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Book of Abstract

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Cell wall structural differences between hardwood and softwood studied by FT-IR, Raman and fluorescence spectroscopy

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ABSTRACT

The cell walls (CWs) of woody tissue are composed predominantly of cellulose, lignin, and hemicelluloses. There are chemical differences between the type of hemicelluloses, as well as between lignin monomeric precursors in the CWs of softwoods and hardwoods. Raman and FT-IR spectroscopy are complementary optical methods for monitoring composition differences in the CWs, as both lignin and polysaccharides have fingerprint regions in these spectra. Fluorescence spectroscopy is an intrinsic property of the cell walls. Deconvolution and modeling of the emission spectra is a sensitive analytical tool in studies of complex molecular structures. Since fluorescence of the cell walls originates from lignin and/or hydroxy-cinnamic bridges between wall polymers, this method gives data about lignin fluorophores in the cell wall.

We compared FT-IR, Raman and fluorescence emission spectra of the CWs isolated from the *Picea omorika* (Panč) *Purkyne* (softwood) and *Acer platanoides* (hardwood). The isolation of the CWs was performed according to the procedure of Chen et al. (Phytochem. Anal. 11, 2000, p 153). Raman and FT-IR spectra were measured using Thermo Scientific Nicolet Almega Visible Raman spectrometer and Termo-Nicolette 6700 FT-IR spectrometer (ATR), respectively. Fluorescence spectra were collected using a Fluorolog-3 spectrofluorimeter (Jobin Yvon Horiba, Paris, France) equipped with a 450W xenon lamp and a photomultiplier tube. In all measurements the cell wall samples were positioned in a front-face configuration in the measuring chamber. For each of the samples, a series of emission spectra were collected by varying excitation wavelengths with 5 nm steps, in order to trace all fluorophores in the cell walls. The deconvolution of all spectra of a sample, using a log-normal model, was performed in order to determine the number of fluorophores in the sample.

The bands in the FT-IR spectra of the *Acer* cell walls are more pronounced in comparison with those of the *P. omorika* cell walls, but there are no substantial differences in the spectral pattern. However, differences are much more pronounced in the Raman spectra of the two CW samples, in the lignin (band region of C = C vibrations being active in Raman) and polysaccharides characteristic regions. The spectral differences reflect different inter- and intramolecular connections in these CWs, caused by the chemical differences in precursors of hardwood and softwood CWs. Thus the results show different C = C bond organisation in the two CW samples. The emission spectra of the two CWs have similar shape, but differ in the spectral width. Deconvolution of the emission spectra has confirmed the difference in the long-wavelength region of the spectra, due to the difference in the corresponding fluorophores (mainly related to the lignin polymer) in the CWs of the two samples. This difference reflects chemical/structural distinction between lignin precursors in the hardwood and softwood (guaiacyl type in *P. omorika* and syringyl/guaiacyl type in *Acer* sp).

Understanding of the distinct interpolymer connections in the CWs of the hardwood and softwood species, may contribute to the studies and modeling of the isolated single polymers

