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Effect of the Location of Hydrogen Abstraction on the Fragmentation of Diuretics in Negative Electrospray Ionization Mass Spectrometry

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Abstract

The diuretic agents bumetanide, xipamide, indapamide and related compounds were investigated in order to determine the effect of different ionization sites on their collisionally activated dissociation and the corresponding fragmentation pathways. Therefore, analytes were selectively alkylated, and structural analogues as well as deuterium labeled compounds synthesized, which contain a reduced number of ionizable hydrogen atoms. Thus, specific hydrogen abstractions and their correlated dissociation routes of the negatively charged molecules were eliminated, providing evidence for the influence of the location of ionization on product ion spectra. Fragment ions such as m/z 78 indicate ionization at the commonly present sulfamoyl residue of diuretics but does not exclude additional ionization sites. Product ion spectra of the investigated diuretic agents proved to be composed by fragmentations initiated from different hydrogen abstractions. Moreover, the generation of radical anions by collision-activated dissociation of even-electron precursor ions was observed, the generation of which is discussed by proposed fragmentation pathways.

For the full paper, please refer to the *Journal of the American Society for Mass Spectrometry* 2003, 14, 658-670