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OZONOLYSIS OF PHOSPHOLIPID DOUBLE BONDS: A COMPARISON BETWEEN *IN-SOURCE* AND *IN VACUO* OZONOLYSIS

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Phospholipids are the main structural component of biological membranes and play a major role in many biochemical pathways. For these reasons there is a need for rapid characterization of phospholipids within lipid extracts. Electrospray ionization tandem mass spectrometry (ESI-MS/MS) can provide a near complete characterization of the molecular structure of phospholipids in a complex mixture [1]. Unfortunately, current ESI-MS/MS methods cannot distinguish isomeric phospholipids that differ only in the position of double bonds [2]. We have previously developed an on-line method that allows for unambiguous assignment of double bond position within phospholipid molecular species [3]. This is achieved by performing ozonolysis in the source of a standard ESI mass spectrometer which results in the formation of two chemically induced fragment ions indicative of double bond position: we have dubbed this technique OzESI. While this has proved to be a powerful method for the characterization of pure compounds and simple mixtures, the interpretation of OzESI spectra obtained from complex mixtures is either difficult or impossible. This problem may be overcome by a tandem mass spectrometric approach whereby *mass selected* ions are allowed to undergo chemically induced fragmentation.

In our laboratory, ozonolysis of unsaturated phospholipid ions has been observed in the ion trap of a modified LTQ mass spectrometer. Differences are noted between spectra acquired under these conditions (i.e., *in vacuo*) and analogous spectra obtained by OzESI, notably, ions arising from reactions with solvent molecules in the source are not formed in the ion trap. Interestingly, in the latter experiment, ions with masses corresponding to reactive intermediates implicated in alkene ozonolysis have been observed. This tandem mass spectrometric approach may allow complete, on-line structural characterization of lipids, even in complex mixtures and has the potential to be integrated into 'shotgun lipdomic' analyses.

References

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