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Determination of multiple toxins in whelk and clam samples collected from the Chukchi and Bering seas

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ABSTRACT

Buccinidae whelk *Neptunea varicifera* (Dall), Cardiidae clam *Serripes laperousii* (Deshayes), and two unknown species of whelk and clam were collected from the Arctic Chukchi Sea and sub-Arctic Bering Sea in July 2014. In this study, the mollusk samples were analyzed by different liquid chromatography-tandem quadrupole mass spectrometry (LC-MS/MS) methods for multiple shellfish toxins, including okadaic acid (OA), pectenotoxin (PTX), yessotoxin (YTX), azaspiracid (AZA), cyclic imines (CI), and saxitoxin (STX) groups. PTX2 ($\approx$2.0 μg kg^{-1} whole tissues) was detected exclusively in the clam *S. laperousii* collected from the Chukchi Sea. OA and dinophysistoxin-1 (DTX1) were restricted to mollusk samples collected from the Bering Sea, and OA was the dominant component of the whelk *N. varicifera* (63 μg kg^{-1} digestive gland) and an unknown species of whelk (6.8 μg kg^{-1} digestive gland). Spirolide-1 (SPX1) was confirmed in most samples except for the whelk *N. varicifera* collected from the Bering Sea. The highest content of SPX1 ($\approx$18.5 μg kg^{-1} digestive gland) occurred in the whelk *N. varicifera* collected from the Chukchi Sea, along with the suspected presence of SPX-C, SPX-D and didesMe-SPX-C. YTX, as well as its derivatives 45-OH-YTX and 45,46,47-Trinor-YTX, were found in all samples, with the highest YTX content (66 μg kg^{-1} digestive gland) present in the whelk *N. varicifera* collected from the Chukchi Sea. Interestingly, STX and dcSTX were measured only in the whelk *N. varicifera* and unknown species of clam collected from the Chukchi Sea. No AZA-group toxins, gymnodimine (GYM), or pinnatoxin G were found in any samples analyzed. Results demonstrated that the mollusk samples were contaminated by multiple shellfish toxins in the Chukchi and Bering seas. This study highlights the need to monitor potentially toxic microalgae in the Arctic and sub-Arctic regions, as well as species of mollusk that may be included in future commercial or subsistence harvests.

1. Introduction

Marine algal toxins, also commonly known as shellfish toxins or marine biotoxins, have been classified into eight groups including okadaic acid and dinophysistoxins (OA-group), pectenotoxin (PTX), yessotoxin (YTX), azaspiracid (AZA), brevetoxin (BTX), cyclic imine (CI), saxitoxin (STX), and domoic acid (DA) (FAO et al., 2004). The chemical structures of shellfish toxins detected in this study are shown in Fig. 1. These toxins can be accumulated by filter-feeding bivalve mollusks, such as mussels, oysters, cockles, clams and scallops, and some zoophagous mollusks, such as whelk and snail. Human poisoning incidents are usually caused by consumption of the seafood products contaminated by high levels of shellfish toxins.

OA-group toxins including OA, dinophysistoxin-1 (DTX1) and DTX2 have been detected in mollusks from almost all regions of the world, whereas Europe and Japan appear to be the most affected areas (EFSA, 2008). These toxins have been identified in picked cells and cultivated strains of most *Dinophysis* spp., such as *Dinophysis acuta* collected from New Zealand waters (Suzuki et al., 2004; Nielsen et al., 2013) and *Dinophysis acuminata* isolated from Woods Hole, MA, USA (Hackett et al., 2009). They have also been isolated from *Prorocentrum lima* (syn. *Prorocentrum arenarium*) collected from various locations (Ten-Hage et al., 2000; Bravo et al., 2001; Heredia-Tapia et al., 2002; Nascimento et al., 2005; Vale et al., 2009).

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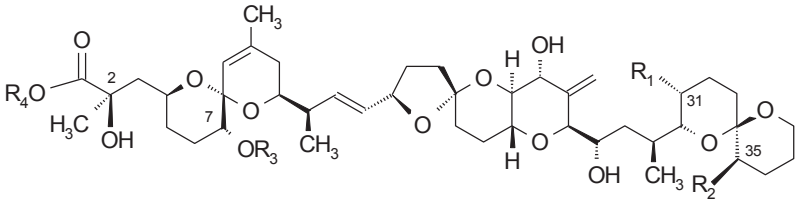
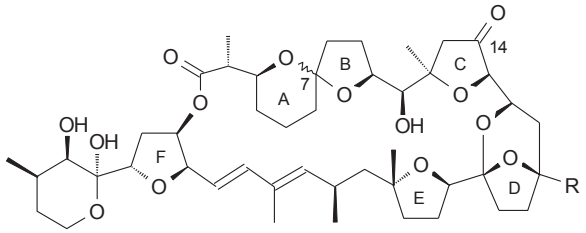
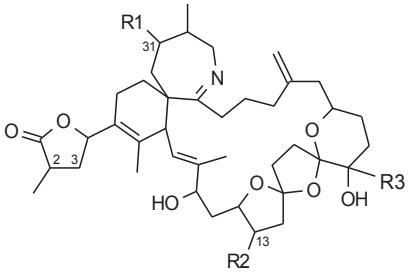


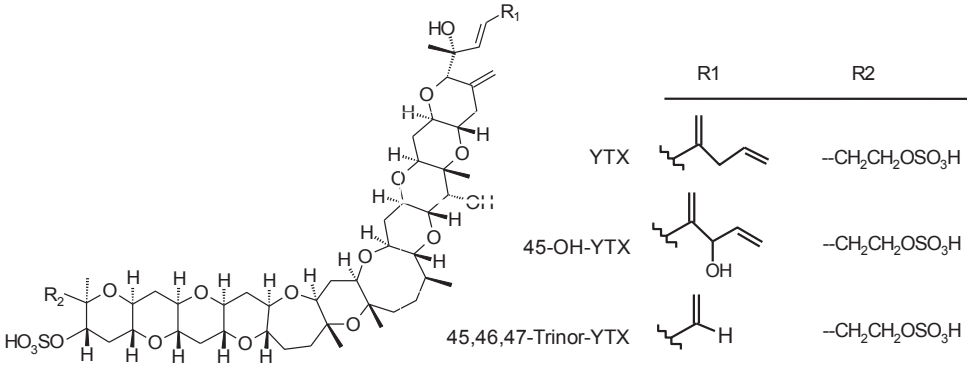
	R1	R2	R3	R4
OA	CH_3	H	H	H
DTX1	CH_3	CH_3	H	H



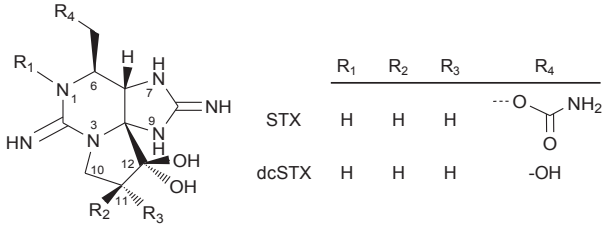
	R	C7
PTX2	CH_3	R



	R1	R2	R3	$\Delta^{2,3}$
SPX-A	H	CH_3	CH_3	√
SPX-B	H	CH_3	CH_3	×
SPX-C	CH_3	CH_3	CH_3	√
SPX-D	CH_3	CH_3	CH_3	×
SPX-1 (13-desMe-C)	CH_3	H	CH_3	√
13,19-didesMe-C	CH_3	H	H	√



	R1	R2
YTX		$-CH_2CH_2OSO_3H$
45-OH-YTX	OH	$-CH_2CH_2OSO_3H$
45,46,47-Trinor-YTX	H	$-CH_2CH_2OSO_3H$



	R_1	R_2	R_3	R_4
STX	H	H	H	$-O-C(=O)-NH_2$
dcSTX	H	H	H	-OH

Fig. 1. Chemical structures of multiple shellfish toxin groups detected in this study.