



## Monomers of cutin biopolymer: sorption and esterification on montmorillonite surfaces

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One of the important precursors for soil organic matter is plant cuticle, a thin layer of predominantly lipids that cover all primary aerial surfaces of vascular plants. In most plant species cutin biopolymer is the major component of the cuticle (30-85% weight). Therefore cutin is the third most abundant plant biopolymer (after lignin and cellulose). Cutin is an insoluble, high molecular weight bio-polyester, which is constructed of inter-esterified cross linked hydroxy-fatty acids and hydroxyepoxy-fatty acids. The most common building blocks of the cutin are derivatives of palmitic acid, among them 9(10),16 dihydroxy palmitic acid (diHPA) is the main component. These fatty acids and their esters are commonly found in major organo-mineral soil fraction-humin. Hence, the complexes of cutin monomers with minerals may serve as model of humin. Both cutin and humin act as adsorption efficient domains for organic contaminants. However, only scarce information is available about the interactions of cutin with soil mineral surfaces, in particular with common soil mineral montmorillonite. The main hypothesis of the study is that adsorbed cutin monomers will be reconstituted on montmorillonite surface due to esterification and oligomerization, and that interactions of cutin monomers with montmorillonite will be affected by the type of exchangeable cation.

Cutin monomers were obtained from the fruits of tomato (*Lycopersicon esculentum*). Adsorption of monomers was measured for crude Wyoming montmorillonites and montmorillonites saturated with Fe<sup>3+</sup> and Ca<sup>2+</sup>. To understand the mechanism of monomer-clay interactions and to evaluate esterification on the clay surface, XRD and FTIR analyses of the montmorillonite-monomers complexes were performed.

Our results demonstrated that the interactions of cutin monomers with montmorillonite are affected by the type of exchangeable cation. Isotherms of adsorption of cutin monomers on montmorillonites were fitted by a dual mode model of sorption, which combines site specific adsorption mechanism (Langmuir) and partitioning mechanism. Adsorption of monomers by Fe<sup>3+</sup>-montmorillonite was higher than for Ca<sup>2+</sup> and crude -montmorillonites. XRD measurements showed expansion of d-spacing of montmorillonite samples with the increase in diHPA loading from 12.32, 12.66 and 12.17 Å for Fe<sup>3+</sup>- Ca<sup>2+</sup>- and crude-montmorillonite up to 16.84, 16.62 and 16.79 Å for organo-clay complexes of Fe<sup>3+</sup>-, Ca<sup>2+</sup>- and crude-montmorillonites respectively. This significant expansion of d-spacing suggests interlayer, and probably, multilayer diHPA adsorption by montmorillonite. Based on FTIR data we suggest that diHPA forms inner-sphere complexes with Fe<sup>3+</sup>-montmorillonite surface but not with Ca<sup>2+</sup> and crude-montmorillonites. However all montmorillonite samples induce esterification and oligomerization of the monomers, which was demonstrated by FTIR spectra of the organo-montmorillonite complexes and by LC-MS analysis of the organic material extracted from organo-clay complexes. These results confirmed our hypothesis about oligomerization of cuticular monomers on mineral surfaces. We assume that esterification and oligomerization of monomers on montmorillonite surfaces simulate similar soil processes, which result in the formation of soil organo-mineral complexes and humin.