

## General Information about Cellulose

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### Abstract

Cellulose has been on Earth since the advent of trees and plants, being the main constituent of plant cell walls. Cellulose is currently the most widespread polysaccharide in nature and is being observed by scientists, with changes in the processing, use and genetics of plants (many farmers are interested in genetic mutations to produce larger amounts of cotton). The formation of cellulose in plants is the result of a process of photochemical biosynthesis. The percentage of plant cellulose varies widely: 7–10% for some legumes, 40–50% for cereal or reed straw, 40–60% for the wood mass of various tree species, up to 85–99% for plants textiles. Cellulose is a natural macromolecular substance in the class of carbohydrates, being the main constituent of plant cell membranes. Cellulose is a polysaccharide that together with lignin (an aromatic macromolecular compound) and other substances, forms the walls of plant cells and gives plants mechanical strength and elasticity.

**Keywords:** cellulose; wood cellulose fibers; pentoses, hexoses; polyuronic acids

### Background

Cellulose is the most widespread natural polymer. The recognition of cellulose as a major constituent of the plant cell was in 1838 due to the discoveries of the French botanist Anselme Payen who isolated cellulose for the first time from wood. Then its structure was understood. It is the basic constituent of plant tissues and the main component of the cell membrane in all higher plants, including woody species. Secondary effects of wood such as lignin, hemicelluloses and extractables. With these substances (encrusting substances) cellulose is simply distributed in a mixture or in combination. It is almost impossible to separate chemically pure cellulose from the wall of the plant cell membrane without a more or less advanced deterioration of its chemical structure. It is necessary to make this statement, in order to distinguish chemically pure cellulose, or native cellulose from technical cellulose which is obtained by descaling or boiling wood. It is in fact a mixture of chemical cellulose and various other components with which it is naturally associated in plants [1]. Wood pulp has a shorter fiber than cotton pulp. Spruce cellulose fibers have a length of 2.6–3.8nm, while beech wood cellulose fibers have a length of 0.7–1.7nm. The length of the cellulose fibers in cotton reaches up to 40–50nm. From a chemical point of view, the notion of cellulose means a natural polysaccharide with fibrillar structure, which results from the condensation of a variable number of D – glucose units, which can be

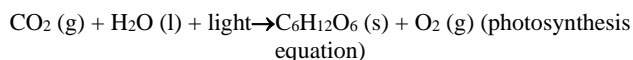
represented by the crude formula:  $(C_6H_{10}O_5)_n$  [2]. The term cellulose does not define a unitary chemical substance, but a supramolecular aggregate consisting of several macromolecular chains of glucan, different in length and associated with each other. It is almost impossible to separate chemically pure cellulose from the wall of the plant cell membrane without a more or less advanced deterioration of its chemical structure. It is necessary to make this statement, in order to distinguish chemically pure cellulose, or native cellulose from technical cellulose which is obtained by descaling or boiling wood. It is in fact a mixture of chemical cellulose and various other components with which it is naturally associated in plants. Wood pulp has a shorter fiber than cotton pulp [3]. Spruce cellulose fibers have a length of 2.6–3.8nm, while beech wood cellulose fibers have a length of 0.7–1.7nm. The length of the cellulose fibers in cotton reaches up to 40–50nm. From a chemical point of view, the notion of cellulose means a natural polysaccharide with fibrillar structure, which results from the condensation of a variable number of D – glucose units, which can be represented by the crude formula:  $(C_6H_{10}O_5)_n$  [4]. The term cellulose does not define a unitary chemical substance, but a supramolecular aggregate consisting of several macromolecular chains of glucan, different in length and associated with each other. Table 1 shows the maximum values in descending order of the cellulose content in the wood of some tree species.

NO.	Wood species	Cellulose content, %
1	Spruce	57.00
2	Fir	55.09
3	Pine tree	55.07
4	Linden	55.74
5	Willow	53.66
6	Sycamore	53.02
7	Poplar	52.56
8	Elm	49.63
9	Beech	49.23
10	Acacia	48.72
11	Birch	48.45
12	Hornbeam	47.83
13	Oak tree	45.08

**Table 1:** Maximum values in descending order of the cellulose content of wood of some tree species

For many years it has been accepted that cellulose is a long chain of polymers made up of glucose. In the 1900's, cellulose was described as more prevalent by Cross and Bevan. They removed the plant parts normally present in cellulose by dissolving them in concentrated sodium dioxide solution. The undissolved part was called  $\alpha$ -cellulose. The soluble material ( $\beta$  – cellulose and  $\gamma$  – cellulose) later proved not to be cellulose but sugars and carbohydrates [5].

The chemical formula is  $(C_6H_{10}O_5)_n$  where  $n$  varies between 700–800 and 2500–3000. Cellulose is made up of glucose molecules joined in the 1–4 position. It is an organic substance, a polymer or more specifically a polysaccharide that is made up of over 3000 molecules of glucose. A polymer is a macromolecule made up of smaller molecules (glucose in this case) that repeats itself. This explains why the structure of cellulose is made up of molecules of glucose or  $C_6H_{12}O_6$ [6]. Glucose is a substance that plays a role in cellular respiration and photosynthesis:



The hydroxyl atoms are grouped in an orderly manner like the crystal structure in the cellulose chain. Hydrogen bonds in crystalline regions are strong leading to insolubility in most solvents (prevents cellulose from melting). In less ordered regions the chains are farther apart and more willing to combine hydrogen with other molecules (water). The components of cellulose are non-metallic; cellulose has covalent bonds. The result is a filiform structure of the cellulosic macromolecular chain. Due to its structure (cellulose is made up of a single monomer) it is called a polysaccharide and cannot be digested by humans. Chemically it is a carbohydrate, cellulose hydroxyls react with aldehydes and form acetates, this reaction leads to stability. Animals (cows, sheep, horses, and other herbivores) have the enzymes needed to digest this material by increasing the rate of cellulose hydrolysis and converting it to glucose. Man does not have these enzymes [7]. Polysaccharides, such as cellulose, are produced by removing water contained in monosaccharide molecules. Cotton companies and other textile mills, along with other methods, use this process to refine cellulose. The purest variety of cellulose is obtained from cotton by degreasing (removing the seeds) and then washing the cotton wool from the capsules of the cotton plant. This variety is used almost

exclusively for textile purposes. A less pure cellulose is obtained from wood, reed or straw. In them cellulose is mixed with various non-cellulosic components, called irecrusts (lignin, oligosaccharides, waxes, resins), which must be removed. The separation is carried out by means of acidic or basic reagents which dissolve the inlays, releasing most of the useful cellulosic material. Among the reagents used, the most commonly used is calcium bisulfite,  $Ca(HSO_3)_2$  (in the bisulfite process) or a mixture of sodium sulfate and sodium hydroxide (in the sulfate process). The resulting pulp is bleached and used for papermaking or chemicalization [8].

### Cellulose biosynthesis

Cellulose is formed in plants during the process of photosynthesis, from  $CO_2$  and  $H_2O$ , under the influence of light and in the presence of chlorophyll. From these substances, through the stationary cycle of photosynthesis, elementary units of D-glucose are reached, capable of forming macromolecular chains of cellulose. According to one of the existing theories, the formation of polysaccharides in plants follows an enzymatic mechanism, in two main directions under the specific action of different enzymes. In a first stage, the D-glucose molecules bind successively under the action of phosphorylase-type enzymes, which favor the appearance of  $C_1$ - $C_4$   $\beta$ -glycosidic bonds between the elementary glucose units. In the second step, the enzyme catalyzes the simultaneous binding of previously made macromolecule fragments, a process also called "copolymerization block". However, it is also necessary to explain how the enzymes catalyze the simultaneous polymerization and crystallization of the macromolecular cellulose chains between them [9]. Theoretically there are two variants:

- In a first embodiment, the elemental cellulose fiber develops from a single spherical enzyme particle with a spherical diameter of 8 nm, which by extrusion in a certain direction elongates and becomes thinner to a thickness of 3.5 nm. This hypothesis is consistent with the actual constant diameter of the elementary fiber, but does not give any information regarding the para-crystalline and amorphous cellulose content of the cellulose fiber, it does not explain a certain length of the elemental cellulose fibril.

- In the second variant, it is considered that the synthesis of the elemental cellulose fibril takes place from several enzymatic particles, their development taking place in the lateral direction. At the points of contact with the enzyme, the network of macromolecular cellulose chains is constructed in a more orderly (parallel) manner, the so-called crystalline zone, while between the enzymatic particles the network is less ordered, constituting the amorphous zone, but the system and the formation of cellulose elementary fibrils has not been fully elucidated [10].

However, some basic conclusions can be drawn from the study of the structure and formation of the walls of the vegetal cell membrane:

- cellulose initially appears in the primary wall along with hemicelluloses, pectins and lignin, serving as a framework for their support. During plant growth, cellulose is formed in the form of microfibrils with a diameter of 10–30 nm thickened in the plane of the primary wall.
- In the secondary wall, however, the cellulose microfibrils have a strictly parallel orientation and with modified dimensions, the biosynthesis process is influenced here by other factors than in the case of the primary wall.
- the final process of cell wall formation also involves the formation of the tertiary wall, which differs in chemical and morphological properties from the other walls of the plant cell membrane [11,12].

The chemical structure of cellulose. The study of the structure of cellulosic fibers is carried out by appropriate means at three different scales:

- At the microscopic scale, when studying the molecular structure of cellulose, various indirect pathways are used, usually chemical and physico-chemical, determining how to bind atoms in the macromolecule, as well as macromolecular chains of cellulose in the elementary structural aggregate (0.5–3nm);
- on a submicroscopic scale, when studying the fine or supramolecular structure. At this scale, it is possible to directly observe the

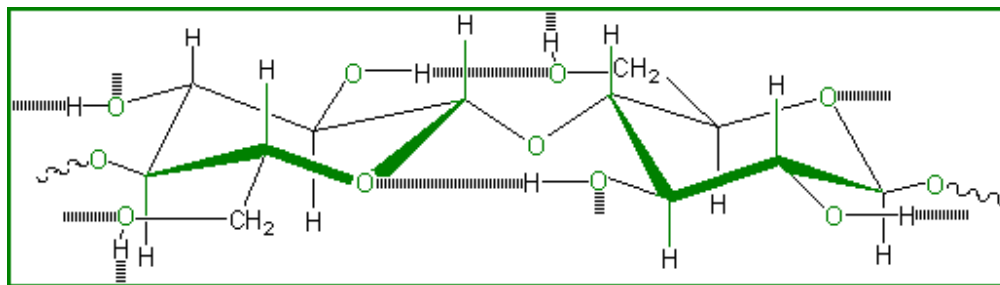
arrangement of specific elements in the cellulose fiber, called fibrils (25–30nm);

- at the microscopic scale, when studying the microscopic structure of the cellulosic aggregate. The study at this scale offers the possibility to observe with the optical microscope the morphological details of the cellulose fiber (over 500nm) [13,14].

### Molecular structure of cellulose

The first evidence on the chemical structure of the macromolecular cellulose chain was provided by the results of its direct hydrolysis process with concentrated mineral acids. At the total hydrolysis of cellulose with 40% hydrochloric acid, it is formed with a yield of 96–98% compared to the theoretical D-glucose. During partial hydrolysis of cellulose, the disaccharide cellobios is formed. The simplest structural unit, also called the elementary structural unit (u.e.s.) of the macromolecular cellulose chain is anhydro- $\beta$ -D-glucopyranose. Only ether and trisubstituted cellulose esters, respectively, can be obtained as final products by the etherification or complete esterification reactions of cellulose. Hydrolysis of these products results in higher amounts of trimethyl glucose and lower amounts of tetramethyl glucose. The elemental unit of anhydro- $\beta$ -D-glucopyranose in cellulose contains three free alcoholic hydroxyl groups, 2,3,6-trimethylglucopyranose (ether). Of the three hydroxyl alcoholic groups of the elementary unit of anhydro- $\beta$ -D-glucopyranose, the one at the C<sub>6</sub> atom is the primary alcohol group, and the other two at the C<sub>2</sub> and C<sub>3</sub> atoms are secondary alcohol groups. Primary alcohol groups are 5-6 times more reactive than secondary groups [15].

The elemental units of anhydro- $\beta$ -D-glucopyranose in the cellulose chain are joined together by specific etheric bonds (C<sub>1</sub>-C<sub>4</sub>  $\beta$ -glycosidic bonds). They are made by removing a water molecule from the C<sub>1</sub> glycosidic hydroxyl of a D-glucose unit and the secondary alcoholic hydroxyl from the C<sub>4</sub> of the neighboring D-glucose unit. The oxygen atom that binds the two elementary structural units (–O–) is called glycosidic oxygen and differs from the oxygen atom in the oxide bridge (C<sub>1</sub> – O – C<sub>5</sub>) that participates in the formation of the pyranose cycle. The elementary unit of anhydro- $\beta$ -D-glucopyranose is in the form of the  $\beta$ -anomer, as this isomer forms the disaccharide cellobios, which is the penultimate product of cellulose hydrolysis.



Namely the existence of the C<sub>1</sub> – O – C<sub>4</sub> – glycosidic bond between the elementary units of the macromolecular cellulose chain determines its low stability to the action of hydrolysis agents. Their action, including water, at high temperatures causes the breakdown of glycosidic bonds and complete depolymerization to D-glucose. In order not to be tense, the pyranose cycle can have two spatial conformations, either in the shape of a "bath" or in the shape of a "chair". The "bathroom" conformation is richer in energy than the "chair" conformation [16].

The former has a lower stability and will be less common in the structure of the macromolecular cellulose chain. If we consider that a water molecule remains bound to the macromolecular chain, the cellulose formula can also be presented: (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>xH<sub>2</sub>O. It is considered that the elementary unit of D-glucopyranose at the left end of the chain has an

extra hydrogen atom, and that at the right end an additional hydroxyl group: H–(C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>-OH. Cellulose has reducing (insignificant) properties. In the case of natural macromolecular compounds, respectively cellulose, the elementary units of anhydro- $\beta$ -D-glucopyranose are able to rotate against each other at 180°, which practically causes a bending of the cellulose chain from place to place. Due to the free rotation of pyranose cycles of anhydro- $\beta$ -D-glucopyranose in both directions to the glycosidic oxygen atom, the macromolecular cellulose chain can adapt to different shapes. The macromolecular cellulose chain is not only made up of D-glucopyranose units, but also contains small amounts of other monosaccharides [17].

The presence of residues of various monosaccharides has been thoroughly proven by the total hydrolysis of cellulose obtained from wood. In

addition to D-glucose, cellulose contains appreciable amounts of mannose and birch cellulose contains xylose residues. Traces of arabinose, mannose, galactose and even glucuronic acid have also been identified in deciduous cellulose. The main carriers of wood pulp are mixed polysaccharides such as pentoses, hexoses and polyuronic acids. In the process of cellulose biosynthesis, in addition to the macromolecular chains of cellulose, macromolecular chains of mixed polysaccharides are formed, in the composition of which, in addition to anhydrous- $\beta$ -D-glucopyranose residues, there are also residues of other monosaccharides with pyranose structure even furanose. When changes in cellulose destruction by internal or external factors occur over time, it is said to undergo an aging process [18].

The aging process of cellulose depends on the number of weaknesses in its supramolecular structure. During such a process cellulose is cornified, i.e., from a supramolecular point of view, its structural elements are merged by welding into larger aggregates due to the multiplication of hydrogen bonds. Aging of fibrous cellulosic materials is often accompanied by a decrease in the degree of whiteness (yellowing). The process is attributed to the appearance of chromophore groups, which results in the oxidation of free functional groups along or at the end of macromolecular cellulose chains [19].

The reactions take place under the action of oxygen, temperature and metal ions as catalysts. Destruction reactions can take place through oxidative, hydrolytic, thermal, mechanical, photochemical and biochemical degradation processes, all of which lead to changes in the properties of cellulose: decrease in the degree of polymerization, reduction of physical-mechanical resistance, increase in solubilization, etc.

### Concluding Remarks and Future Perspectives

Cellulose is a natural organic compound in the category of polysaccharides, being the main constituent of plant cell membranes. Together with lignin (an aromatic macromolecular compound) and other macromolecular compounds, it enters the structure of plant cell walls and gives plant organisms mechanical strength and elasticity. It has the same crude formula as starch,  $(C_6H_{10}O_5)_n$ , where  $n$  can reach thousands. Cellulose consists of a linear chain, in which there are thousands of D-glucose units, linked together by  $\beta$  bonds (1  $\rightarrow$  4). Cellulose is used to make smoke-free explosive substances; artificial viscose silk (Milanese) and acetate silk; of nitrolacs and nitroemails (fast-drying and high-gloss coating varnishes); of cellophane. It is a raw material of great economic value and is the starting point in the manufacture of important products, of which paper occupies a major place (it has been used to obtain paper since the second century). It is found in large quantities in almost all plants and is a major source of food. It has the properties of reducing the caloric value of some foods if crystallized cellulose is added to them. Viscose silk is used in the manufacture of various fabrics as well as tire cord. If the viscose solution is spun through a fine cast iron in a bath of dilute sulfuric acid and glycerin, foils are obtained from a widely used product - cellophane. Products containing cellulose: sponges, allergy or powder sprays, medical tapes. Cellulose is very cheap because it is very abundant.

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### Conflicts of interest/Competing interests

The authors declare no conflict of interest.

### Availability of data and material

Not applicable.

### Code availability

Not applicable.

### Authors' contributions

Conceptualization, G.V.P. and M.B.; methodology, G.V.P.; validation, G.V.P.; investigation, G.V.P.; data curation, G.V.P. and M.B.; writing—original draft preparation, M.B.; writing—review and editing, G.V.P. and M.B.; visualization, M.B.; supervision, M.B. All authors have read and agreed to the published version of the manuscript.

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### Ethics approval

Not applicable.

### Consent to participate

Not applicable.

### Consent for publication

Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

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