

## A STUDY OF CAROTENOIDS AND XANTHOPHYLLS IONISATION AND FRAGMENTATION, IN ELECTROSPRAY OR NANOSPRAY MS.

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The difference in the source and ionisation conditions for nanospray makes it a process with much lower energy. Analysis of retinal showed an unexpected difference in the balance of ionisation between radical molecular ion and protonated molecule formation in nanospray, when compared to that previously published for ESI. The purpose of this study is to establish a sound basis for the ionisation of 16 polyenes in nanospray in comparison to ESI, and fragmentation analysis.

$\beta$ -carotene (in nanospray) showed unexpected behavior with the protonated molecule occurring as the major ion. Systematic studies of all xanthophylls also confirmed the protonated molecule as the major ion independently of the presence of heteroatoms. Detailed analysis suggests that in nanospray ionisation it is easier to obtain the protonated molecule in neutral solutions than in acidic solutions in ESI. Considering the lower potentials applied to the nanospray chip, these results showed a better correlation between the loss of an electron from their highest occupied molecular orbital and the potential applied. The fragmentation pathway showed a general mechanism for the elimination of aromatic molecules from polyenes in tandem MS. The same behavior was observed in the MS/MS spectra from molecular ion, protonated or sodiated molecule. Taken together, all this data will help structural elucidation of polyenes at different sources.

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