Acetylation of woody lignocellulose: significance and regulation

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OCCURRENCE OF O-ACYETYLATION IN LIGNOCELLULOSSE

O-acetyl and methyl esterification are the most common substitutions in different cell wall matrix polysaccharides (Figure 1). While the role of methyl esterification in plant cell walls has been a focus of many studies, that of O-acetylation has received much less attention in the past. O-acetylation may occur on the backbones or branches of many cell wall polymers (recently reviewed by Gille and Pauly, 2012), but the nature of acylated polymer and the extent of acetylation differ between species, tissues and types of cell walls (Figure 1; Table 1).

Table 1: Occurrence of O-acetylation in lignocellulosic polymers.

| Polysaccharide | Type of substitution | Extent of acetylation |
|----------------|----------------------|-----------------------|
| Xylans         | Acetyl groups        | Varies from 0.3 to 0.4 in (galacto)glucomannan in the wood of aspen, birch and spruce |
| Mannan         | Acetyl groups        | DA varied from 0.60 to 0.75 in aspen wood glucuronoxylan and from 0.3 to 0.4 in (galacto)glucomannan in wood of aspen, birch and spruce |
| Lignin         | Acetyl groups        | Levels, up to DA 0.8 of S monomers, are found in extraxylary fibers in jute, abaca, and kenaf |

Non-cellulosic cell wall polysaccharides constitute approximately one quarter of usable biomass for human exploitation. In contrast to cellulose, these components are usually substituted by O-acetyl groups, which affect their properties and interactions with other polymers, thus affecting their solubility and extractability. However, details of these interactions are still largely obscure. Moreover, polysaccharide hydrolysis to constituent monosaccharides is hampered by the presence of O-acetyl groups, necessitating either enzymatic (esterase) or chemical de-acetylation, increasing the costs and chemical consumption. Reduction of polysaccharide acetyl content in planta is a way to modify lignocellulose toward improved saccharification. In this review we: (1) summarize literature on lignocellulose acetylation in different tree species, (2) present data and current hypotheses concerning the role of O-acetylation in determining woody lignocellulose properties, (3) describe plant proteins involved in lignocellulose O-acetylation, (4) give examples of microbial enzymes capable to de-acetylate lignocellulose, and (5) discuss prospects for exploiting these enzymes in planta to modify xylan acetylation.

Keywords: cell wall, wood, biofuel, saccharification, O-acetylation, hemicellulose, acetyl esterase

Figure 1: Schematic representation of cell wall structure and the type of substitutions that can be found in different cell wall polymers.

MOLECULES POLYMER ACETYLATION AFFECTS ITS INTERACTIONS WITH POLAR MOLECULES

Lignocellulose polysaccharides can be de-acetylated by alkali and re-acetylated by acetic anhydride, providing materials for studying of physico-chemical properties affected by acetylation.

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O-acetyle groups are also found in lignin, linked to the gamma-carbon of the aliphatic side chain of lignin S and G monomers and can be very variable (Del Rio et al., 2007). The highest levels, up to DA 0.8 of S monomers, are found in extraxylary fibers in jute, abaca, and kenaf. In hardwood xylem, lignin acetylation varies between 1 and 50% (w/w) whereas in softwood xylem it has not been reported. The function and consequences of such variability in lignin acetylation are unknown.

The presence of O-acetyl groups on hemicelluloses indicates that xylan differs between softwoods and hardwoods. Typical positions of acetyl groups in these polymers are shown in Figure 1, but species-specific positions also may exist (Hayashi, 1989; Pauly, 1999; Jacobs et al., 2002; Jia et al., 2003), and spontaneous migration of acetyl group between the neighboring free hydroxyls is possible (Kabel et al., 2003; Mastihubová and Biely, 2004). Acetylation level is described as degree of acetylation (DA), which is the molecular ratio between the total content of acetyl groups and the total content of monomers that can bear them. DA varied from 0.60 to 0.75 in aspen wood glucuronoxylan and from 0.3 to 0.4 in (galacto)glucomannan in the wood of aspen, birch and spruce (Teleman et al., 2008, 2003). Therefore the overall acyl content is lower in softwoods than in hardwoods. Existence of specific domains with respect to acetylation, as known for pectin methyl esterification, is an intriguing possibility (Jacobs et al., 2002; Ralet et al., 2008).
FIGURE 1. O-acetylation of cell wall polysaccharides. (A) Generic representation of O-acetyl group as found at different -OH positions in many cell wall polysaccharides. Note the structural similarity between O-acetyl- and methyl ester-groups that decorate carboxylic acid residues in polygalacturonic acid. (B) Occurrence of O-acetyl groups in cell wall matrix polysaccharides (Voragen et al., 1986; Pauly and Scheller, 2000; MacKinnon et al., 2002; Teleman et al., 2002; Glushka et al., 2003; O’Neill et al., 2004; Rakić et al., 2005).
Such comparisons show that de-acetylated xylan absorbs more moisture than highly acetylated xylan because it offers more hydrogen bonding to water molecules (Grendahl et al., 2003). The weakly acetylated xylan (DA ≈ 0.5) is totally soluble in water, whereas the totally acetylated xylan (DA 2.0) only dissolves in non-polar solvents like chloroform or polar aprotic solvents like dimethyl sulfoxide. The non-acetylated xylan (DA 0) is only partially soluble in hot water, due to spontaneous intra-molecular hydrogen bonding. De-acetylation of xylan also facilitates its bonding to cellulose (Kabel et al., 2007), whereas its acetylation could be a means of increasing its interaction with hydrophobic substances like plastic used for making composite wood-based products (Lisperguer et al., 2007) or naturally occurring biocides like plastic used for making composite wood-based products. Wood acetic anhydride treatment, resulting in ∼ 0.5) is totally soluble in water, whereas the totally acetylated xylan (DA 2.0) only dissolves in non-polar solvents like chloroform or polar aprotic solvents like dimethyl sulfoxide. The non-acetylated xylan (DA 0) is only partially soluble in hot water, due to spontaneous intra-molecular hydrogen bonding. De-acetylation of xylan also facilitates its bonding to cellulose (Kabel et al., 2007), whereas its acetylation could be a means of increasing its interaction with hydrophobic substances like plastic used for making composite wood-based products (Lisperguer et al., 2007) or naturally occurring lignin.

### WOODY BIOMASS DE-ACETYLATION IS IMPORTANT FOR PULPING, SACCHARIFICATION AND FERMENTATION

Wood is de-acetylated during the initial phases of chemical pulping, which consumes most of alkali during Kraft cooking (Zanuttini et al., 2003), and results in the accumulation of acetate in the spent liquor (Sjöström, 1993). Following de-acetylation, fibers swell, which improves their ion transport capacity and facilitates pulping (Sumi, 1964). In mechanical pulping, de-acetylation takes place after the refining step during the alkaline peroxide bleaching. In both pulping processes, de-acetylation of hemicelluloses improves their adsorption to cellulose (Kabel et al., 2007), whereas its acetylation could be a means of increasing its interaction with hydrophobic substances like plastic used for making composite wood-based products (Lisperguer et al., 2007) or naturally occurring lignin.

### ACETYLATION OF SECONDARY BUT NOT PRIMARY WALLS INCREASES MECHANICAL STRENGTH

While the high hemicellulose acetylation is disadvantageous for pulping and biofuel production, it is often desirable in solid wood products. Wood acetic anhydride treatment, resulting in ∼ 5-15% of weight gain, increases wood mechanical strength (modulus of elasticity and rupture) in both tension and compression experiments, but higher levels of acetylation are damaging (Ramsden et al., 1997; Papadopoulos and Pougliola, 2004). Interestingly, the acetylation is initially introduced to the secondary wall layers where hydroxyl groups of hemicelluloses are likely the main reactants, whereas prolonged treatment introduces acetyl to the middle lamella where pectins and lignin are the main targets (Rowell, 2009). Most likely it is the acetylation of xylan and mannan in secondary wall layers that is responsible for the increased stiffness, possibly by allowing more hydrophobic interactions with lignin. Such a mechanism is not possible in non-lignified primary walls. Indeed, it has been shown that overexpression of pectin acetyl esterase (PAE) inhibited cell elongation in tobacco (Gou et al., 2012) and led to stiffer cell walls in potato tubers based on mechanical stress-strain experiments (Orfila et al., 2012). Moreover, primary cell wall acetylation was negatively correlated with cell adhesion (Li et al., 1994). Since pectin acetylation, similarly, to methyl esterification, interferes with binding of calcium to polygalacturonic acid and formation of “egg-box” domains in

| Species | % d.w. | Reference |
|---------|--------|-----------|
| Wheat (straw) | 2.2 | Surv (1984) |
| Populus tremuloides Michx. (wood) | 3.7 | Timell (1967); Sjöström (1993) |
| Eucalyptus globulus Labill. (wood) | 3.9 | Timell (1967) |
| Salix sachalinensis Marsh. (wood) | 4.4 | Timell (1967) |
| Populus trichocarpa Torr. & Gray (wood) | 1.3 | Laffend (1967); Timell (1967) |
| Abies balsamea Mill. (wood) | 1.5 | Timell (1967) |
cell wall (Ralet et al., 2003), pectin acetylation decreases cell wall stiffness.

**ACRYLATION AFFECTS WOOD BIOTIC RESISTANCE**

Since acetylation of xylan and mannan hinders their hydrolysis, chemical acetylation of wood has been used to increase its durability and resistance to fungi, bacteria, and termites (Peterson and Thomas, 1978; Moehlby, 2003; Rowell, 2009). It was therefore surprising to find that reduced acetylation in different polymers, XG and pectin—in rw2 mutants, xylan—in lines overexpressing acetyl xylan esterase (AXE) from family carboxylic esterase 1 (CE1), and pectin—in lines overexpressing rhomboalacturonan acetyl esterase (RGAe), induced resistance to necrotrophic fungi (Manabe et al., 2011; Pogorelko et al., 2013). Moreover, whereas digestibility of pectins by Aspergillus pectinase was actually reduced by their de-acetylation (Gou et al., 2012), digestibility of cell walls of plants expressing either PAE or RGAe by pectinase/PME mixture was increased (Orilla et al., 2012; Pogorelko et al., 2013). Overexpressed esterases were shown to activate plant acetylation and defense pathways, and it has been proposed that the cell wall fragments generated as a result of deacetylation may trigger the activation of plant innate immune responses (Pogorelko et al., 2013). Clearly, more studies are needed to understand how acetylation of different polymers affects their digestibilities in vivo and in vitro by different hydrolyases to gain understanding of the role of their acetylation in biotic stress resistance.

**ENZYMES DE-ACYLATING LIGNOCELLULOSE POLYSACCHARIDES**

**DE-ACYLATION OF XYLAN AND MANNAN**

Polymeric xylan and xylo-oligosaccharides are de-acetylated by AXEs (EC 3.1.1.72). Short xylo-oligosaccharides can be also deacetylated by non-specific acetyl esterases (AE; EC 3.1.1.6), which act mainly on the non-reducing end residues (Poutanen et al., 1990; Linden et al., 1994). AXEs and AEs have been found in wood-degrading fungi and bacteria (Bidy et al., 1985; Dupont et al., 1990; Bidy, 2012). The occurrence of true AXEs in plants has not been reported, although poplar PAE1 had some activity toward acetylated xylan (Gou et al., 2012). Acetyl xylan esterases fall presently into eight of the 16 CE families (http://www Sega.org/), including CE1—CE7, and CE16 (Table 2; Dodd and Cann, 2009; Bidy, 2012; Gou et al., 2012). Most CE1—CE7 enzymes are serine esterases having Ser-His-Asp (Glu) triad or Ser-His diad in their active sites and use the catalytic mechanism with the formation of enzyme-Ser complex (acylation), followed by the de-acylation by activated water molecule. CE4 enzymes have a unique, Asp-His and divalent cation-dependent activity (Taylor et al., 2006; Bidy, 2012).

Different AEs and AXEs may exhibit preferences to different acetyl positions (Christov and Prior, 1993; Linden et al., 1994; Bidy, 2012). For example, CE1, CE4, and CE5 AXEs have preference for position O-2, CE16 AEs for positions O-3 and O-4 (Bidy et al., 2011) and CE2 AXEs for position O-6 in hexoses (Topakas et al., 2009). Many CE1 and CE2 AXEs have broad specificities for xylan and mannan. Acetyl xymenan one esterase (AGME, EC 3.1.1.-) activity was shown in Aspergillus sp., and the enzyme was also capable of slow de-acetylation of xylan (Tenkanen et al., 1995). CE family for this enzyme remains to be identified.

**DE-ACYLATION OF PECTINS**

Pectin acetyl esterases (EC 3.1.1.-) were found in plant and microbial species (Williamson, 1991; Breton et al., 1996; Shevchik and Hugouvieux-Cotte-Pattat, 1997, 2003; Gou et al., 2012). Plant PAEs belong to family CE13 and are secreted enzymes acting on O-2 and O-3 acetyl in HG. Arabidopsis and Populah have 12 and 9 CE13 members, respectively (Ceasar-Lee et al., 2006). Genomic sequencing identified similar proteins in animals and bacteria, but corresponding activities have not been characterized. Bacterial PAEs of Erwinia chrysanthemi PAEx and PAe1, acting on demethylated oligomeric and polymeric HG, respectively, are classified in CE10 (Shevchik and Hugouvieux-Cotte-Pattat, 1997, 2003).

Rhamnogalacturonan acetyl esterase (EC 3.1.1.86) deacetylates RGI at GaA O-2 and O-3 positions and belongs to CE12 (Molgaard et al., 2000). This activity has been shown in Aspergillus aculeatus (Schols et al., 1990), and in bacteria where it has broad substrate specificity including acetylated xylan and cephalosporin C (Martinez-Martinez et al., 2008; Navarro-Fernandez et al., 2008).

**BIOSYNTHESIS OF ACETYLATED POLYSACCHARIDES IN PLANTS**

O-acetylation of plant cell wall-polysaccharides takes place in the Golgi. In the case of HG, RGI, and XG, acetyl-CoA has been identified as a donor substrate (Pauly and Scheller, 2000). Proteins involved in polysaccharide acetylation are conserved in pro and eukaryotes (Gille and Pauly, 2012). In fungi, animals and Gram-positive bacteria, the acetyl transfer to extra- cytoplasmic compartment and catalysis are performed by a single multifunctional protein Carlp identified first in Cryptococcus neoformans. Caslp has a set of 12 transmembrane domains (called Carlp domain) that are proposed to form a channel for acetyl-CoA transfer, and two other domains, TRICHOME-BIREFRINGENCE-LIKE (TBL)-domain and DUF231 located at the extra-cytoplasmic side, that are involved in esterification and are conserved in serine esterases/lipases of SGNH superfamily including AXIs (Dodd and Cann, 2009).

In plants, two separate gene families are needed for acetylation of cell wall polymers. REDUCED WALL ACETYLATION (RWA) family, which has the Caslp domain (Lee et al., 2011; Manabe et al., 2011), and TBL family, which has TBL and DUF231 domains (Anantharaman and Aravind, 2010; Bischoff et al., 2010a; Gille et al., 2011a).

Arabidopsis RWA family has four members. RWA1, RWA3, and RWA4 were suggested to redundantly regulate acetylation in secondary walls (Lee et al., 2011) whereas RWA2 was shown to be responsible for acetylation of XG and pectin (Manabe et al., 2011). Quadruple rwa2/2/3/4 mutants show 42% loss of acetyl groups in xylan and 40% reduction in stem acetyl content (Lee et al., 2011). These results indicate that RWA regulates acetylation in several polymers and is partially redundant with some other presently unknown proteins. Arabidopsis TBL family has 45 members (Anantharaman and Aravind, 2010). Two of
Table 2 | Examples of enzymes deacetylating plant cell wall poly and oligosaccharides.

| CAZY | Species | Activity1 | Reference | pH | Protein name(s) | Accession number |
|------|---------|-----------|-----------|-----|----------------|-----------------|
| CE1  | Aspergillus awamori | AXE | Koseki et al. (2005) | 6–7 | AXEA | BAA13434 |
| CE1  | Aspergillus oryzae | AXE | Koseki et al. (2006) | 6–7 | AXE | BAD12626 |
| CE1  | Aspergillus niger | AXE | Komai et al. (1993) | 5.5 | AXEA | CAJ46215 |
| CE2  | Neocallimastix patriciarum | AXE | Dainymple et al. (1997) | 7 | BNA1, BNA2 | AAAB9090 |
| CE2  | Cellvibrio japonicus | AXE and AGME | Montanier et al. (2009) | 7 | AXE2B, CE2C | ACE85140 |
| CE3  | Clostridium thermosaccharoxidans | AXE | Correia et al. (2008) | 7 | CES3 | ABN62033 |
| CE4  | Streptomyces lividans | AXE | Dupont et al. (1996) | 6–7 | AXEA | AAC68115 |
| CE5  | Trichoderma reesei | AXE | Sundberg and Poutanen (1991); Margolis-Clark et al. (1996) | 5–6 | AXE | Z69256 |
| CE6  | Fibrobacter succinogenes | AXE | Yoshida et al. (2010) | 75 | AXE6A | AF180309 |
| CE7  | Thermotoga maritima | AXE and CCD | Shao and Wiegand (1995) | 6 | AXE1 | AF901926 |
| CE8  | Bacillus pumilus | AXE and CCD | Degrazia et al. (2000) | 7 | AXE | AJ256997 |
| CE9  | Erwinia chrysanthemi | PAE | Shevchenko and Hugouvieux-Cotte-Pattat (1997) | 8 | PAEX | CAC70971 |
| CE10 | Erwinia chrysanthemi | PAE enhanced by PEL | Shevchenko and Hugouvieux-Cotte-Pattat (2003) | 8.5 | PAEX | CAD45188 |
| CE11 | Bacillus subtilis | RGAE, CCD, and AXE enhanced by Xyn10 | Martinez-Martinez et al. (2008) | 8.5 | YEST | CAB12521 |
| CE12 | Paenibacillus polymyxa | PAE and AXE enhanced by Xyn10 | Gou et al. (2012) | 70 | PAE1, CE13_S | HQ232420 |
| CE16 | Trichoderma reesei | AE enhanced by xylanases and mannanases | Poutanen et al. (1990); Li et al. (2008) | 5.5 | AES1 | AB344486 |

1 AXE, acetyl esterases (EC 3.1.1.6); AGME, acetyl glucomannan esterase (EC 3.1.1.41); AXE, acetyl xylan esterase (EC 3.1.1.72); CCD, cephalosporin C deacetylase (EC 3.1.1.41); RGAE, rhamnogalacturonan acetyl esterase (EC 3.1.1.86); PAE, pectin acetyl esterase (EC 3.1.1.7); PEL, pectate lyase (EC 4.2.2.2).
that D-glucuronan of different polymers is an important target for the feedstock improvement. Surprisingly, the knowledge of natural variation of these traits in tree species is virtually missing.

One major obstacle for gathering such data and including acetylation traits in conventional breeding programs is the shortage of high throughput analytical tools for detailed analysis of degree and position of acetylation in different plant cell wall polysaccharides.

However, genetic engineering of feedstocks with altered acetylation seems feasible in a near future. Based on studies published since 2011, it appears that modifies (by ∼20%) reduction of general acetylation levels, in planta by mutating biosynthetic genes (Lee et al., 2011; Manabe et al., 2011) or by introducing an AXE to the haplotype for post-synthetic acetyl removal (Pogorelko et al., 2011) is tolerated by herbaceous species, however, too strong de-acetylation of xylan might lead to undesirable molecular changes in cell wall (Postuma et al., 1990) resulting in growth defects as observed in the rinal2/2/4 and tbl-29 mutants (Lee et al., 2011; Xiong et al., 2013). Also, post-synthetic de-acetylation of pectins was shown to affect stem and reproductive organ growth (Gou et al., 2012). Thus, the kind of polymer affected, and the degree of de-acetylation matter for plant performance and might need to be optimized. Increased acetylation in plants, which might be desirable in solid wood products, has not been so far demonstrated.

The overexpression of TBL2 did not result in higher acetyl content in Arabidopsis (Xiong et al., 2013). Thus it is not yet known if increase of cell wall acetyl content can be obtained and tolerated by plants.

Little is known about the performance of acetyl-modified plants in various applications or about the goals for acetyl optimization. For example, extractability of polymers is likely a key parameter that is affected by acetylation, and has not received much attention. Saccharification is another matter – although xylan acetylation restricts its hydrolysis, opposite results have been obtained with pectin (Gou et al., 2012). Only a few reports exist on acetyl-modified plants where the cell wall context and type of pretreatment come into play: saccharification yields of rinal2/2/4 mutants were not increased compared to wild type in tests without pretreatment (Lee et al., 2011) whereas tbl-29 mutant showed a 10% decrease in glucose yield per cell wall mass (Xiong et al., 2013). However, taking into account ∼20% reduction in cellulose content in tbl-29 would reveal that a higher proportion of cellulose was hydrolyzed in the mutant than in wild type. ∼20% reduction in acetyl content in plants overexpressing AXE did not improve saccharification after acid pretreatment (Pogorelko et al., 2011). Clearly, analysis of a range of transgenic lines with different levels of de-acetylation, using standardized protocols is needed to optimize their acetyl level taking into account both plant and lignocellulose performance in a process.

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