DIRECT EVIDENCE THAT SUGAR BEET PECTINS ARE COVALENTLY CROSS-LINKED BY OXYDATIVELY COUPLED FERULATES IN THE CELL WALL

Plant cell walls are complex multifunctional structures constructed principally of polysaccharides. A distinctive specific feature of cell walls of species belonging to the commelinoid monocotyledons, the *Amaranthaceae* and the gymnosperms is the abundance of cell wall bound phenolics such as ferulic acid and coumaric acid. In species of the *Amaranthaceae*, such as sugar beet and spinach, it is pectic polymers that are feruloylated. Pectin main structural features include homogalacturonic and rhamnogalacturonic regions. In the last, some rhamnosyl residues are substituted by arabinose- and galactose-containing side chains. Feruloyl groups are mainly ester-linked to *O*-2 of Ara residues of the main core of α-(1∏5)-linked arabinan chains and to *O*-6 of Gal residues of the main core of β-(1∏4)-linked type I galactan chains.

Biological interest in ferulic acids arises from the fact that they can undergo *in vivo* oxidative coupling reactions to form dehydrodimers, thereby covalently cross-linking the polysaccharides they esterify. Such coupling may contribute to wall assembly, promote tissue cohesion and restrict cell expansion. Dehydrodiferulates have been identified in various plant tissues including sugar beet and spinach cell walls. However, the isolation of dehydrodiferulates linked to neutral sugars – hence providing direct evidence for these cross-links in the cell wall – has only been reported for monocotyledons. We describe here the isolation, by enzymatic hydrolysis followed by hydrophobic interaction chromatography, of several dehydrodiferuloylated oligosaccharides. Structural identification of these compounds by hpaec, ESI-IT-MS and ^{1}H-NMR provides direct evidence for covalent (intra- or inter-molecular) cross-linking of pectic arabinans and galactans through diferulic bridges in sugar beet cell wall.