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Investigation of the Detailed Molecular Structure of the Human Stratum Corneum Ceramides [NP] and [EOS] by APCI and Nano-ESI Mass Spectrometry

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The aim of this study was to characterize two ceramide subclasses, CER[NP] and CER[EOS], of human stratum corneum (SC) and to identify the chemical structures of their subspecies. High performance thin layer chromatography (HPTLC) and normal phase high performance liquid chromatography (NP-HPLC) were used for the separation of CER fractions of interest, whereas nanoelectrospray tandem mass spectrometry was applied to identify the chemical structures in detail. Thus, CER[EOS] fragmentation revealed that in addition to linoleic acid other esterified fatty acids occur in the ω -hydroxylated-position (part E). Of particular interest is the identification of a 17:2 fatty acid located in this part of the molecule.

Several subspecies of CER[NP], including subspecies with odd numbers of carbon atoms in both chains, the non- α -hydroxylated fatty acid moiety (part N) and the phytosphingosine (part P) were detected. Furthermore, 12% of CER[NP] subspecies with an odd number of carbon atoms in more than one chain for one molecule were detected.

Similar results were obtained for CER[EOS]. Both, the esterified fatty acid (part E) and the sphingosine base (part S) were found to contain odd-numbered chain lengths.

The combination of the analytical techniques presented allows complete new insights into the molecular structure of the SC ceramides. Now the techniques are used to identify differences in the detailed molecular structure of the ceramides in healthy and diseased skin.