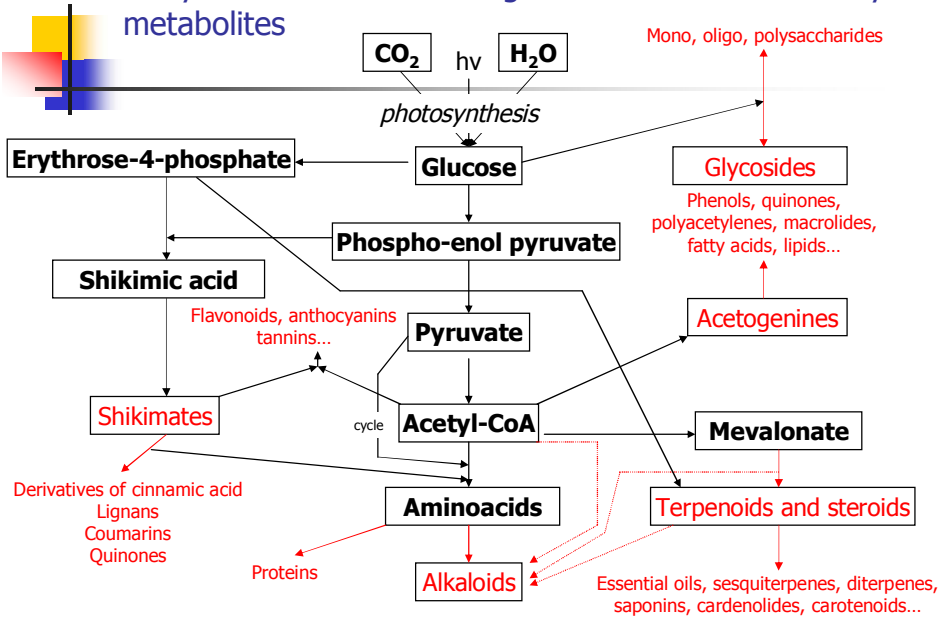
Biosynthetic relations of sugars and further secondary metabolites



SACCHARIDES – CARBOHYDRATES – SUGARS

UNIVERSAL COMPONENTS OF LIVING ORGANISMS

COMPOUNDS POSSESSING:

- CARBONYL GROUP (ALDEHYDE OR KETONE)
- MORE HYDROXYL GROUPS

CAN POSSESS

- OXIDIZED CARBONYL (URONIC ACIDS)
- REDUCED CARBONYL (POLYALCOHOLS)
- DERIVATIVES (ETHERS, ESTERS, AMINES)

FUNCTION IN PLANTS

- SUPPORTING SUBSTANCES (CELLULOSE A OTHER „BUILDING" POLYSACCHARIDES)
- ENERGY POOL (STARCH)
- PART OF DIFFERENT METABOLITES (NUCLEIC ACIDS, COENZYMES, GLYCOSIDES)
- NECCESSARY PRECURSORS OF ALL OTHER METABOLITES OF THE LIVING WORLD

CLASSICAL DIVISION

- MONOSACCHARIDES $C_n(H_2O)_n$
- (n-1) HYDROXYL GROUPS (EXCEPTION DEOXYSUGARS = (n-2))
- ALDEHYDIC or KETONE CARBONYL FUNCTION (aldoses, ketoses)
- NUMBER OF C- ATOMS 3 TO 9, MOSTLY FIVE OR SIX (tetroses, pentoses, hexoses, heptoses)
- Couplet designation – glucose = aldohexose, ribulosa = ketopentose
- Majority of natural monosaccharides belongs to D-line
- To L-line belong L-rhamnose, L-arabinose, L-fucose
- Abbreviations: glucose – Glc; fructose – Fru; arabinose – Ara; ribose – Rib; xylose – Xyl; rhamnose – Rha; galactose – Gal; manose – Man; deoxyribose – deRib; glucuronic acid – GlcUA; galacturonic acid – GalUA; gluconic acid - GlcA

CLASSICAL DIVISION

OLIGOMERIC SACCHARIDES
GLYCOSIDIC BOND BETWEEN LESS THAN 10 MONOSACCHARIDES

POLYMERIC SACCHARIDES
GLYCOSIDIC BOND BETWEEN MORE THAN 10 MONOSACCHARIDES

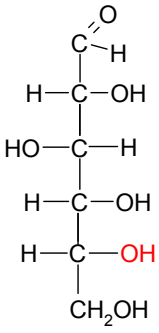
COMPOSITE SACCHARIDES
CONTAIN ALSO LIPIDIC, PROTEIN, PEPTIDES

GLYCOSIDES (-O; -N; -S; -C)

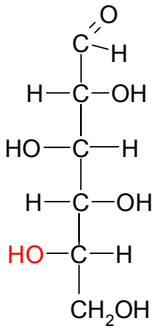
USAGE

- MONOSACCHARIDES AND OLIGOSACCHARIDES – THERAPEUTICALLY LESS IMPORTANT
- POLYSACCHARIDES - PHARMACEUTICALLY AND INDUSTRIALLY MORE IMPORTANT, AS THE MOTHER PLANTS AND CORRESPONDING DRUGS
- MANY TIMES DIETETICS AND NUTRITIVES, LESS FOR PHARMACOLOGY EFFECTS - IMMUNOMODULANTS

CHEMISTRY OF SUGARS



D-glucose

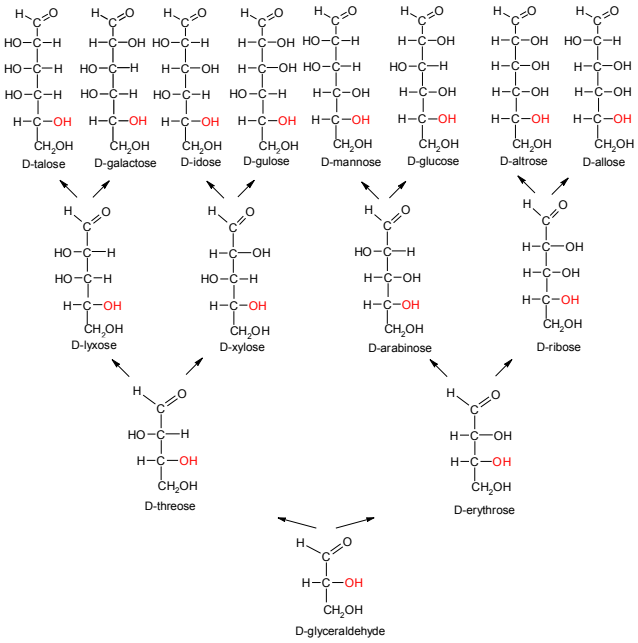


L-glucose

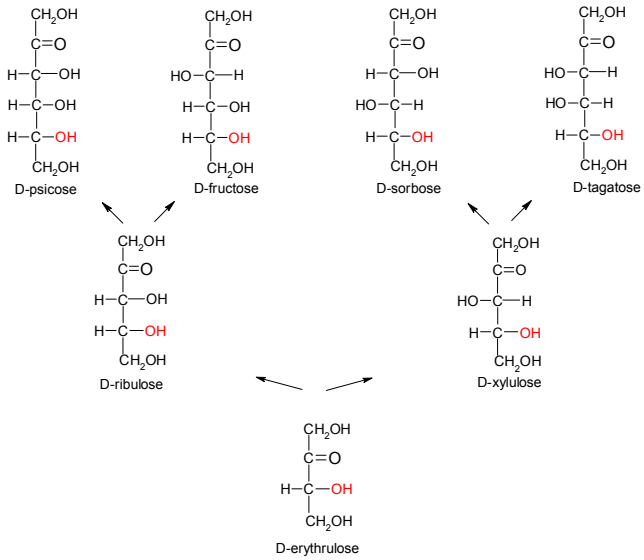
Symbols of D- and L- express absolute configuration at asymetric carbon atom furthermost from carbonyl group in Fischer projection.

Optic rotation: (+); (-)

CONFIGURATION CONNECTIONS OF D-ALDOS

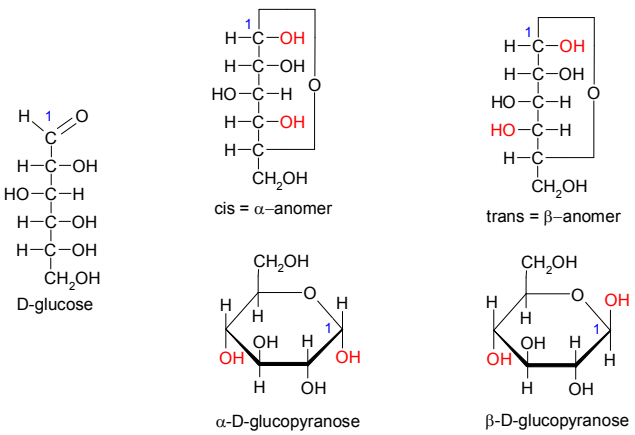


CONFIGURATION CONNECTIONS OF D-KETOSES



CHEMISTRY OF SUGARS

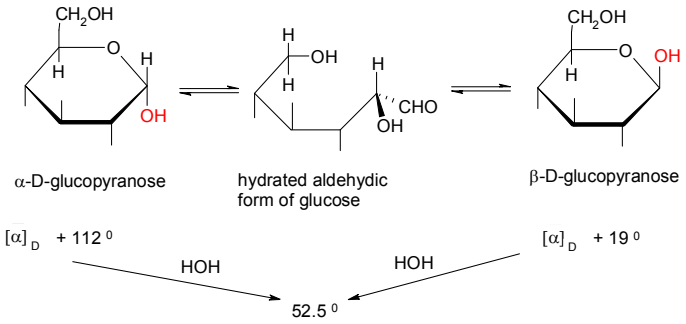
Spontanneous intramolecular addition of one from hydroxyl group (primary or secondary hydroxyl group) on a carbonyl group gives rise to cyclic poloacetals (pyranoses, furanoses). This reaction produces new chiral centre.



CHEMISTRY OF SUGARS

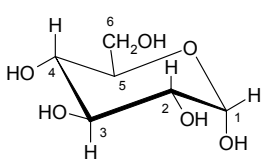
In crystal form monosaccharides exist exclusively in cyclic structures, therefore as α- or β-anomers

Mutarotation - spontanneous change of optic rotation of freshly prepared solution of stereomer.
It confirmes the occurence of sugars in cyclic form.

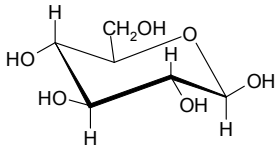


CHEMISTRY OF SUGARS

Cyclic forms of saccharides are not planar formations. Thermodynamically best conformations of pyranoses are chair conformation.



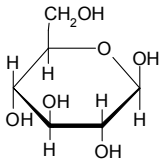
α-D-glucopyranose



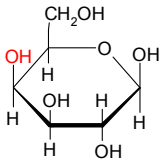
β-D-glucopyranose

CHEMISTRY OF SUGARS

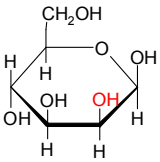
Epimers are isomers, which are different in configuration at one asymetric centre.



β-D-glucose



β-D-galactose



β-D-mannose

BASIC MONOSACCHARIDES

TETROSES

FOUR possible isomers produces two pairs of enantiomers:

- D- and L-threose
- D- and L-erythrose

They do not occure free.

- D-erythroso-4-phosphate possess key role in formation of aromatics.
- Erythrulose is formed as intermediate for example during photosynthesis

BASIC MONOSACCHARIDES

PENTOSES

- D-ribose is universal, its phosphates are metabolites of basic importance, components of nucleic acids and nucleotide coenzymes
- D-ribulose is ketopentose corresponding to ribose, P and P-P esters found during interconversion of sugars
- D-xylulose = C-3 epimer of ribulose, part of plant polysaccharides
- L-arabinose and D-xylose – usually components of complex polysaccharides, hemicelluloses, pectines and polymeric plant secrets (gummms and mucilages). Found also as sugar component of phenolic glycosides.

BASIC MONOSACCHARIDES

HEXOSES – usually ubiquitous

- D-glukose found in free form (fruits), found in polysaccharides (starch, cellulose and other glucanes); important are phosphate esters
- D-mannose = C-2 epimer of glucose, component of polysaccharides, at animals component of glycoproteins, mucopolysaccharides
- D-galactose = C-4 epimer of glucose, component of milk sugar and oligosaccharides, in agar L-galactose is present
- D-fructose (levulose); free in form of pyranose, furanoid form in oligosaccharides only (saccharose) and polysaccharides (inuline); part of honey; P-esters intermediates of glucose metabolism

SPECIFIC MONOSACCHARIDES

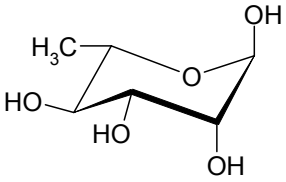
DEOXYSUGARS

- 2-deoxyribose – ubiquitous as component of DNA

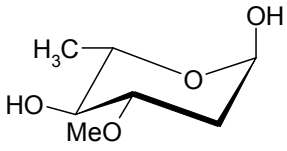
In plants as sugars, in which were one or two hydroxyl groups eliminated by reduction – part of some glycosides

- L-rhamnose (6-deoxy-L-mannose) component of heterogeneous polysaccharides nad of many glycosides
- L-fucose (6-deoxy-L-galactose) as component of Phaeophyceae algae polymers and chosen gums (Tragacanta)
- D-quinovose (6-deoxy-D-glukosae sugar part of triterpenoid saponine present in *Cinchona*
- Some 6-deoxyhexosyes in form of methylethers are specific in cardioactive glycosides, for example L-thevetose (= 6-deoxy-3-O-methyl- L-glucose) and D-digitalose (6-deoxy-3-O-methyl-D-galactose)

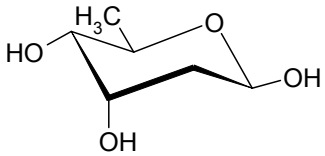
SPECIFIC MONOSACCHARIDES



α-L-Rhamnose



α-L-Oleandrose



β-D-Digitoxose

URONIC ACIDS

HEXOSES → SPECIFIC DEHYDROGENASES → CH_2OH → -COOH

- D-GLUCURONIC ACID
- D-GALAKTURONIC ACID

↓

↓

- PECTINE, GUMS

POLYALCOHOLS

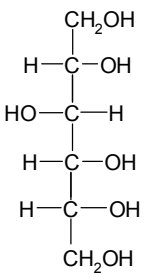
CARBONYL FUNCTION OF MONOSACCHARIDE
→ REDUCTION → POLYALCOHOL

+ 2 H in molecule

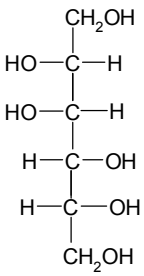
Non-reducing Fehling solution

Are not subjects of alcoholic fermentation

The most occurring are D-sorbitol a D-manitol



D-Sorbitol

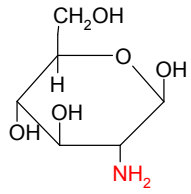


D-Manitol

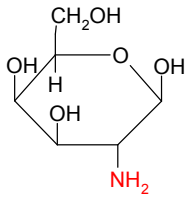
AMINOSUGARS

- BASIC COMPONENTS OF BACTERIAL POLYSACCHARIDES
- COMPONENTS ANTHRACYCLINE ANTIBIOTICS – CYTOSTATICS (Adriamycine, Daunorubicine, Aclarubicine)
- POLYMERS OF ANTHROPODS AND CRUSTACEANS (CHITINE)
- COMPONENTS OF ANIMAL GLYCOPROTEINS
- IN SOME FUNGI
- RARE IN HIGHER PLANTS

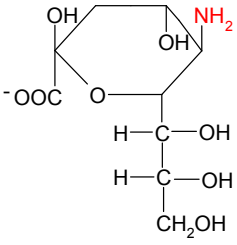
AMINOSUGARS



β-D-glucosamine
(chitosamine)



β-D-galactosamine
(chondrosamine)



neuraminic acid
membrane glycolipides
"bifidus factors"

RAMIFIED SUGARS

- OFTEN PRESENT IN FUNGI
- EXCEPTIONALLY IN HIGHER PLANTS (bonded as esters or glycosides

GLUCOSE

Prepared by enzymatic hydrolysis of starch using effect of α-amylase and amyloglucosidase

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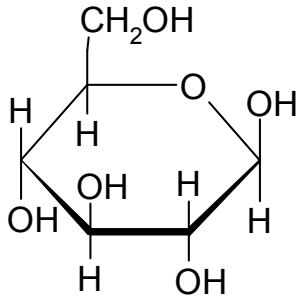
- *Glucosum anhydricum*
- *Glucosum liquidum*
- *Glucosum liquidum dispersione desiccatum*
- *Glucosum monohydricum*

Rigorous test on solubility, neutral character, absence of starch and dextrin, limit assays to detect presence of sulphides, chlorides, sulphates and Ba, As, Cd and Pb



β-D-glucose

GLUCOSE

Prepared:

- water solutions for parenteral application
- solutions for injection (5% and 10%)
- Hypertonic solutions for injection (15%, 20%, 30% and 50 %)

Used for:

- re-hydration, when loss of water is higher than loss of natrium chloride and other electrolytes
- prevention of dehydration
- prophylaxis and correction of ketosis during malnutrition
- vehicle for application of drugs in pre- or post surgery period

Solution of glucose are indifferent in caloric intake.

GLUCOSE

Solutions of glucose:

- are administered very slowly
- recommended biologic monitoring (glycosuria, acetonuria, levels of K^+ in blood)
- If necessary, supplementation of insulin and potassium

Contraindication in case of water retention.

FRUCTOSE

Prepared by hydrolysis v inuline (Asteraceae) – *Helianthus tuberosus* – topinambour, *Cichorium intybus* – chicory

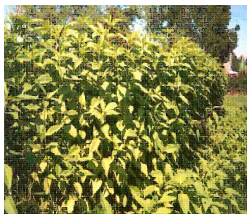
Present in all fruits and honey

Rigorous assays to control solubility, neutral character, absence of starch and dextrin, limit tests to detect presence of sulphides, chlorides, sulphates and Ba, As, Cd and Pb

Usage: ČL 2009 *Fructosum*

- parenteral nutrition
- in diet of diabetics
- Gut resorption is slow, does not trigger secretion of insuline
- metabolisms hepatal
- sweetener – 1.7 × higher sweet taste than saccharose

Helianthus tuberosus



Cichorium intybus

D-SORBITOL

Prepared via catalytic hydrogenation under high pressure or electrolytic reduction of glucose

In nature:

- fruits of Rosaceae plants – *Sorbus aucuparia* – mountain ash, European rowan
- insoles of sea algae

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- *Sorbitolum*
- *Sorbitolum 70% cristallisabile*
- *Sorbitolum 70% non cristallisabile*
- Mixtures with aliphatic acids

D-SORBITOL

Usage:

Pro infusione:

- 5% and 10% solution – for rehydration, caloric indifferent, prophylaxis of ketosis, adjuvant for drug administration

Others:

- cholagogue
- during dyspepsia and as supporting and additive remedy during constipation
- Sweetener for diabetics, metabolized to D-fructose → glycogen
- pharm. technology – regulation of humidity in powders, plasticizer of gelatin, sugar crystallization retardant
- Food industry – excellent solubility, hygroscopic, non cariogenic, does not undergo microbial degradation
- EU code: E420

D-MANNITOL

Prepared *via* D-glucose epimerization under alkaline conditions and following catalytic or electrolytic reduction

In nature:

- Manna (*Fraxinus ornus* – manna ash, Oleaceae)
- Insoles of brown algae (*Laminaria*)

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- Mannitolum

D-MANNITOL

Usage:

Pro infusione:

- intravenous 10% or 20% solution slowly administered during oligouria and anuria, diuretic – very difficult to metabolize – when parenteraly administered rapid glomerular filtration and no tubular resorption

Others

- per os – cholecystokinetic, laxative
- preparation of patient for colonoscopy
- Food industry
- EU code: E421

MANNA - MANA

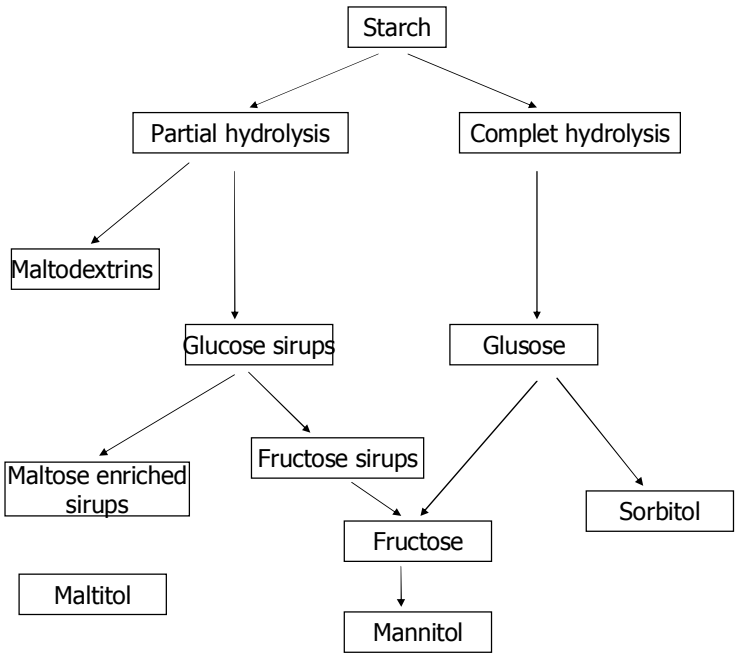
Fraxinus ornus L., manna ash (Oleaceae)

- Occurrence: South Europe
- Used part: Air dried juice obtained by cutting the tree bark
- Collection and adjustment: after drying the excretes are removed and collected
- Macro: Rounded pieces of whitish and weak yellowish mass, sweet taste
- Content compounds: Mannitol
- Effect: dilution of gut content
- Usage: mild laxative in pediatrics

Fraxinus ornus L., manna ash (Oleaceae)

MANNA

STARCH INDUSTRY



MEL - HONEY
Apis mellifica L., honey bee (Apidae)

- Description: From honeycombs obtained liquid, in time grainy crystalline
- Collection and adjustment: VII-VIII, removal of mechanic admixtures
- Macro: Pale yellow to brown-yellow viscose liquid, characteristic odor, (lime honey, acacia honey, forest honey), sweet taste
- Content compounds: - invert sugar (80 %)
  - glucose, fructose, saccharose
  - acetylcholine, choline
  - vitamins
  - bacteriostatic compounds (traces)
  - pollen grain

MEL – HONEY

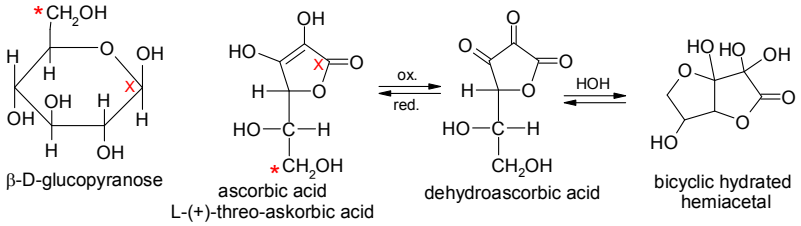
- Usage: - nutritious and tonic remedy
  - during diseases from cold
  - sweetener
  - mild laxative
- Note: individual intolerance
- MEL FOENICULI
- MEL ANISATI
- GELÉE ROYALE
- PROPOLIS

Apis mellifica

PROPOLIS

Apis mellifica

SUGAR DERIVATIVES
ASCORBIC ACID



β-D-glucopyranose

ascorbic acid
L-(+)-threo-askorbic acid

dehydroascorbic acid

bicyclic hydrated hemiacetal

Rosa canina L.
Capsicum annuum L
Hippophae rhamnoides L.
Actinidia chinensis Planch. (kiwi)