Plant Xyloglucan Xyloglucosyl Transferases

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Plant xyloglucan xyloglucosyl transferases or xyloglucan endo-transglycosylases (XET; EC 2.4.1.207) catalogued in the glycoside hydrolase family 16 constitute cell wall-modifying enzymes that play a fundamental role in the cell wall expansion and re-modelling. Over the past thirty years, it has been established that XET enzymes catalyse homo-transglycosylation reactions with xyloglucan (XG)-derived substrates and hetero-transglycosylation reactions with neutral and charged donor and acceptor substrates other than XG-derived. This broad specificity in XET isoforms is credited to a high degree of structural and catalytic plasticity that has evolved ubiquitously in algal, moss, fern, basic Angiosperm, monocot, and eudicot enzymes. These XET isoforms constitute gene families that are differentially expressed in tissues in time- and space-dependent manners during plant growth and development, and in response to biotic and abiotic stresses.

Keywords: enzyme structure and function ; GH16 family ; homo- and hetero-transglycosylation reactions ; molecular modelling and simulations ; plant cell walls loosening and re-modelling

1. Plant Cell Walls and Structure, and Key Components

The presence of polysaccharide-rich cell walls (CWs) is a characteristic feature of plants and fungi. Throughout the evolution of plants, CWs have conformed to multiple roles, including mechanical support, diffusion and growth regulation, defence against biotic and abiotic stresses, and cell-to-cell communication. CWs are highly complex structural entities largely composed of organic polymeric molecules interlinked by covalent and non-covalent linkages. Properties of CWs depend on the composition and chemical linkages of individual adjoined components, and their structure [1][2][3][4][5][6].

All land plants classified in *Embryophytes* evolved from *Charophytes* green algae (Figure 1A) contain CWs assumed to be one of the most decisive factors that allowed for terrestrialisation [7][8][9][10]. Despite certain common components, the composition of CWs varies in species [11][12] and tissues [13][14][15][16][17]. The structure of plant CWs could also be affected by growth conditions [18] and some common distributions of main structural polysaccharides are observed that depend on the evolutionary history of a plant including algae [19][20][21][22]. However, certain polysaccharides could have evolved independently several times [16], and this is observed in (1,3;1,4)-β-d-glucans (mix-linkage glucans, MLGs) in *Pteridophytes* (ferns, whisk ferns, horsetails) [23][24][25] and *Poales* (grasses) [26] (Figure 1A). CWs of grasses differ from those of other higher plants in a lower content of xyloglucans (XGs) and pectins but in a higher content of heteroxylans.

Plants are known to construct two types of CWs, termed primary cell walls (PCWs) and secondary cell walls (SCWs) that differ in composition, structure, and function. The dynamic PCW structures comprise of the networks of cellulose micro-fibrils tethered by cross-linking glycans [27] that are embedded in the matrix of pectin substances [28][29] and glycoproteins. Glycans or hemicelluloses include variously substituted XGs, which are the major form of cross-linking glycans in dicotyledonous plants, while xylan(s)—Xyl(s), arabinoxylan(s)—AraXyl(s), glucuronoarabinoxylan(s), mannan(s)—Man(s), galactomannan(s)—GalMan(s), glucomannan(s)—GlcMan(s) and galactoglucomannan(s)—GalGlcMan(s), and MLGs largely replace XGs in monocots and lower plants [30]. Pectins [31] composed of the homogalacturonan (HG) part are cross-linked via Ca^{2+} bridges that causes the gelling effect, while the 'hairy' regions of pectins are made of rhamnogalacturonan I (RG I) and rhamnogalacturonan II (RG II) [32][33][34][35]. Conversely, SCWs that are more typical for woody and vascular tissues after their growth ceases are more rigid compared to PCWs since they contain more of other cross-linking glycans than pectins, and are reinforced by lignin, a hydrophobic phenylpropanoid polymer [36][37][38].

Cellulose, as the most abundant organic compound on Earth [39], consists of the repeating glucopyranose moieties linked through (1,4)-β-d-linkages that form micro-fibrils tightly bound via hydrogen bonds—these supra-molecular structures form the backbone of PCWs [40]. Cellulose is found not only in CWs of green algae and higher plants but also in *Rhodophyta* (red algae), *Phaeophyceae* (brown algae), *Oomycetes* (fungus-like microorganisms), *Ameobozoa*, animals, and in some *Procaryotes* (*Cyanobacteria*).

The biosynthesis of XGs [41] seems to be reserved for plants including certain green algae [42]. XG was not detected in red and brown algae, and this absence is also supported by the lack of XG modifying enzymes in these organisms [43]. XG consists of repeating (1,4)-β-d-linked glucopyranosyl moieties [44], which contain the C-6 carbon branching by α-d-xylopyranosyl residues. Xylosyl moieties could be further substituted by galactopyranosyl residues on C-2 carbons (β-d-Galp-(1,2)-α-d-Xylp) and the galactosyl moieties could carry the fucopyranosyl branching (α-l-Fucp-(1,2)-β-d-Galp-(1,2)-α-d-Xylp). In certain instances, the arabinopyranosyl [45][46] and galacturonate [47][48] substituents are found, which suggests that the structure of XG differs from plant to plant, but also between the parts of the same plant [49][50][51]. The XG backbone is synthesised by a XG:glucan synthase encoded by members of the C subfamily of *cellulose synthase-like (CSL)* genes [52], but only when both UDP-glucose and UDP-xylose are present [53][54], meaning that the activity of another enzyme XG:xylosyltransferase is required to produce XG [53]. Most of XG residues are substituted with d-Gal by XG:galactosyltransferases and further modified with l-fucose by XG:fucosyltransferases [53][54], although more work is required to clarify all aspect of XG biosynthesis. A recent study with the C subfamily CSL synthases and their genes found a quintuple mutant with disruptions in five C subfamily *CSL* genes that had no detectable XG, and did not display the significant alteration of gene expression at the whole genome level [41].

Figure 1. Polysaccharides form the structural foundation of plant CWs. (**A**) distinct polysaccharides emerge in plant CWs in phyla during the evolutionary history of plants [55]; (**B**,**C**) intuitive CW structural models by Albersheim et al. [56] (**B**), and Park and Cosgrove [57] (**C**); (**D**) mechanisms of action of XET enzymes leading to the loosening of CWs through homo-transglycosylation reactions (top panel) [1], and cross-linking cellulose and XGs through hetero-transglycosylation reactions (bottom panel) that could enhance tighter packing of cellulose micro-fibrils and other polysaccharides [58]. Cellulose micro-fibrils are in green and XGs in red in (**B**–**D**); pectins are in yellow in (**B**,**C**); XETs are in cyan in **D**; the plasma membrane is in blue in (**B**,**C**).

The similarity between the structure of XG and cellulose underlies the conformational homology of these polysaccharides, which results in their strong noncovalent associations . Networks of cellulose and XGs were for a long time considered to support the structure of PCWs, which also trigger their flexibility and strength [59][60][61][62][63]. The most recognised PCW model of dicotyledons [56] is based on linear micro-fibrils of cellulose, each consisting of 32 cellulosic micro-fibrils inter-connected through hydrogen bonds. These para-crystalline micro-fibrils are interwoven and bridged to polymeric XGs. According to this model (Figure 1B), the function of pectin is attributed to a gelling material that pervades the space between the cellulosic and XG structures. The advances in the field of microscopic techniques allowed for the development of advanced CW models based on so-called hot spots of cellulose micro-fibrils, where these micro-fibrils composed of eight or sixteen cellulosic subunits [64], come to close contacts with each other (Figure 1C). These hot spots of cellulosic micro-fibrils are isolated from each other by a thin layer of XGs, which according to this model are isolated in PCWs [57]. Here, pectins serve as the filling material between the cellulosic and XGs structures, and take over the major role of the XGs, compared to the first model. Various pectins interact both with cellulose and XGs, thus ensuring the flexibility and strength of CWs [65]. The processes of hot spots formation remain unknown, although one possibility is that they are formed spontaneously during the cellulose deposition into CWs, or that they could be formed enzymatically [66].

While there are numerous studies focused on the role of XGs in CW modifications during plant growth and development, little information is available as to how XGs participate in the CW formation. Recent work focused on the regeneration of CWs in wild-type *Arabidopsis thaliana* and a double mutant *xxt1 xxt2* lacking any detectable XGs, suggested that the formation of cellulosic networks is XG-independent [67].

As already noted, CWs show a remarkable diversity that underlies the function of each cell, which is directly linked to the basic and subtle structure of polymers, their quantity, ratios, and underpins mutual interactions. The syntheses of CW polysaccharides occur due to the cooperative activities of prodigious numbers of biosynthetic glycosyl transferases (GTs) or synthases [68][69][70][71][72][73][74][75][76][77][78][79][80][81][82][83][84], localised mostly in the Golgi apparatus [85]. The products of these GTs and synthases are transported to CWs by secretory vesicles, although the exception includes the superfamilies of cellulose synthases [85][86][87][88][89][90] and callose synthases [91] locating in the plasma membrane [92]. In the latter instances, polysaccharides synthesised by these enzymes could be exported directly to CWs. However, the structural polysaccharides that are observed in CWs are often heterogeneous. This is assumed to be achieved through a wide range of available activated sugar donors required for GTs activities, which could give rise to a variety of glycosidic linkages using different sugar isomers.

Life processes in plants are underscored by CWs structure and re-organisation, which involves disintegration, elongation and expansion. In addition to GTs, these processes are governed by hydrolases and lyases, and non-catalytic expansin proteins [93][94][95][96]. As in the case of GTs, there is a vast number of enzymes that could modify structural polysaccharides in muro by cleaving bonds, esterifying or de-esterifying saccharide moieties [97][98], and incorporating new

material into CWs or re-constructing CW polymers by cross-linking. The last two processes are secured by xyloglucan xyloglucosyl transferase also known as xyloglucan endo-transglycosylase (XET) enzymes (Figure 1D), which could either loosen or enhance the packing of cellulosic micro-fibrils and other polysaccharides in CWs [99].

Xyloglucan xyloglucosyl transferases or XET enzymes (EC 2.4.1.207) as one of the key glycosidic bond-formation enzymes participating in plant CW expansion, reconstruction, and re-modelling [100][101][102][103][104] were independently discovered by three groups [105][106][107]. According to the Enzyme Commission [108], these enzymes are also named as endo-xyloglucan transferases.

2. Roles of Xyloglucan Xyloglucosyl Transferases in Cell Wall Formation and Re-Modelling

Catalysis, and remarks on the nomenclature and classification—The nomenclature of xyloglucan xyloglucosyl transferases or XET enzymes is defined by the International Union of Biochemistry and Molecular Biology (IUBMB)/International Union of Pure and Applied Chemistry (IUPAC) Biochemical Nomenclature Committee [108] that is also implemented in the Kyoto Encyclopaedia of Genes and Genomes Enzyme Database (KEGG). These enzymes are classified amongst transferases by the Enzyme Commission (EC) and listed under the primary identifier EC 2.4.1.207 in IUBMB/IUPAC and the BRENDA collection of enzyme functional data [109]. The differences in the used nomenclature are based on whether the authors consider the transfer of 'glycosyl' (xyloglucan endo-transglycosylase) or 'glucosyl' (xyloglucan endo-transglucosylase) groups [110][111][112][113][114][115][116][117], although given that XETs primarily transfer XG fragments, the usage of the first name should be preferred. The fundamental feature of the catalysis mediated by XETs is the breaking of a bond between 1,4-β-d-linked glucosyl residues of XGs and the transfer of an XG fragment onto O-4 of the non-reducing terminal end of the glucose moiety of the acceptor, which can be XG or its oligosaccharide (XG-OS). This constitutes a so-called ping-pong bi bi reaction mechanism rather than a sequential one [118][119]. It is of note that the definition by the Enzyme Commission contains a strict note 'does not use cello-oligosaccharides as either donor or acceptor', although, in the light of the current knowledge, this specification is obsolete [120][121][122][123][124][125].

A more objective view on the XET enzyme nomenclature and classification is given by the Carbohydrate-Active enZYmes Database (CAZy; CAZypedia Consortium 2018) [126], which is based on protein tertiary structures and substrate specificities or activities. According to CAZy, XETs are classified in a glycoside hydrolase (GH16 family) and not in a glycoside transferase (GT) group. According to this classification, the latter group contains enzymes which utilise activated sugar donors. In accordance with tertiary structures of XET enzymes, the first steps of both transglycosylation and hydrolytic reactions are binding and cleavage of donor substrates. The difference occurs in the second step, in which the fragment with the original non-reducing end of the substrate is transferred to an acceptor, which in the case of a typical transglycosylase is another saccharide, while, in the case of a hydrolase, it is a water molecule (Figure 2A) [127]. This second step of the reaction has the key importance for the nomenclature and classification of transglycosylases as transferases. Commonly, most hydrolases could also transglycosylate, but this only occurs under high substrate concentrations [128], when in the later stages the products accumulate and shift the chemical equilibrium of the reaction towards transglycosylation reactions, due to a specific response of the biocatalyst. Contrary to this, 'true' transglycosylases, which include XETs, catalyse primarily the transfer on a saccharide from the beginning of the reaction. While hydrolytic reactions catalysed by hydrolases reflect the increased concentrations of reducing groups in the reaction system, this is not the case for 'true' transglycosylases. Furthermore, during reactions with endo-transglycosylases, no dramatic decrease in the viscosity of the polymeric substrates is observed at the early stages of reactions, contrary to endo-hydrolases. Besides XETs, other transglycosylases or enzymes with potential transglycosylase activities were described in plants as endo-transglycosylases/hydrolases recognising (1,4)-β-d-mannan-derived polysaccharides [129][130], xylan endo-transglycosylases functionalising heteroxylan polysaccharides [131][132][133], MLG: xyloglucan endotransglucosylases [134][135] recognising MLGs, and the hetero-trans-β-glucanase (HTG) that functionalise cellulose [136], although designating these enzymes as such hides the fact that the latter enzymes are broad specific or poly-specific XET enzymes.

XET enzymes are classified in GH family 16 (GH16) in CAZy. A GH16 family is a large group, which was according to specific features in tertiary structures further sub-divided into 23 subfamilies [137]. Subfamily GH16_20 includes XETs and xyloglucan endohydrolases (XEHs, EC 3.2.1.151) [138][139] with predominantly hydrolytic activities towards XGs. This group of enzymes contains the products of *XTH* (xyloglucan transglycosylase/hydrolase) genes encoding both types of XG-modifying enzymes which display close similarity in their tertiary structures [140].

Figure 2. The GH16_20 subfamily of the XTH enzymes. (**A**) reaction mechanism leading to transglycosylation or hydrolytic reactions; (**B**) superposition of the crystal structure of poplar PttXET16A transglycosylase (PDB accession 1UN1; red) and the nasturtium TmNXG1 hydrolase (green) points to structural differences that underlie their distinct activities; differences in selected signatures that underlie these activities are indicated by sequence alignments, and some of these residues shown in the inset; (**C**) unrooted phylogenetic tree of the GH16 subfamily (MEGA v7.0.26; [141]) shows clustering of entries into three subgroups, where subgroups I and II consist of transglycosylases and subgroup III of hydrolases .

Currently, the best characterised XET enzyme is the PttXET16A isoform from hybrid aspen, *Populus tremulus x tremuloides* . After its expression in a recombinant host achieved in high yields in *Pichia*, the crystal structure of PttXET16A (Protein Data Bank—PDB accessions 1UN1 and 1UMZ) revealed that the enzyme folds into two antiparallel β-sheets, which form a β-sandwich consisting of convex and concave regions. The catalytic machinery, formed by two glutamic acid residues Glu85 and Glu89, with an aspartate Asp87, is located approximately mid-way in the convex region. The C-terminal end is elongated compared to other XTH family members and located near the convex region of the β-sheet, forming an α-helix and another β-strand on the concave side of the molecule; this part of the structure is stabilised by two disulphide bridges. PttXET16A is N-glycosylated at Asn93 with two N-acetylglucosaminyl and mannosyl moieties that are stabilised by hydrogen bonds. The structures of other plant XET enzymes are yet to be determined, however, the structural features of barley and nasturtium XETs (Figures 2B, 3B, and 4B) and HTG were defined through homology modelling, an approach that could introduce local approximations in structural features of modelled XETs [142].

The mechanism of transglycosylation catalysed by XET enzymes proceeds in two stages that incorporate two transition states (Figure 2A). The first step is the deprotonation of the carboxyl acid residue acting as the nucleophile that attacks the anomeric carbon forming the glycosyl-enzyme intermediate complex with acidic assistance provided by the acidic carboxylate. In PttXET16A, the nucleophile attacking the anomeric carbon is Glu85, while Glu89 acts as an acid/base, which protonates the released saccharide and subsequently de-protonates the glycosyl acceptor. The Asp87 residue located mid-way between both catalysts Glu85 and Glu89 controls the protonation state of the catalytic machinery and operates through hydrogen bonding interactions. The nucleophile must be de-protonated during the donor substrate attack, while Asp87 and Glu89 are protonated and donate the proton to a leaving saccharide. During the later stages of the transfer reaction, the glycosyl-enzyme intermediate complex dissociates after the nucleophile attack on the anomeric carbon, and a new glycosidic bond is formed .

Interactions between residues in PttXET16A and dimeric XG nonasaccharide were obtained using molecular dynamics simulations . The substrate was modelled in active site in a way, in which one of the XG nonasaccharide dimers occupied the donor site creating a stable intermediate with the enzyme, while the second XG nonasaccharide occupied the acceptor site. It was important to observe that the XG nonasaccharide of the reducing-end glucose moiety changed its conformation into a boat at the beginning of the simulation and kept this conformation during the whole simulation time. This was the case not only for PttXET16A, but also for XEHs.

Attention was paid to structural differences, which determine whether the XET/XEH enzymes act as transglycosylases (PDB accessions 1UN1, 1UMZ) or hydrolases (TmNXG1; PDB accession 2UWA) [143]; here, the information of their primary and crystal structures was compared including the TmNXG1-DELTAYNIIG mutant (PDB accession 2VH9). Minor differences in structures lead to stronger binding of a donor substrate combined with larger loop flexibility at the acceptor binding site, and the higher conformational flexibility of specific residues underlined the hydrolytic preference [143] (Figure 2B). This was also reflected by the phylogenetic analyses, which showed that the distribution of XTH gene products was segregated into three groups, with XEHs belonging to the XTH III clade, while XETs were placed in both XTH I and XTH II clades (Figure 2C, Supplementary Data Set S1) [144]. Based on these structural and phylogeny insights, it was postulated that GH16 hydrolases could have evolved from XET transglycosylases [143], although the research including a gradual cross-genome survey and the whole GH16 family phylogeny continues [145]].

Enzyme activity assays methods—Preferred methods of XET activity assays are based on the use of radiochemically or fluorescently labelled acceptor oligosaccharides and an unlabelled donor polysaccharide. Alternatively, radiolabelled donor and unlabelled acceptor substrates could be used . Products then contain labelled components that are incorporated into products, and remaining unincorporated donors or acceptors are removed through washing on a filter-paper [146], through a gel [147][149], size-exclusion chromatography, or ethanol precipitation [148]. Labelled oligosaccharides could also be used in high-throughput activity assays [149] and for visualisations of XET activities in vivo [150][151][152][153]. Despite an undeniable advantage of the latter technique for screening of XET activities, it is important to consider ongoing

reactions amongst polysaccharides in muro. For the selection of activity assays, it is crucial to consider the choice of fluorescent tags [154][155] and the removal of unreacted donors or acceptors. Other XET activity assays include viscometry and colorimetry [156].

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