A Methodological Approach to Elucidate the Effect of Balsam Woolly Adelgid Infestation on the Structure of Wood and Bark

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Traditional analytical methods used in wood chemistry require a significant amount of time and labor to obtain comprehensive information. Better understanding of the mechanisms of pest-host interaction requires new methodological developments to elucidate changes in the chemical structures in components of various parts of the tree (wood, bark, foliage) triggered by infestation. This paper reports development of a rapid and informative approach to elucidate the structures of lignin and polyphenolics with nuclear magnetic resonance (NMR) spectroscopy and its application to track the effect of balsam woolly adelgid (BWA) infestation on the chemical composition of Fraser fir wood and bark. Components of wood and bark have been characterized by wet chemistry methods, correlation 2D NMR techniques (HMQC, HMBC, TOCSY), and quantitative ^{13}C and ^{1}H NMR.

In response to infestation, Fraser fir produces reddish wood (*rotholz*) with a high density and low conductivity that is eventually responsible for the tree death. The *rotholz* wood has a ~15% higher amount of lignin and much higher amount of galactans than that of unifested trees. *Rotholz* lignin has higher amounts of p-hydroxyphenyl (H) units and aliphatic Ohio groups and lower amount of interunit linkages, implying that it is less crosslinked. The degree of condensation of the *rotholz* lignin is not higher than that of normal wood.

Chemical analysis of inner and outer bark samples from infested *A. fraseri*, unifested *A. fraseri*, and resistant *A. veitchii* showed a tendency toward lower amounts of lipophilic extractives and higher amounts of low molecular mass phenols and polyphenols in the bark of the infested trees as compared to the bark of the uninfested trees. An NMR approach developed for comparative analysis of ethanol- and water-soluble fractions allows for the characterization of the phenolic compounds without tedious chromatographic separation. These fractions consist predominantly of flavanoids and condensed tannins with small amounts of phenylpropanoids and lignans. The bark polyphenolics of the infested trees contain much higher amounts of p-hydroxyphenyl moieties and lower amount of guaiacyl (G) aromatic moieties than that of uninfested Fraser fir. The amount of H-moieties in bark polyphenolics of the resistant Veitch fir is also high, but this does not result in a decrease in the G-unit content, in contrast to infested Fraser fir.