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RESEARCH PAPER

Mediterranean *Azadinium dexteroporum* (Dinophyceae) produces six novel azaspiracids and azaspiracid-35: a structural study by a multi-platform mass spectrometry approach

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Abstract *Azadinium dexteroporum* is the first species of the genus described from the Mediterranean Sea and it produces different azaspiracids (AZA). The aims of this work were to characterize the toxin profile of the species and gain structural information on azaspiracids produced by the *A. dexteroporum* strain SZN-B848 isolated from the Gulf of Naples. Liquid chromatography-mass spectrometry (LC-MS) analyses were carried out on three MS systems having different ion source geometries (ESI, TurboIonSpray®, ESI ION MAX) and different MS analyzers operating either at unit resolution or at high resolution, namely a hybrid triple quadrupole-linear ion trap (Q-Trap MS), a time of flight (TOF MS), and a hybrid linear ion trap Orbitrap XL Fourier transform mass spectrometer (LTQ Orbitrap XL FTMS). As a combined result of these different analyses, *A. dexteroporum* showed to produce AZA-35, previously reported from *Azadinium spinosum*, and six compounds that represent new additions to the AZA-group of toxins, including AZA-54 to AZA-58 and 3-epiAZA-7, a stereoisomer of the shellfish metabolite AZA-7. Based on the interpretation of fragmentation patterns, we propose that all these molecules, except AZA-55, have the same A to I ring system as AZA-1, with structural modifications all located in the carboxylic side chain. Considering that none of the azaspiracids produced by the Mediterranean strain of *A. dexteroporum* is currently regulated by European food safety authorities, monitoring programs of marine biotoxins in the Mediterranean area should take into account the occurrence of the new analogues to avoid an underestimation of the AZA-related risk for seafood consumers.

Keywords Azaspiracids · *Azadinium dexteroporum* · Marine toxins · LC-MS/MS · LC-HRMS^n · LC-TOFMS

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Introduction

Azaspiracids (AZAs) are a group of polyether toxins first reported to cause seafood poisoning in the Netherlands in 1995, following the ingestion of contaminated shellfish from Killary Harbour, Ireland [1]. Shellfish were contaminated by a unique marine toxin, originally named "Killary-toxin" and shortly after structurally elucidated and renamed azaspiracid-1 (AZA-1) [2–4] (Fig. 1). The name was consistent with its chemical features which includes a six-membered cyclic amine (AZA), a unique tri-spiro assembly (SPIRO), and a carboxylic acid group (ACID). The rest of the molecule consisted of a linear carbon chain cyclized at several points through ether bridges. The biogenetic origin of azaspiracids causing the Killary Harbour shellfish contamination was initially identified in the heterotrophic dinoflagellates

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