



Profiles and levels of fatty acid esters of okadaic acid group toxins and pectenotoxins during toxin depuration. Part II: Blue mussels (*Mytilus edulis*) and flat oyster (*Ostrea edulis*)

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ABSTRACT

Bivalve molluscs accumulate toxins of the okadaic acid (OA) and pectenotoxin (PTX) groups, which are frequently found in *Dinophysis* spp. Transformation of the OA-group toxins into fatty acid ester derivatives (often designated “DTX3”) is common in many bivalve species but the degree to which these toxins are transformed vary between species, and is also depending on the parent toxin involved. In this paper, detailed profiles and levels of fatty acid esters of OA, DTX1, DTX2 and PTX2 SA were studied in blue mussels (*Mytilus edulis*) and European flat oysters (*Ostrea edulis*), collected during a bloom of *Dinophysis* spp. and after 3 and 6 weeks of depuration. Analysis of samples by HPLC-MS/MS and HPLC-MS² revealed some differences in identity and abundance of fatty acid moieties of the OA-group esters between species, but the 16:0 fatty acid esters dominated in both oysters and mussels, which is in accordance with the free fatty acid profiles in these species. A wider range of PTX2 SA-esters were detected compared to esters of the OA-group toxins in both mussels and oysters, and in oysters, both 14:0, 18:4 and 20:5 fatty acid side chains were more common than 16:0. OA-group toxins were esterified to a larger degree in oysters (83–93%) compared to mussels (21–41%), and in mussels a higher proportion of OA was esterified compared to DTX1 and DTX2. Contrary to what was observed for OA-group toxins, PTX2 SA was esterified to a larger degree in mussels (81%) compared to oysters (64%). Calculations of depuration rates for all individual esters of each parent compound showed that the esters of DTX1 depurated significantly slower from both mussels and oysters compared to esters of OA, DTX2 and PTX2 SA, but overall the depuration rates of esters of both toxin group were highly similar for both species. This indicated that differences in depuration rates are not causing the large species-specific differences in levels and profiles of these toxins. Instead, the results for the OA-group toxins suggested that a higher rate of esterification in oysters is the main factor causing the observed differences in the proportion of esters to free toxin. For PTX2 SA, large differences in ester profiles and a higher proportion of esters of PTX2 SA in mussels compared to oysters suggested differential assimilation and metabolic rate processes for the PTXs compared to OA-group toxins between these species. Hence, although produced by the same *Dinophysis* species, conclusions about the dynamics of one toxin group based on results from the other group should be avoided in future studies.

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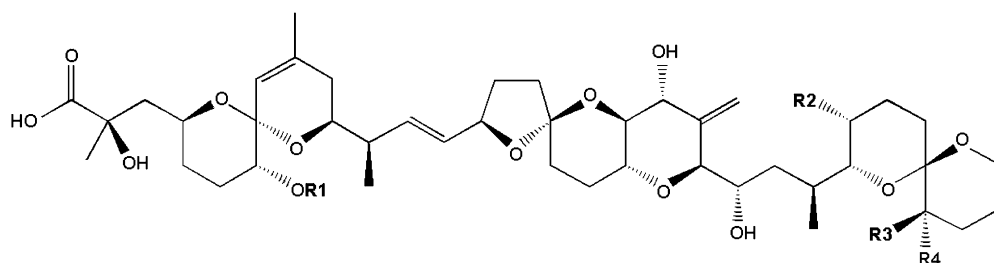
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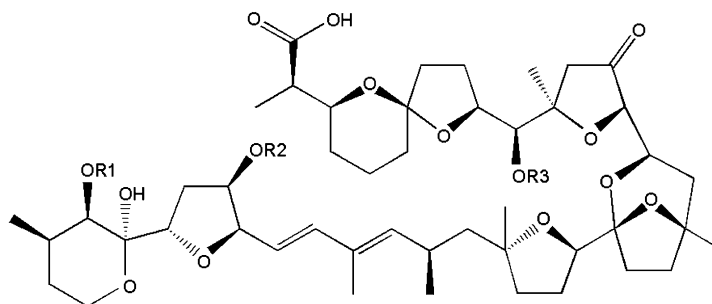
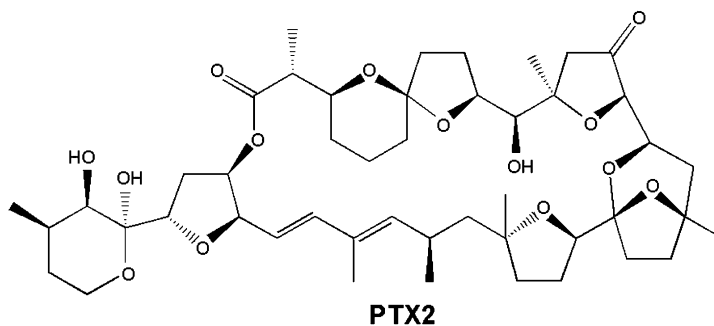
1. Introduction

Filter-feeding bivalve molluscs, such as mussels and oysters, accumulate secondary metabolites produced by various phytoplankton species (i.e. algal toxins), which may be toxic to humans (Daranas et al., 2001).

Dinoflagellates of the genera *Dinophysis* produce toxins belonging to the okadaic acid (OA) group and the pectenotoxin (PTX) group (Yasumoto et al., 1989). The OA-group toxins (Fig. 1) consist of okadaic acid and its analogues dinophysistoxin-1 (DTX1) and dinophysistoxin-2 (DTX2) (Hu et al., 1992; Murata et al., 1982; Yasumoto



<u>Toxin</u>	<u>R1</u>	<u>R2</u>	<u>R3</u>	<u>R4</u>
OA	H	CH ₃	H	H
DTX1	H	CH ₃	CH ₃	H
DTX2	H	H	H	CH ₃
7-O-acyl OA	Fatty acid	CH ₃	H	H
7-O-acyl DTX1	Fatty acid	CH ₃	CH ₃	H
7-O-acyl DTX2	Fatty acid	H	H	CH ₃



<u>Toxin</u>	<u>R1</u>	<u>R2</u>	<u>R3</u>
PTX2 SA	H	H	H
37-O-acyl PTX2 SA	Fatty acid	H	H
33-O-acyl PTX2 SA	H	Fatty acid	H
11-O-acyl PTX2 SA	H	H	Fatty acid

Fig. 1. Structures of okadaic acid group toxins and pectenotoxins.

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