

ABSTRAKT (EN)

This doctoral thesis summarizes the use of modern mass spectrometric methods for the structural identification of fatty acids and triacylglycerol estolides (TG-EST) and their subsequent characterization in the lipidome of *vernix caseosa*, i.e., the biofilm covering the skin of the human fetus during the last trimester of *in-utero* development. *Vernix caseosa* has mainly antimicrobial properties and the ability to heal wounds and burns.

The first part of the doctoral thesis focuses on the diversity of fatty acids in the lipidome of *vernix caseosa*. These acids form the structural subunits of complex lipids, such as the abundant triacylglycerols and wax esters. By studying fatty acids and their structural features, this thesis has provided valuable insights into the structural variability of the *vernix caseosa* lipidome. Without a full understanding of the structure of these key subunits, it would be impossible to complete the analysis of this lipidome in the future. In this thesis, fatty acids using high-performance liquid chromatography (HPLC) and modern mass spectrometry methods, namely ultraviolet photodissociation (UVPD) and ozone-induced dissociation (OzID), were characterized. The coupling of HPLC and mass spectrometry (HPLC-MS) provided unambiguous information on the positions and geometry of double bonds and methyl-branching positions within fatty acyl chains. Fatty acids that have not been previously described in existing lipid databases, e.g., LIPID MAPS®, were discovered.

The second part of the thesis focuses on developing and optimizing mass spectrometric methods based on collision-induced dissociation (CID), higher-energy collision dissociation (HCD), OzID, and UVPD for structural analysis of TG-EST. TG-EST molecules are known for their anti-inflammatory effects. Fragmentation of ammonium, lithium, and sodium molecular adducts of structural isomers of TG-EST was studied. It was possible to distinguish structural isomers of TG-EST by selecting molecular adduct and activation methods. Detailed characterization of the fatty acid composition and positional isomerism of the estolide subunits by fragmentation of the lithium adducts of TG-EST was achieved. Based on these results, the HPLC-MS method for separating TG-EST standards and TG-EST in *vernix caseosa* was optimized.