

Biosynthesis of Food Constituents: Saccharides.

2. Polysaccharides – a Review

JAN VELÍŠEK and KAREL CEJPEK

Department of Food Chemistry and Analysis, Faculty of Food and Biochemical Technology, Institute of Chemical Technology Prague, Prague, Czech Republic

Abstract

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This review article gives a survey of the selected principal biosynthetic pathways that lead to the most important polysaccharides occurring in foods and in food raw materials and informs non-specialist readers about new scientific advances as reported in recently published papers. Subdivision of the topic is predominantly done via biosynthesis and includes reserve polysaccharides (starch and glycogen, fructans), plant cell wall polysaccharides (cellulose and callose, pectin), and animal polysaccharides (chitin and glycosaminoglycans). Extensively used are the reaction schemes, sequences, and mechanisms with the enzymes involved and detailed explanations using sound chemical principles and mechanisms.

Keywords: biosynthesis; polysaccharides; starch; glycogen; fructans; cellulose; callose; pectin; chitin; glycosylaminoglycans; mucopolysaccharides

Polysaccharides fulfil two main functions in living organisms, as structural elements and food reserves (VOET & VOET 1990; DEWICK 2002; VELÍŠEK 2002). Most of the photosynthetically fixed carbon in plants is incorporated into cell wall polysaccharides. The central process of polysaccharide synthesis is the action of glycosyltransferases (also called glycosylsynthases). These enzymes form glycosidic bonds by attaching a sugar moiety of an appropriate donor substrate, mainly a nucleotide sugar, to a specific acceptor substrate (VELÍŠEK & CEJPEK 2005). Whereas amylose, callose, cellulose, and other linear polysaccharides are synthesised in a single-step reaction involving no intermediates, the assembly of the branched polysaccharides, such as xyloglucan, galactomannan, and pectin, requires a number of enzyme activities.

1 RESERVE POLYSACCHARIDES

1.1 Starch and glycogen

The starch biosynthetic pathway plays a distinct role in the plant metabolism. In the plastids of higher plants, either transient or reserve starch is formed. The former is synthesised in leaves and serves as a temporary sugar reserve. It is accumulated in chloroplasts during the day and serves as a major source for saccharose synthesis at night. Saccharose is then transported to the storage organs of plants, such as seeds, fruits, tubers, and roots. Eventually, reserve starch is biosynthesised in amyloplasts (VELÍŠEK 2002).

Starch is composed entirely of D-glucose (D-Glc) and is a mixture of two types of macromolecules,

amylose and amylopectin. Amylose is a linear polymer containing 1000–2000 glucose units linked by α -(1→4) bonds. The repeating unit is the disaccharide maltose, α -D-glucopyranosyl-(1→4)-D-glucopyranose (BALL *et al.* 1998). Amylopectin is a branched-chain polysaccharide with a much larger molecule. The number of glucose residues varies widely but may be as high as 10^6 . In addition to α -(1→4) linkages, amylopectin has branches at about every 24–30 glucose units through α -(1→6) linkages. The repeating unit in the amylopectin branches is the disaccharide isomaltose, α -D-glucopyranosyl-(1→6)-D-glucopyranose. These branches continue with α -(1→4) linkages, but then they may have subsidiary branching giving a tree-like structure (BULÉON *et al.* 1998).

Animals, bacteria, and yeasts store glucose as glycogen. The mammalian storage polysaccharide glycogen is analogous to starch amylopectin in structure and biosynthesis, but it has a larger molecule (more than 10^6 glucose residues) and contains more frequent branching, at about every 8–12 glucose residues.

Glycogen and starch biosynthetic processes are quite similar (VOET & VOET 1990; FRANSON *et al.* 2000). The biosynthesis of glycogen is a three-step reaction. The first step, catalysed by UDP-glucose 1-phosphate uridylyltransferase (UDP-glucose pyrophosphorylase, EC 2.7.7.9), is a transformation of D-glucose 1-phosphate (Glc1P) to the active form of glucose, UDP-D-glucose (UDP-Glc). In

the second step, glycogen biosynthesis is initiated on a self-glucosylating specific protein glycogenin. A limited number (6–10) of glucose residues can be transferred to one molecule of glycogenin by glycogenin glucosyltransferase (EC 2.4.1.186) and bound to the protein through the hydroxyl group of L-tyrosine. This glucose chain having glycosidic α -(1→4) bonds then serves as a template for glycogen synthase (EC 2.4.1.11)¹. Glycogen synthase extends the already existing maltosaccharide molecule as it transfers UDP-Glc molecules to its not reducing end. The reaction proceeds through the corresponding carbenium cation (Figure 1).

The third step, the branching of glycogen, is achieved by the enzymic removal of a portion of about 7 glucose residues of the α -(1→4) linked straight chain consisting of at least 11 glucose residues, then transferring this short chain to a suitable C-6 hydroxyl group of glucose. The new branching must be at least 4 glucose units apart from the already existing branching (Figure 2). The reaction is catalysed by amylo-(1,4→1,6) transglycosylase (so called branching enzyme, EC 2.4.1.18).

The biosynthesis of both starch amylose and amylopectin from saccharose proceeds via ADP-D-Glc (MUKERJEA *et al.* 2002; JAMES *et al.* 2003; VANDEPUTTE & DELCOURT 2004). Sucrose synthase (EC 2.4.1.13) converts saccharose into D-fructose and UDP-D-Glc. UDP-D-Glc is then further metabolised to D-Glc1P by the action of UDP-glucose

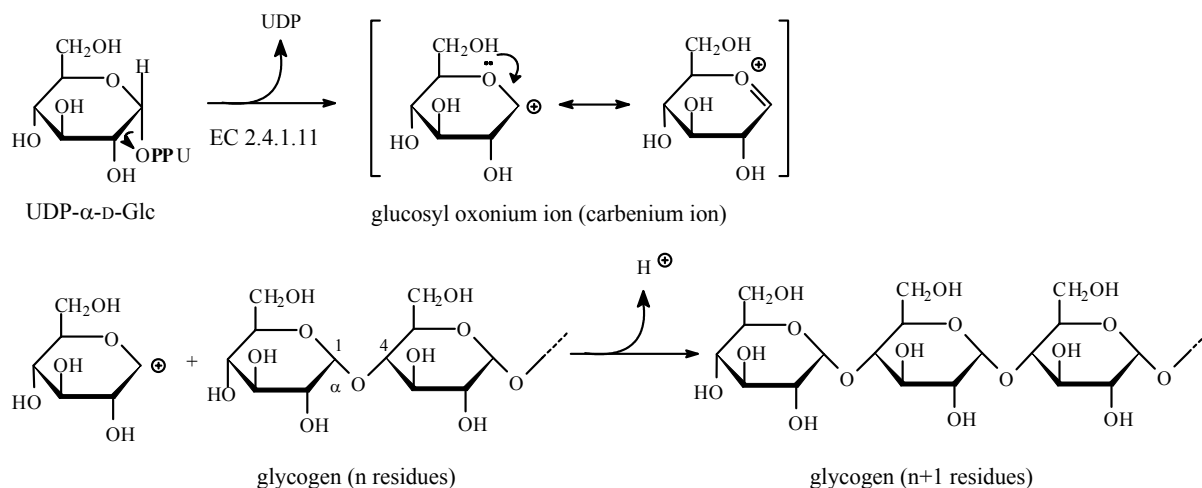


Figure 1

¹Glycogen synthase (EC 2.4.1.11) from animal tissues is a complex of a catalytic sub-unit and the protein glycogenin. The enzyme is only able to elongate the already existing α -(1→4) polysaccharide chain and in the initial reaction step requires glucosylated glycogenin as a primer, i.e. the enzyme catalyses its own autoglucosylation.

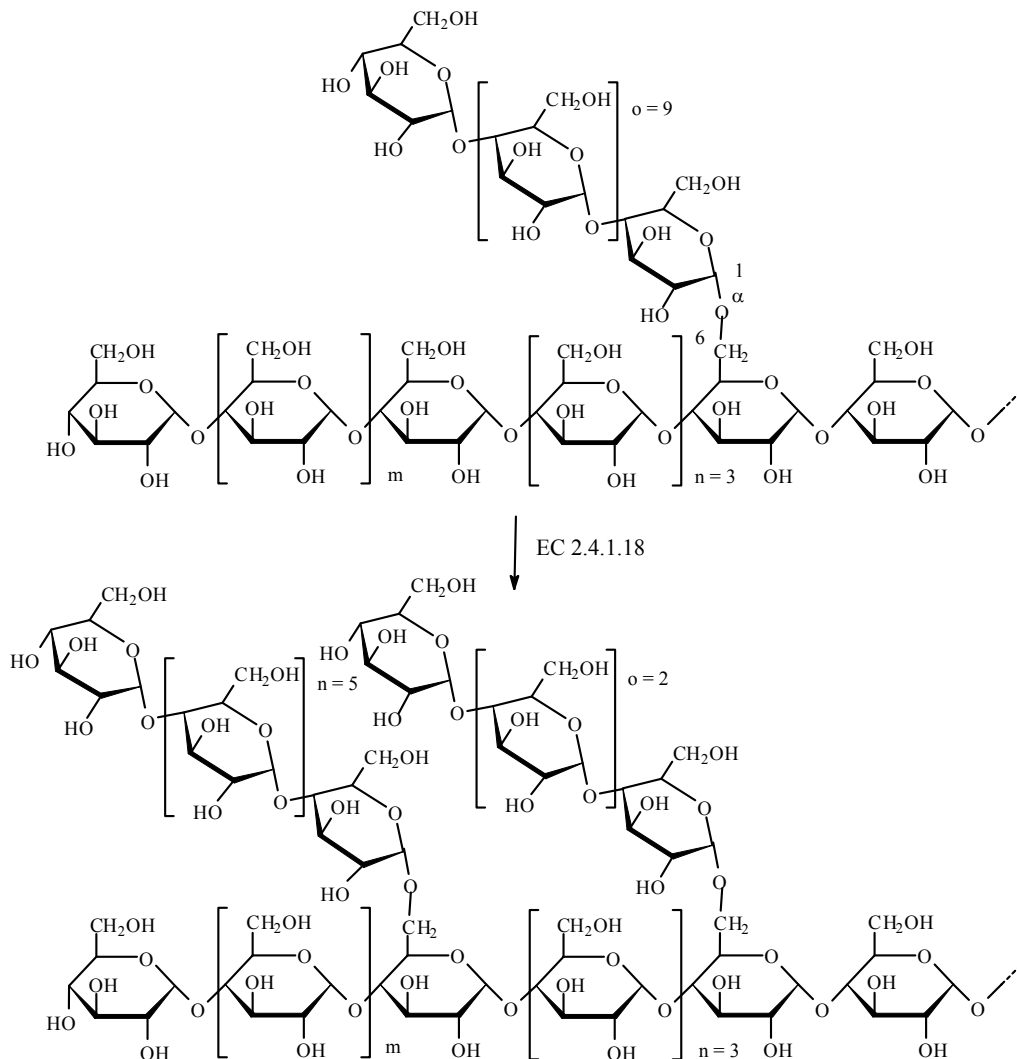


Figure 2

pyrophosphorylase (EC 2.7.7.9). The formation of ADP-Glc from Glc1P and ATP (catalysed by ADP glucose pyrophosphorylase, EC 2.7.7.27) is the first step of the starch biosynthetic pathway. Starch synthase (EC 2.4.1.21) catalyses the transfer of the glucosyl unit from ADP-glucose to the reducing end of the growing starch chain, attached to the protein acceptor² (SINGH *et al.*

1995), via an α -(1→4) linkage (CHATTERJEE *et al.* 2005). After the elongation of the α -glucan chain by starch synthase, starch branching enzyme (EC 2.4.1.18) catalyses hydrolysis of α -(1→4) bonds and the transfer of the released reducing end to a C-6 glucosyl unit resulting in an α -(1→6) branch point. Amylopectin debranching enzymes are also involved in starch biosynthesis³.

²In plants, starch synthases require primers (analogous to glycogenin in animals) for starch biosynthesis. Whether priming molecules for starch biosynthesis exist in plants is still controversial. Earlier claims concerning the existence of such a protein called amylogenin were subsequently dismissed, but a glycogenin-like starch initiation protein has been recently discovered.

³Following starch branching, starch debranching enzyme oligo-1,6-glucosidase (EC 3.2.1.10) catalyses the hydrolysis of α -(1→6) bonds. Two other debranching enzymes with different substrate specificity have been distinguished: isoamylase (EC 3.2.1.68) and pullulanase (EC 3.2.1.41). Isoamylase debranches both, glycogen and amylopectin. In contrast, pullulanase attacks amylopectin, but not glycogen. Oligo-1,6-glucosidase can release an α -(1→6)-linked glucose, whereas the shortest chain that can be released by pullulanase and isoamylase is maltose.

1.2 Fructans

Fructans are polymers of D-fructofuranose and most often contain D-glucose as the end unit (glucofructans). Fructans are used as storage polysaccharides by almost 15% of all flowering plant species. Fructans can be stored in different types of organs, including leaves and stems (wheat, barley), bulbs (onion), taproots (chicory) or tubers (Jerusalem artichoke, *Helianthus tuberosus*) (VELÍŠEK 2002).

Fructans consisting of linear β -(1→2) linked fructose polymers are called inulins. Typical inulins occur, e.g. in the Jerusalem artichoke tubers. Levans are β -(2→6) branched fructose polymers. Typical levans are synthesised by some microorganisms, e.g. by *Bacillus subtilis*, using saccharose as a precursor. In wheat, barley, and onion fructans, both linkage types occur. The degree of polymerisation of the plant fructans can vary between 10 and 250 fructose units. For instance, in the Jerusalem artichoke, fructans (inulins) have a degree of polymerisation of up to 30 while the globe artichoke (*Cynara scolymus*) synthesises inulin molecules with a chain length of up to 200, which is the highest degree of polymerisation of inulin molecules known in plants.

Inulins are synthesised from saccharose by a concerted action of at least two fructosyltransferases, i.e. in two steps (VAN DER MEER *et al.* 1998; HELLWEGE *et al.* 2000). In the first step, the

trisaccharide 1-kestose (GF₂) forms by transferring a fructose unit from a saccharose donor onto a saccharose (GF) acceptor molecule (Figure 3). This reaction is catalysed by sucrose:sucrose 1-fructosyl transferase⁴ (EC 2.4.1.99). A second enzyme, 1-fructan:fructan fructosyl transferase (EC 2.4.1.100), is required to synthesise fructans with a higher degree of polymerisation by transferring fructosyl units between GF₂ and larger fructans according to the equation: $[\beta$ -(1→2)-D-Fru]_m + $[\beta$ -(1→2)-D-Fru]_n = $[\beta$ -(1→2)-D-Fru]_{m-1} + $[\beta$ -(1→2)-D-Fru]_{n+1}, producing a mixture of fructans with different chain lengths, i.e. the tetrasaccharide 1,1-nystose (GF₃), pentasaccharide 1,1,1-fructosylnystose (GF₄) etc.

2 Plant cell wall polysaccharides

2.1 Cellulose and callose

Cellulose is the major polysaccharide in the primary and secondary cell walls (BROWN *et al.* 1996). Enzymes of this group catalyse glycosyl transfer reactions that involve inversion at the anomeric carbon leading to the formation of β -(1→4)-linked D-glucan, which is then stabilised by hydrogen bonds. The repeating unit in the cellulose chain is therefore the disaccharide cellobiose, β -D-glucopyranosyl-(1→4)-D-glucopyranose. In nature, cellulose never occurs as a single chain, but from

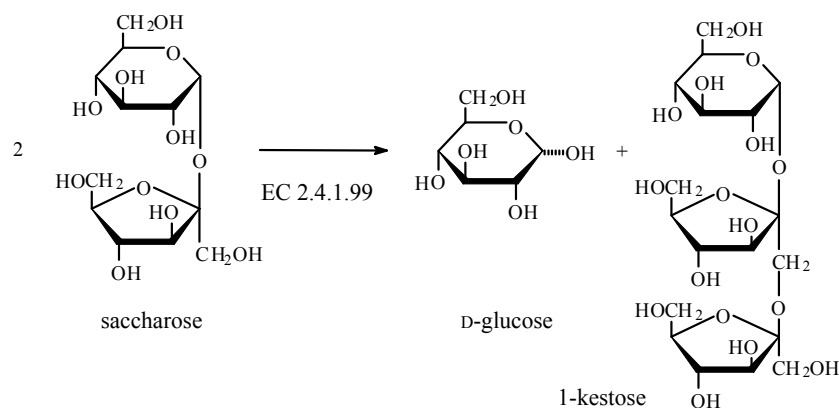


Figure 3

⁴The enzymes EC 2.4.1.9 (inulosucrase, sucrose 1-fructosyltransferase) and EC 2.4.1.99 (sucrose-sucrose 1-fructosyltransferase) have overlapping substrate specificities, each being able to use two sucrose molecules. When the predominant product is 1-kestose the enzyme is classified as EC 2.4.1.99, when the predominant products are higher fructooligosaccharides the enzyme is classified as EC 2.4.1.9. Analogously, levans are synthesised from saccharose by the action of levansucrase (sucrose 6-fructosyltransferase, EC 2.4.1.10).

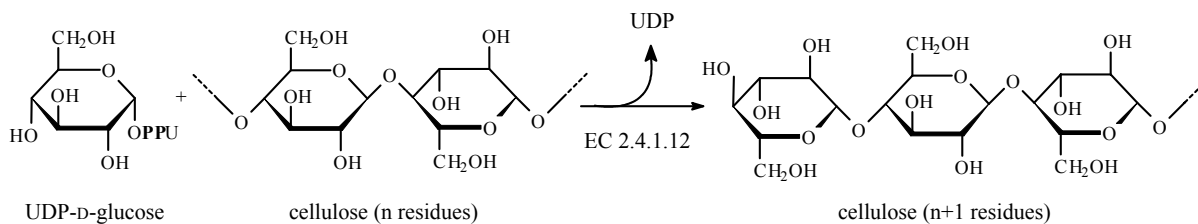


Figure 4

the moment of its biosynthesis as a crystalline array of microfibrils each of which contains an estimated 36 parallel polysaccharide chains stiffened by intra- and intermolecular hydrogen bonds. Cellulose biosynthesis from UDP-glucose by cellulose synthase (EC 2.4.1.12) does not require a primer (SAXENA & BROWN 2000) (Figure 4).

The amorphous β -(1 \rightarrow 3) glucan called callose is less abundant than cellulose during normal plant growth (BROWN *et al.* 1996) (Figure 5). The repeating unit in the callose chain is the disaccharide laminarabiose, β -D-glucopyranosyl-(1 \rightarrow 3)-D-glucopyranose. Most plants make this polysaccharide upon wounding and in some cells it is made at a specific stage of the wall development from UDP-glucose by callose synthase (EC 2.4.1.34).

2.2 Pectin

Pectin is a complex acidic polysaccharide that contains α -1,4-linked D-galacturonic acid (D-GalA) residues found in the primary wall of all higher land plant cells other than the grasses and their likes. The pectic polysaccharides play a critical role in the cell wall structure and in the plant growth and development. Three major domains of pectin, homogalacturonan, rhamnogalacturonan I, and rhamnogalacturonan II, have been found in the primary wall of all plants (RIDLEY *et al.* 2001, VELÍŠEK 2002).

The homogalacturonan chain consists of blocks of methyl-esterified (neutral) D-GalA residues alternating with blocks of non-esterified (negatively charged) GalA residues. The charged blocks can be cross-linked by Ca^{2+} ions. Some GalA residues are also O-acetylated, which increases the hydrophobicity of the molecule. Rhamnogalacturonan I (degree of polymerisation \cong 1000) contains a backbone of repeating D-galacturonic acid/L-rhamnose (L-Rha) units, α -D-GalpA-(1 \rightarrow 2)- α -L-Rhap-(1 \rightarrow 4). Some GalA residues occur as their 4-O-methyl ethers. Rhamnogalacturonan II (degree of polymerisation \cong 60) has a backbone rich in α -(1 \rightarrow 4)-linked GalA, to which several different side-chains are attached. These side-chains include the following residues: α - and β -D-GalpA, α - and β -D-Rhap, α -D-Galp, α -L-Fucp, α -L-Arap, β -L-Araf, α -D-Xylp, D-GlcpA, and four unusual sugar residues, i.e. 3-C-(hydroxymethyl)- β -D-erythrofurano- β -D-Apif, apiose), 3-C-carboxy-5-deoxy- β -L-xylofuranose (β -L-AcefA, aceric acid), 3-deoxy- β -D-lyxo-hept-2-ulopyranaric acid (β -D-Dhap, derived from the trivial name deoxyheptonic acid), and 3-deoxy- β -D-manno-oct-2-ulopyranosonic acid (β -D-Kdop, derived from the trivial name ketodeoxyoctonic acid) (Figure 6). The xylose and some of the fucose occur as their 2-O-methyl ethers. Rhamnogalacturonan II has recently been shown to become dimerised via a borate tetraester cross-link. The

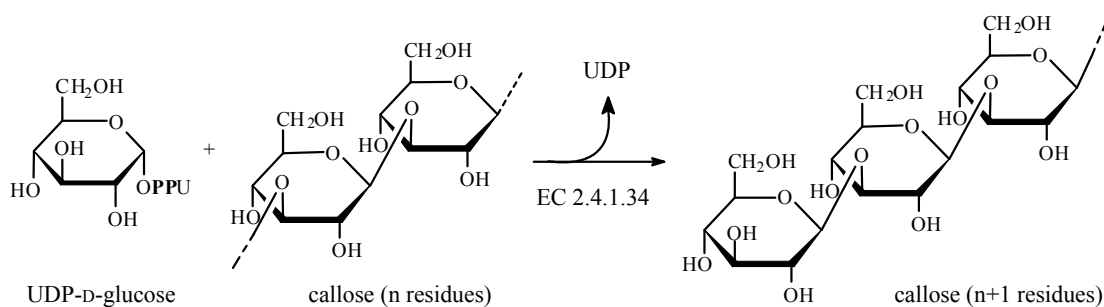


Figure 5

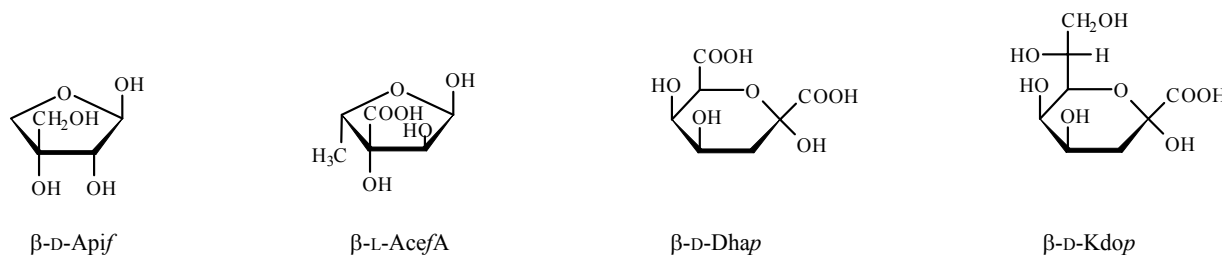


Figure 6

borate is believed to bind tightly to the *cis*-hydroxyls at C-2 and C-3 of an apiose moiety creating a borate diester, which can then react with the apiose moiety of another rhamnogalacturonan II molecule to form a tetraester bond. The establishment of this cross-link has recently been shown to reduce the wall porosity, a property that may be highly significant for the cell wall function and integrity. Some pectins from the members of the *Chenopodiaceae* family (spinach, beet, etc.) appear to carry sugar residues esterified by ferulic acid (PUVANESARAJAH *et al.* 1991; MØLHØJ *et al.* 2003).

The biosynthesis of pectin proceeds in two steps, the backbone synthesis and its subsequent modification. The galacturonosyltransferase (EC 2.4.1.43) is responsible for the biosynthesis of non-esterified homogalacturonan (pectate) (Figure 7). The substrate for the homogalacturonan synthesis is UDP-GalA that is also a likely substrate for the biosynthesis of rhamnogalacturonan I and rhamnogalacturonan II backbones. The formed pectate is partly methylated. The enzymes that methylate pectin are not well characterised (GOUBET & MÖHNEN 1999; BOURLAND *et al.* 2001). They are typically referred to as pectin methyltransferases (or homogalacturonan methyltransferases, EC 2.1.1.6.x). These pectin methyltransferases use *S*-adenosyl-*L*-methionine (SAM, AdoMet) as the methyl donor, which is formed from *L*-methionine

and ATP. The formation of SAM is catalysed by methionine adenosyltransferase (EC 2.5.1.6). SAM has positively charged sulfur, which facilitates the biosynthetic methylation of suitable acceptors yielding the corresponding methylated acceptors and *S*-adenosyl-*L*-homocysteine (AdoHcy), a potent inhibitor of most methyltransferases (Figure 8).

The major known plant enzymes that can attack homogalacturonans are exo-polygalacturonase (α -D-galacturonidase, EC 3.2.1.67), endo-polygalacturonase (pectinase, EC 3.2.1.15), and pectin methylesterase (pectinesterase, EC 3.1.1.11). Exo-polygalacturonase and pectin methylesterase are probably universal in the growing plant tissues; endo-polygalacturonase activity is largely restricted to specific tissues, e.g. ripening fruit.

3 Chitin

Chitin is a biopolymer composed of D-glucosamine and *N*-acetylated glucosamine (2-acetylaminoglycoside-2-deoxy-D-glucose) units linked by β -(1 \rightarrow 4) glycosidic bonds. Chitin constitutes shells of arthropods such as crabs, shrimps, lobsters, and insects, and is produced extracellularly also by fungi and brown algae (KOIDE 1998). Chitin synthase (EC 2.4.1.16) is the enzyme responsible for the conversion of UDP-*N*-acetyl-D-glucosamine (UDP-D-GlcNAc) into chitin polymeric chains of β -(1 \rightarrow 4)-linked *N*-acetyl-D-glucosamine⁵ (Fig-

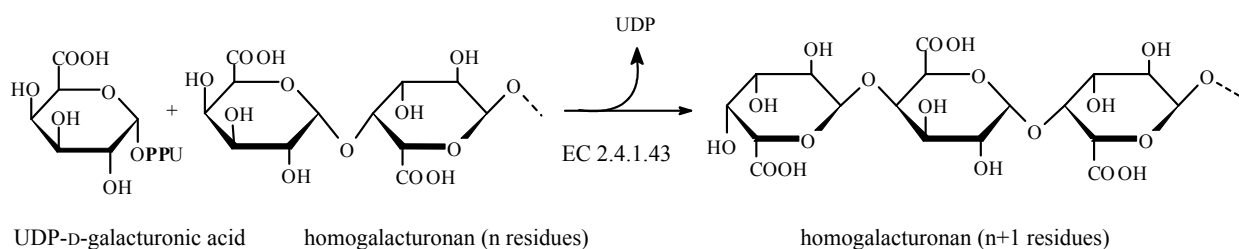


Figure 7

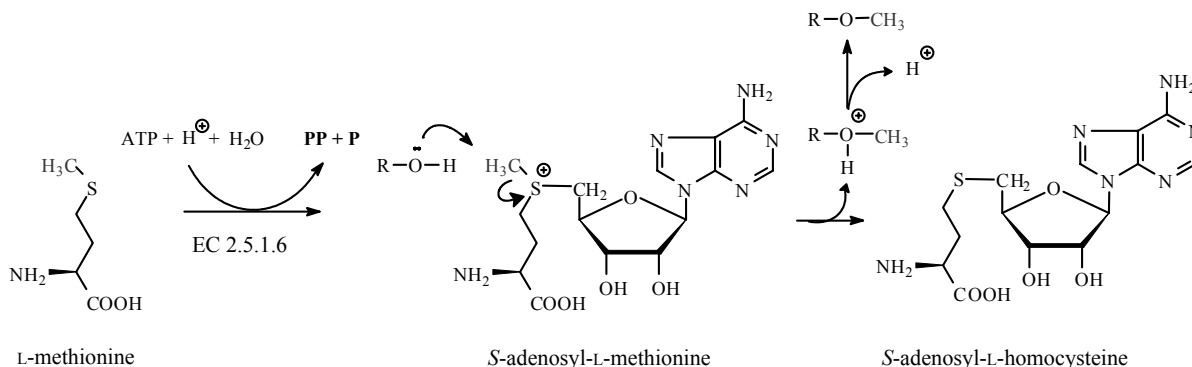


Figure 8

ure 9) that are partially deacetylated to chitosan by chitin deacetylase (EC 3.5.1.41) (YEAGER & FINNEY 2004).

4 Glycosaminoglycans

Glycosaminoglycans (mucopolysaccharides) function in various biological systems as constituents of proteoglycans (mucoproteins) and glycoproteins. Proteoglycans are the principal components of extracellular epithelium layers and various connective tissues (skin, blood vessels, cartilages, and bones). In cells, they also have important protective roles. Glycosylaminoglycans-based glycoproteins are constituents of various gelatinous materials (saliva, egg white, etc.).

Glycosylaminoglycans are composed of characteristic repeating disaccharide units with sulfate groups at various positions and various combinations (HABUCHI 2000; SUGAHARA & KITAGAWA 2000). Linear sulfated glycosaminoglycans are classified into two types, chondroitin sulfate/

dermatan sulfate, and heparan sulfate/heparin, the former being galactosaminoglycans and the latter glucosaminoglycans. Both types of glycosaminoglycan chains are covalently attached to their respective core proteins through the so-called glycosaminoglycan-protein linkage region, β -D-GlcA-(1 \rightarrow 3)- β -D-Galp-(1 \rightarrow 3)- β -D-Galp-(1 \rightarrow 4)- β -D-Xylp-(1 \rightarrow , attached to selected L-serine residue in the core protein (Figure 10).

The biosynthesis of this linkage region starts with the addition of Xyl from UDP-D-Xyl to a serine residue by the protein xylosyl transferase (FRANSON *et al.* 2000) (EC 2.4.2.26). Two Gal units (from UDP-D-Gal) and one D-glucuronic acid (D-GlcA) residue (from UDP-D-GlcA) are then added by three distinct transferases, i.e. galactosyltransferase I (EC 2.4.1.133), galactosyltransferase II (EC 2.4.1.134), and glucuronyltransferase I (EC 2.4.1.135), respectively. The glycosaminoglycans are then built up on this linkage region by the alternative additions of *N*-acetylhexosamine (UDP-D-GalNAc or UDP-D-GlcNAc) and D-GlcA residues. Chondroi-

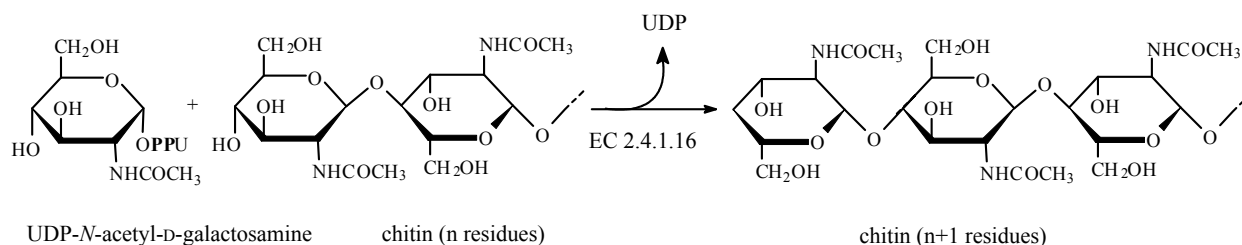


Figure 9

⁵Chitinase (EC 3.2.1.14) hydrolyses chitin to monomers, chitin deacetylase (EC 3.5.1.41) transforms chitin to chitosan by hydrolysing the acetamido groups of polymeric *N*-acetyl-D-glucosamine, and *N*-acetylglucosamine deacetylase (EC 3.5.1.33) converts monomeric *N*-acetyl-D-glucosamine to D-glucosamine and acetic acid.

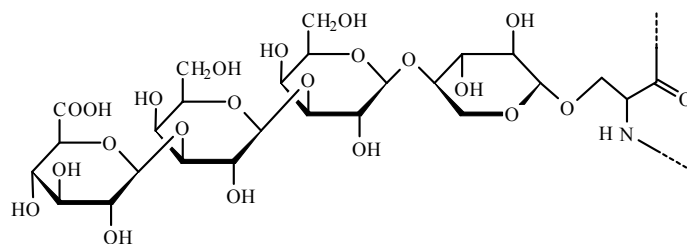


Figure 10

tin sulfate/dermatan sulfate glycosaminoglycan is formed if *D*-GalNAc is transferred to the common linkage region by *N*-acetylgalactosaminyltransferase I (EC 2.4.1.174). Analogously, heparan sulfate/heparin glycosaminoglycan is formed if *D*-GlcNAc is first added by *N*-acetylglucosaminyltransferase I (EC 2.4.1.223).

The elongation of a chondroitin sulfate/dermatan sulfate chain then proceeds via alternating additions of *D*-GlcA (chondroitin glucuronyltransferase II, EC 2.4.1.226) and *D*-GalNAc (*N*-acetylgalactosaminyltransferase II, EC 2.4.1.175) (Figure 11).

Sufation using 3'-phosphoadenosine-5'-phosphosulfate (PAPS) as the donor (KUSCHE-GULLBERG & KJELLÉN 2003) then occurs at either C-4 (chondroitin 4-*O*-sulfotransferase, EC 2.8.2.5) or C-6 (chondroitin 6-*O*-sulfotransferase, EC 2.8.2.17) of GalNAc, producing a chondroitin sulfate chain (Figure 12).

When 5'-epimerase (chondroitin *D*-glucuronosyl 5-epimerase, EC 5.1.3.19) catalyses the conversion of *D*-GlcA to *L*-iduronic acid (*L*-IdoA), a dermatan/chondroitin co-polymer is formed (Figure 13). Finally, IdoA can be partially sulfated at C-2 (dermatan 2-*O*-sulfotransferase), forming a typical dermatan chain⁶.

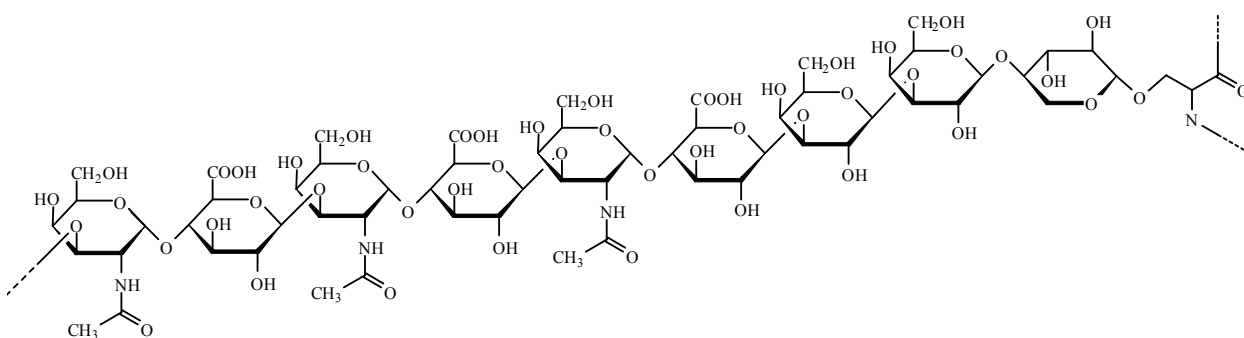


Figure 11

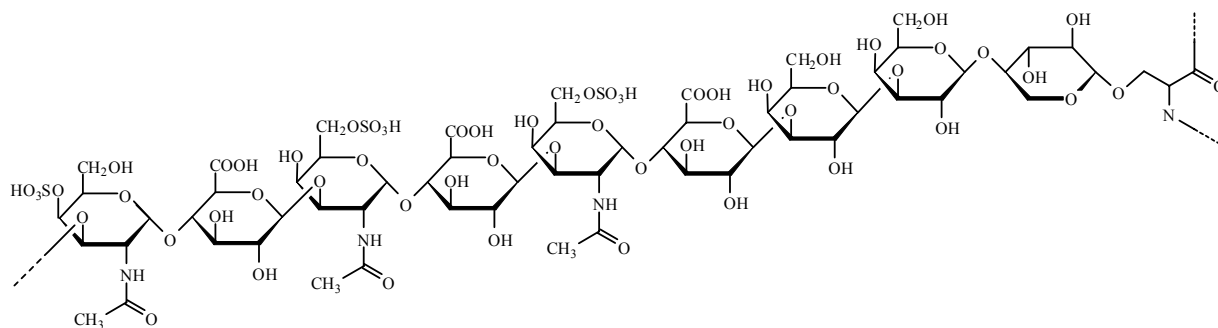


Figure 12

⁶The sulfotransferases involved in the biosynthesis of chondroitin sulfate/dermatan sulfate chain belong to three different families that transfer sulfate groups to C-4 of GalNAc residues, to C-6 GalNAc residues, and to C-2 of the hexuronic acid moieties.

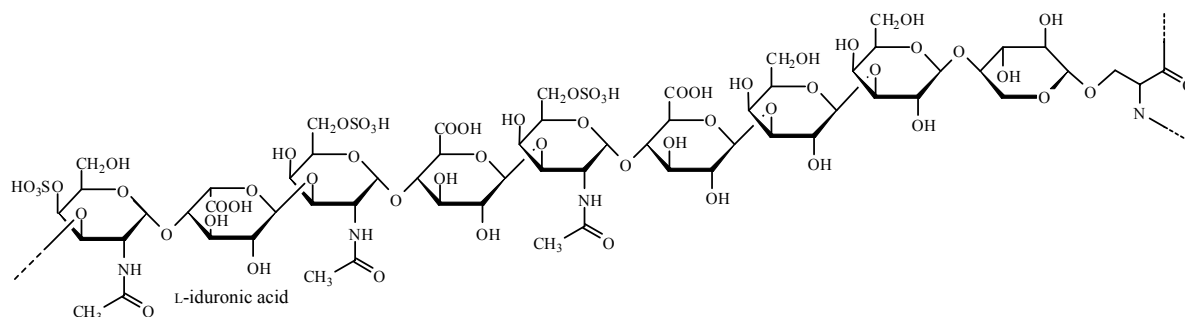


Figure 13

Generally, the formation of PAPS is a two-step reaction⁷. The enzyme ATP sulfurylase (EC 2.7.7.4) catalyses the formation of adenosine-5'-phosphosulfate (APS) from ATP and sulfuric acid. The product, APS, then reacts with ATP and forms PAPS. The second reaction is catalysed by APS kinase (EC 2.7.1.25). Finally, PAPS reacts with chondroitin yielding e.g. chondroitin 6'-sulfate (EC 2.8.2.17) and adenosine-3',5'-diphosphate (Figure 14).

EC (Enzyme Commission) numbers and some common abbreviations

EC (Enzyme Commission) numbers, assigned by IUPAC-IUBMB, were taken from KEGG: Kyoto Encyclopedia of Genes and Genomes, <http://www.biologie.uni-hamburg.de>. In many structures, the abbreviation **P** is used to represent the phosphate group and **PP** the diphosphate group. At physiological pH, these and some other groups will be

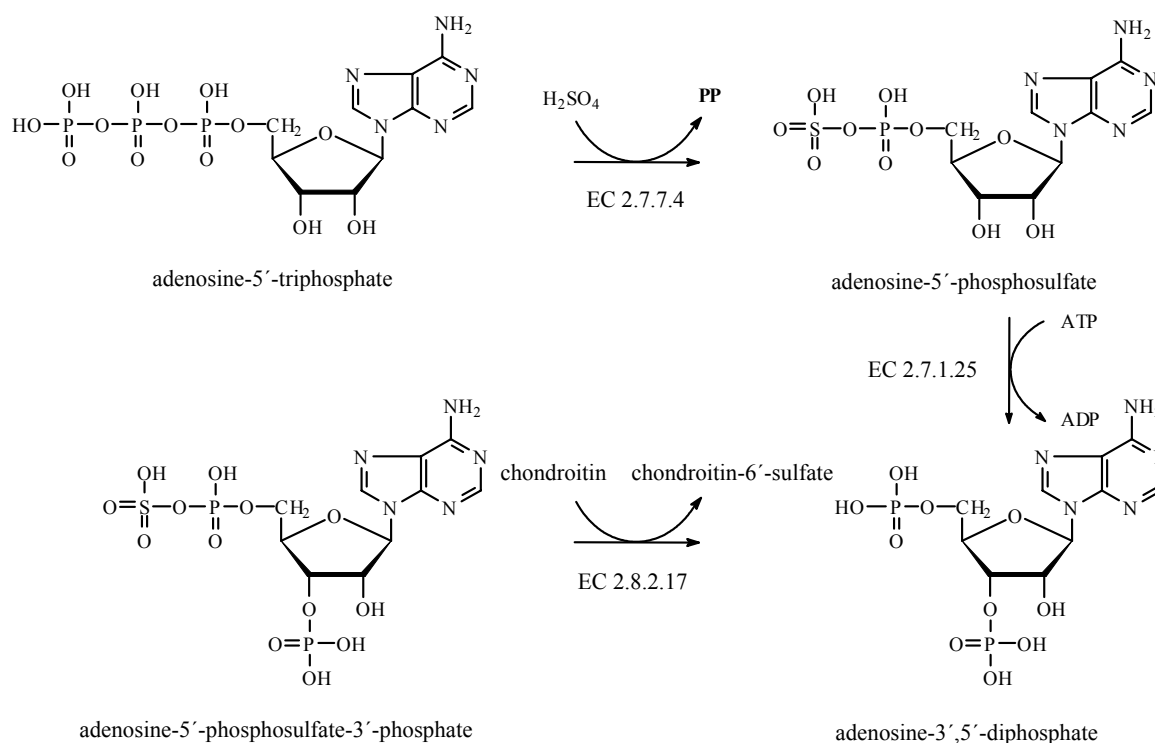


Figure 14

⁷In bacteria, yeast, fungi, and plants, the formation of PAPS is carried out by two individual polypeptides, ATP-sulfurylase (EC 2.7.7.4) and APS kinase (EC 2.7.1.25). In contrast, the human PAPS synthase system is a bifunctional enzyme (fusion product of two catalytic activities).

ionised, but in pictures the unionised forms are depicted to simplify the structures, to eliminate the need for counter-ions, and to avoid the mechanistic confusion.

AceA	aceric acid
AdoHcy	S-adenosyl-L-homocysteine
AdoMet	S-adenosyl-L-methionine
ADP	adenosine-5'-diphosphate
Api	apiose
APS	adenosine-5'-phosphosulfate
Ara	arabinose
ATP	adenosine-5'-triphosphate
Dha	deoxyheptonic acid
Fru	fructose
Gal	galactose
GalA	galacturonic acid
GalNAc	N-acetyl-D-galactosamine
Glc	glucose
GlcA	glucuronic acid
GlcNAc	N-acetylglucosamine
IdoA	iduronic acid
Kdo	ketodeoxyoctonic acid
P	phosphoric acid
PAPS	3'-phosphoadenosine-5'-phosphosulfate
PP	diphosphoric acid
Rha	rhamnose
SAM	S-adenosyl-L-methionine
UDP	uridine-5'-diphosphate
UTP	uridine-5'-triphosphate

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Corresponding author:

Prof. Ing. JAN VELÍŠEK, DrSc., Vysoká škola chemicko-technologická v Praze, Fakulta potravinářské a biochemické technologie, Ústav chemie a analýzy potravin, Technická 5, 166 28 Praha 6, Česká republika
tel.: + 420 220 443 177, fax: + 420 233 339 990, e-mail: jan.velisek@vscht.cz
