OLIGOSACCHARIDES

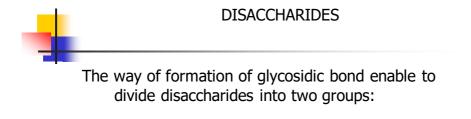
Products of condensation of two-ten monosaccharides, connected by glycosidic bond.

Glycosidic bond is formed:

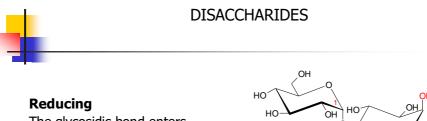
- by hemi-acetal hydroxyl (at anomeric carbon of monosaccharide)
- and whichever hydroxyl of further monosaccharide (if formating disaccharides),
- hydroxyl longer or shorter saccharide chain (if formating oligo- or polysaccharides)

Glycosidic bond is cleaved:

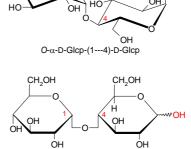
- easily by hydrolysis (in acids)
- enzymatically (significant enzymatic specifity)



- Reducing
- Non-reducing

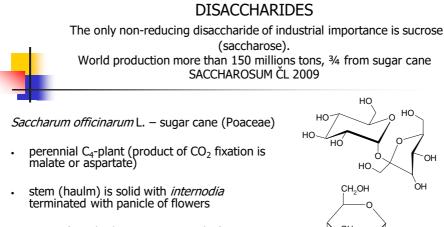


The glycosidic bond enters hemi-acetyl hydroxyl of one sugar only. The other hemiacetyl-hydroxyl is free, disaccharide possesses reducing power, can mutarotate and can formate glycosides. These disaccharides are known as "maltose type"

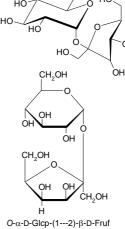


4-*O*-α-D-glukosyl-D-glucose

DISACCHARIDES Non-reducing The glycosidic bond enter hemi-CH₂OH OН acetyl hydroxyl groups of both reacting ^{он}носн Ĥ monosaccharides. These QН ÓН sachcharides do not ÓН mutarotate, do not make óн osazones. Trehalose is found O-α-D-Glcp-(1---1)-α-D-Glcp in fungi and other nonphotosynthetising organisms. "Blood sugar of insects" "Trehalose type"



- Juice of crushed stems removal of proteins, filtration, and concentration, crystallization of raw "brown" sugar. The brown sugar is further refined.
- Asia, South America and Caribbean islands are main producers, cca 100 millions tons/year



 Beta vulgaris L. – sugar beet (Chenopodiaceae)

 . biennial plant cultivated as annual, from the beginning of 19th century used as raw material of production of sucrose.

 . contains 16 – 17 % of sucrose, cca 77 % of water

 . Tubers are sliced to sugar beet "cossettes", extracted with hot water, the obtained juice is purified. Concentration, crystallization (the residue is molasses). Rafination.

 . 1000 kg of sugar beet → 130 kg sucrose

 Acer saccharophorum (A. saccharum) C. Koch – sugar maple (Aceraceae)

 . three of eastern part of North American continent

 . saccharose excreted from leaves and from rupture of bark (three courted by bees)

 Phoenix dactylifera L. – date palm (Palmae)

• Fruits are rich on sucrose



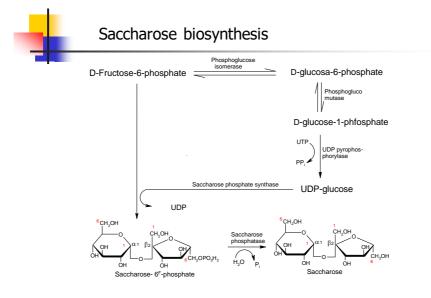
http://www.food-info.net/images/sugarcane2.jpg

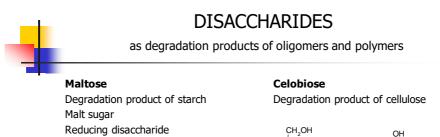


http://www.recipetips.com/images/glossary/b/beets_sugar.jpg



http://wahyuinqatar.files.wordpress.com/2009/06/16062009692.jpg





CH₂OH

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4-O-α-D-glucopyranosyl-D-glucose

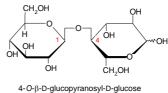
OH

ÇH₂OH

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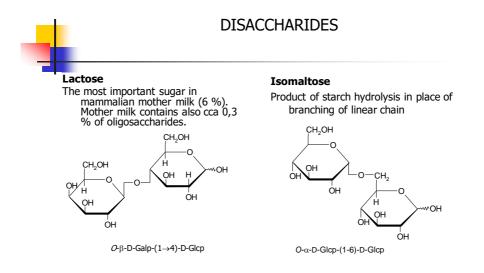
OH

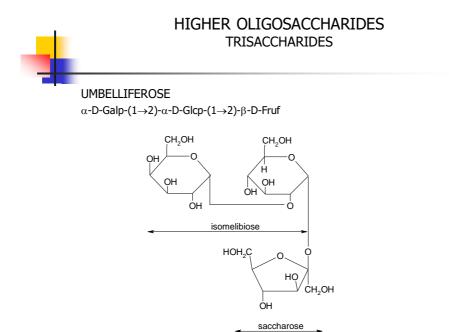
OH

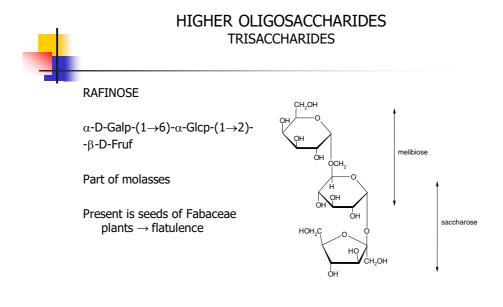


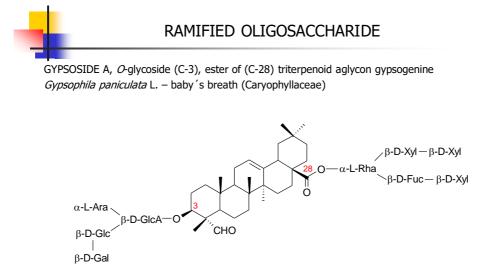
 $\begin{array}{c} \textbf{DISACCHARIDES} \\ reducing disaccharides as part of glycosides, especially flavonoids \\ \bullet & \text{RUTINOSE} & \text{O-}\alpha\text{-L-Rhap-}(1\rightarrow2)\text{-D-Glcp} \\ \bullet & \text{NEOHESPERIDOSE} & \text{O-}\alpha\text{-L-Rhap-}(1\rightarrow6)\text{-D-Glcp} \\ \bullet & \text{MALTOSE} & \text{O-}\alpha\text{-D-Glcp-}(1\rightarrow4)\text{-D-Glcp} \end{array}$

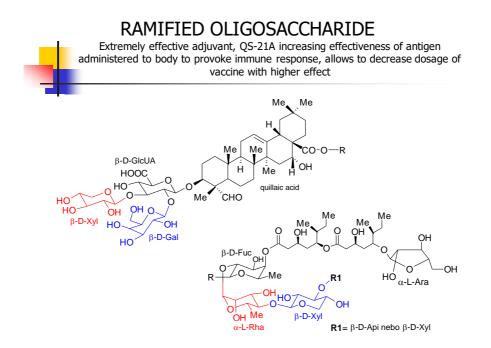
	CELLOBIOSE	O-β-D-Glcp-(1→4)-D-Glcp
•	SOPHOROSE	$O-\beta$ -D-Glcp-(1 \rightarrow 2)-D-Glcp
•	LAMINARIBIOSE	O-β-D-Glcp-(1→3)-D-Glcp
	GENTIOBIOSE	$O-\beta$ -D-Glcp-(1 \rightarrow 6)-D-Glcp
	LACTOSE	$O-\beta$ -D-Galp-(1 \rightarrow 4)-D-Glcp
	SCILLABIOSE	$O-\beta-D-Galp-(1\rightarrow 3)-\alpha-L-Rhap$
•	SAMBUBIOSE	$O-\beta$ -D-Xylp-(1 \rightarrow 2)-D-Glcp
•	PRIMEVEROSE	$O-\beta$ -D-Xylp-(1 \rightarrow 6)-D-Glcp

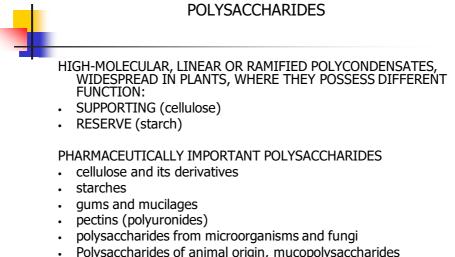












Polysaccharides of animal origin, mucopolysaccharides



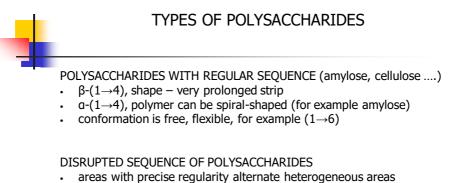
HOMOGENIC Composed from large number of the molecules of the same sugar unit

HETEROGENIC

Produced by condensation of molecules of different sugar types

- Hexoses
- Pentoses
- Anhydrohexoses
- Sugar ethers
- Sugar sulphates
- Aminosugars •

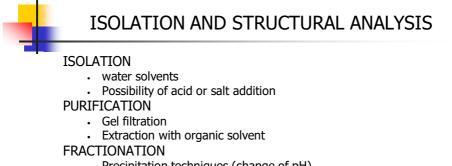
LINEAR RAMIFIED



• potential interaction "polymer – polymer" enables the formation of gel

POLYSACCHARIDES COMPLETELY HETEROGENOUS

interaction of "polymer – solvent" can be found



- Precipitation techniques (change of pH)
- Chromatography (active char coal, ion exchange)

PURITY VALIDATION

- Optical rotary power
- Molecular weight
- Electrophoresis

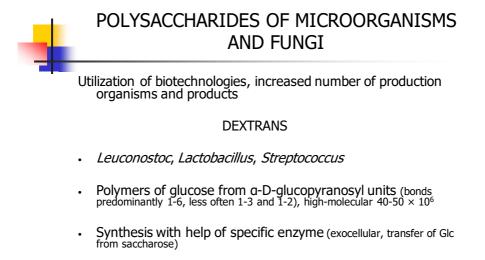


Physical methods:

- spectrometry
 - MS, NMR

Chemical methods

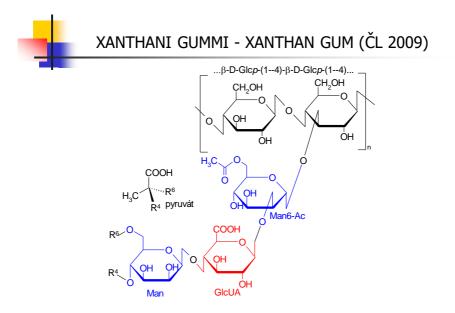
- partial hydrolysis
- derivatives formation
- controlled degradation

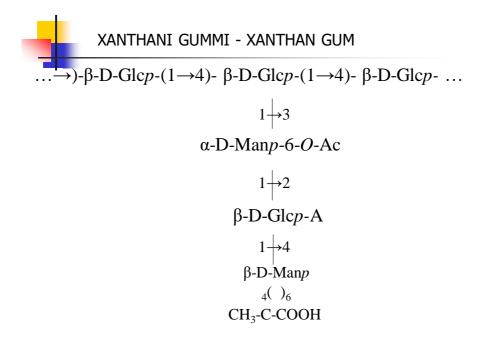


 Adjustment by partial hydrolysis to 40000-75000 (acid hydrolysis, sonication, bacteria)

XANTHANI GUMMI - XANTHAN GUM (ČL 2009)

- high-molecular anionic polysaccharide, in form of natrium, potassium or calcium salt
- produced during the sugar fermentation (glucose or sucrose) with help of microorganic species *Xanthomonas campestris*
- composed from main chain derived from $\beta(1\rightarrow 4)$ bonded D-glucose units with trisaccharide secondary chains (at exchanging anhydroglucose units) composed of glucuronic acid between two mannose units. Majority of terminal units is substituted with pyruvic acid and mannose neighboring the main chain can bee C-6 acetyled maleulary actions and the provide the transformation of the second seco
- molecular weight approximately 1 × 10⁶
- properties: white or yellowish loose powder; well dissolve-able in hot and cold water (making highly viscous solution), viscosity does not change with changing temperature
- insoluble in organic solvents; resistant to enzymes, rare incompatibilities, tolerate up to 50 % of alcohol
- E number E415.







USAGE (E415)

Pharmacy: stabilizer of emulsions, adjuvant

Does not contain gluten, used in gluten-free bakery (makes the dough adhesive). Coeliac disease – gluten intoleration (shorter protein cuts – gliadin in wheat, secalin in rye, hordein in barley, avenin in oat)

Food industry: Stabilisators, thickener of products based on water (milk products, dressings, dips, sauces, instant soups, sirups), ice-creams (prevent formation of ice crystals); Activia, Pribináček, Tartar sauce, Tisíc ostrovů, Křemílek, Thai Kari, Hermelin salad and others.

Cosmetics: creams, tooth pasts (stabilizer)

POLYSACCHARIDES OF FUNGI

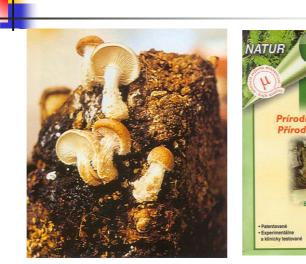
Lentinan (Lentinus edodes – SHIITAKE)

Homogenous polyglucan

- β -(1-3) bonds, rarely 1-6 bonds
- Immune-modulating effects
- Antitumor activity
 - human clinical studies showed higher survival rate, higher quality of life, and lower recurrence of cancer
 - (1) prevention of onset of cancer by oral consumption of mushrooms or their preparations
 (2) direct inhibition of growth of various types of cancer cells
 - (3) immuno-stimulating activity against cancers in combination with chemotherapy
 (4) preventive effect on spreading or migration of cancer cells in the body

Basidiomycetes:

Pachymaran Schizophyllan Krestin *(Coriolus versicolor)*







POLYSACCHARIDES OF ALGAE

- Phaeophyta Alginic acids (alginate), fucans
- *Rhodophyta* Sulphated galactans (agar, carrageen)
- Chlorophyta
 Complex polysaccharides, often sulphated



Laminaria spp.

Brown alga, seacoast of France and England Industrial processing, colloid chemistry

Macrocystis pyrifera Californian kelp, giant algae of Pacific

Fucus serratus, F. vesiculosus Seacoast of England

-







Laminaria digitata

Fucus vesiculosus

Macrocystis pyrifera

http://diver.net/californiadiveboats.com/OceanOdyssey/2008.02.23/ http://www.dermaxime.com/seaweed-extracts.htm

Alginic acid, alginates

Mixture of uronic acids, 19-25 % of carboxyls Linear polymer of D-mannuronic acid- $\beta(1\rightarrow 4)$ -L-guluronic acid Blocks of same acids alternate in linear chain In form of salt (Na, Mg, Ca)

Properties

- Salts with Na and Mg \rightarrow colloid solution
- Salts with $Ca \rightarrow elastic gel$

Usage

- · Antacids in combination with NaHCO₃ a Al(OH)₃
- · Haemostatic stomatology, superficial wounds
- · Pharmaceutical technology
- Food industry E400-405

HOOC HO O.HO HO ноос но

block of mannuronic acids

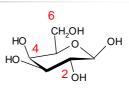
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block of guluronic acid

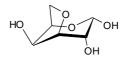
CARRAGEENAN – Karagen, Irish moss syn. Alga carrageen, *Chondrus crispus* and *Gigartina mamillosa* (Gigartinaceae)

Polymers of D-galactose, anionic character, sulphated, molecular weight 10⁵-10⁶

- Bonds $1 \rightarrow 3$ (A unit) and $1 \rightarrow 4$ (B unit)
- Sulphatation at positions 2 and 6 or 2 and 4
- · Different structural subtypes
- · Properties
 - Based on subtype
 - · Usually soluble in hot water
 - · Some of them produce gel
- Usage:
 - Technology
 - Laxative
 - · Cosmetics
 - · Additives of food



D-galactose



anhydro-D-galactose

	CARRAGEENAN types	
A unit	B unit	Туре
D-galactose-4-sulphate	D-galactose-6-sulphate	μ
	D-galactose-2,6-disulphate	υ
	3,6-anhydro-D-galactose	κ
	3,6-anhydro-D-galactose-2-sulphate	ι
D-galactose-2-sulphate	D-galactose-2-sulphate	ζ
	D-galactose-2,6-disulphate	λ
	3,6-anhydro-D-galactose-2-sulphate	θ

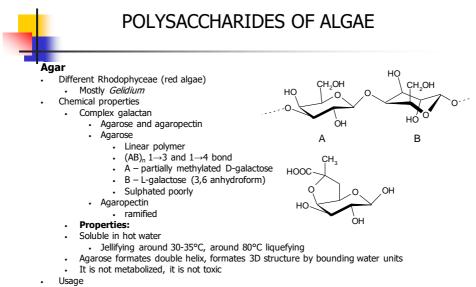
18



Chondrus crispus – Irish moss



- Karageenans
- Chlorophyll A and D
- Fycoerythrin
- Starch typical for red algae





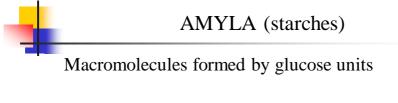
Gelidium amansii

http://www2.naris.go.kr/v2/naris_search/search_result_detail.jsp?inst_id=1165083

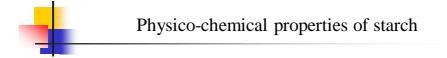


POLYSACCHARIDES OF HIGHER PLANTS

- Starches
- Cellulose
- Polyfructosans
- Dietary fibre



- Amylose (20-30 %)
 - 250-300 Glc residues; $(1\rightarrow 4)$ - α -D-glykosidic bond
 - · Basic building block is maltose
- Amylopectin (70 %)
 - 1000 Glc residues; (1→4)-α-D-glycosidic bond and (1→6)-α-D-glycosidic bond – branching cca after 25 units of Glc



Insoluble in cold water and organic solvents

Swelling in cold water

- Soluble in hot water \rightarrow formation of wheatpaste colloid starch solution
- According to the origin grains of different shape, size and structure

Careful hydrolysis gives arise to dextrins

MODIFIED STARCHES

Physical modification

· Boiling and dehydration

Chemical modification

- Oxidation
- Esterification
- Cationisation or anionisation
- Etherification
- Hydrogenation

Controlled depolymerisation

- Partial hydrolysis
- Enzymatically
- Debranching enzymes



- · Pharmaceutical additive
- Reagent for production of dextrin
- Textile industry
- Paper mills

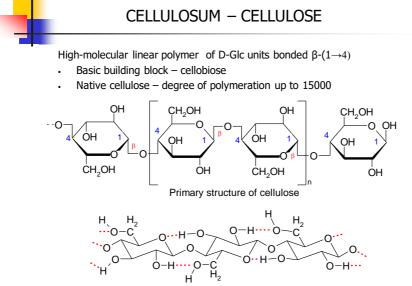
NATURAL SOURCES OF STARCH

Oryza sativa (Poaceae), rise – Oryzae amylum

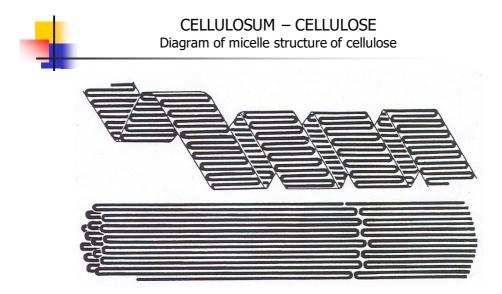
Triticum aestivum (Poaceae), wheat - Tritici amylum

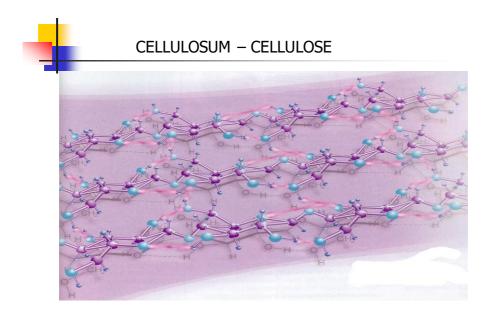
Solanum tuberosum (Solanaceae), potatoe - Solani amylum

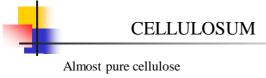
Zea mays (Poaceae), corn – Maydis amylum



Linear cellulose chain stabilized by hydrogen bridges







• Cotton wool fibers – trichomes from seeds of plants from *Gossypium* species

Technical cellulose

- wood of conifers
- Purification from lignin and admixtures

Acetobacter xylinum

Lana gossypii depurata – bandage cotton wool purified from cotton seeds

Gossypium spp. - cotton plant (Bombacaceae)

Gossypium spp.

- Asian variety
 - G. arboreum and G. herbaceum
- American variety *G. hirsutum* and *G. barbadense*

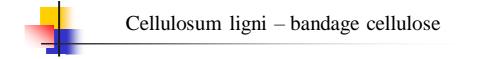
Uni-cellular fibers

- 15-40 mm long
- 12-25 microns in diameter
- During ripening their distortion textile quality

Processing

- Seeds separated mechanically
- Sorting according to the quality



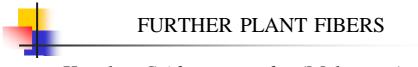


Bleached cellulose from wood of Coniferae trees

Delignification in acid or under neutral conditions

Possibility of esterification

- Nitrate, acetate (different utilization)
- Soluble in water
- · Solubility depends on degree of esterification DS 0-3



Kapok – Ceidra pentandra (Malvaceae)

Flax fibers - Linum usitatissimum (Linaceae)

Hemp fiber - Cannabis sativa (Cannabaceae)

Jute – Corchorus capsularis (Tiliaceae)



Mixture of polysaccharides

Produced by mild hydrolysis of starches

- Heating
- Mineral acids



Plant polyfructosan (furanoid form)

Bond β -(2 \rightarrow 1) between D-fructose units

Less than 100 units of Fru

Well soluble in water

Occurrence - storage organs of Asteraceae plants and Poaceae plants

- Inula helenium
- Cichorium intybus
- Helianthus tuberosus

DIETARY FIBERS

- Dietary, chemical, physiological definitions
 - Plant (vegetables) residues of non-digestible by enzymes of GIT of human
 - Macromolecules of cell wall and intracellular polysaccharides
 - Lignin
 - · Polysaccharides of different type than a-glucans
 - cellulose
 - pectins (glycano-galactans)
 - Hemicelluloses
 - · galactomannans, heteroxylans, pentosans
 - Glycoproteins
- Sources: fruits, vegetables, dried fruits, brans



- Physiologic effects:
 - · Gastro-intestinal tract
 - · Increase of faeces volume (insoluble fraction)
 - Affection of food passage through guts (insoluble fraction)
 - Effect of intestinal microflora
 - Possible prevention of creation of colorectal carcinoma
 - · Affection of metabolic activity
 - · Interaction with intake of mineral compounds
 - Level of blood cholesterol
 - Level of blood sugar



Under term gums and mucilages can be found:

- · Macromolecules of polysaccharides
- · More or less soluble in water, usually format colloid solutions or gels

Today under naming "plant hydrocolloids"

Plant hydrocolloids are of interest in health care and industry.

Mucilages – protectives of mucose layers, expectorants/antitussics, laxatives Gums – laxatives, anobesics, emulgators, stabilizers



Mucilages – normal content compounds pre-existing in specialized histological formations (cells or tubules), which are generally found in external covers of seeds.

Widely distributed, mostly in *Malvales* (acidic mucilages) and *Fabales* (neutral mucilages of endosperm)

Swelling in water – active role in seed germination.



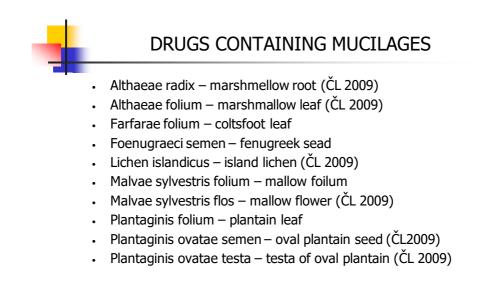
MUCILAGES

Mucilages - high-molecular polysaccharides

- strongly swelling in water (micellar solubility)
- · dissolving into viscose colloid hydrophilic solutions
- · Insoluble in ethanol and organic solvents

Hydrolysis

- · hexoses and pentoses (mostly galactose and arabinose)
- sugar derivatives (anhydrides, uronic acids, esters with sulphuric acid)



Cyamopsidis seminis pulvis (ČL 2009) Cyamopsis tetragonolobus – Guar (Fabaceae)

Annual plant planted in USA, India, Pakistan

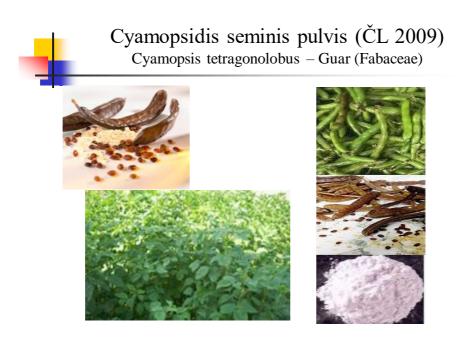
Commercial product is grinded endosperm (not exudate)

White powder, with water formats a mucilage of different viscosity, insoluble in EtOH.

Content compounds: polysaccharides D-galacto-D-mannane $(1\rightarrow 4)$

Usage:

- hypercholesterolemia (prevention of cardiovascular diseases); lowers the level of serum cholesterol and LDL without affection of other lipoproteins and triglycerides;
- DM2; lowering of hyperglycaemia and post-prandial insulinemia (after food intake)
- In combination with montmorillonite symptomatic treatment of colonopathy with constipation



MANNOSE DERIVED MUCILAGES (NEUTRAL MUCILAGES)

Rarely pure mannan

- Glucomannans

20-50 % of D-mannose replaced by D-glucose, β -(1 \rightarrow 4) Amorphophallus konjak

Galactomannans

Part of D-mannose replaced by D-galactose

Ceratonia siliqua (Caesalpiniaceae), Annonaceae, Palmae

· Galactoglucomannans

Cercis siliquastrum Caesalpiniaceae

CERATONIAE SEMEN; KARRUBIN; LOCUST BEAN

GUM

Ceratonia siliqua (Caesalpiniaceae); Karob tree

Subtropic, evergreen, dioecious caulifloric woody plant. Pods ripen in following year. Seeds are exceptional with regular weight, from ancient times weight for measurement of amount of gold and gems: from Greec *kerátion* \rightarrow carat = 200 mg

Content compounds:

galactomannan karrubin (up to 80 % of endosperm); flavones, oils with linolenic acid; $\beta\mbox{-sitosterol}$

Usage:

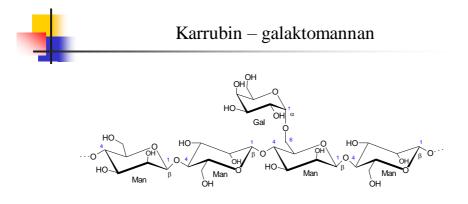
- dietary fibers lowers the level of cholesterol, triglycerides, and blood glucose
- retains water in intestinal lumen
- roasted seeds \rightarrow substitution of coffee, for production of chocolate for allergic people and for dogs
- E410 thickener, stabilizer of emulsions



Ceratonia siliqua (Caesalpiniaceae)







MANNOSE DERIVED MUCILAGES (NEUTRAL MUCILAGES)

Trigonella foenum graecum Fabaceae

Composition

- mucilages galactomannans
- saponins
- essential oil sesquiterpens
- · lipids, proteins
- flavonoids
- cellulose

Usage

- compress, kataplasmata
- lowering of blood cholesterol
- adjuvant therapy of DM2



ACID HETROGENOUS POLYSACHARIDES (ACIDIC MUCILAGES)

Mucilages of Plantaginaceae

Psyllium

Planatago afra (syn. P. psyllium) P. indica (syn. P. arenaria • Mediterranian

Ispaghula

Plantago ovata (syn. P. ispaghula) • India

Composition

 heteroxylan (D-xylose (70 %), Larabinose (10 %), D-galaktose, α-Dgalakturonyl-(1→4)-L-xylose)

Usage

- mechanical laxative
- · lowering of blood glucose
- lowering of LDL and total
- cholesterol
- $\cdot \quad \text{Irritable colon syndrom}$



ACIDIC HETEROGENOUS POLYSACCHARIDES

Mucilages of Malvaceae

- Malva silvestris
- Althaea officinalis

Strongly ramified structure

- · Similar to pectins
- D-galactose, L-rhamnose, D-glucuronic acid, D-galacturonic acid

Usage

- Symptomatic treatment of constipation
- · Symptomatic treatment of cough
- · Protective at GIT



Lini semen Linum usitatissimum (Linaceae)

Containing:

- Oil, proteins
- Ramified mucilage: D-xylose, D-glucose, L-arabinose, D-galactose
- Lignans

Usage

- Laxative
- Mucose layer protective
- Compresses



http://caliban.mpiz-koeln.mpg.de/~stueber/thome/band3/tafel_001.html

GUMS

Gums - clovatins

Common occurrence mainly at Mimosaceae, Rosaceae, Rutaceae, Burseraceae

Characteristics:

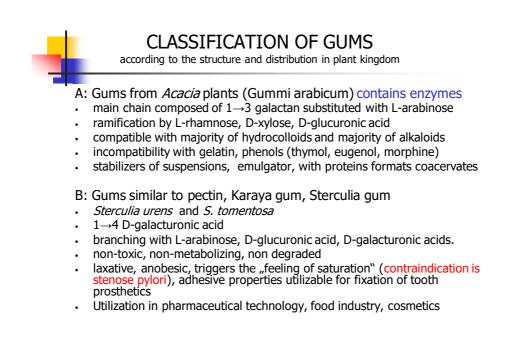
- Optically active compounds, molecular weight $2 \times 10^4 2 \times 10^6$; complex molecules, always heterogeneous and ramified, containing uronic acids together with galactose, arabinose and xylose. Often partially methylated or acetylated. Carboxylic groups can occurre in form of salt.
 - Pathologic products flowing from plants after wounding (with exception of Tragacantha).

Formation:

transformation of other polysaccharides (probably also starches)

Characteristics

- · amorphous optically active compounds
- · soluble in water to format colloid hydrophilic solution, weakly acidic reaction in EtOH
- in organic solvents insoluble
- · water solutions tends to glue



CLASSIFICATION OF GUMS

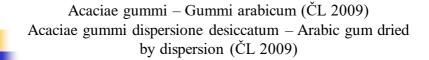
according to the structure and distribution in plant kingdom

C:

- Uncommon 1→4 bonded xylans
- Often substitution with monosaccharides (L-Ara, D-Gal, D-GlcUA)

D:

- Main chain formed by repetition of (1–4 and 1–2) D-GlcUA and D-Man
- C3-OH of majority of D-Man substituted with further sugars
- India, Sri Lanka
- Formation of emulsions, stabilizer
- Ghatti gum (Anogeissus latifolia, Combretaceae)



Acacia senegal – gum arabic tree (Mimosaceae). African trees (Sudan). On the air hardened clovatine flowing spontaneously or after cutting of

branches and stem, flowing gum desiccates into yellowish or jantar oval pieces friable, opaque, without odor and taste.

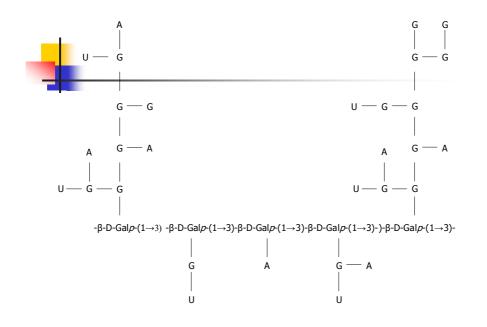
Slowly soluble in doubled amount of water. Obtained liquid is dense, yellowish, showing acidic reaction. Insoluble in ethanol.

Fresh gum is formed from:

- arabin arabinic acid (salts of Ca, K, Mg), 1→3 galactan, side sugars are: L-Ara, L-Rha, D-Gal, D-GlcUA.
- enzymes incompatible with glycosides, therefore *Acaciae gummi desenzymatum* is prepared

Utilization: stabilizer of suspensions, emulgator, adhesive. Production of colorants, glues.





TRAGACANTHA – TRAGANT

Astragalus gummifer (Fabaceae)

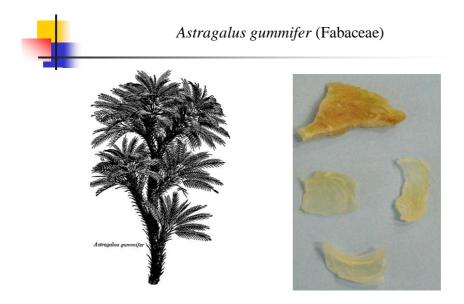
Trees of Western Asia.

Obtained after cutting of branches and stems, flowing gums is without odor, taste. Consists of thin strips $(30 \times 10 \times 1 \text{ mm})$ or their segments.

Fresh gum is formed from:

- tragacanthin (arabinogalactan, neutral, soluble in water and water/alcoholic solvents)
- · bassorin (partially methylated glycanogalacturonan, acidic)

Utilization: stabilizer of suspensions; bifunctional emulgator (increases viscosity of water fraction and lowers superficial tension at interface O/W emulsions), E413



Gums similar to pectin Karaya gum, Sterculia gum

Sterculia urens a S. tomentosa

- $1 \rightarrow 4$ D-galacturonic acid with L-rhamnose
- · branching with D-glucuronic acid, D-galaktose
- Non-toxic, non-metabolizing, non-degraded
- laxative, anobesic, triggers the "feeling of saturation" (contraindication at stenose pylori) adhesive properties utilizable for fixation of dental prosthetics
- Usage in pharmaceutical technology, food industry, cosmetics



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