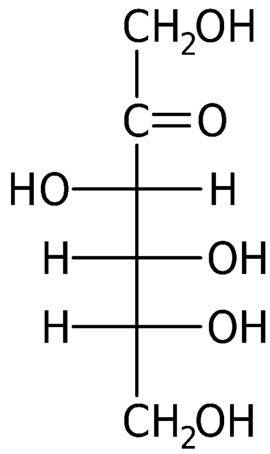


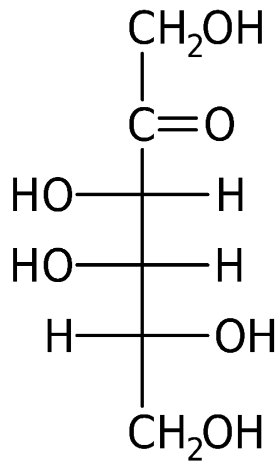
Galactose

4.3 ALDOSES AND KETOSES

Some important D-ketoses







Optically inactive !

Dihydroxy-acetone

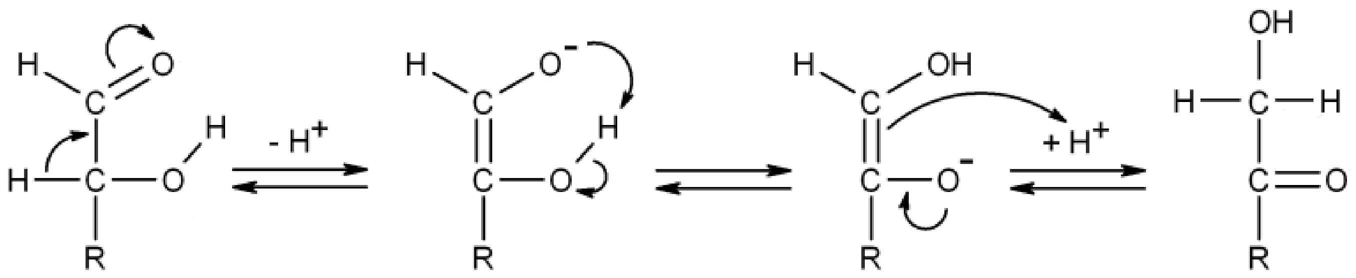
Fructose

Tagatose

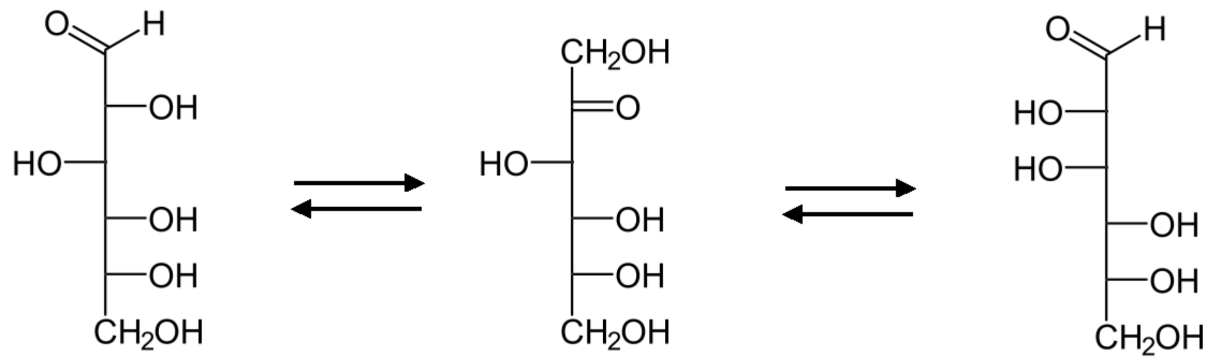
Functional sweetener

4.3 ALDOSES AND KETOSES

Lobry-de Bruyn-van Eckenstein reaction *dT*



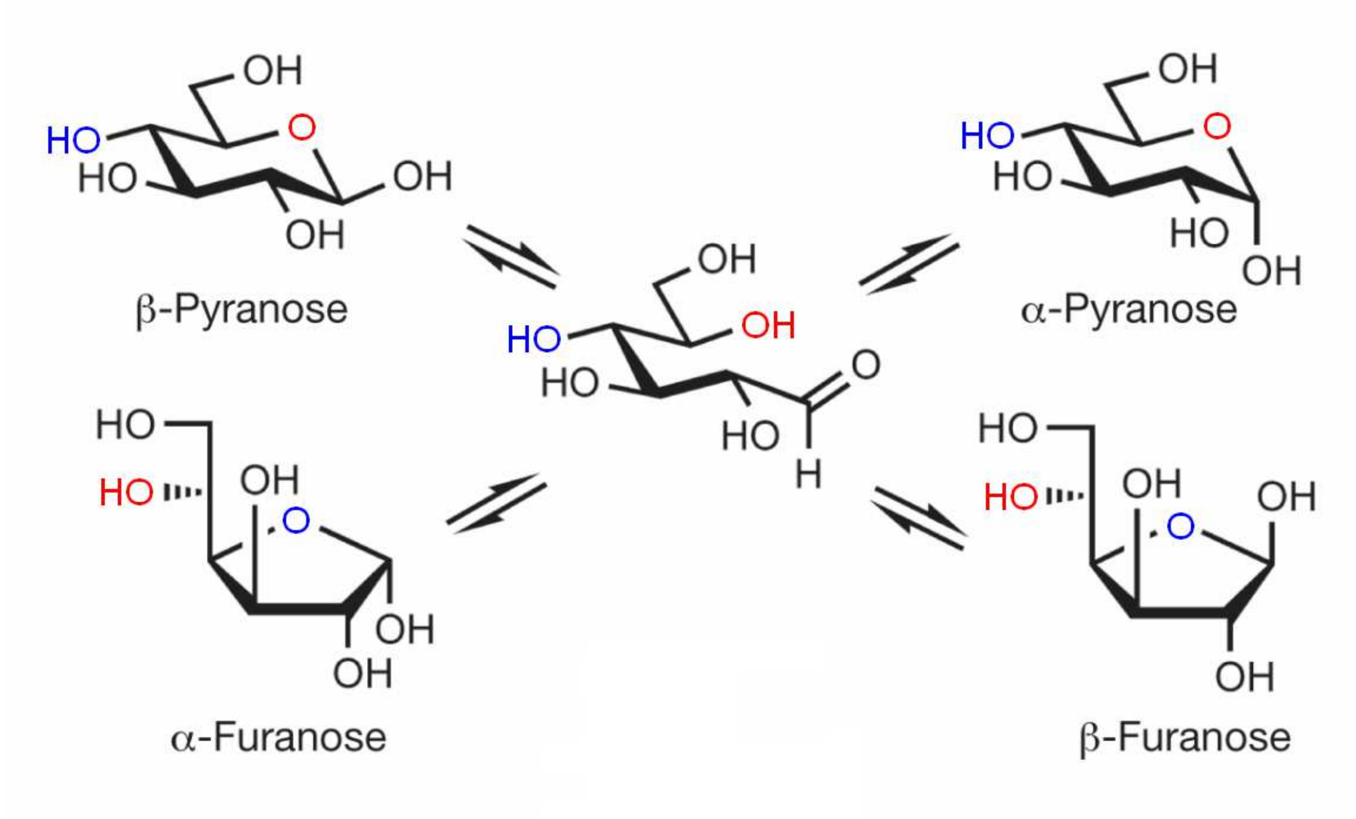
Aldose **Deprotonated enediol** **Ketose**



D-glucose D-fructose D-mannose

4.4 PYRANOSES AND FURANOSES

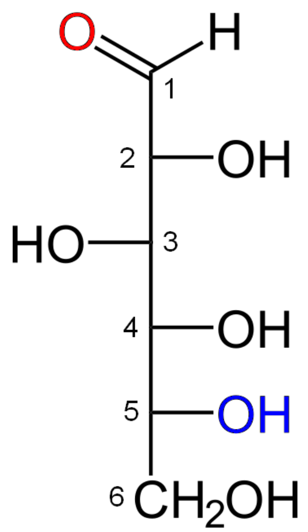
Cyclization reactions of D-glucose

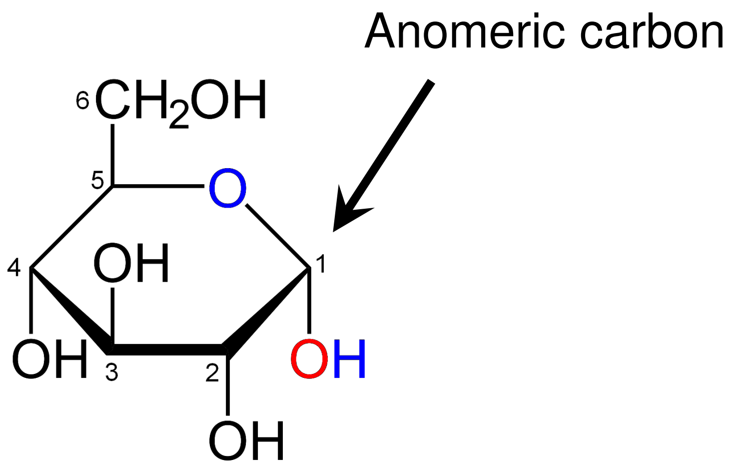


4.4 PYRANOSES AND FURANOSES

From Fisher to Haworth representations (I)

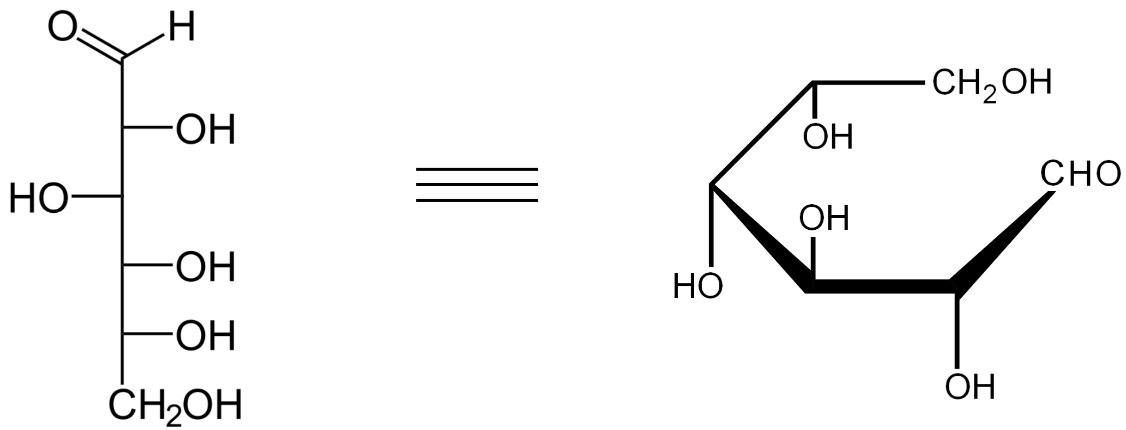
The groups on the right side become the groups on the bottom of the ring and the groups on the left become the groups on the top. The carbon at the very bottom is placed on top of the ring

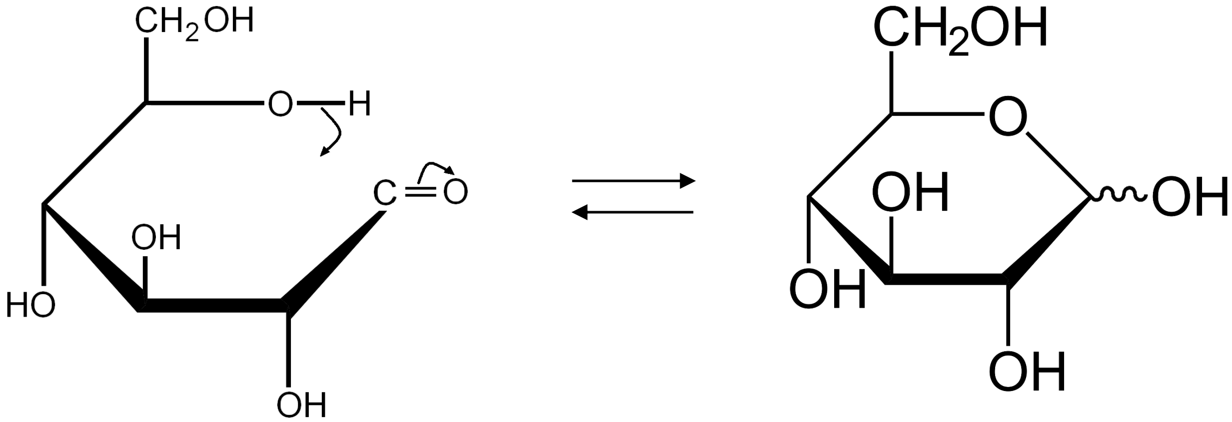




4.4 PYRANOSES AND FURANOSES

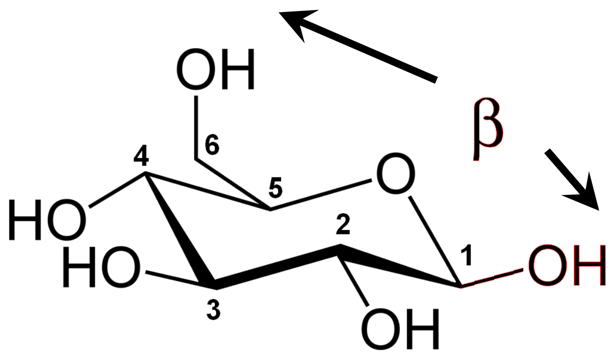
From Fisher to Haworth representations (II)



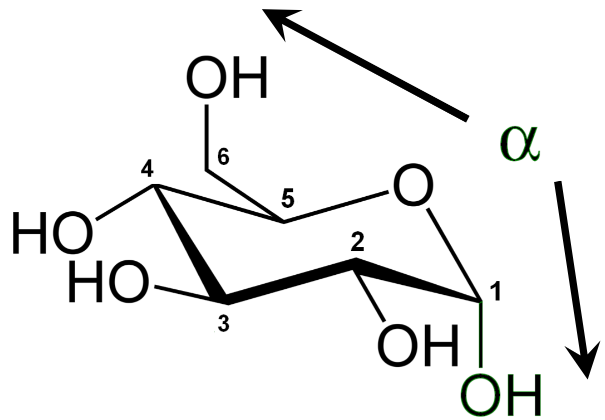


4.4 PYRANOSES AND FURANOSES

α- and β-anomers of D-glucopyranose



β - cis

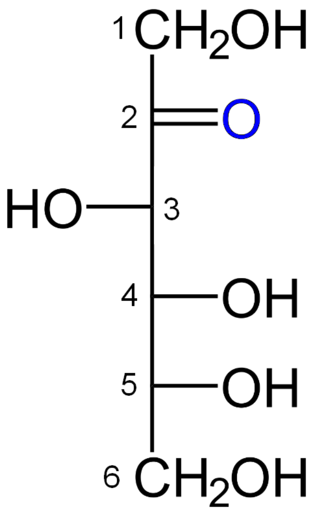


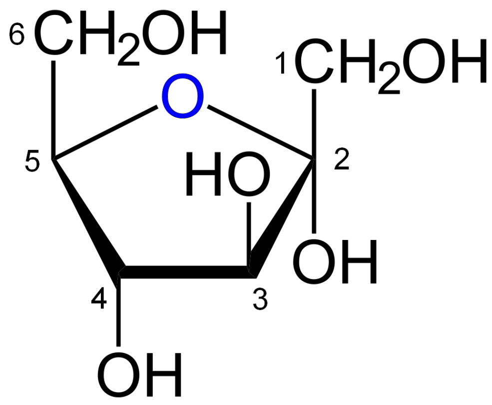
α - trans

The carbon atom in position 1 is a new asymmetric center.

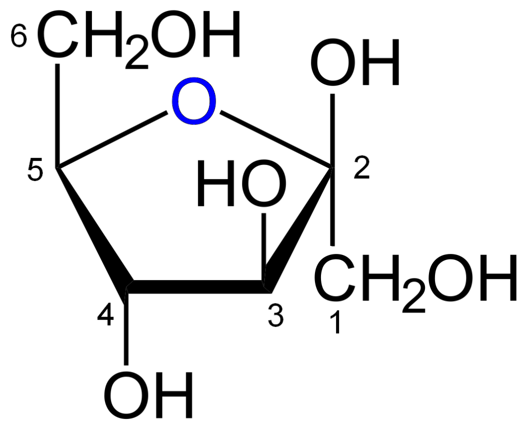
4.4 PYRANOSES AND FURANOSES

Fructofuranose anomers





α-anomer



β-anomer

4.4 PYRANOSES AND FURANOSES

Mutarotation of sugars

β – glucopyranose

$[\alpha]_D^{20} = 18.7°$

α – glucopyranose

$[\alpha]_D^{20} = 112.2°$

In aqueous media, there is a rapid conversion, called MUTAROTATION

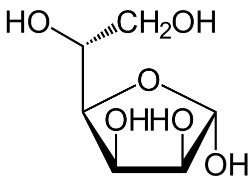
At equilibrium, $[\alpha]_D^{20} = 52.5°$

Therefore, β – glucopyranose = 64 % and α – glucopyranose = 36 %

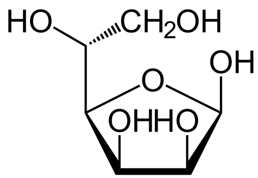
4.4 PYRANOSES AND FURANOSES

Forms of monosaccharide in aqueous solutions (in %)

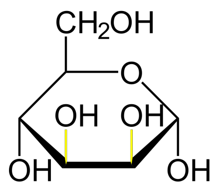
Compound	***α-pyranose***	***β-pyranose***	***α -furanose***	***β-furanose***	***Open chain***
Glucose	36.0	63.0	0.5	0.5	0.002
Galactose	30.0	64.0	2.5	3.5	0.02
Fructose	2.5	65.0	6.5	25.0	0.8
Mannose	65.5	34.5	0.6	0.3	0.005



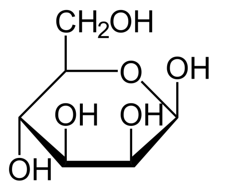
α -D-mannofuranose



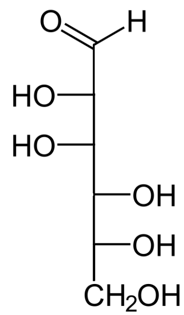
β -D-mannofuranose



α -D-mannopyranose



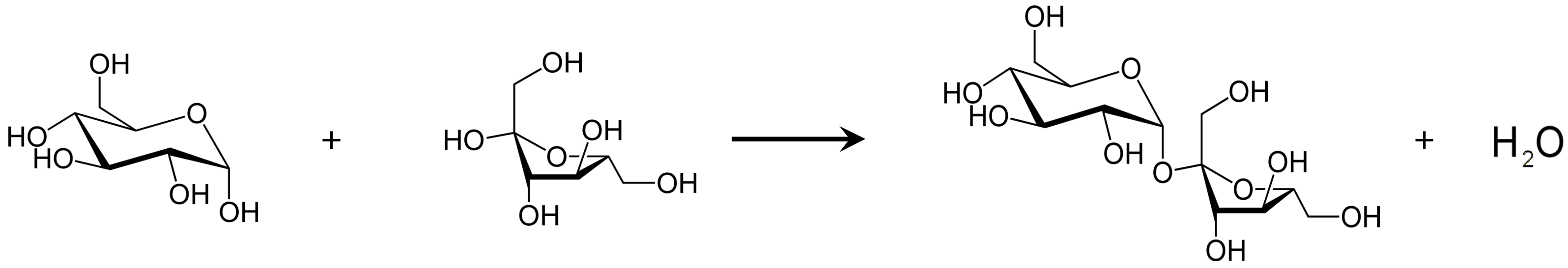
β -D-mannopyranose



D-mannose

4.5 DISACCHARIDES
General nomenclature

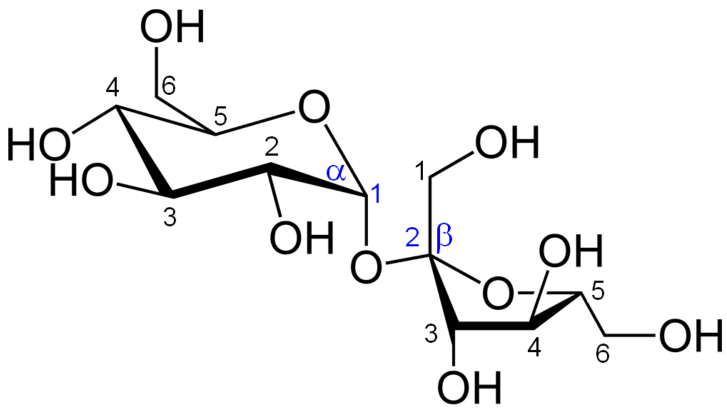
Condensation reaction between glucose and fructose, yielding sucrose



α – D – glucopyranosyl – (1→2) – β – D – fructofuranose

4.5 DISACCHARIDES

Bonding nomenclature



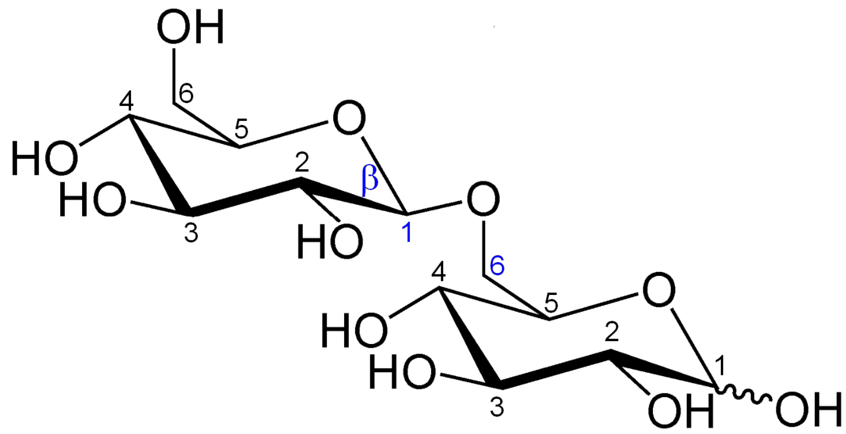
Sucrose

Glucose-α(1→2)β-fructose

Gentiobiose

Glucose-β(1-6)-glucose

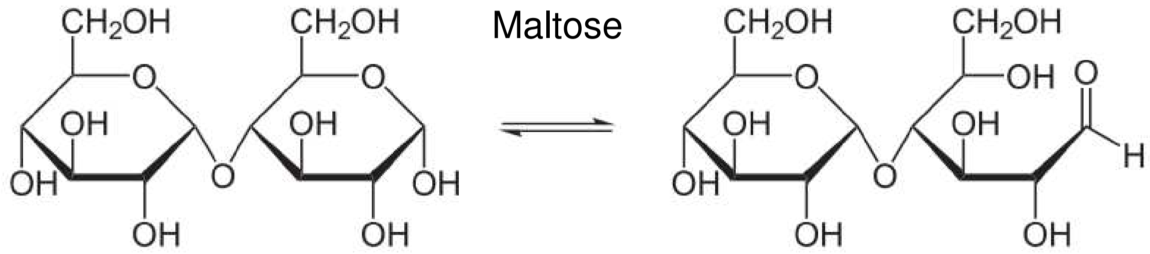
Heteroside/ amygdalin



4.5 DISACCHARIDES
Reducing and non reducing sugars

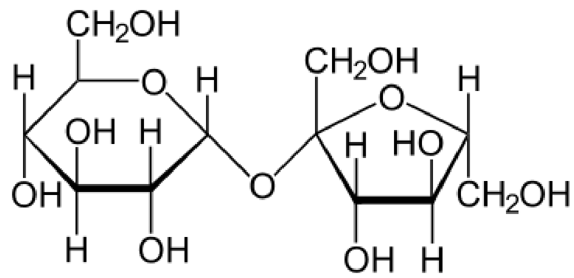
All monosaccharides are reducing compounds (aldehydes or ketones)

Disaccharides containing an hemiacetal can generate an aldehyde and are also reducing.



Maltose

Disaccharides without an hemiacetal cannot open their rings and are non reducing.



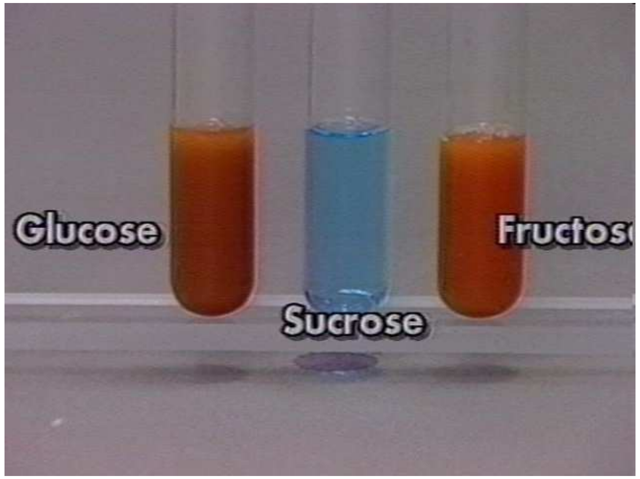
Sucrose

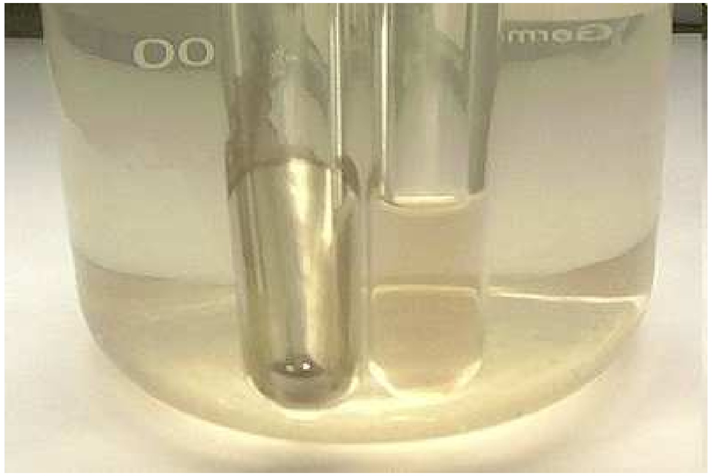
4.5 DISACCHARIDES

Some characteristic reducing sugars reactions

Tollens reaction $2\,[Ag(NH_3)_2]^+ + RCHO + 3\,OH^- \rightarrow 2\,Ag\,(s) + 4\,NH_3 + 2\,H_2O + RCOO^-$

Ag complex



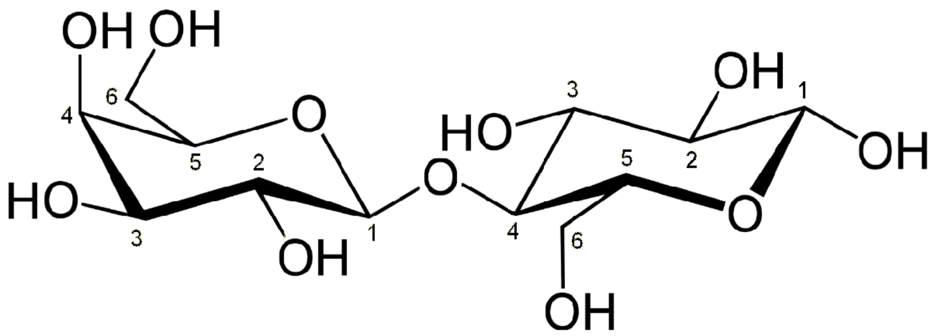


Benedict reaction $2\,Cu^{2+} + RCHO + OH^- + H_2O \rightarrow Cu_2O + 4\,H^+ + RCOO^-$

4.5 DISACCHARIDES

Some important disaccharides

Disaccharide	***Unit 1***	***Unit 2***	***Bond***
Sucrose	Glucose	Fructose	α (1→2)
Maltose	Glucose	Glucose	α (1→4)
Lactulose	Galactose	Fructose	β (1→4)
Lactose	Galactose	Glucose	β (1→4)



4.5 DISACCHARIDES

Frequencies of dietary intolerances in Switzerland

		Estimated frequencies
Non-immunological intolerances		
Fructose malabsorption		12 - 16 %
Hereditary fructose intolerance		1 : 30’000
Lactose intolerance		15 – 20 %
Primary lactase deficiency		< 2 %
Immunological intolerances		
Coeliac disease		1 %
Food allergies	Adults	2 – 4 %
	Children up to 17 years	3 – 4 %
	Babies	2 – 6 %

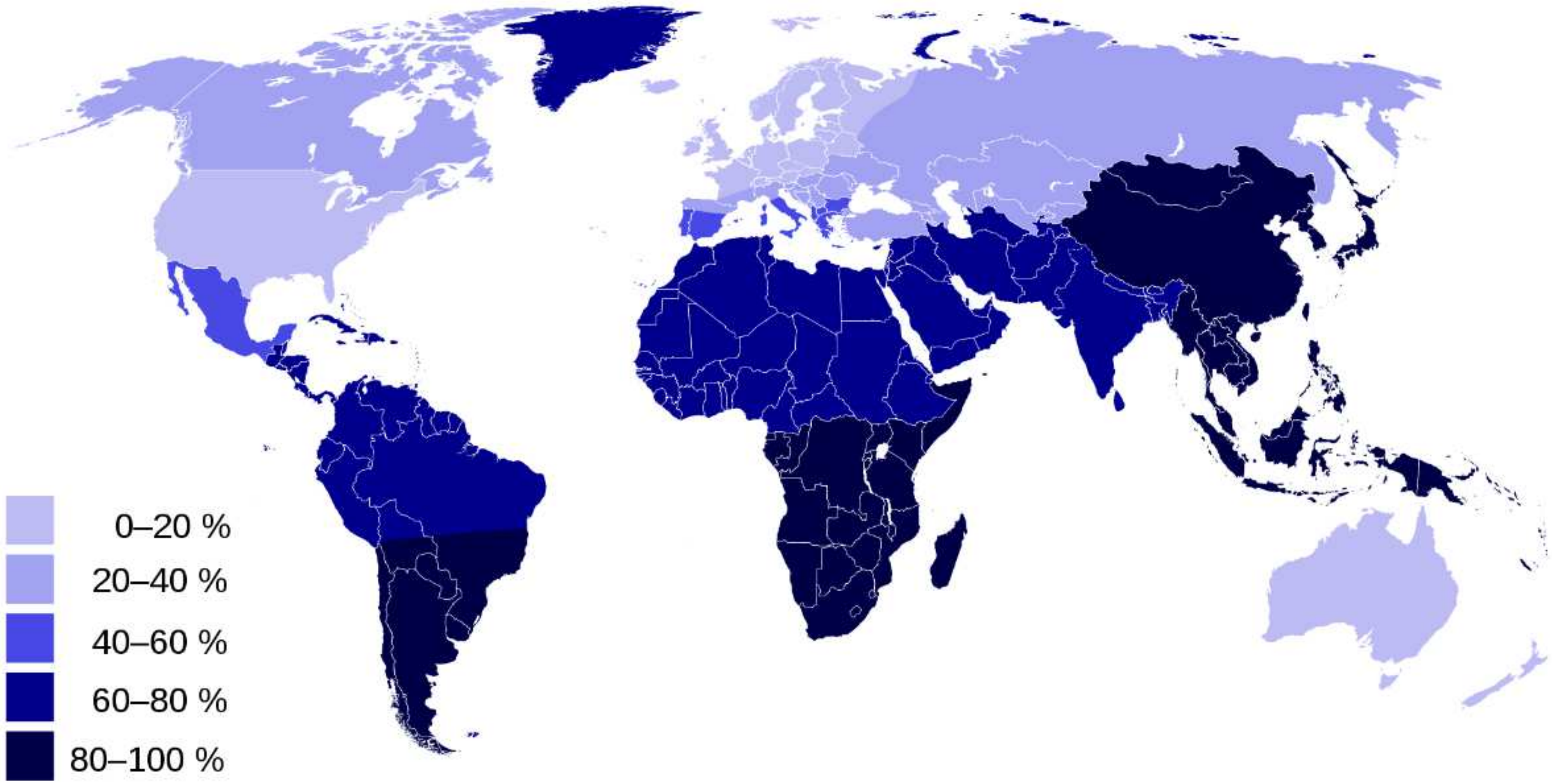
4.5 DISACCHARIDES
Lactose intolerance

Lactose intolerance : lack of the enzyme lactase in the digestive system.

- In mammals, the young experience reduced lactase production at the end of the weaning period (a species-specific length of time).
- In human non-dairy consuming societies, lactase production usually drops about 90% during the first four years of life.
- The frequency of decreased lactase activity ranges from as little as 5% in northern Europe, up to 70% for Sicily, to more than 90% in some African and Asian countries, and even 100% for native americans.
- Certain human populations have a mutation on chromosome 2 which eliminates the shutdown in lactase production, allowing them to drink milk even at adulthood.
- This is an evolutionarily adaptation to dairy consumption, and has occurred in populations with a pastoral lifestyle.

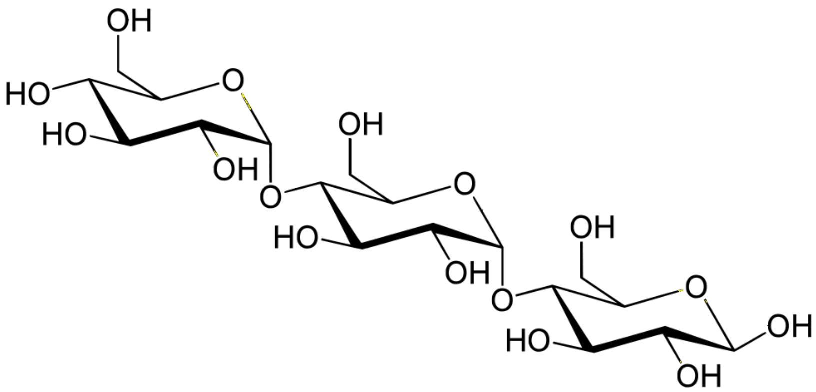
4.5 DISACCHARIDES

Distribution of lactose intolerance



4.6 OLIGO- AND POLYSACCHARIDES

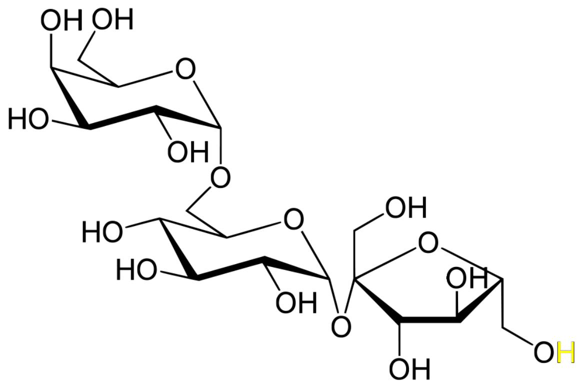
Some trisaccharides



Maltotriose

Glucose α (1→4) glucose α (1→4) glucose

saliva

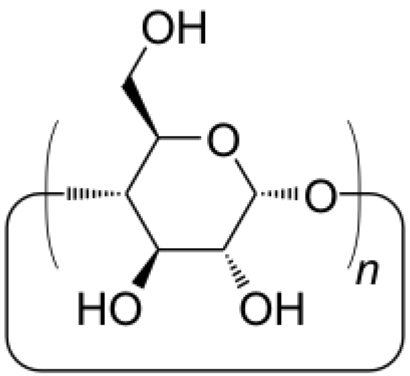


Raffinose

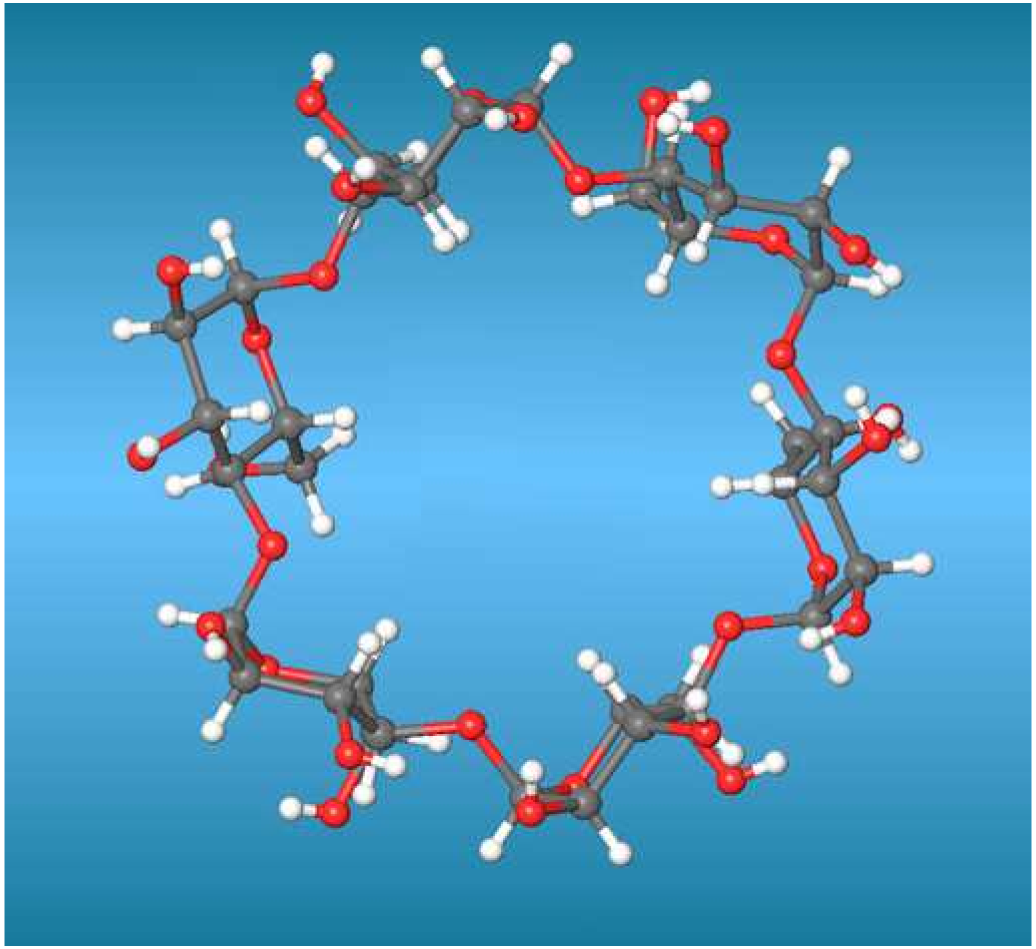
Galactose α (1→6) glucose β (1→2) fructose

α-GAL enzyme break down RFOs

4.6 OLIGO- AND POLYSACCHARIDES
Structures of cyclodextrins



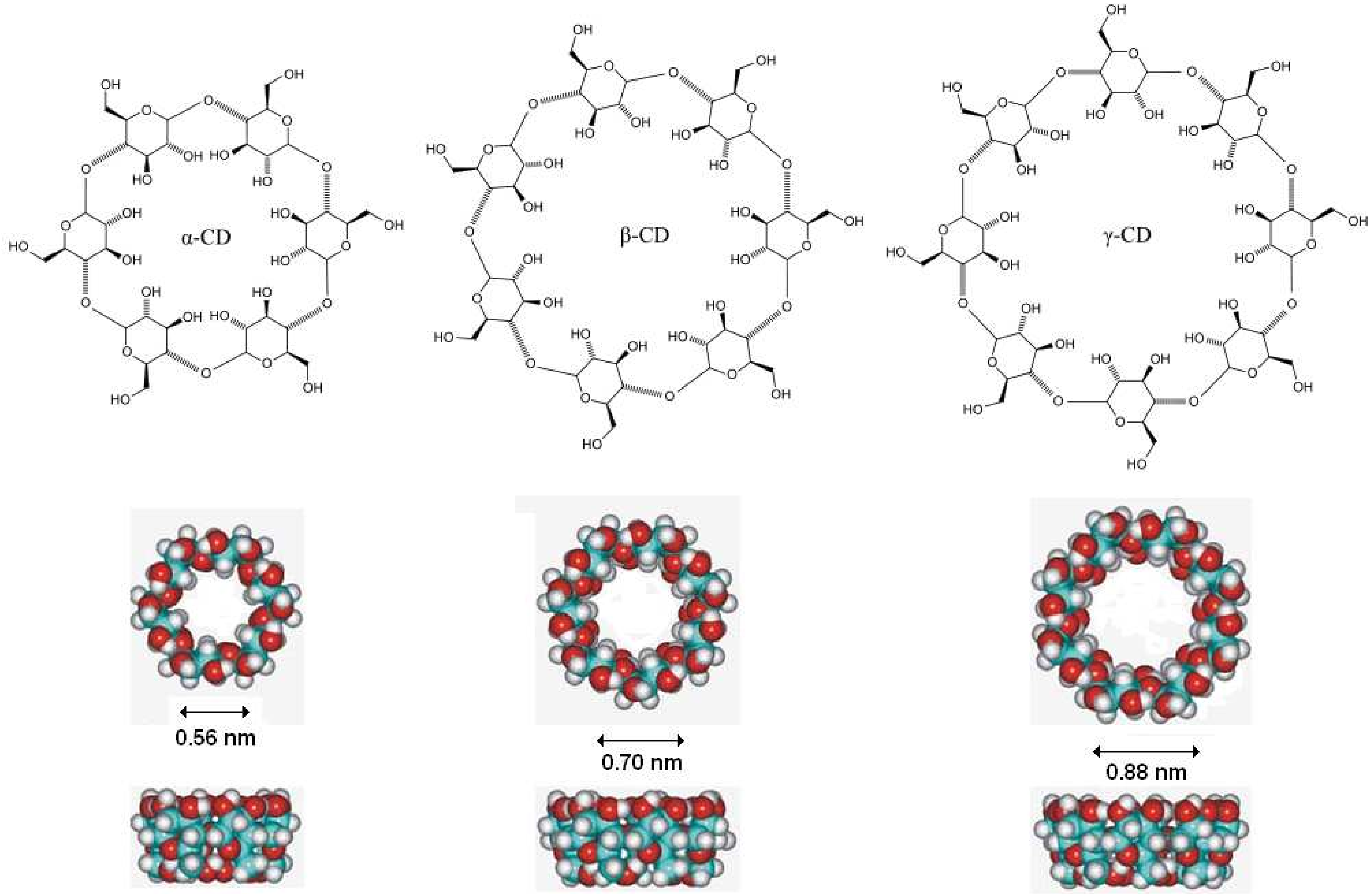
α-(1,4) glucopyranose rings



4.6 OLIGO- AND POLYSACCHARIDES

Cyclodextrins cavities

Starch degradation by Bacillus macerans



4.6 OLIGO- AND POLYSACCHARIDES
Use of cyclodextrins

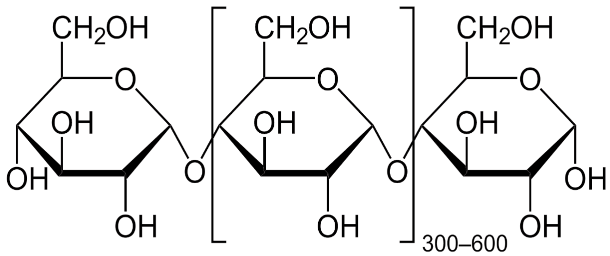
Cyclodextrins can encapsulate odorous molecules, which can

- block unpleasant smell
- control the release of aroma

4.6 OLIGO- AND POLYSACCHARIDES
Starch

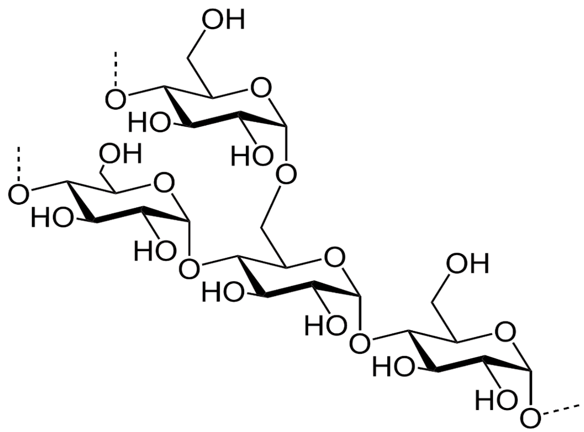
Amylose

Roughly 20-30% by weight. Linear molecules Containing 300-600 glucose units. Adopt a coiled conformation giving rise to a helix structure with 6 to 8 glucose units on each turn. Water insoluble.

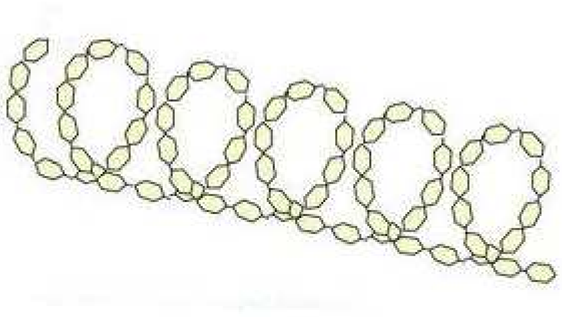


Amylopectin

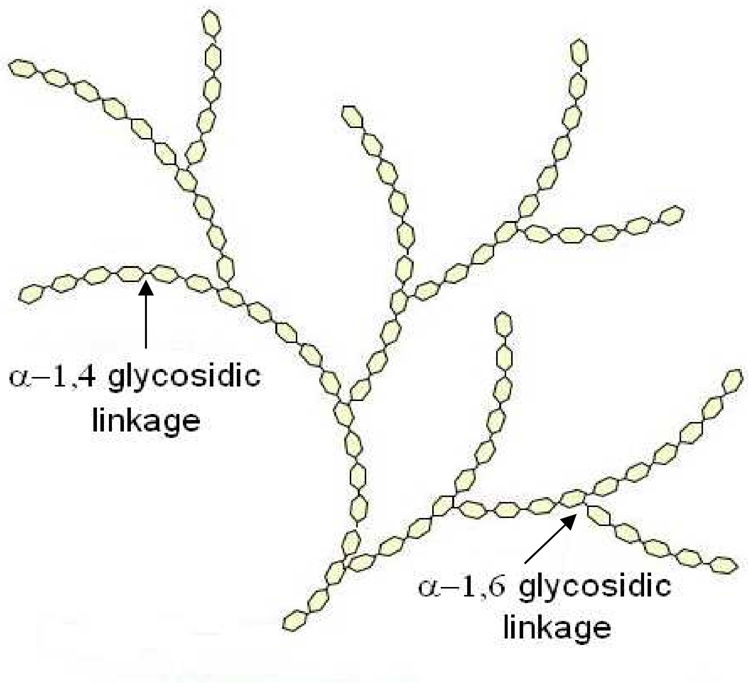
Roughly 70% by weight (up to 100% in waxy rice or waxy starch). Molecules are highly branched, being formed of 2,000 to 200,000 glucose units. Inner-chains are formed of 20-24 glucose subunits. Water soluble.



4.6 OLIGO- AND POLYSACCHARIDES
Amylose and amylopectin



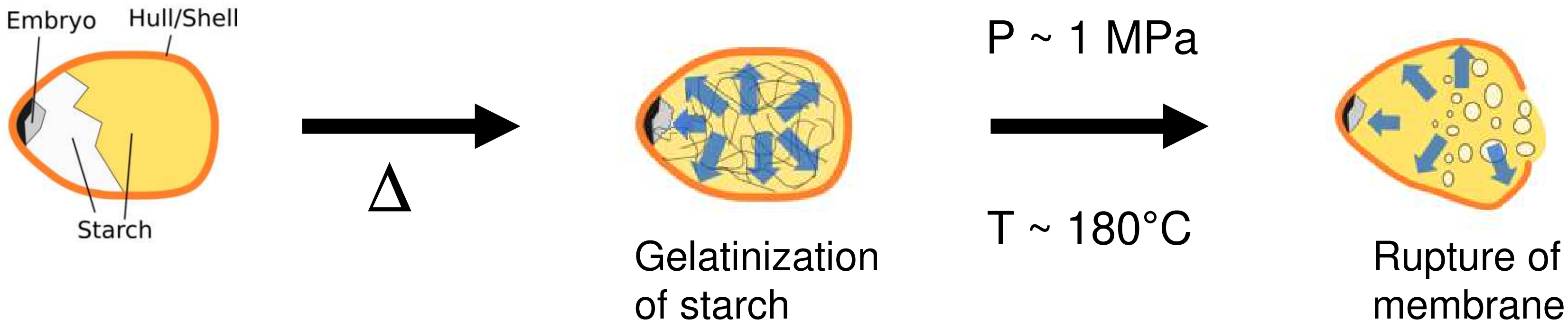
Amylose



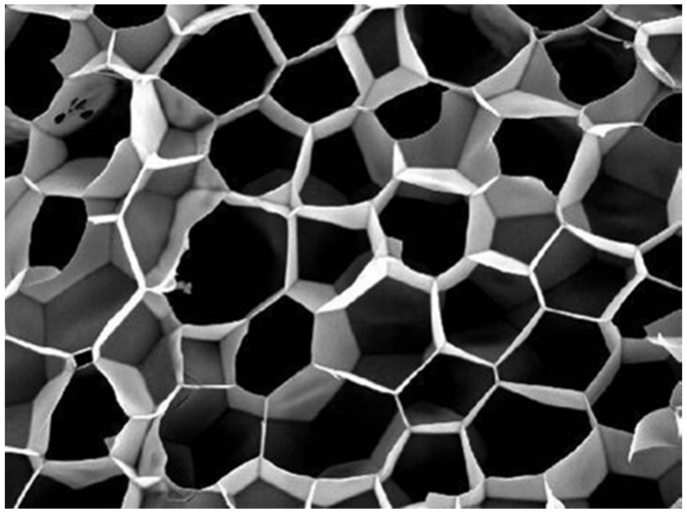
Amylopectin

4.6 OLIGO- AND POLYSACCHARIDES

The physico-chemistry of pop-corn



Scanning electron microscopy of pop corn slice



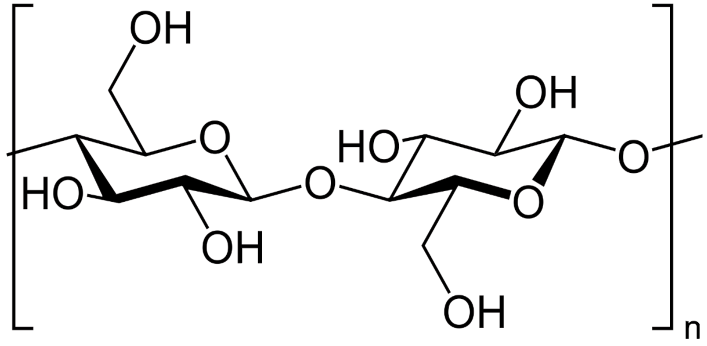
4.6 OLIGO- AND POLYSACCHARIDES
Modified starches used in the food industry

- E1400 dextrin, roasted starch with hydrochloric acid
- E1402 alkaline-modified starch, treated with KOH or NaOH
- E1403 bleached starch, treated with hydrogen peroxide
- E1404 oxidized starch, treated with sodium hypochlorite
- E1412 distarch phosphate, esterified with H_3PO_4
- E1413 phosphated distarch phosphate
- E1420 acetylated starch, esterified with acetic anhydride
- E1440 hydroxypropylated starch, treated with propylene oxide
- E1442 hydroxypropyl distarch phosphate
- E1450 octenyl succinic anhydride starch
- E1451 acetylated oxidized starch
- Maltodextrin, enzyme-treated starch
- Glucose syrup, enzyme treated starch

4.6 OLIGO- AND POLYSACCHARIDES

Cellulose

Cellulose is a linear chain of several hundred to over ten thousand β (1→4) linked D-glucose units.



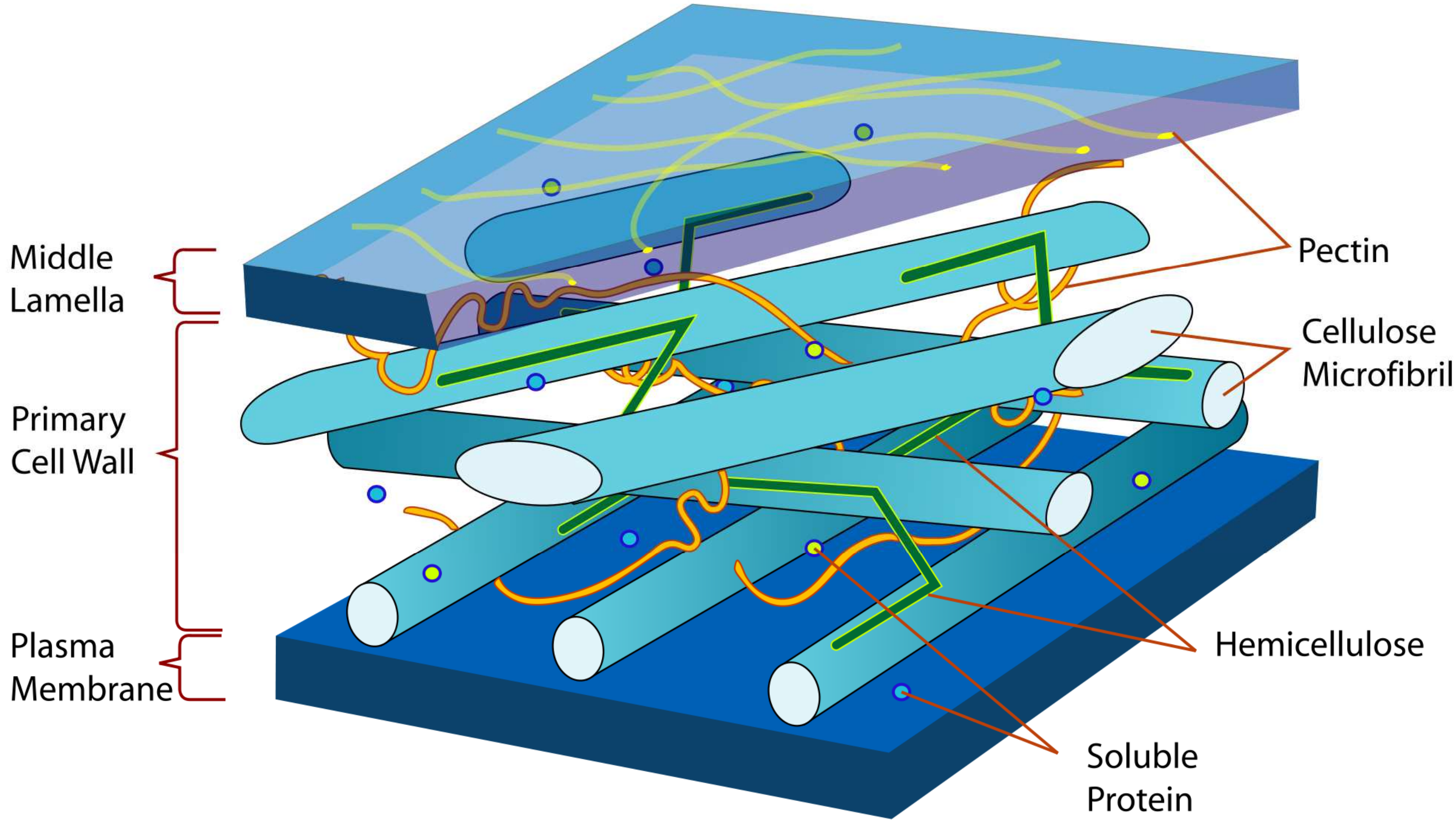
Cellulose is the main component of the cell walls of green plants. It is the most common organic compound on Earth.

Pure cellulose can be obtained by dissolving plant fibers in acetic and nitric acid to remove lignin, hemicellulose, and xylosans.

The portion that does not dissolve in a 17.5 % solution of sodium hydroxide at 20 °C is α cellulose. Acidification of the extract precipitates β cellulose. The portion that dissolves in base but does not precipitate with acid is γ cellulose.

4.6 OLIGO- AND POLYSACCHARIDES

Cellulose and cell-wall structure

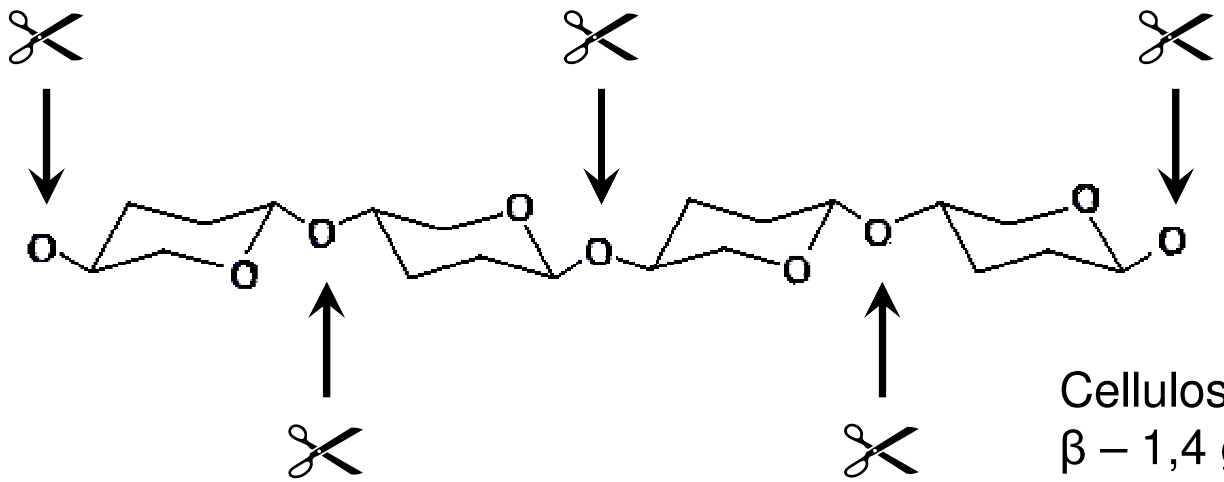


4.6 OLIGO- AND POLYSACCHARIDES
Modified celluloses used in the food industry

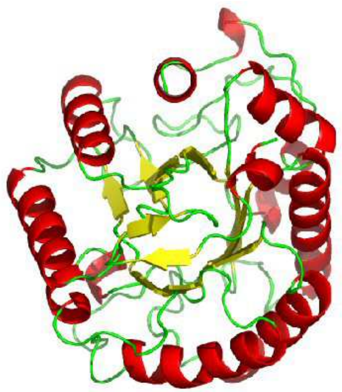
- E460(i) Microcrystalline cellulose
- E460(ii) Cellulose powder
- E461 Methylcellulose
- E462 Ethylcellulose
- E463 Hydroxypropylcellulose
- E464 Hydroxypropylmethylcellulose
- E465 Ethylmethylcellulose
- E466 Carboxymethylcellulose

4.6 OLIGO- AND POLYSACCHARIDES

Degradation of cellulose



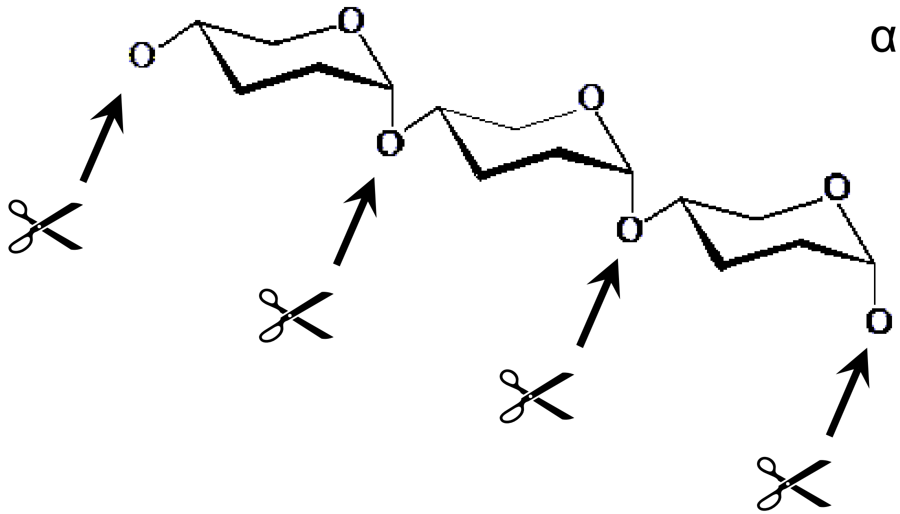
Cellulose :
β – 1,4 glucose chain



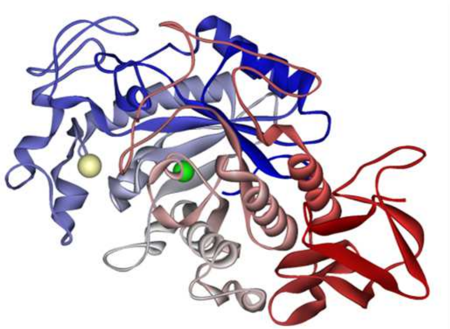
Cellulase (mushrooms, bacteria)

4.6 OLIGO- AND POLYSACCHARIDES

Digestion of starch



Amylose :
α – 1,4 Glucose chain



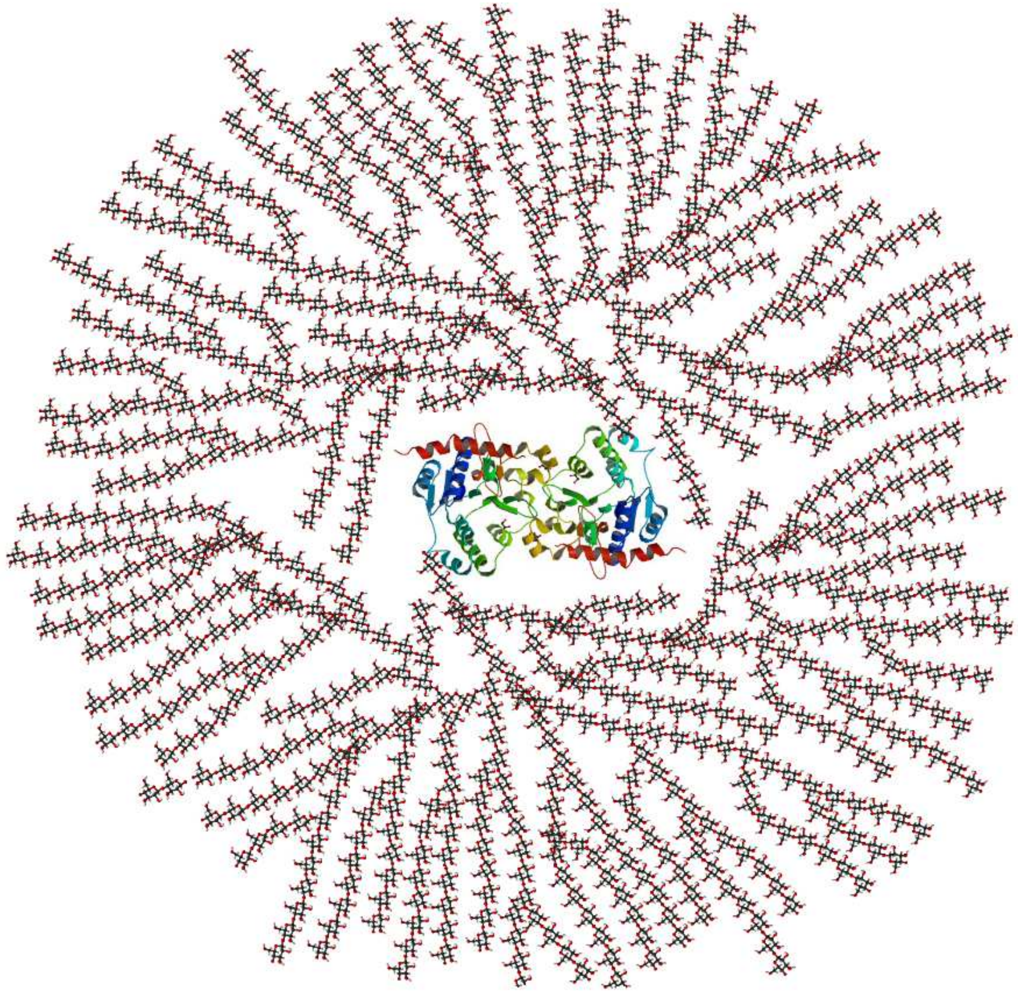
Amylase (saliva, pancreatic juice)

4.6 OLIGO- AND POLYSACCHARIDES

Glycogen

Energy storage in animals and fungi

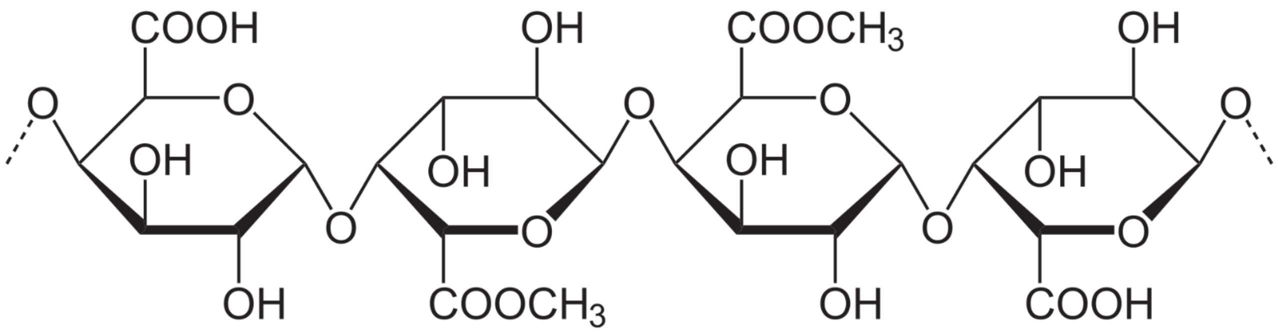
Insulin stimulates the action of several enzymes, including glycogen synthase. Glucose molecules are added to the chains of glycogen as long as insulin and glucose remain plentiful.



Glycogenin enzyme surrounded by highly branched glucose units

4.6 OLIGO- AND POLYSACCHARIDES
Derivatized polysaccharides

Pectin



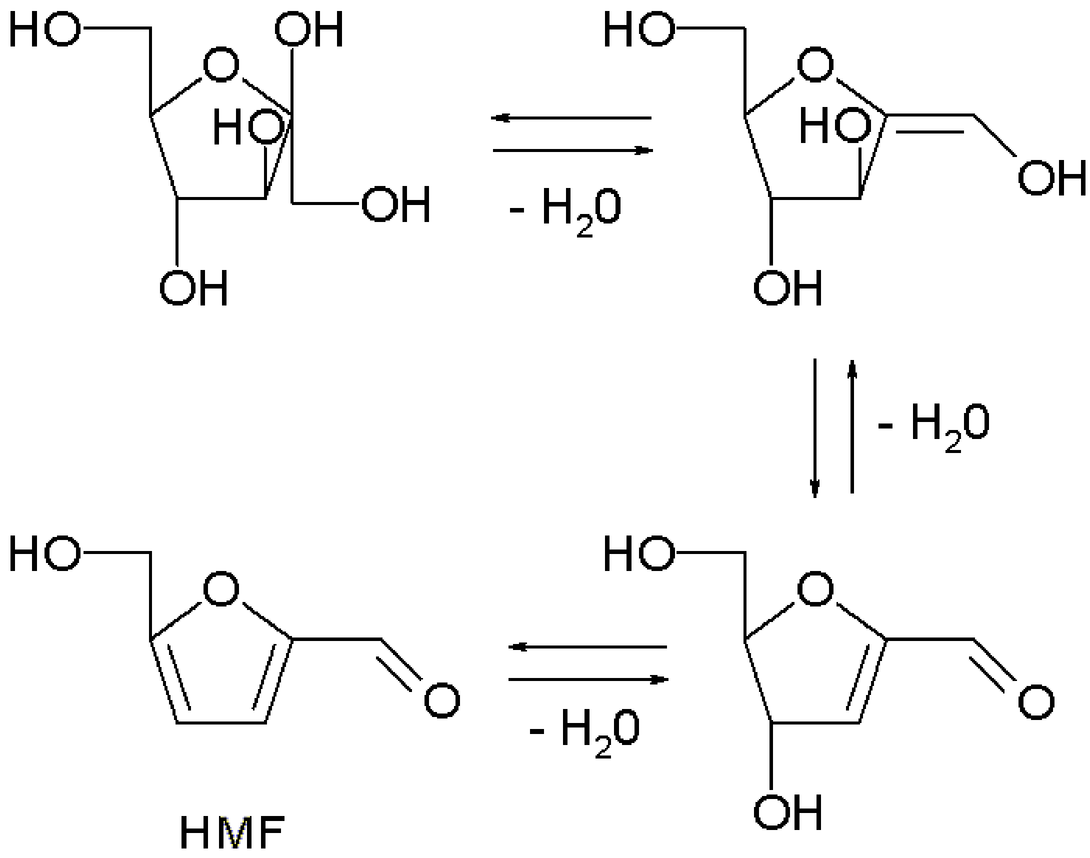
Partially methylated 1,4-polygalacturonic acid

Gelling agent found in vegetal cell walls (apple peels ans seeds)

Its chelating properties have been used to prevent ^{134}Cs and ^{137}Cs irradiations

4.7 THERMAL REACTIONS

Dehydration of fructose yielding hydroxy-methyl-furan



4.7 THERMAL REACTIONS
Caramelization reactions E-150

Caramelans

$$2\ C_{12}H_{22}O_{11} \longrightarrow C_{24}H_{36}O_{18} + 4\ H_2O$$

Caramelens

$$3\ C_{12}H_{22}O_{11} \longrightarrow C_{36}H_{50}O_{25} + 8\ H_2O$$

Caramelins

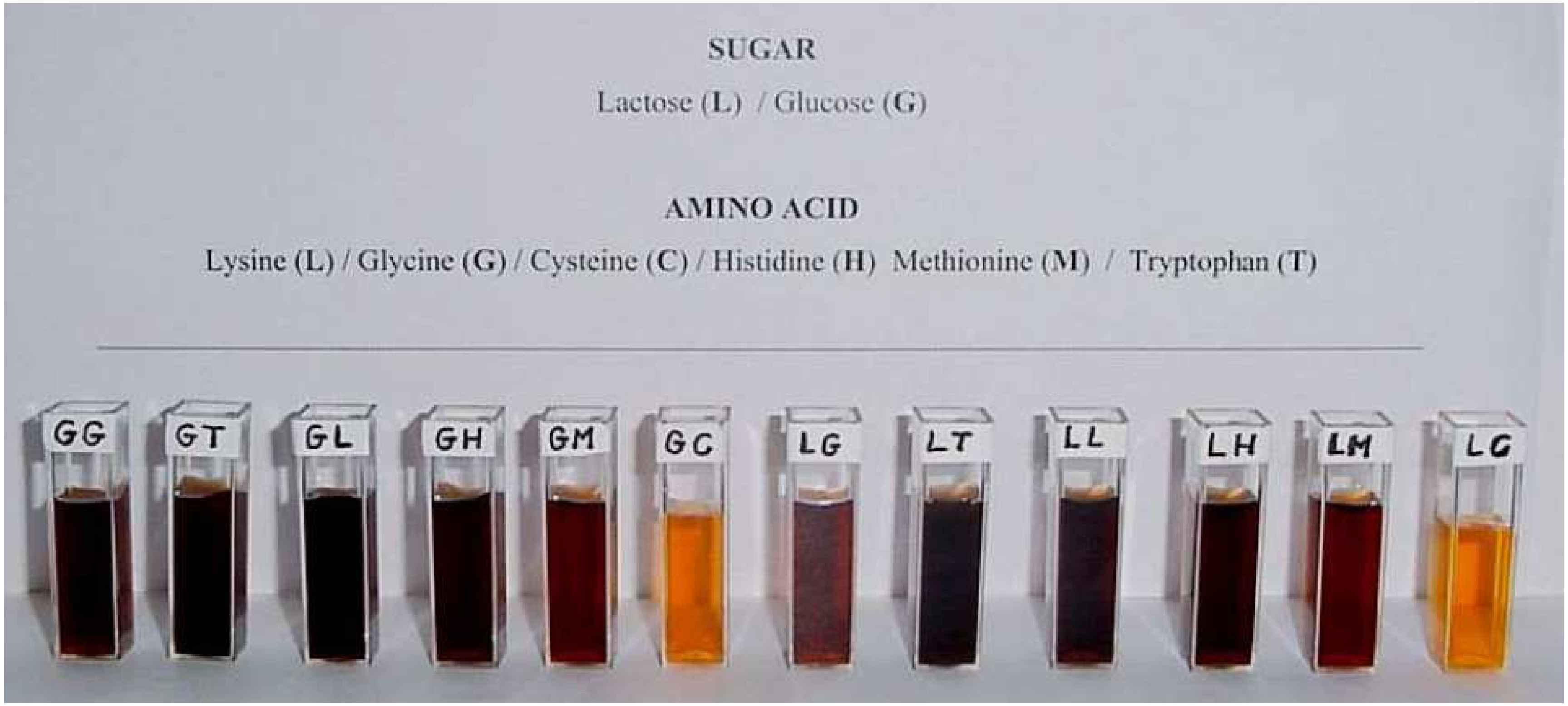
Condensations yielding polymers of mean formula

$C_{125}H_{188}O_{80}$

4.8 MAILLARD REACTION
Louis-Camille Maillard (1878 – 1936)

Thesis (1913)
Action of Glycerol and Sugar on the amino Acids : Cyclo-glycyl-glycine, Polypeptides, Melanoidins and humic Substances.

4.8 MAILLARD REACTION
Model mixtures of the Maillard reaction



4.8 MAILLARD REACTION

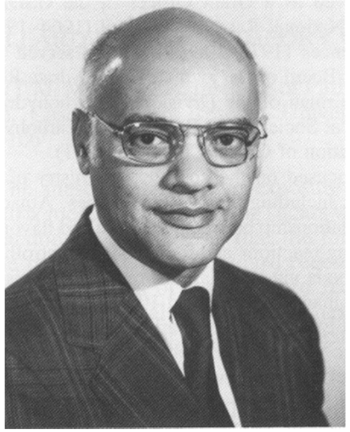
Aromas of reactions between glucose and amino acids

Amino acid	***Colour***	***Aroma***
Alanine	Brown	Fruity (persimmon)
Aspartic acid	Very light brown	Fruity (fresh dates)
Glycine	Brown	Caramel
Leucine	Brown	Burnt
Methionine	Brown	Fried potatoes, prawn cracker
Phenylalanine	Dark yellow	Flowery (dried roses)

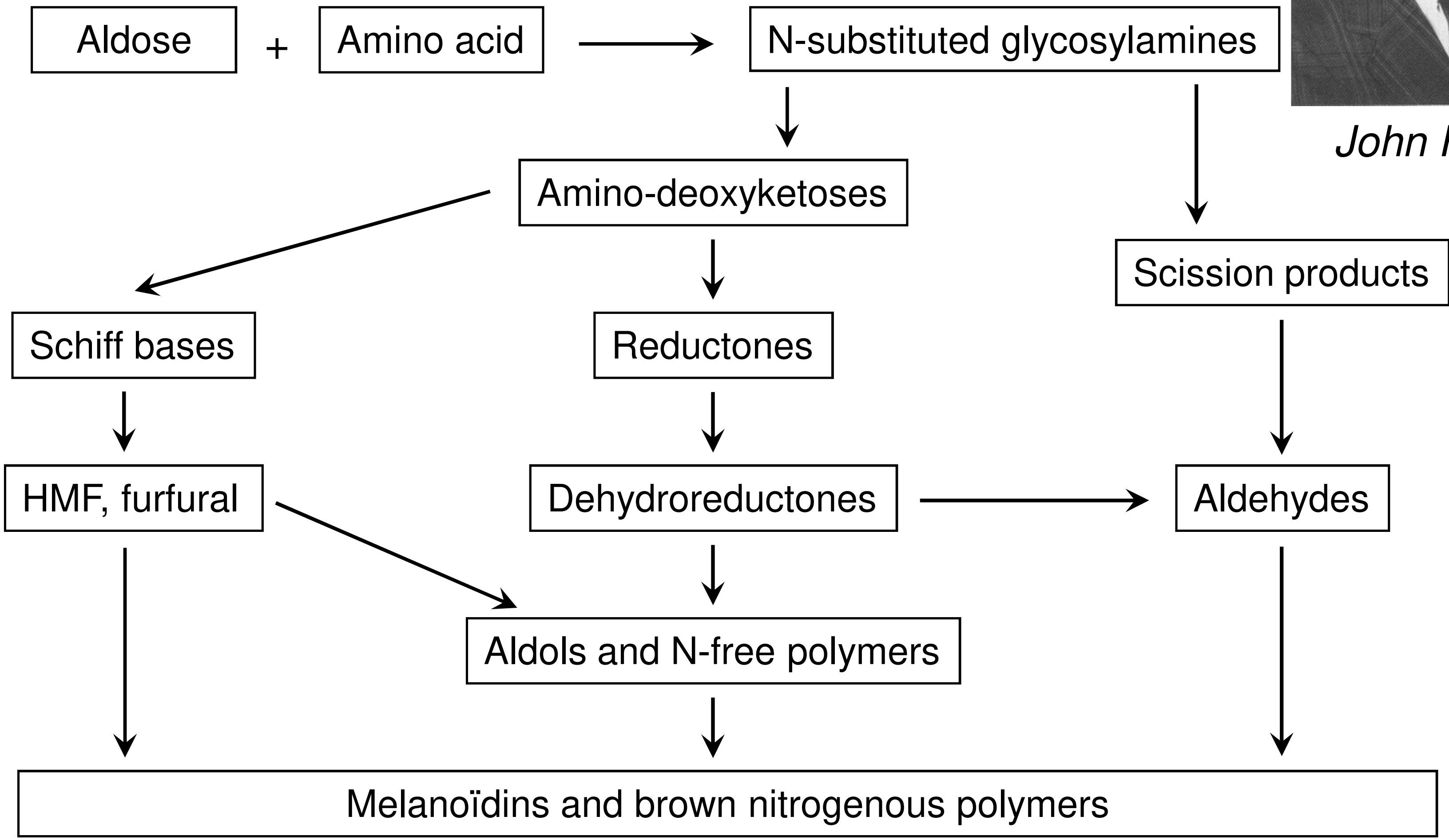
Conditions : D-glucose 20 mmol/l + AA 3 mmol/l at 100°C during 14 h

4.8 MAILLARD REACTION

The « non-enzymatic browning »

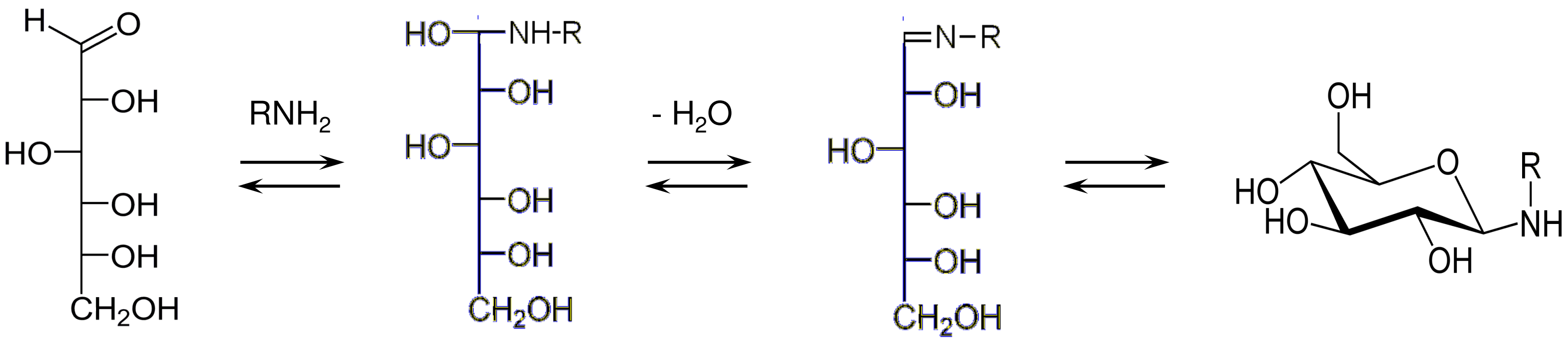


John Hodge



4.8 MAILLARD REACTION

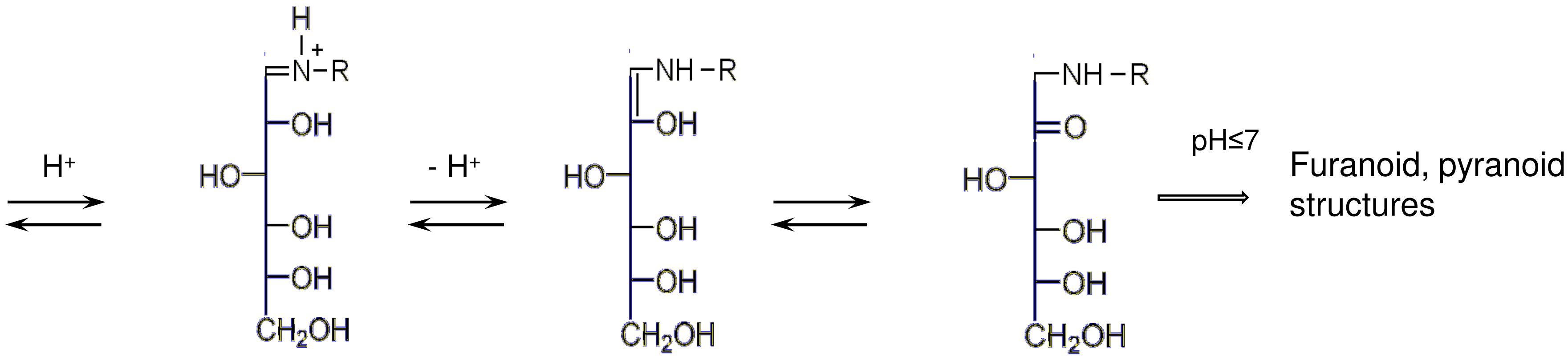
Formation of Amadori compounds (aldosylamine reactions)



Glucose

Schiff base (imine)

N-glycosylamine



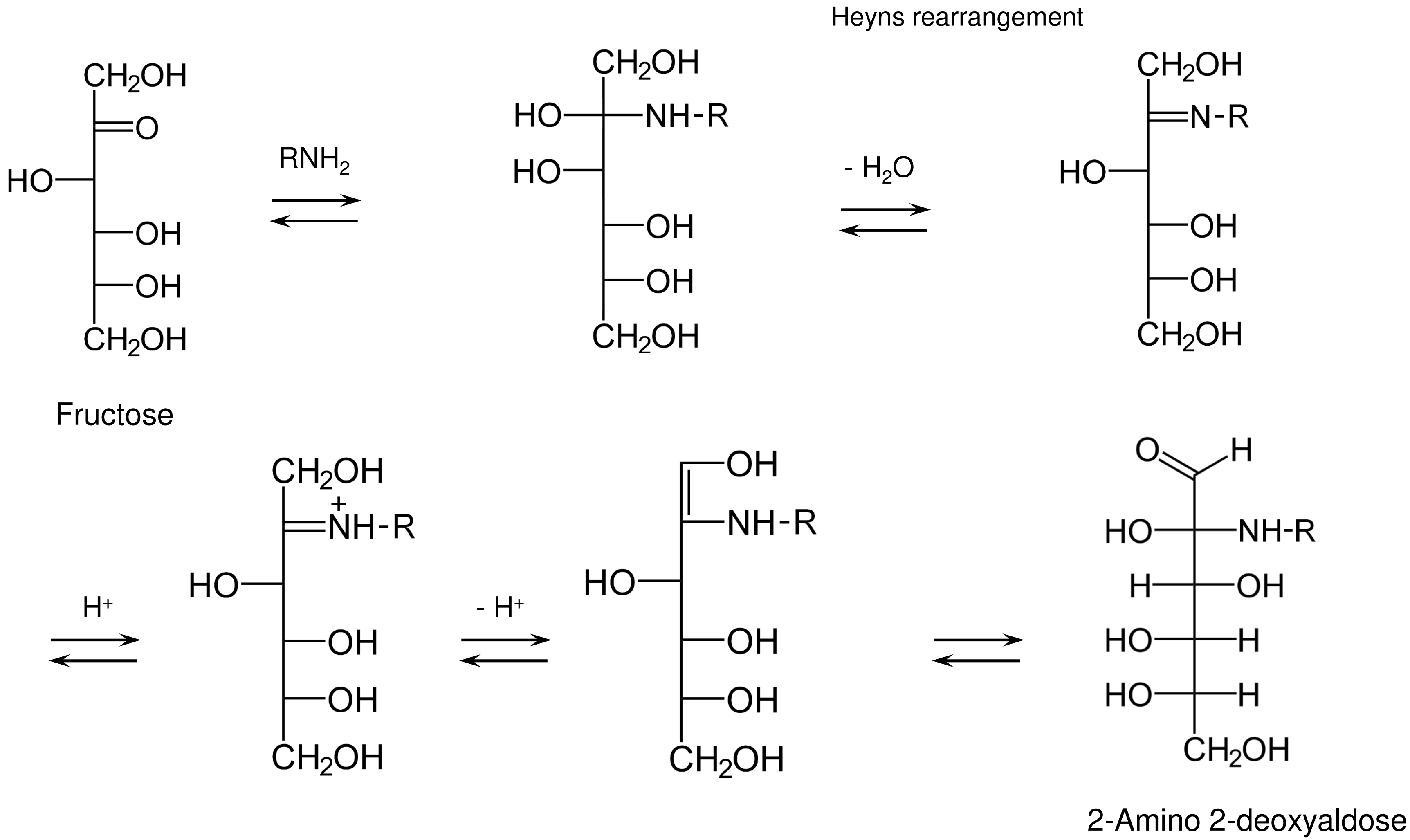
Amadori rearrangement

Eneaminol

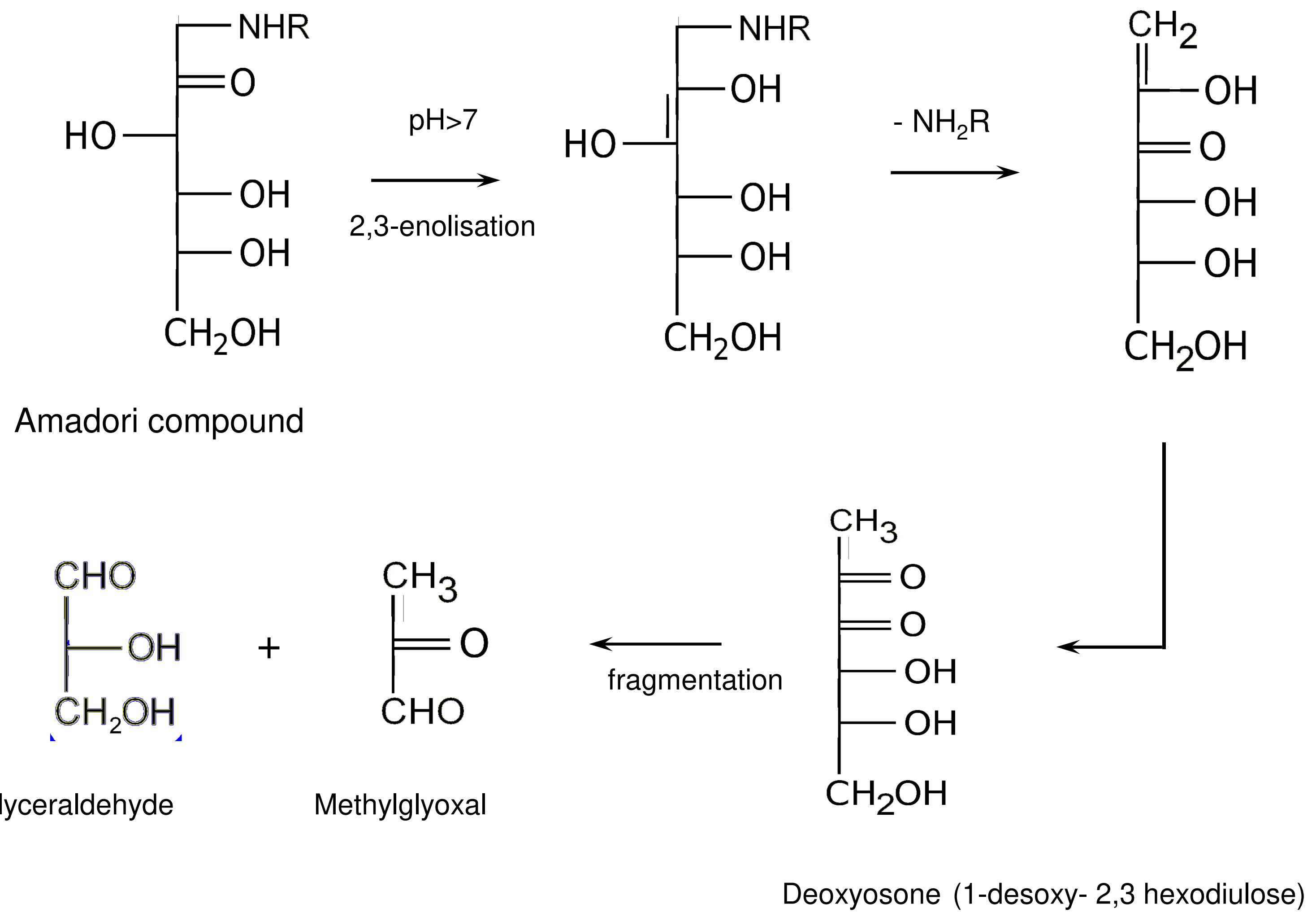
Amadori compound (1-amino 1-deoxycetose)

4.8 MAILLARD REACTION

Formation of Heyns compounds (ketosylamine reactions)

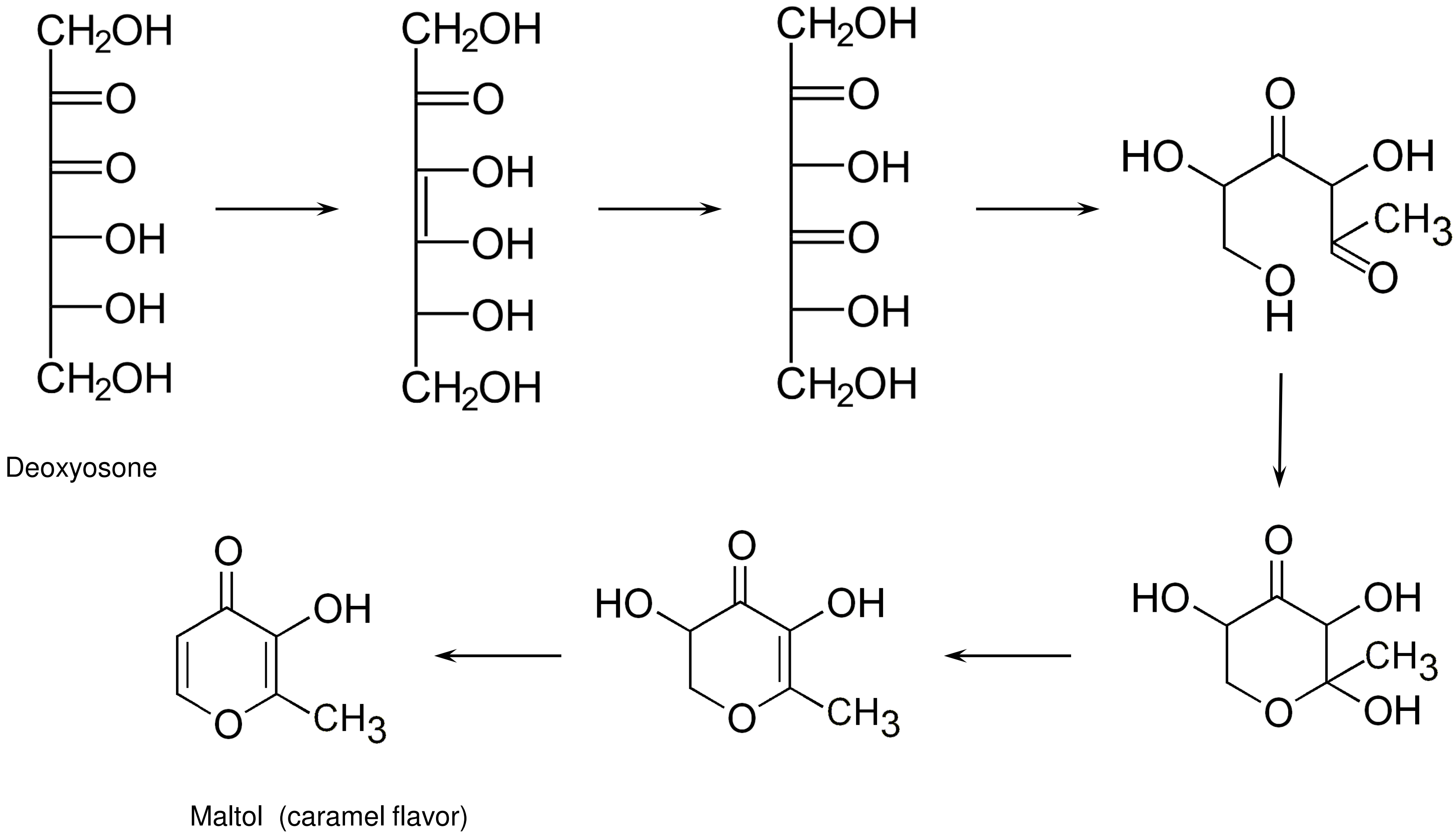


4.8 MAILLARD REACTION
Formation of aldehydes



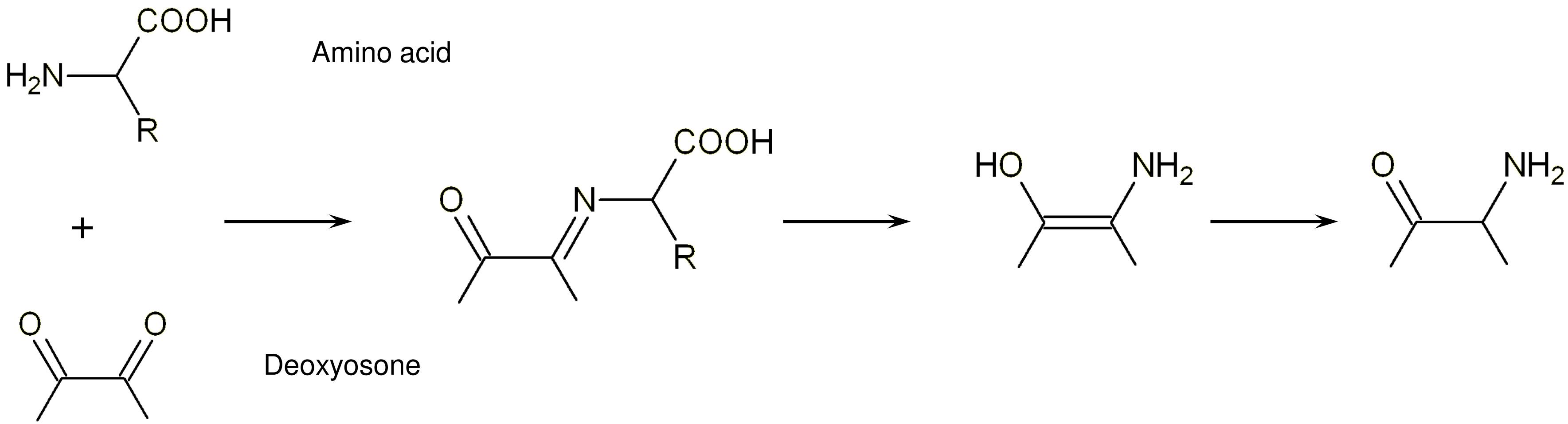
4.8 MAILLARD REACTION

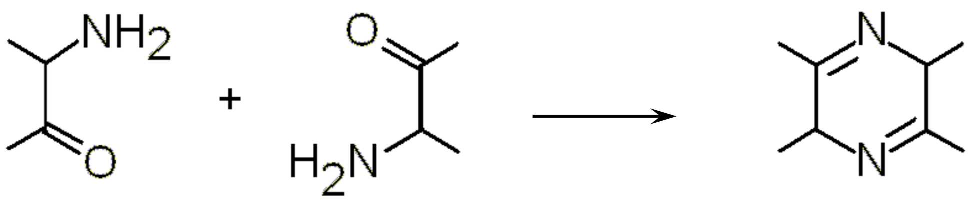
Cyclisation of deoxyosones



4.8 MAILLARD REACTION

Strecker degradation *(volatile flavour compounds)*





Pyrazine

4.8 MAILLARD REACTION

A review of Maillard reaction in food and implications to kinetic modelling

Trends in Food Science & Technology 11 (2001)364–373

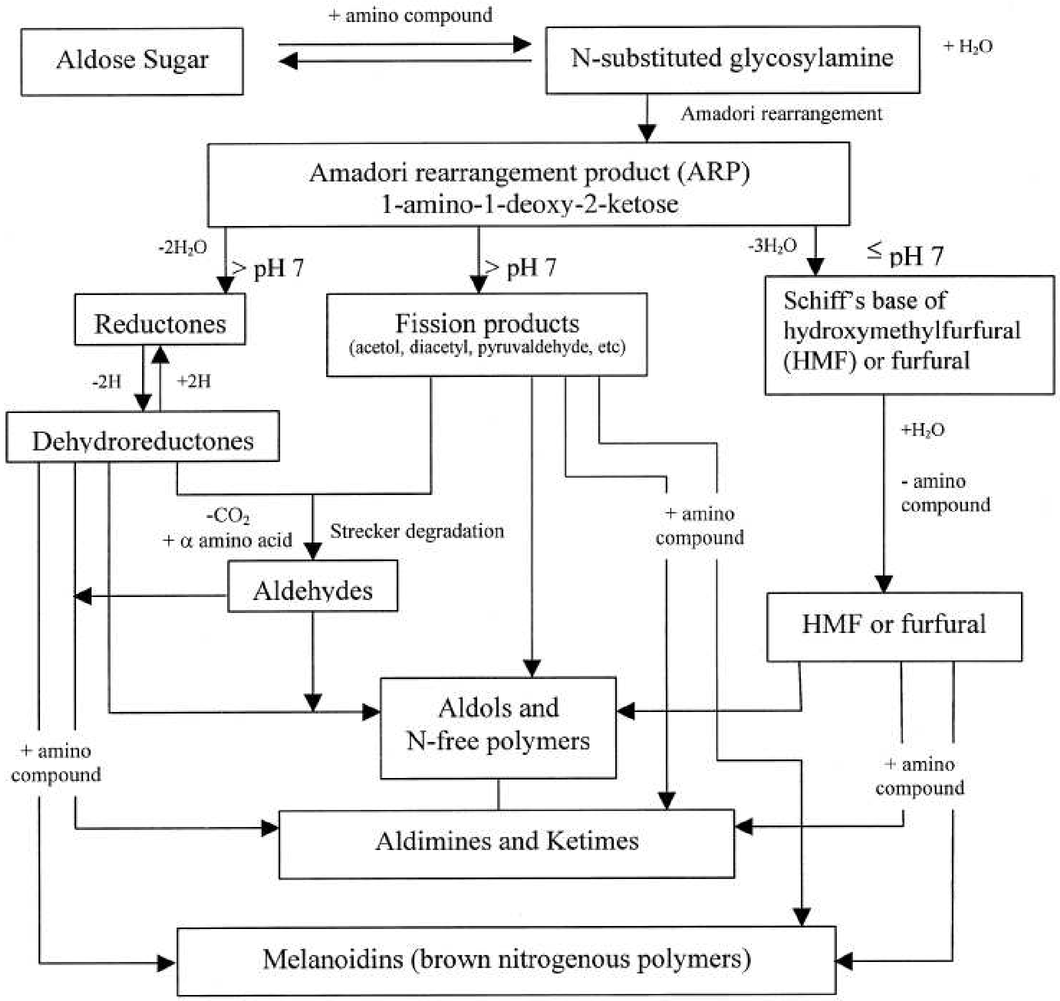


Figure 1. Maillard reaction scheme adapted from Hodge [1].

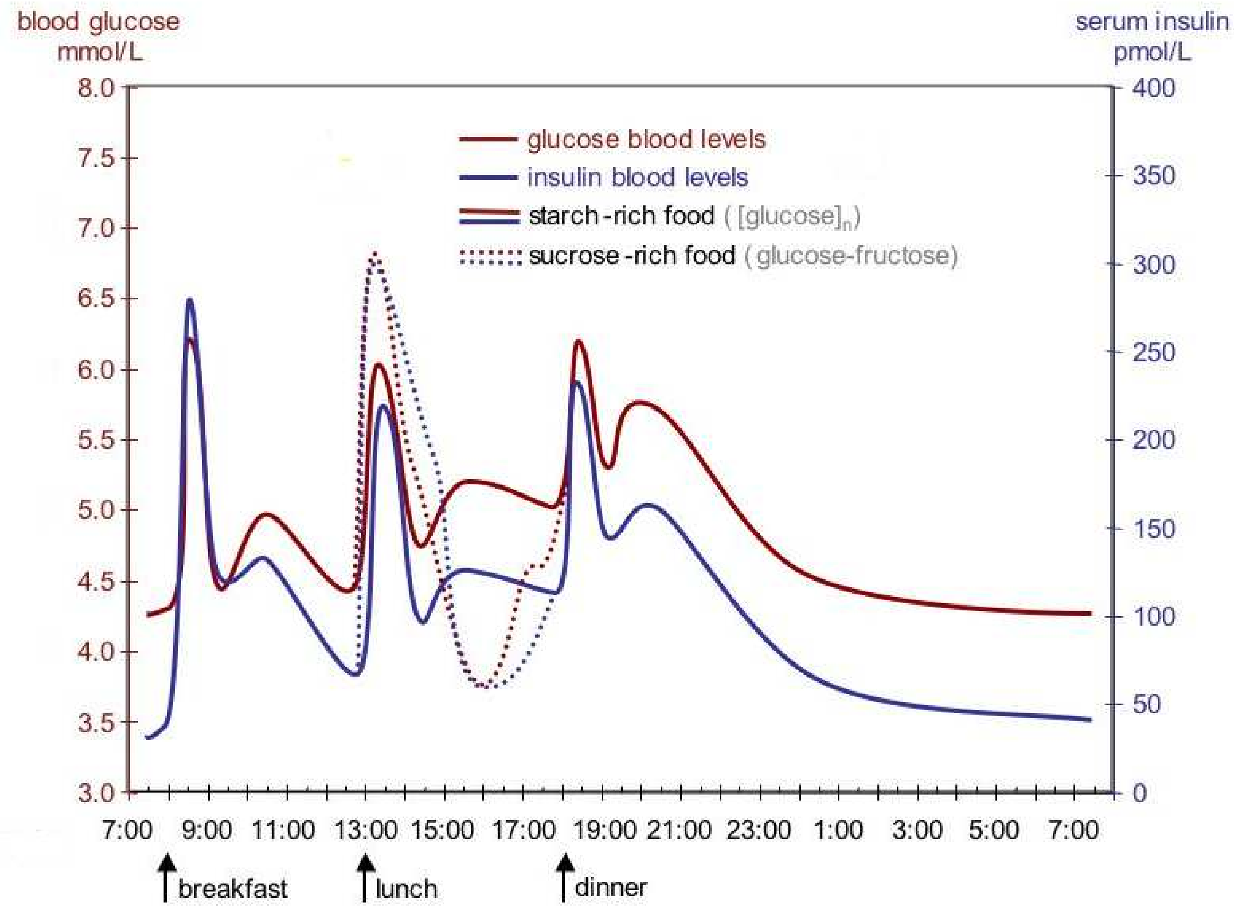
4.9 NUTRITIONAL ASPECTS

Relative sweetness of carbohydrates

Sugar	***Sweetness***
Fructose	114
Saccharose	100
Glucose	69
Galactose	63
Maltose	46
Lactose	39

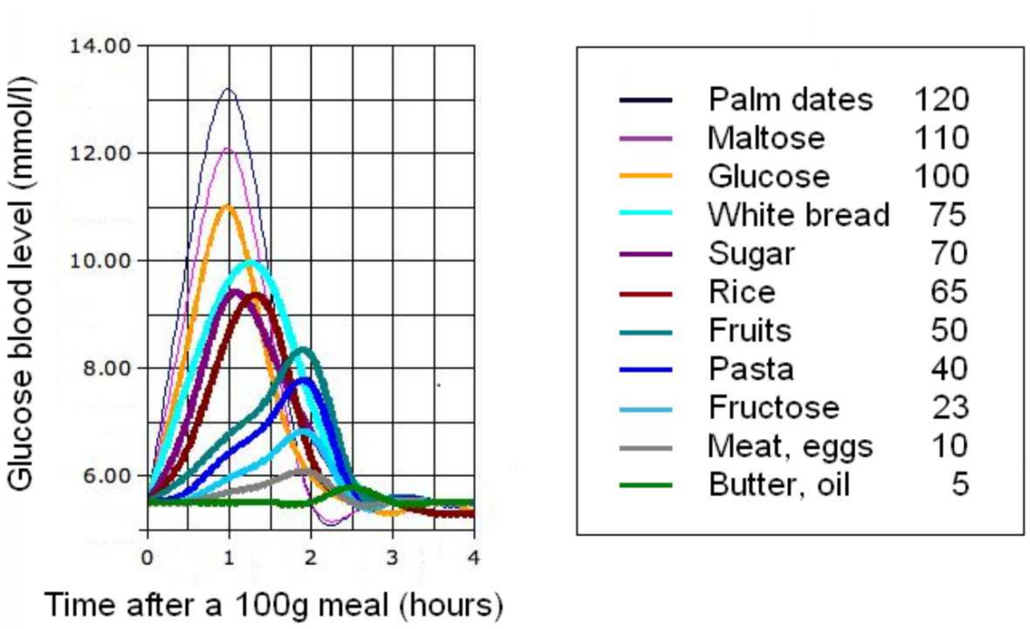
4.9 NUTRITIONAL ASPECTS

Glucose blood levels after meals



4.9 NUTRITIONAL ASPECTS

Glucose blood levels and glycemic index (GI)



$$\text{Glycemic index (x)} = \Sigma_{x} / \Sigma_{glucose} * 100$$

how quickly the levels of glucose in the blood are expected to rise after consuming different of type of food

4.9 NUTRITIONAL ASPECTS

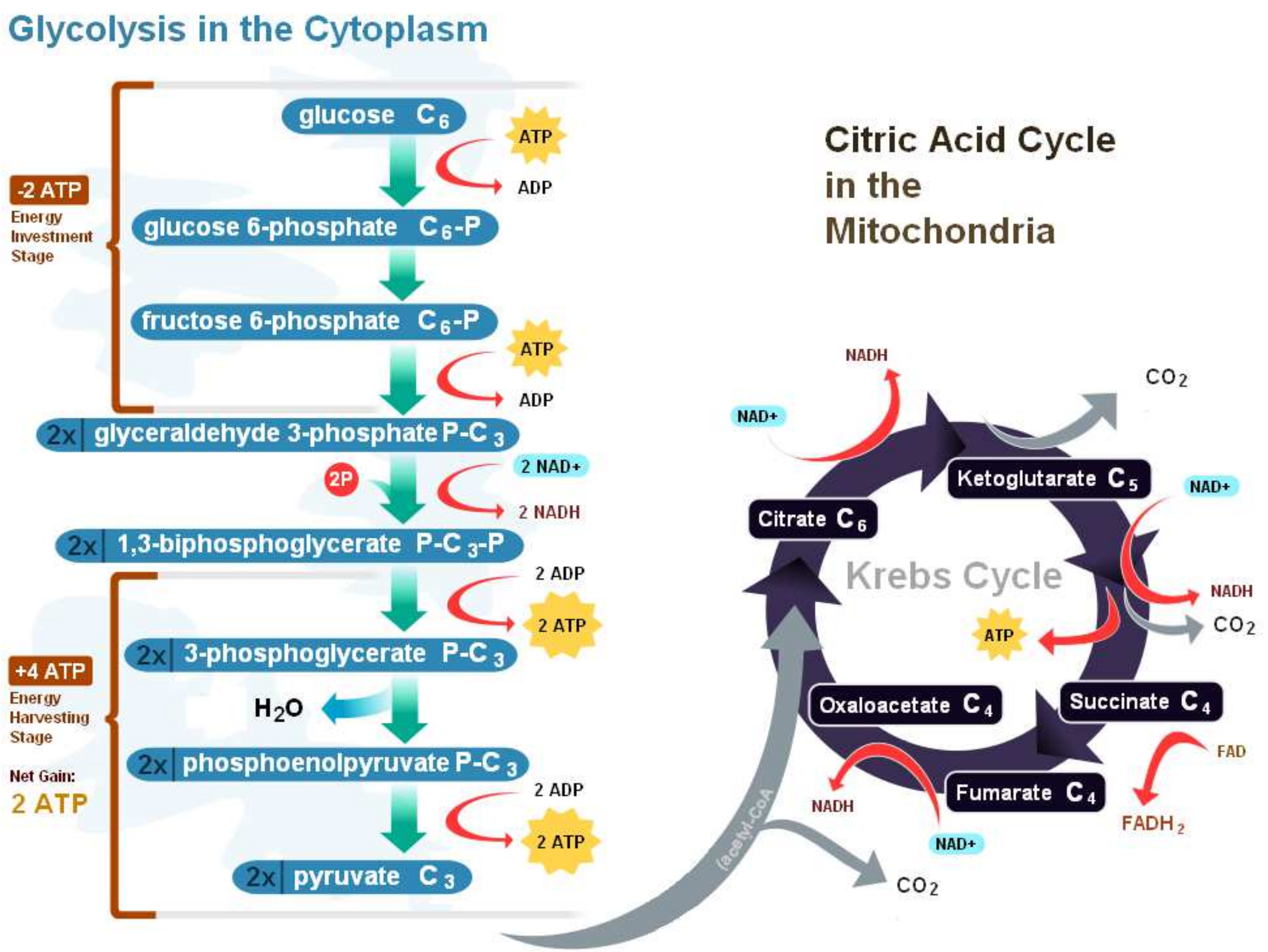
Glycemic load (GL)

Glycemic load = Glycemic index * carbohydrate contents per portion / 100

Product	***Glycemic Index***	***Portion (g)***	***Carbohydrate contents (g)***	***Glycemic load***
White bread	70	40	20	14
Bananas	50	100	24	12
Carrots	42	80	3	1.3
Potatoes	83	150	23	19
Watermelon	75	120	9	7

GL: measures the amount of carbohydrates in a serving of food.

4.9 NUTRITIONAL ASPECTS
Glucose metabolism



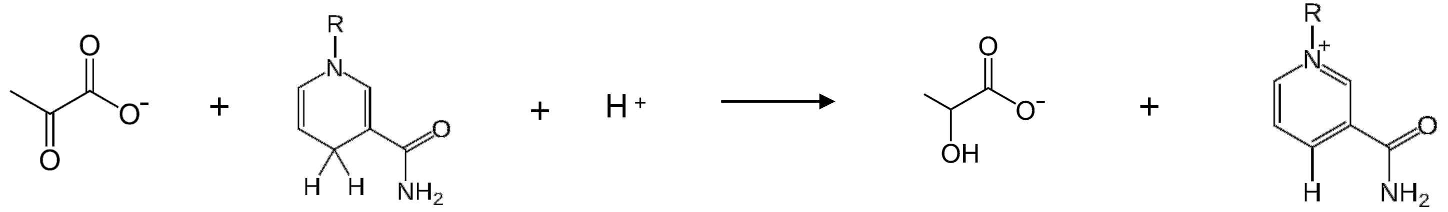
4.9 NUTRITIONAL ASPECTS

Overall glucose oxydation

Glycolysis

$C_6H_{12}O_6 + 2\ NAD^+ + 2\ ADP + 2\ H_3PO_4 \rightarrow 2\ CH_3COCOOH + 2\ NADH + 2\ H^+ + 2\ ATP + 2\ H_2O$

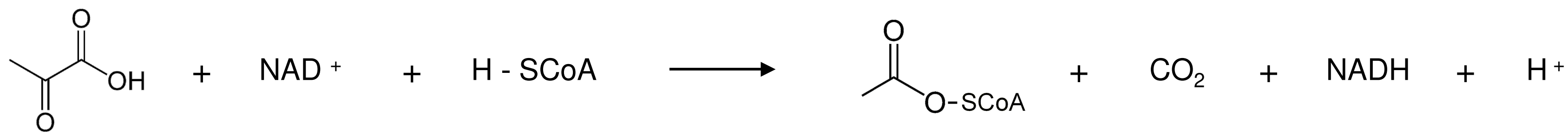
Anaerobiosis



pyruvate

Lactic acid

Aerobiosis



4.9 NUTRITIONAL ASPECTS
Dietary fibers

Edible parts of plants or similar carbohydrates resistant to digestion and absorption in the human small intestine with complete or partial fermentation in the large intestine. They are usually not « fibers » !

Cellulose

Hemicellulose (cellulose with random, amorphous structure)

β-Glucans (polysaccharides consisting of glucose units linked by β (1,3) and β (1,4) bonds

Pectins (polysaccharides that contain β (1,4) linked α-D-galactosyluronic acid residues)

Inulins (polysaccharides with 100 to 6'000 fructose units joined by a β (2,1) glycosidic bond)

Fructooligosaccharides (polymer of 20 - 60 fructose units with a terminal glucose)

4.9 NUTRITIONAL ASPECTS

Health effects of dietary fibers

Functions	***Benefits***
Increases food volume without increasing caloric content, providing satiety	May reduce appetite
Attracts water and turns to gel during digestion, trapping carbohydrates and slowing absorption of glucose	Lowers variation of blood sugar levels
Lowers total and LDL cholesterol	May reduce risk of heart disease
Regulates blood sugar	May reduce risk of metabolic syndrome and diabetes
Balances intestinal pH and stimulates intestinal fermentation and production of short-chain fatty acids	May reduce risk of colorectal cancer

4.10 SACCHAROSE PRODUCTION

Simplified process