Comparative Analysis of the Gas-Phase Reactions of Protonated and Sodiated Cylindrospermopsin

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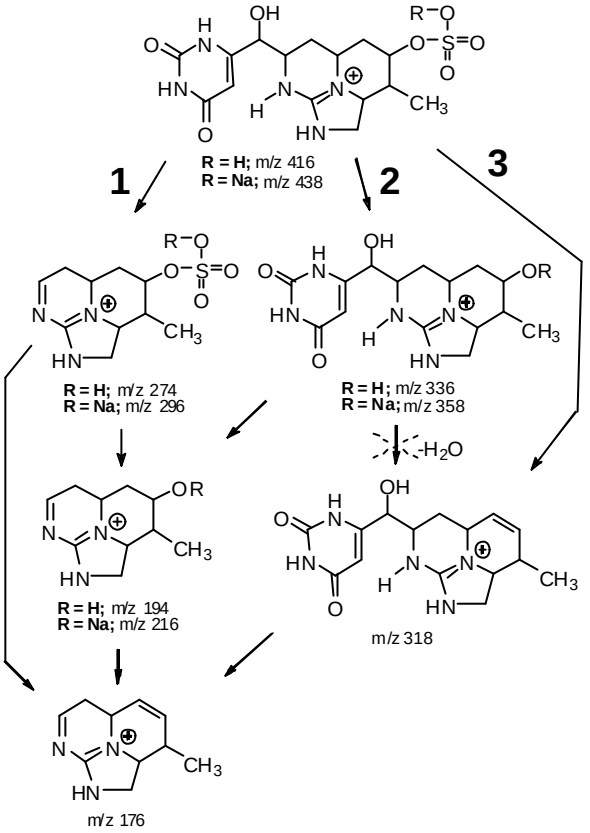
Introduction

Cylindrospermopsin (CYL) belongs to a group of toxins naturally produced by several strains of freshwater cyanobacteria. It is a compact zwitterionic molecule composed of an uracil section and a tricyclic guanidinium portion, that yields a positive center. The fragmentation reactions of CYL are not only important from analytical perspectives, but it can also be a model for the identification of new CYL derivatives in cyanobacteria. Considering the importance of this toxin for human health, we examined in this work the gas phase mechanisms of fragmentation for protonated and sodiated CYL using MS^n and high resolution mass spectrometry

Results and Discussion

Protonated (m/z 416) and sodiated (m/z 438) ions were formed via electrospray ionization on Bruker® equipments (Esquire HCT and UltrO-TOF) under standard isolation and excitation procedures. The MS^n spectra obtained on both instruments at neutral pH revealed the presence of three major initial pathways of fragmentation (Scheme 1). Pathway 1 is characterized by the neutral elimination of the uracil moiety directly from the protonated or sodiated molecule, while pathways 2 and 3 are characterized by the neutral eliminations of SO_3 and SO_4R, respectively. High resolution spectra are also dominated by neutral losses. Although protonated and sodiated molecules were found to fragment with similar number of ions under standard conditions, ion intensities were markedly different, especially for those ions generated by neutral losses that involve migration of **R** (Na or H). The opposite intensities are a consequence of the differential Na and H mobility. Since proton migration is easily accomplished when compared to sodium, the protonated molecule follows preferentially pathways 2 and 3, whereas the sodiated molecule follows preferentially pathway 1.



Scheme 1: Proposed fragmentation route for protonated (m/z 416) and sodiated (m/z 438) cylindrospermopsin.

Conclusions

The present study shows the fragmentation pathways for CYN and CYN sodium salt and the differential mobility of H and Na. Experiments with other metal cations are in course and will be reported. Data obtained in this way provide complementary structural information that will be of significant use for future identification of metabolites and biosynthetically generated derivatives.

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