

Fragmentation studies of protonated xanthophylls from marine organisms by accurate-mass electrospray tandem mass spectrometry.

Fausto Carnevale Neto^{1*} (PQ), Thais Guaratini² (PQ), Leticia V. Costa-Lotuf³ (PQ), Pio Colepicolo⁴ (PQ), Norberto P. Lopes¹ (PQ).

*fausto_pos@yahoo.com

(1) Núcleo de Pesquisa em Produtos Naturais e Sintéticos (NPPNS), Faculdade de Ciências Farmacêuticas de Ribeirão Preto da Universidade de São Paulo (FCFRP-USP), Ribeirão Preto, SP, Brazil,

(2) Lychnoflora Pesquisa e Desenvolvimento em Produtos Naturais LTDA, Incubadora SUPERA, Campus da Universidade de São Paulo (USP), Ribeirão Preto, SP, Brazil,

(3) Departamento de Farmacologia, Instituto de Ciências Biomédicas, Universidade de São Paulo (USP), São Paulo, SP, Brazil,

(4) Departamento de Bioquímica, Instituto de Química de São Paulo, Universidade de São Paulo (USP), São Paulo, SP, Brazil.

Keywords: xanthophylls, marine organisms, tandem mass spectrometry, electrospray ionization.

Introduction

Carotenoids and xanthophylls are 40-carbon isoprene derivatives with a conjugated polyene chain - usually up to 15 double bonds. These molecules are widely distributed in nature where they play a key role in photosynthesis and photoprotection, specially for marine organisms - exposed to stress factors, such as UV radiation, salinity, temperature, and desiccation.¹

Several analytical methods have been developed to detect and quantify carotenoids based on their unique chemical reactivity and light-absorbing properties. LC-UV is by far the most common, but the UV spectra similarity demand a complete LC resolution to assure identity. LC-MS can overcome the coelution issue by offering high selectivity, however it requires mechanistically and structurally dependent fragmentation studies on complex gas-phase ion chemistry of carotenoids.^{2,3}

The purpose of this study is to establish the fragmentation study of protonated xanthophylls $[M+H]^+$ by high-resolution ESI-CID-MSⁿ.

Results and Discussion

Ionization of protonated carotenoids $[M+H]^+$ gave rise to several conjugated carbocation ions with different *cis-trans* isomerisation of the polyene chain.⁴ The presence of heteroatoms (hydroxyl and carbonyl groups) in xanthophylls promoted acid-base ionization and intramolecular rearrangements, as proton transfer, by assistance of the lone pair of electrons from oxygen atom (Figure 1-A₁).

The main fragmentation route proposed for the xanthophylls $[M+H]^+$ consisted in pericyclic reactions as retro-ene (Figure 1-A₂) and electrocyclic eliminations (Figure 1-B₁).

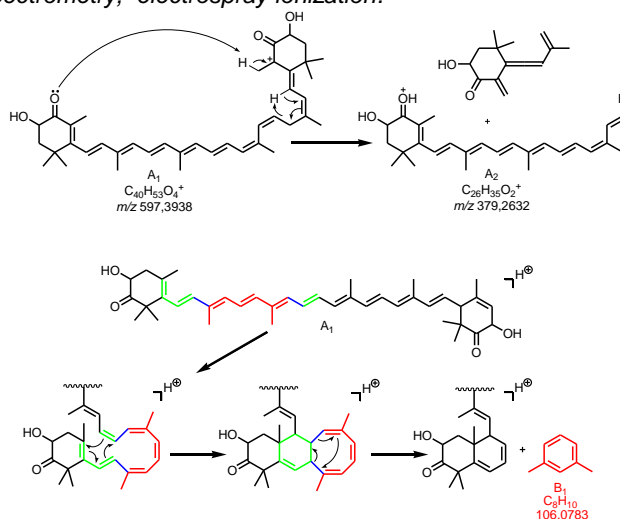


Figure 1. Proposed mechanisms for the retro-ene elimination (A₂) and electrocyclic aromatic elimination (B₁) derived from the astaxanthin (A₁).

Conclusion

Characteristic fragmentation pathways were proposed for protonated xanthophylls and may assisted carotenoid identification by ESI-MS/MS.

Acknowledgements

CNPq, CAPES and FAPESP for fellowship support (F.C.N. FAPESP n. 2014/12343-2).

¹ Rastogi, R. P.; Richa, Sinha, R. P.; Singh, S. P., Häder, D. P. *J. Ind. Microbiol. Biotechnol.* **2010**, *37*, 537.

² Guaratini, T.; Vessecchi, R.; Pinto, E.; Colepicolo, P.; Lopes, N. P. *J. Mass Spectrom.* **2005**, *40*, 963.

³ Guaratini, T.; Lopes, N. P.; Pinto, E.; Colepicolo, P.; Gates, P. J. *Chem. Commun.* **2006**, *39*, 4110.

⁴ Mormann, M.; Kuck, D. *J. Phys. Org. Chem.* **2003**, *16*, 746.