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Structural Elucidation of Archeal Diether Phospholipids by High-Energy CID/tandem TOF-MS

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In contrast to most other living organisms (animals, plants, bacteria etc.) archeae are representing nowadays an own kingdom. Even their cell wall lipids differ markedly as they possess typically ether bonds with only minor structural variations in their alkyl chains constituting regular methyl-branched C_{20}-building blocks called phytanol instead of ester bonds. The identity of the polar head group ranges from PI, PC and PE to saccharide-moieties. Additionally, also C-C-linked tetraether lipids are formed representing very big carbocyclic compounds. Structural elucidation of such unusual phospholipids was previously typically performed with ESI low-energy CID MS/MS or MALDI-TOFMS with post source decay (PSD) yielding spectra of poor quality. Here, we present for the first time MALDI high-energy CID-data on selected diether phospholipids including two synthetic ether derivatives selecting all types of precursor ions formed ($[M-H]^-$, $[M+H]^+$, $[M+Na]^+$ and $[M+2Na-H]^+$). All diether derivatives forming $[M-H]^-$-precursor ions (PI, PE) show abundant charge-remote fragmentation of the alkyl chains with 14 Da-spacing except for the methyl-branchings spaced by 28 Da. Low mass ions typically identify the polar head group of the lipid species. Protonated precursor ions (PC, PE) yield strongly differing spectra as the PE derivative shows an unexpected loss of H_3PO_4 from the precursor ion and a McLafferty rearrangement. No diagnostic low-mass head group product ions could be detected. Among PC-derivatives, an unexpected rearrangement involving the transfer of one alkoxy group to the phosphate-moiety was detected - besides high-mass charge remote fragmentation - yielding most likely an O-alkyl-phosphocholine product ion. For sodiated and disodiated species only the latter ones seem to be of interest for high-energy CID-experiments as only these precursor ions yield abundant charge-remote fragmentation – comparable to high-energy CID-spectra of $[M-H]^-$-precursor ions. The low-mass region identifies the type of polar head group. In conclusion, several unique and new, previously undescribed fragmentations/ rearrangements are shown and discussed in detail.

References

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