Carbohydrates (1. LF UK, NT)

Classification

According to the number of sugar units

- **Monosaccharides**
- **Oligosaccharides** (2–10 monosaccharide units)
- **Polysaccharides** (more than 10 monosaccharide units)
- **Complex (conjugated) carbohydrates**

By attachment:

- **loosely**
- **bound**
  - homoglycosides
  - heteroglycosides
  - aglycone (non-sugar component)

Monosaccharides

- polyhydroxyalkyl substituted aldehydes and ketones, derived compounds
- main nutrients, biologically and sensorially active substances
- characteristic: sweet taste

Structure and classification

According to the type of carbonyl group

- aldos
- ketosis

By number of carbon atoms (3–8), (multiples of CH2O (formaldehyde))

- *trios*
  - D-(+)-glyceraldehyde (D-glycero-triose)
  - L-(-)-glyceraldehyde
  - 1,3-dihydroxyacetone (1,3-dihydroxypropan-2-on)
- *tetros*
- *pentoses*
- *hexoses*
  - D-glukose (D-gluko-hexose) = dextrose, grape sugar
  - D-fructose (D-arabino-hex-2-ulose) = levulose, fruit sugar

According to the arrangement of the string

- with a direct chain
- with a branched chain

According to the type of lactol

- furanoses
- pyranoses

Mutarotation

- anomers, anomeric C, anomeric OH

Conformation

- furanoses (envelope E, crossed T)
- pyranoses (chairs $^{4}C_{1}$, $^{1}C_{4}$)
- acyclic forms (conformation cik-cak)

Occurrence

- component of almost all foods
- atypical monosaccharides
  - D-apiosa (branched sugar), root vegetables
  - L-sorbose (L-series sugar), rowan berries

    - D-manno-hept-2-ulose (ketoheptose), avocado

(abbreviations: glucose Glc, furanose f, fructose Fru, pyranose p, mannose Man, acid A, apiose Api, sorbose Sor, β-D-glucopyranose β-D-Glcp)

Derivates of monosaccharides

chemical reactions of their formation:

- **oxidation (rearrangement)** – sugar acids, ketoaldoses, diketoses
- **reduction** – sugar alcohols, deoxysugars
- **dehydration** – anhydrosugars
- **reaction with other compounds** – glycosides, ethers, esters

Sugar acids

- aldonic (glykonic) – (glucose oxidase, Ca-gluconan (medicine), δ-lactone (fermented salami, 0.1%)
- alduronic (glycuronic) – polysaccharides: D-GlcA6 (glycoproteins), D-GalA6 (pectins), D-ManA6 and L-GulA6 (alginates)
- aldaric (glycaric), e.g. tartaric and malic acid
- content in chicory and malt

Ketoaldoses, diketoses

- key products of the Maillard reaction and oxidation
    - 3-deoxyglykosulose, 1-deoxyglykodiulose, 4-deoxyglykodiulose

Sugas alcohols

- alditols, glycitols (glycerol derivatives)
- reduction of hemiacetal hydroxyl of mono- and oligosaccharides

- natural food ingredients
    - ribitol – riboflavin
    - arabinitol – mushrooms
    - xylitol – mushrooms
    - D-glucitol – plums, rowanberries, pears
    - D-mannitol – mushrooms, rowan berries, celery, green coffee
    - galaktitol – mushrooms, fermented milk products
- synthetic (reduction of H2/cat., NaHgx, substitute sweeteners)
    - xylitol, D-glucitol

- cyclitols - content
- cyklohexane-1,2,3,4,5,6-hexols (inositols, cykloses)
    - myo-inositol (meso-inositol)

widespread, phospholipids, phytates, pseudo-oligosaccharides (legumes)

Deoxysugars

- reduction of primary / secondary hydroxyl - natural, Maillard reaction

2-deoxysugars

- 2-deoxy-D-ribose (thyminose), deoxyribonucleic acid

6-deoxysugars (6-deoxyhexosis = methylpentosis)

Anhydrosugars

sugar anhydrides, glycosans, elimination of water, mainly hemiacetal and other OH

- natural polysaccharide components CH2O
    - 3,6-anhydro-α-D-galaktopyranose (carrageenans)
    - 3,6-anhydro-α-L-galaktopyranose (agar)
- products of thermal reactions
    - 1,6-anhydro-β-D-glukopyranose (β-glucosan, levoglucosan) (caramel)

Glycosides, ethers, esters and other derivates

- O-glycosides – very widespread
- ethers: 4-O-methyl-D-GlcpA (hemicelluloses), 2-O-methyl-D-Xylp (pectins)
- esters – natural (phosphates, acetates, benzoates, etc.), synthetic (fatty acids, emulsifiers)

- S-glycosides – glucosinolates
- N-glycosides - natural (ATP, NADH), Maillard reaction (glycosylamines)
- aminodeoxysugars – natural (chitosamine), Maillard reaction (Amadori products)
- C-glycosides

Oligosaccharides

- homoglycosides
- pentoses, hexoses, sugar acids, etc. derivatives
- furanoses, pyranoses

Classification

By number of monosaccharides (monos, 2-10)

- disaccharides (bioses) – decasaccharides (decaoses)

According to the presence of hemiacetal OH

- reducing (glycosides)
- non-reducing (glycosylglycosides)

According to the predominant monosaccharide

- glucooligosaccharides
  - maltose, maltooligosacharides
- fructooligosaccharides
  - sucrose
- galactooligosaccharides
  - lactose, α-galactosides

According to digestibility

- digestible
- indigestible

According to biological effects

- prebiotic effects (stimulate growth and metabolism of desirable microflora)
- probiotic effects (with fiber they influence and regulate peristalsis)
- synbiotic effects (both prebiotic and probiotic)

Nomenclature

- maltose
  - α-D-glukopyranosyl-(1→4)-D-glukopyranose,
  - 4-O-α-D-glukopyranosyl-D-glukopyranose
  - α-D-Glcp-(1→4)-D-Glcp
- α,α-trehalose
  - α-D-glukopyranosyl-α-D-glukopyranoside
  - α-D-Glcp-(1↔1)-α-D-Glcp

Gluco-oligosaccharides

maltose = α-D-Glcp-(1→4)-D-Glcp (malt sugar)

Occurrence

- starch hydrolysis product, glucose reversion
- malt, bread (1.7-4.3%), honey (2.7-16%)

Production

- maltose (85%), glucose syrups (acids, enzymes)
- maltose
- isomerization to maltulose, α-D-Glcp-(1→4)-D-Fruf
- reduction to maltitol, α-D-Glcp-(1→4)-D-glucitol

Frukto-oligosaccharides

sacharóza = α-D-Glcp-(1↔2)-β-D-Fruf (beet sugar)

Occurence

fruit	to 8 %	.
vegetables	0,1–12 %	.
green coffee	6–7 % (0,2 %)	.
beet sugar	15–20 %	beet sugar
cane sugar	12–26 %	cane sugar
sugar maple (juice)	5 %	maple sirup
dates	81 %	date sugar

Production (from sugar beet)

- cuttings extraction (diffusion)
- purification (epuration) of raw juice, clarification of Ca(OH)2
- CO2 saturation
- filtration, light juice
- thickening - heavy juice (61-67% sucrose, 68-72% solids)
- raw (brown) sugar - 96% sucrose, 2-3% non-sugars, 1-2% water (1.0-1.2% organic, 0.8-1.0% inorganic)
- affinade
- refining – molasses (feed, substrate for fermentation processes), production of invert sugar, other products

Galakto-oligosaccharides

laktosis = β-D-Galp-(1→4)-D-Glcp (milk sugar)

Occurrence

- cow's milk 4-5%
- human milk 5.5-7%

Production (from whey)

- by ultrafiltration
- after thickening by crystallization – production of galactose, galactitol, lactulose, lactitol

other β-galactooligosaccharides of milk

α-galaktooligosacharides of legumes

content

Reactions of saccharides

- complex enzymatic and non-enzymatic reactions
- carbonyl, anomeric OH, primary OH, secondary OH

Non-enzymatic browning reaction

- reactions of the carbohydrates themselves
- Maillard reaction (reaction with proteins, amino compounds)
- caramelization

Reaction of carbohydrates

- Reactants
  - reducing mono- and oligosaccharides
  - non-reducing oligo- and polysaccharides after hydrolysis

Main reactions of monosaccharides (reactions catalyzed by acid-base)

- in an acidic environment (other factors: temperature, time)
  - formation (hydrolysis) of glycosides, dehydration, formation of reductones
- in an alkaline environment
  - mutarotation, isomerization, rearrangements, fragmentation, oxidation

Formation and hydrolysis of glycosides

- reaction of hemiacetal OH

Hydrolysis (inversion)

- production of starch syrups
- invert sugar
- galaktose

Formation (reversion, Fischer reaction)

- inversion by-products (starch syrups: 5-6%)
- byproducts of caramelization
- low energy products
- counterfeit indicators

Dehydratation

- reaction of hemiacetal OH and other OH
- hemiacetal OH / other OH → anhydrosugars (glycosans)
- another OH / another OH → deoxysugars

Anhydrosugars

- β-D-Glcp → 1,6-anhydro-β-D-Glcp (β-glukosan)
- inversion by-products (glucose < 1%)
- byproducts of caramelization (more)

Deoxysugars

- 1,2-enolisation (series of isomerisations and dehydrations)
- 2,3-enolisation (caramel aroma)

Formation of reductones

- antioxidants
  - reduction of organic substances, metal ions
  - pH < 6 (similar to enediolates) monoanionts
  - pH > 6 dianionts

Isomeration

- aldose → ketose
- aldose → aldose (epimerization) .

Isomerization of disaccharides

- laktosis – β-D-Galp-(1→4)-D-Glcp
- laktulosis – β-D-Galp-(1→4)-D-Fruf
- epilaktosis – β-D-Galp-(1→4)-D-Manp

Changes to acids

- 1-ene-1,2-diol, Cannizzaro reaction, benzyl rearrangement

Fragmentation

- formation of very reactive compounds
  - retroaldolization
  - by oxidation (after isomerization, dehydration)

Malliard reaction

non-enzymatic browning reaction

Reactants

- sugars (carbonyl compounds)
  - monosaccharides and reducing oligosaccharides
  - (non-reducing oligosaccharides, polysaccharides, glycosides)
    - triosa > …. > pentose > hexose (acyclic form)
    - aldose > ketose
    - α-dicarbonyls > aldehydes > ketones > carbohydrates
- proteins (amino compounds)
  - ε-NH2 Lys, N-terminal NH2, guanidyl Arg, SH Cys
  - free amino acids, amines, ammonia
  - ε-NH2 > …. > β-NH2 > α-NH2
  - NH3 > R-NH2 > amino acid

Reaction conditions

- water activity (aw 0.3–0.7)
- pH (9–10)
- other (temperature, reaction time, other components)

Consequences positive, negative

- formation of aromatic substances
- formation of yellow, brown, black melanoidin pigments
- reduction of nutritional value
- potentially toxic products
- in vivo reaction (glycosylation of proteins)

Reaction mechanisms – 3 reaction phases

- initial phase
  - formation of glycosylamine (Amadori rearrangement) and aminodeoxysugar (Amadori product)
- middle phase
  - breakdown of carbohydrates, glycosylamines, aminodeoxysugars (dehydration, fragmentation)
  - breakdown of amino acids (Strecker degradation)
- final stage
  - reaction of products and decomposition products, formation of aromatic, taste and colored substances (melanoidins)

Glykosylamines and aminodeoxysugars

- ketoses → ketosylamine → aldosamine (2-amino-2-deoxyaldose), Heyns' p.

- mechanisms (reactions of acyclic forms)

Decomposition of aminodeoxysugars

- 1,2-enolization, acidic environment
- 2,3-enolization, neutral and alkaline environment
  - the formation of glycosulos and glycodiulos (aldoketos and diketos)

Analogy with the reactions of sugars themselves

- lower activation energy
- products contain N and S
- qualitatively and quantitatively more products

parallel breakdown of the sugars and amino acids themselves

Important heterocyclic products

Malliard reaction in major commodities

- positive and negative consequences, desirable and undesirable reactions

technology (aroma, taste, color, nutritional value)

- roasting
- cooking, baking, frying
- drying
- extrusion, microwave heating
- milk, dairy products - Lys: 10-30% traditional drying, 3% spray drying
- cereals, cereal products - Lys: 70% bread crust, 10% total
- meat, meat products – mutagens
- fruit vegetables
- coffee, cocoa, nuts

Reaction during milk processing unusable (blocked) Lys

- isomerization of lactose → lactulose + epilactose
- lysinoalanine

Maillard reaction inhibition

- creating unfavorable conditions
  - water content (activity), temperature reduction, pH adjustment
- removal of one of the partners
- use of inhibitors

Caramelization

- sugars (sucrose, glucose, fructose, starch syrups, invert sugar)
- temperature 150–190 °C (240 °C)
- reaction time 5-10 hours
- catalyst

- caramel – a solid product
- cooler - solution

class		name of cooler	another substances	usage
I	CP	caustic	Na_2C0_3, K_2CO_3, NaOH. KOH, H_2S0_4, acetic acid, citric acid	spirits (high alcohol content)
II	CCS	caustic sulfite	$S0_2$, H_2S0_4, Na_2S0_3, K_2S0_3, NaOH, KOH	vinegar, beer, spirits, flavored wines, mead
III	AC	ammoniacal	NH_3, $(NH_4)2S0_4$, Na_2C0_3, H_2S0_4, NaOH, KOH	beer etc. alcoholic beverages, acidic foods
IV	SAC	ammonia-sulphite	NH_3, $S0_2$, $(NH_4)2S0_3$, Na_2S0_3, K_2S0_3, Na_2C0_3, K_2C0_3, NaOH, KOH, H_2S0_4	acidic foods, soft drinks

Source

- DAVÍDEK, Jiří. *5. CARBOHYDRATES* [online]. [cit. 2012-03-12]. <https://el.lf1.cuni.cz/p46134582/>