

Polysaccharide Biotechnology essay

Introduction: what are polysaccharides?

Polysaccharides are a class of polymeric organic compounds consisting of carbohydrates as building blocks. Most polysaccharides have structural formula $C_x(H_2O)_y$, where x can be in the range of several hundreds or thousands. Building blocks are covalently linked via glycosidic bonds. Glycosidic bond is formed between hemiacetal group of one monosaccharide and hydroxyl group of another monosaccharide.

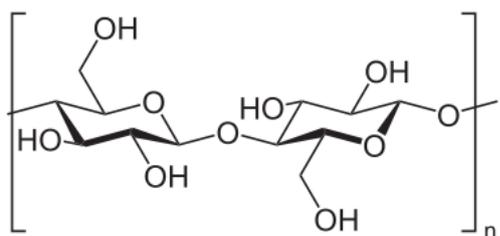
Carbohydrates, or monosaccharides, have structural formula $(CH_2O)_n$, where n is 3 or more. In many carbohydrates used as building blocks of polymers $n = 6$. Individual monosaccharides have one aldehyde or ketone group and several hydroxyl groups. They can exist in both linear and circular forms. Circular carbohydrates are formed as a result of intramolecular reaction between carbonyl group of aldehyde or ketone and one of hydroxyl groups in the molecule. The reaction results in the formation of hemiacetal. Hemiacetal can be easily hydrolysed by water returning back to linear form. This ability to undergo easy hydrolysis is lost in polysaccharides due to formation of covalent glycosidic bond which involves hemiacetal group (Clayden et al., 2001).

Despite a significant similarity in the structures of monomeric building blocks between different polysaccharides, the resulting polymers have surprisingly large differences in their properties. This is caused by several factors. Polysaccharides can be linear or branched and may consist of one (homopolysaccharides) or several (heteropolysaccharides) varieties of monosaccharide residues. The residues can be connected to each other in different ways and can have additional substitutions and modifications with various functional groups. As a result of this variability, polysaccharides can play very different biological functions and found a large array of industrial and medical applications.

Examples of polysaccharides and their characteristics

Cellulose

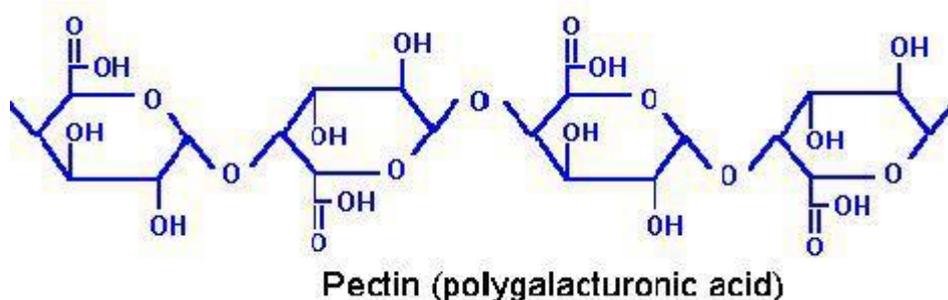
Cellulose is a structural polysaccharide and a major building block of cell walls in plants and some other organisms. Wood, cotton and flax are examples of natural products rich on cellulose. This is a linear polymers consisting of D-glucose molecules connected via $\beta(1\rightarrow4)$ glycosidic bonds. The number of monomeric blocks runs from hundreds to tens of thousands. Cellulose is mainly used to produce paper and, to a smaller degree, to make other polymers such as cellophane and rayon. It is also used as a source of biofuel (ethanol). Cellulose is insoluble in water and has rather rigid structure. The polymeric threads can form multiple hydrogen bonds between themselves making the structure even more rigid. Microfibrils formed this way are major structural blocks of cell walls. Properties of cellulose such as mechanical strength depend in significant degree on the length of polymeric chains (Klemm et al., 2005).



Cellulose is a huge potential source of glucose and ethanol, but its enzymatic hydrolysis by cellulase is too slow and produces disaccharide product, which has to be cleaved further. As a result, economically the process of saccharification of cellulose is not optimal, with the cost of enzyme representing a half of the whole process cost (Tombs and Harding, 1997).

Pectins

Pectin is another major component of cell walls in terrestrial plants, particularly non-woody plants. The polymer has a linear backbone of α -galacturonic acid connected via $\alpha(1\rightarrow4)$ glycosidic bonds. Pectin is heteropolysaccharide, and its structure, composition and degree of branching depends on a particular type and source. In some cases a number of other sugar residues can be connected to the linear backbone of α -galacturonic acid residues forming branches. These monosaccharides include D-xylose and D-apiose. In other cases the linear backbone itself can contain additional monosaccharide residues such as L-rhamnose alternating with α -galacturonic acids, and various sugars such as D-galactose, L-arabinose and D-xylose on the side chains. The carboxylic groups of α -galacturonic acid residues are usually esterified forming methyl esters but some residues stay in the form of acid or salt (Buchanan et al., 2000)



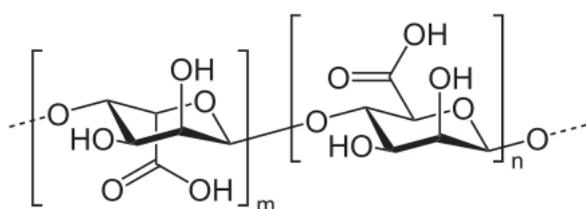
Pectin is used as thickening agent in the food industry (for example in production of jams) since it can form gels with sugar. Gels are formed at low pH when the carboxylate residues are protonated. At higher pH the negative charge of these residues prevent the gels formation due to electrostatic repulsion. Gel strength depends on the pH and calcium concentration. These parameters can be easily manipulated to achieve a desirable result. Pectins are also used in medicine against constipation and diarrhea.

Carboxylic acid residues are convenient sites for chemical modification. Degree of their esterification can be controlled, and this parameter influences the change and properties of polymer.

Alginate

Alginate is an anionic polysaccharide from cell walls of brown algae. This is a linear copolymer of (1-4)-linked β -D-mannuronate (M) and α -L-glucuronate (G) residues. Blocks of β -D-mannuronate and α -L-glucuronate residues can have different lengths and vary from alternating sequences to long homopolymeric stretches. Proportion of M and G residue can vary significantly in different alga.

Alginate quickly absorbs water and can hold it in 200-300 times amount of its dry weight. It is used for waterproofing, as gelling, emulsifying and thickening agent, agent for wound healing and in manufacture of paper and textile. Gel strength depends on concentration of calcium ions and M:G ratio of polymer. The gels are thermo-irreversible, they don't re-melt upon heating. Alginate is also used for microencapsulation and controlled drug release applications.

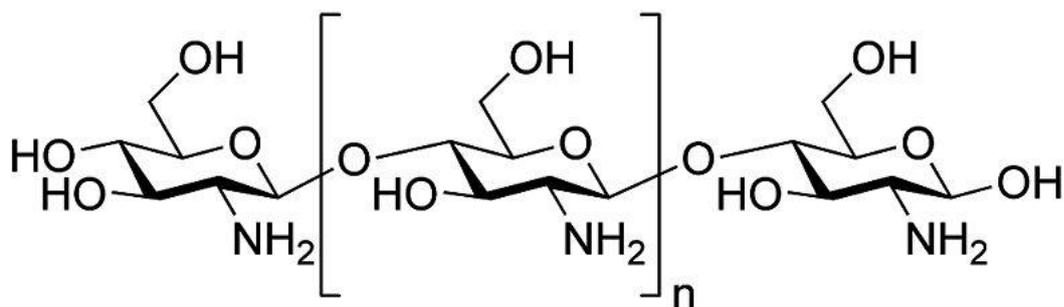


Annual production of alginate is currently around 30,000 tonnes. Unfortunately, due to the fact that most algae grow in geographically remote areas, there is a lack of raw material on the market. Alginates with low M:G ratio have better commercial value. M:G contents depend on the species of alga, geographic region and plant age.

M residues are convenient sites for biomodification, which can manipulate the charge of polymer.

Chitosan

Chitosan is a linear polysaccharide found in the shells of shrimps and some other marine organisms, as well as in mushrooms and insects. It consists of β -(1-4)-linked D-glucosamine residues. Some of these residues are acetylated at random positions forming N-acetyl-D-glucosamine. Polymer has rigid linear structure due to electrostatic repulsion of positively charged amino groups.

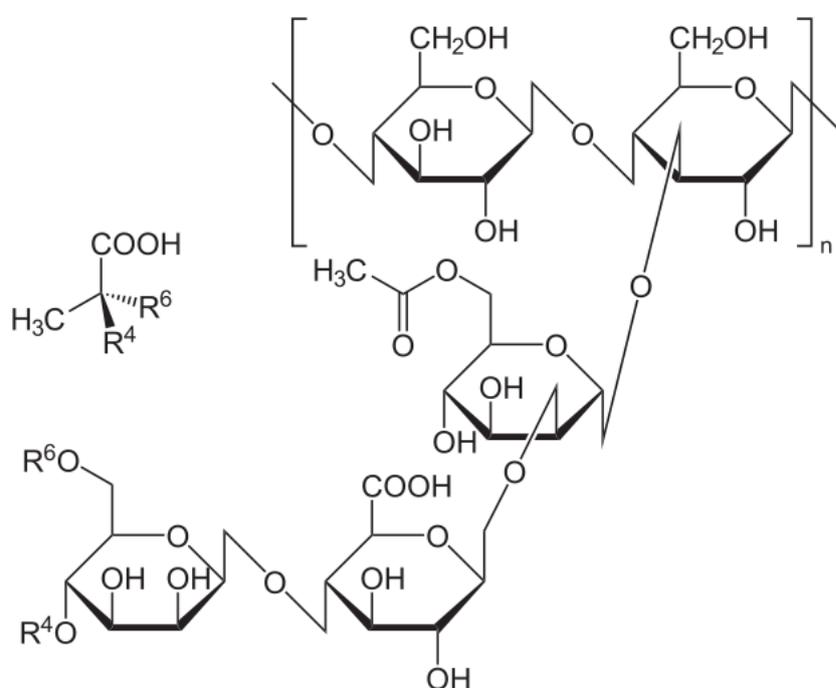


Chitosan enjoys a variety of industrial and medical applications. It is used as insecticide and antifungal agent in agriculture. In medicine, it is used in bandages to

reduce bleeding, and as an antibacterial agent. Important medical application of chitosan is as a drug delivery agent. Due to the presence of amino group, the polymer is insoluble at neutral pH but become soluble in acidic conditions upon protonation (at pH < 6). As a result, chitosan can be used to transport the drug to acidic environment, where the chitosan package degrades, dissolves and release the drug. Delivery of insulin is one of such important applications (Sunil et al., 2004)

Due to its positive charge, biodegradability and low antigenicity, the polymer attracted attention as a non-viral gene delivery vector. It easily forms complexes with negatively charged DNA, the capsules can be delivered to target cells in the body.

Around 2000 tonnes of chitosan produced annually. The N-acetyl group of polymer is an easy target for biomodification (control of acetylation degree) (Tombs and Harding, 1997).



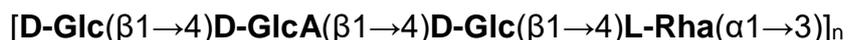
Xanthan gum

Xanthan gum is a branched heteropolysaccharide produced by bacterium *Xanthomonas campestris*. Fermentation of sucrose, glucose and lactose by these bacteria produces the polymer which is precipitated and later added to liquid media to form gums. Xanthan gum is able to significantly increase viscosity upon addition of very small amount of compound to liquid. It has one of the highest viscosities for polysaccharides. This property is retained at wide range of temperatures and pH. Xanthan gum is used as food additive (food thickening agent is salad dresses) and rheology modifier (stabilized for cosmetic products, to prevent the ingredients from separating) (Becker and Vorholter, 2009). Due to high acid stability, xanthan gum is used for preparation of sauces, salad dressings and syrups. This is an emulsifying agent and has skin hydrating properties. It is also used for microencapsulation and controlled release pills. Xanthan gum is also used in the oil industry to thicken the drilling mud (Tombs and Harding, 1997).

Xanthan costs approximately 14\$ per kg, over 10,000 tonnes of polymer produced annually.

Gellan gum

This polysaccharide is produced by bacterium *Pseudomonas elodea*. Gellan gum consists of tetrasaccharide units (two residues of D-glucose, one of L-rhamnose and one of D-glucuronic acid) connected to each other by ($\alpha 1 \rightarrow 3$) linkages. Inside the tetrasaccharide unit, the monomers are connected by ($\beta 1 \rightarrow 4$) bonds:



Gellan gum is used as a thickener, emulsifier, gelling agent and stabiliser in food industry. It also has a number of applications as microbiological gelling agent instead of agar. One of distinctive feature of this polymer is ability to withstand high temperatures (up to 120°C) which makes it very useful for cultivation of thermophilic organisms.

Conclusion

Polysaccharides do look rather simple when their structure is considered. Comparing to other biological molecules such as DNA and proteins, their structure is relatively simple, they have limited number of functional group, and rather small number of monomeric building blocks is used to produce these polymeric molecules. However, due to the possibility of connecting monomers in a large number of different ways (the property completely absent in natural peptides and nucleic acids where the backbone structure of biopolymers is firmly fixed), polysaccharides enjoy a remarkable variety of structural forms. This variety is responsible for broad range of characteristics and properties found among natural polysaccharides. This variety lies in the heart of multiple industrial and biomedical applications of these polymers.

References:

Becker and Vorholter (2009) Xanthan Biosynthesis by Xanthomonas Bacteria: An Overview of the Current Biochemical and Genomic Data. *Microbial Production of Biopolymers and Polymer Precursors*. Caister Academic Press.

Buchanan, B. B.; Gruissem, W.; Jones, R. L. (2000). *Biochemistry and Molecular Biology of Plants*. Rockville, MD USA: American Society of Plant Biologists.

Clayden, J., Greeves, N., Warren, S. and Wothers, P. (2001) *Organic Chemistry*. Oxford University Press: Oxford, New York.

Klemm, D., Heublein, B., Fink, H.-P. and Bohn, A. (2005), Cellulose: Fascinating Biopolymer and Sustainable Raw Material. *ChemInform*, 36: no. doi: 10.1002/chin.200536238

Sunil A. Agnihotri, Nadagouda N. Mallikarjuna and Tejraj M. Aminabhavi (2004). Recent advances on chitosan-based micro- and nanoparticles in drug delivery. *Journal of Controlled Release* 100 (1): 5–28

Tombs, M.P. and Harding, S.E. (1997) *An Introduction to Polysaccharide Biotechnology*, Taylor & Francis, London.