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Chasing a moving target:

The intriguing diversity of goniodomins (GD)

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Goniodomins and their producers: an overview

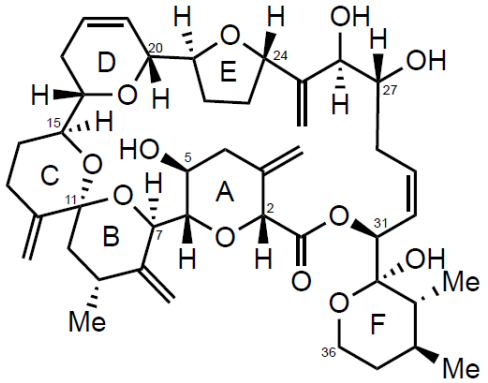
Goniodomin A (GDA) was isolated in 1968 from an unidentified *Alexandrium* species from Puerto Rico (Sharma, G.M. et al. (1968) Antibiotics, *21*, 659-664)

GDA was rediscovered 20 years later by Murakami et al. from *Alexandrium hiranoi* (initially named *Goniodoma pseudogonyaulax*) (Murakami, M. et al. (1988) Tetrahedron Lett. *29*, 1149-1152.)

Hsia et al. reported GDA from *Alexandrium monilatum*
(Hsia, M.H., et al. (2006) Harmful Algae *5,* 290-299)

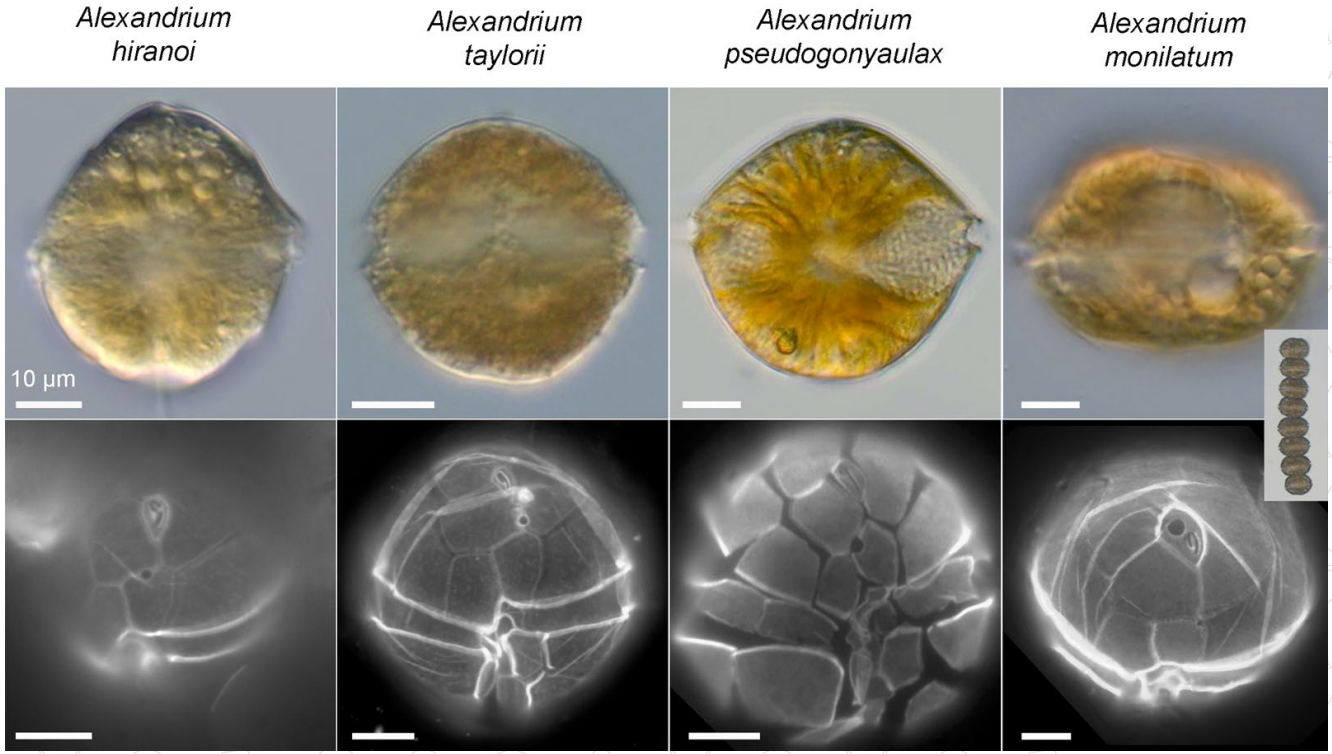
Alexandrium pseudogonyaulax was reported to produce GDA
(Zmerli Triki, H. et al. (2016) Toxicon *111*, 91-99)

Tillmann et al. described *Alexandrium taylorii* as a GDA-producer
(Tillmann, U. et al. (2020) Toxins *12(9)*, 564)

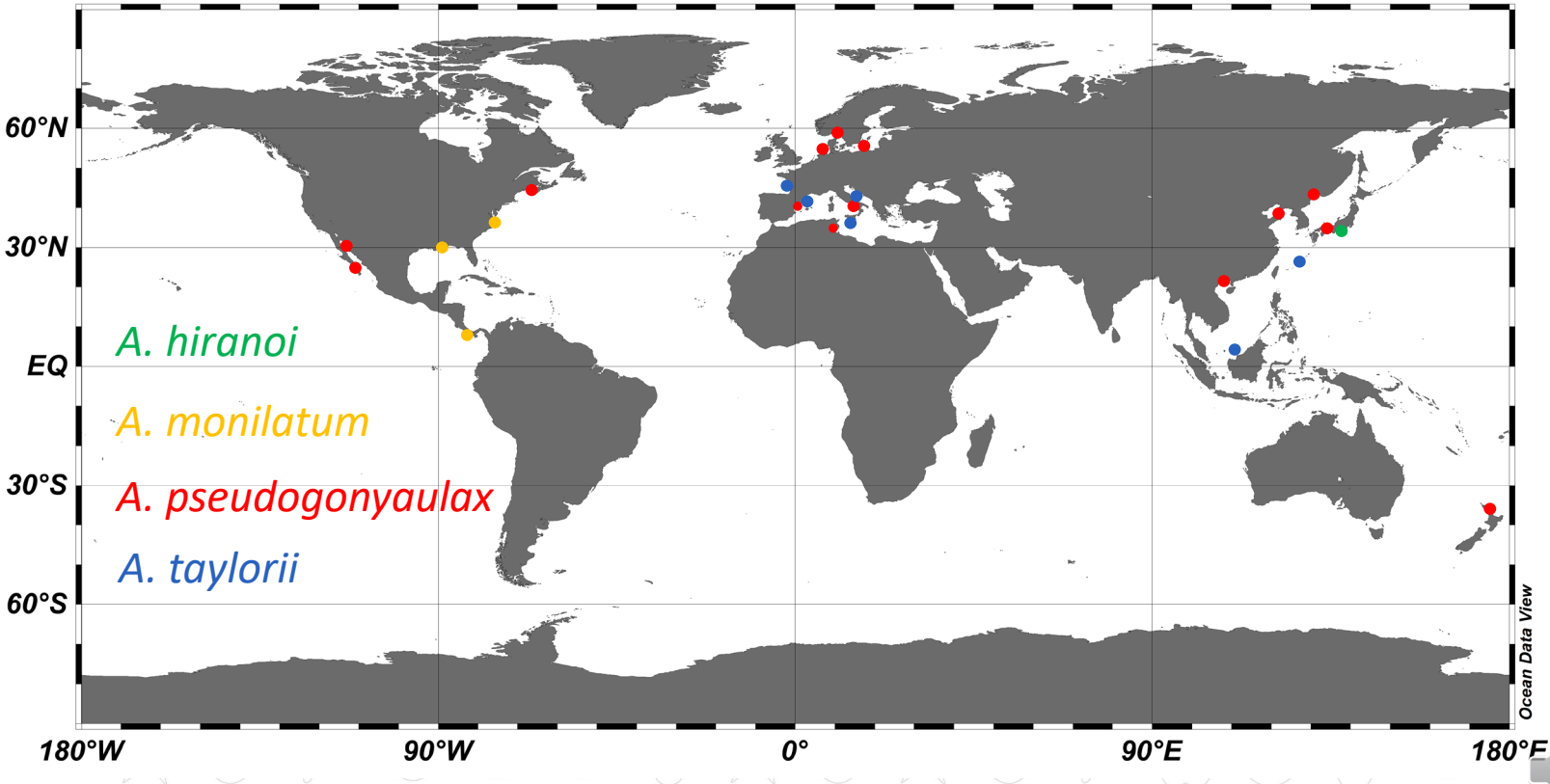


Goniodomin A (GDA)

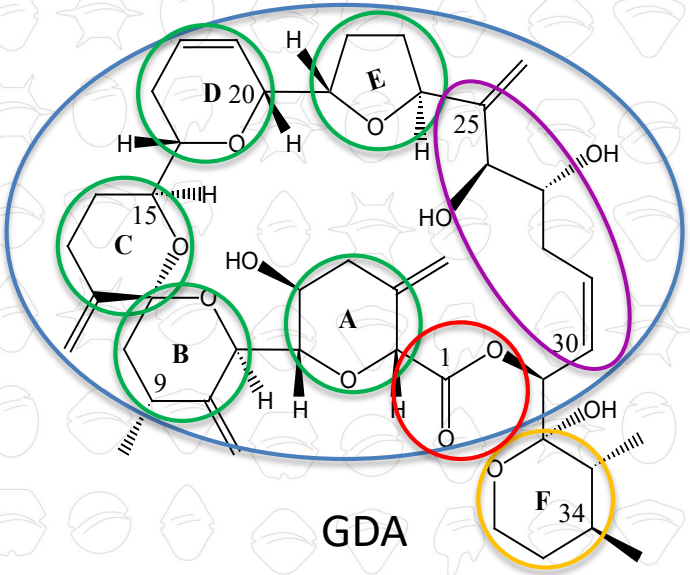
Currently known goniodomin-producers



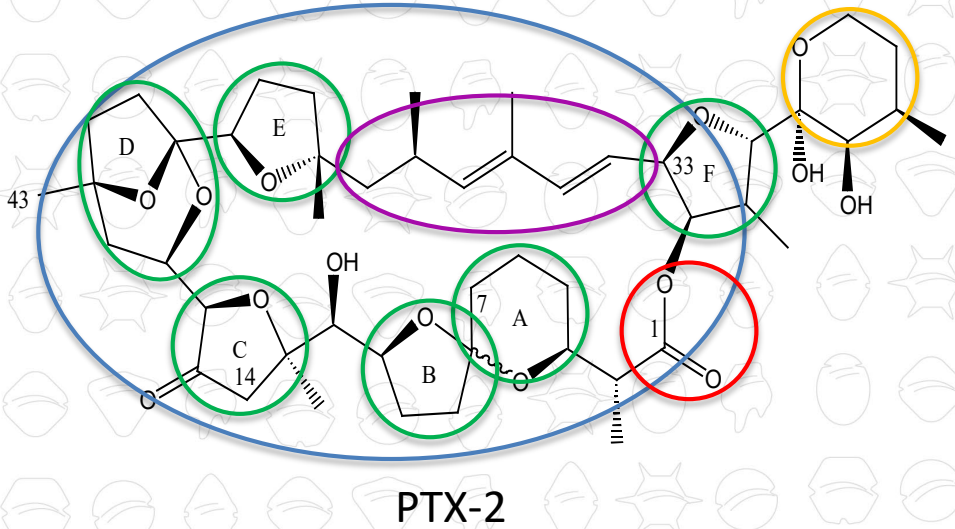
Global distribution of goniodomin-producers



Chemical characteristics of goniodomins



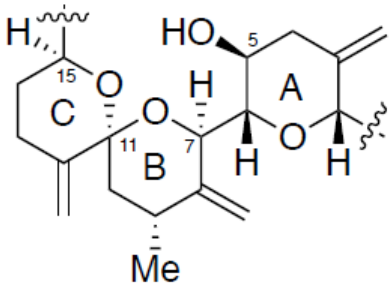
GDA



PTX-2

Macrocycle, exocyclic ether ring, ether rings, 6-membered carbon chain, lactone function

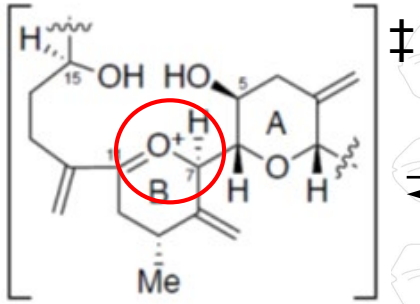
Conversion of goniodomin A (GDA)



GDA

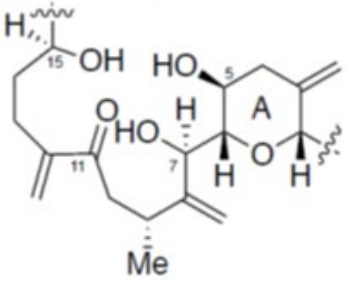
H^+

H^+

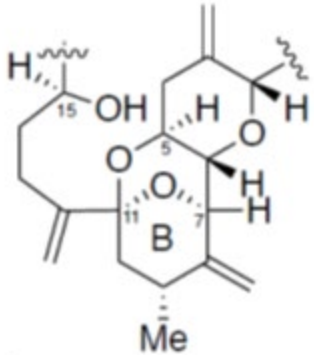


‡

H_2O



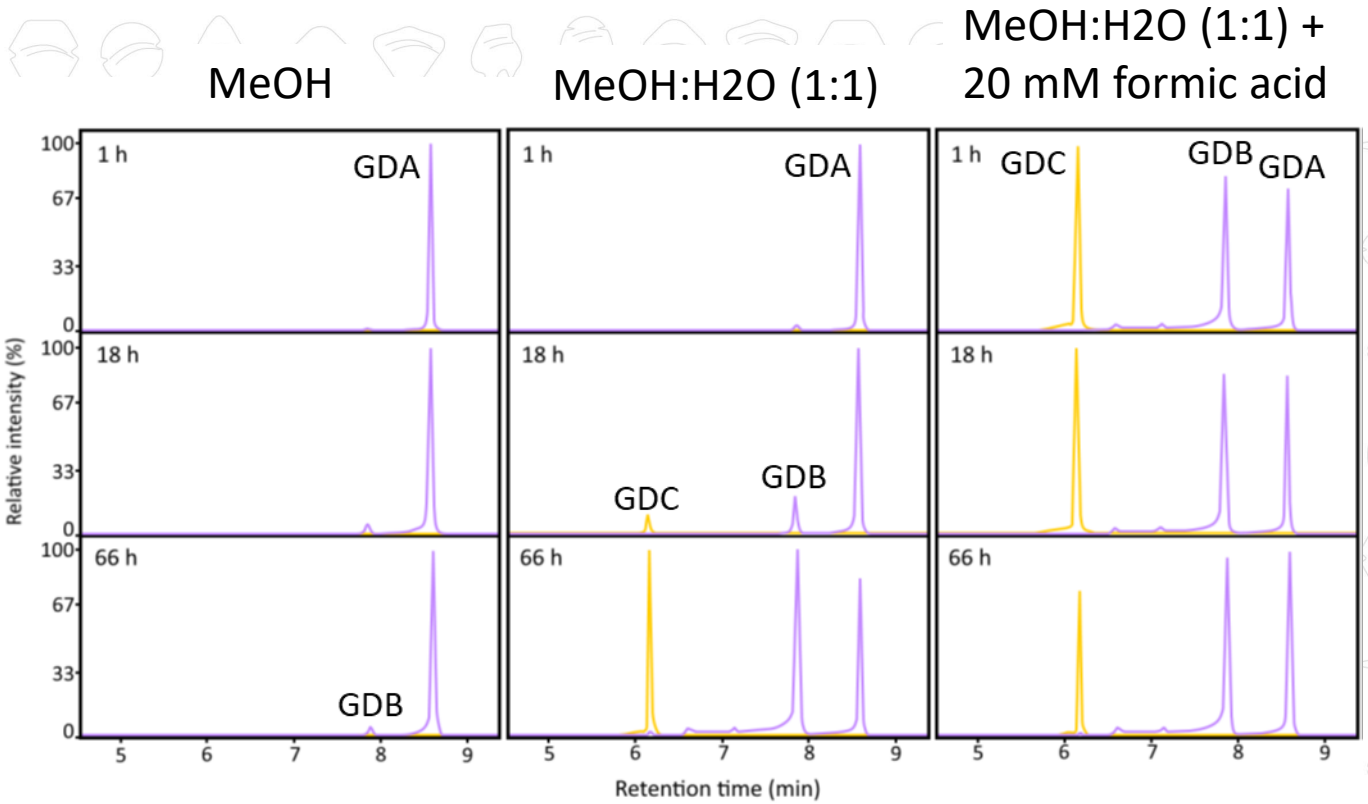
GDC



GDB

GDA oxonium ion

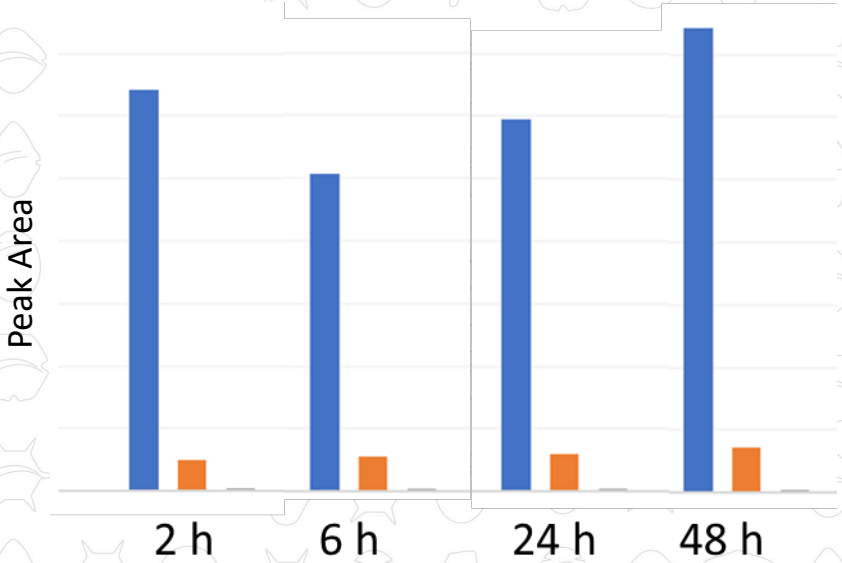
Conversion of goniodomin A (GDA)



Stability of GDA under chromatographic conditions

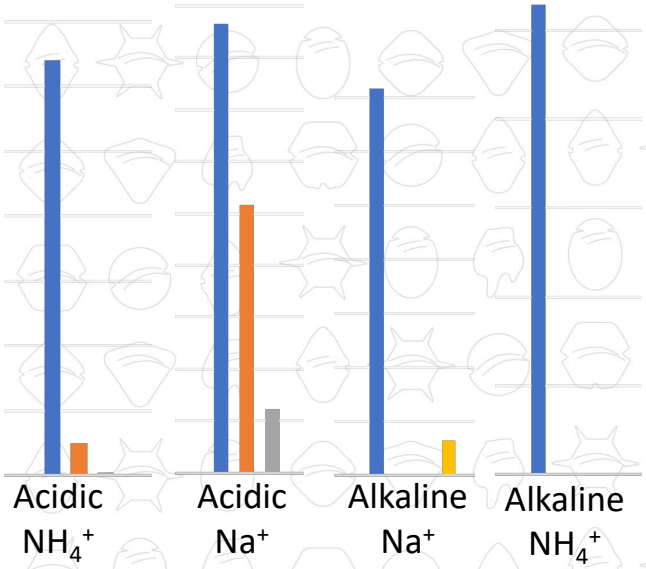
GDA GDB GDC GDA-sa

Ammonium Adducts with Acidic Eluent



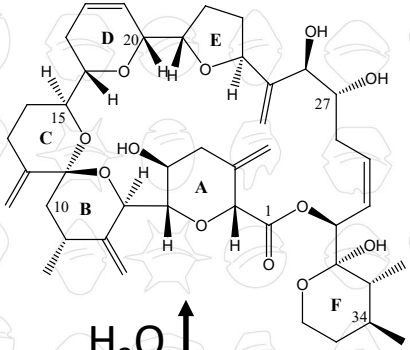
Chromatographic conditions

UPLC, retention time 3 min

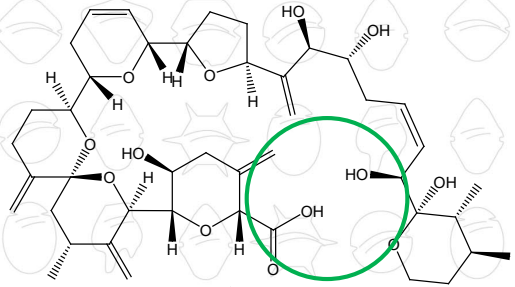


Conversions of GDA in the aquatic environment

GDA



H_2O

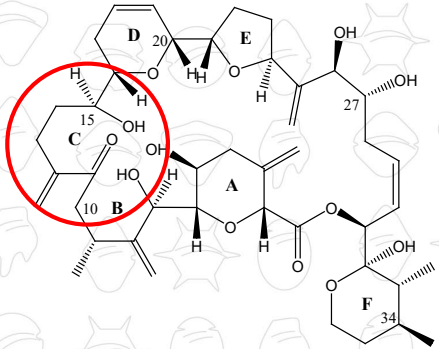


GDA-sa

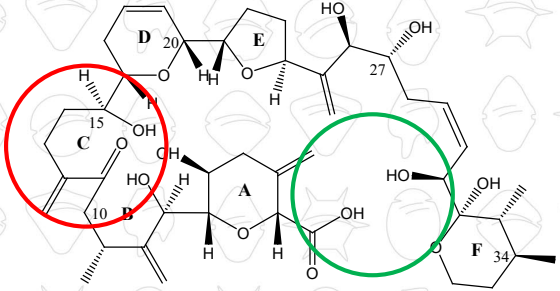
H_2O

H_2O

GDC



H_2O

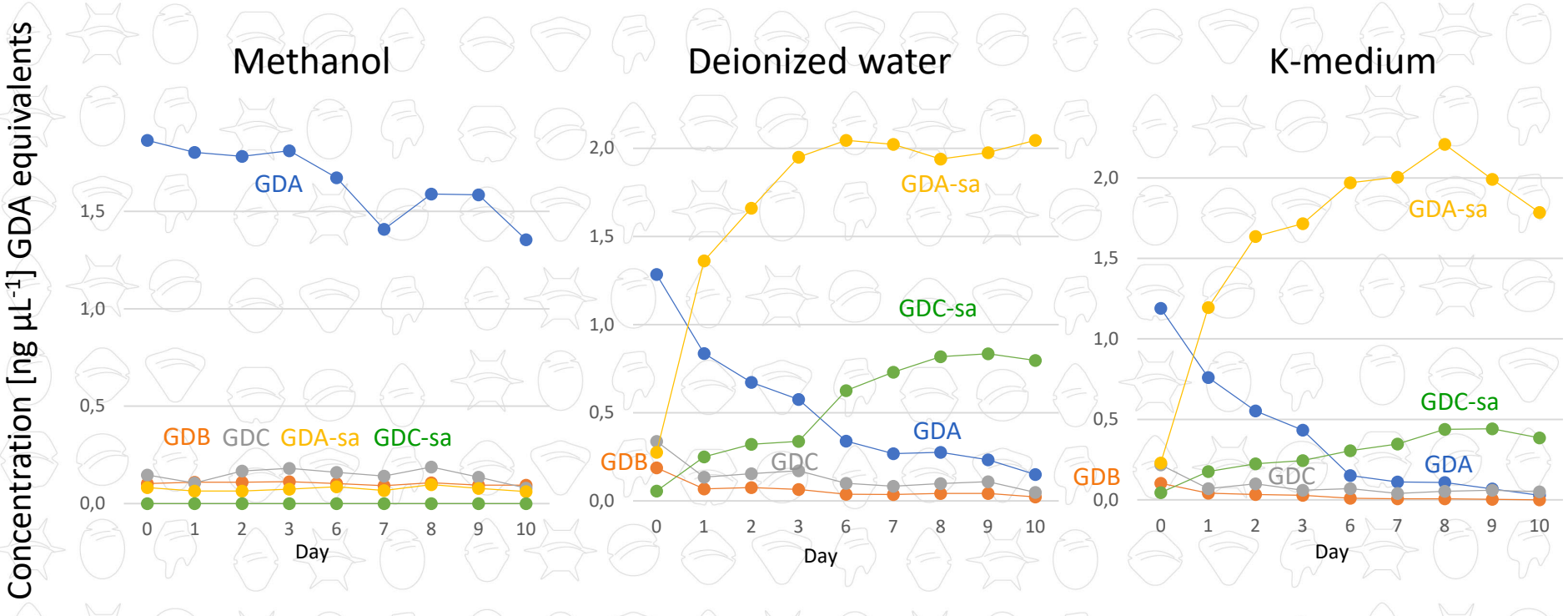


GDC-sa

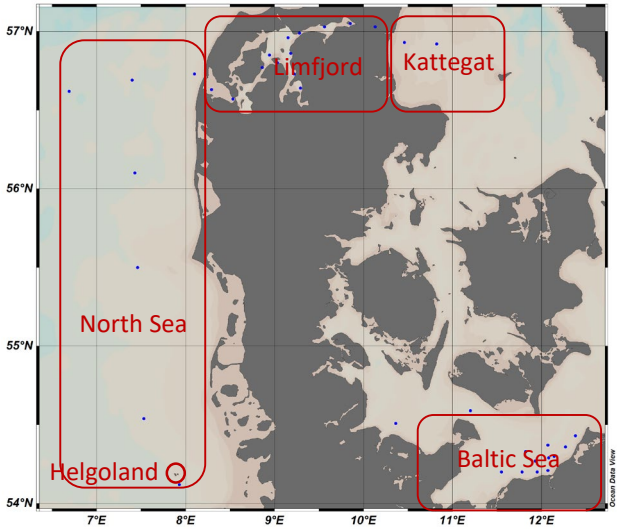
Hydrolytic ether ring opening

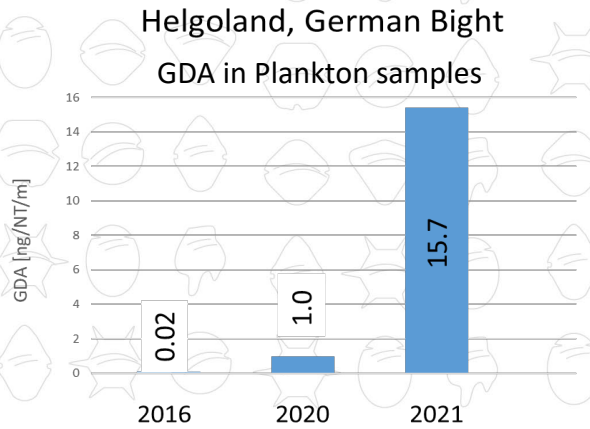
Lactone hydrolysis

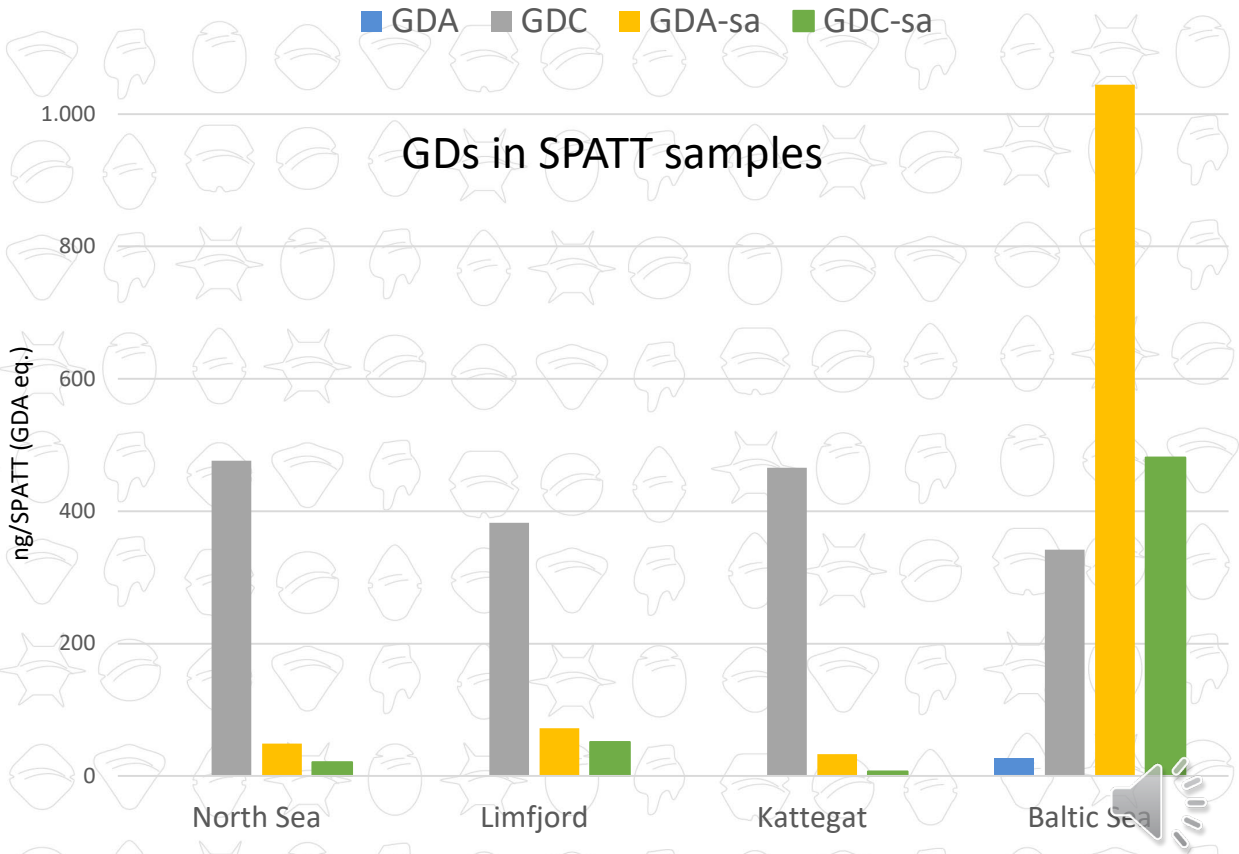
Conversions of GDA in the aquatic environment



Goniodomins in the field

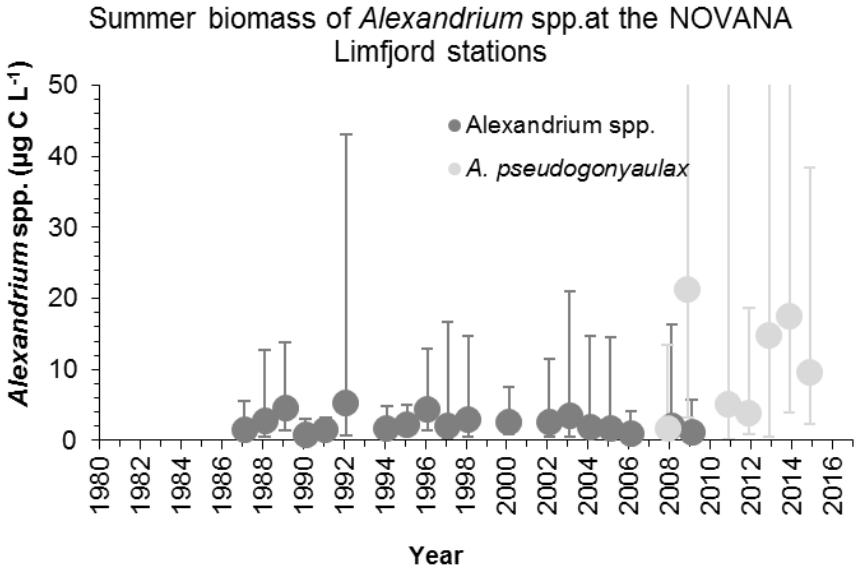






Alexandrium pseudogonyaulax: an expanding species

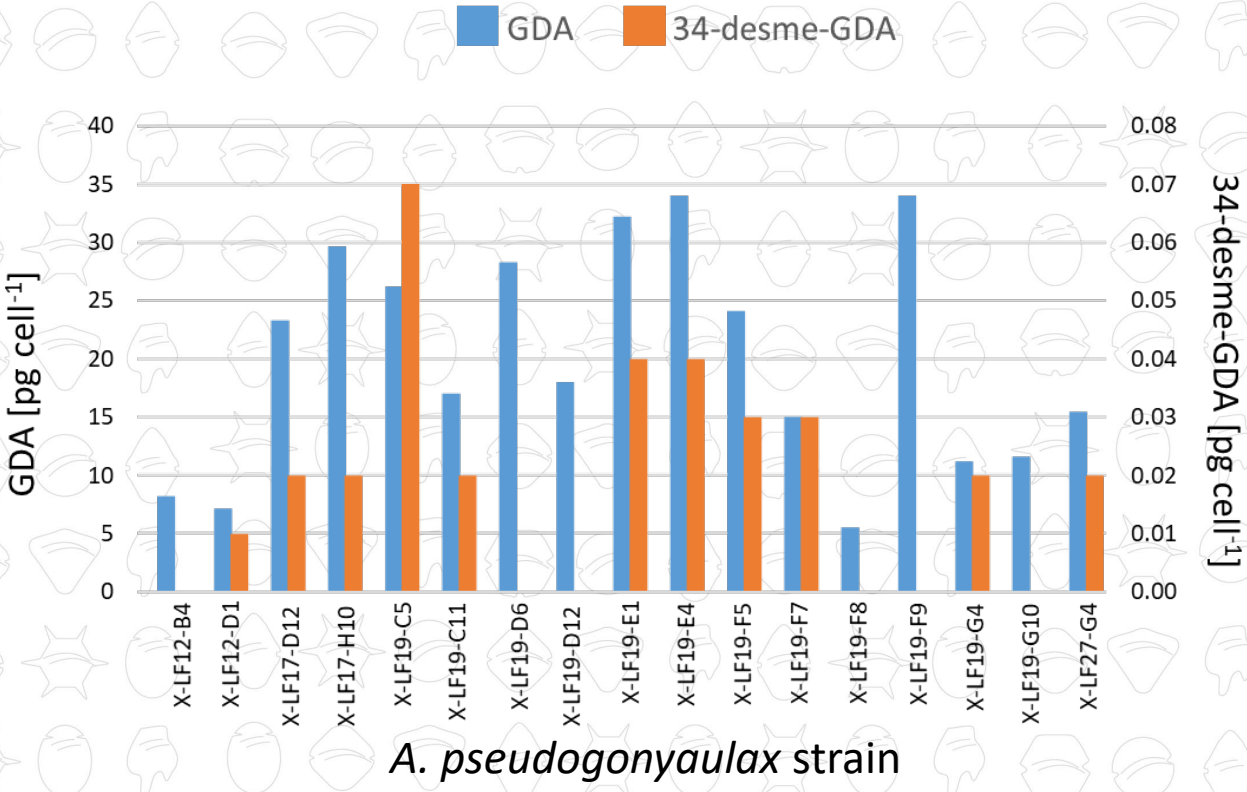
Temporal trend



Kremp, A. et al. (2019) Harmful Algae 87, 101622

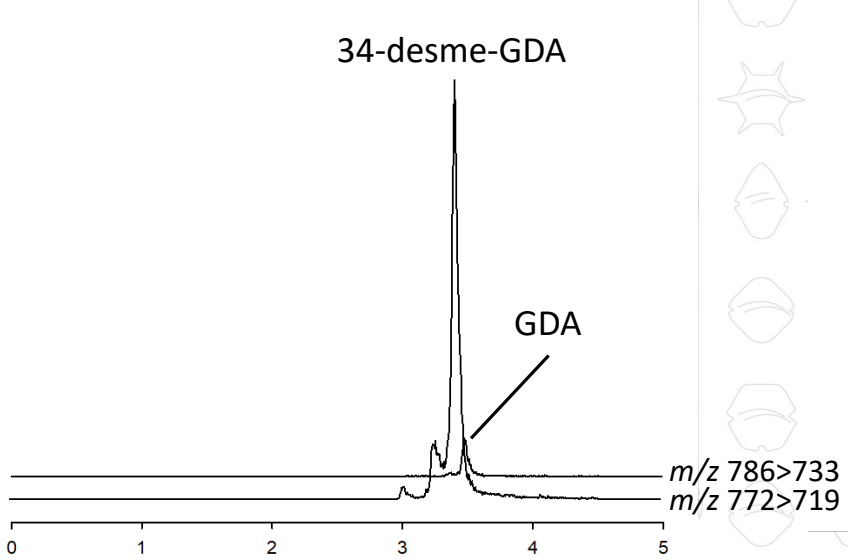
Community shift from an *Alexandrium catenella/ostenfeldii* to *A. pseudogonyaulax* population

Other goniodomin variants

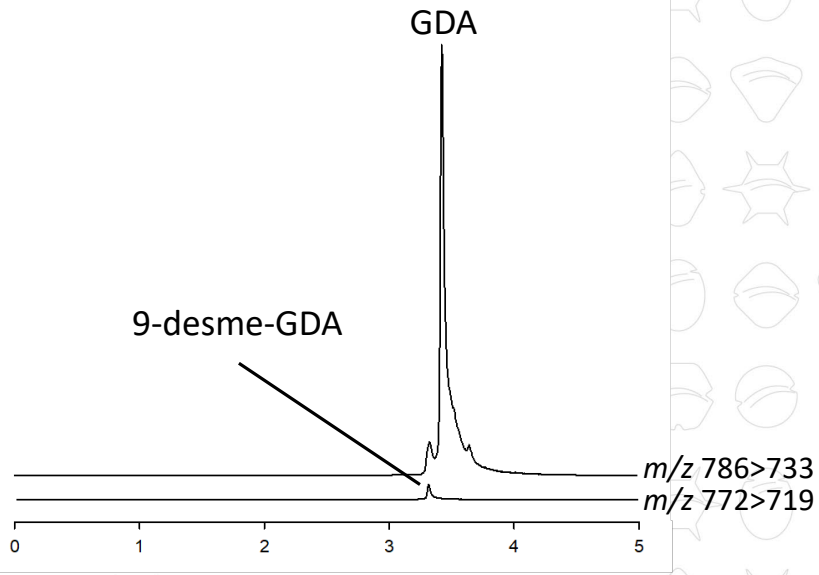


Other goniodomin variants

A. taylorii strain Atay99Shio-02
(Okinawa, Japan)



A. taylorii strain AY7T
(Adriatic Sea)



Other goniodomin variants

A. pseudogonyaulax		*A. taylorii*			
$[M+NH_4]^+$	$[M+Na]^+$	$[M+NH_4]^+$	$[M+Na]^+$	Molecular weight	Goniodomin
772	777	772	777	754	desme-GDA
786	791	786	791	768	GDA/B
790	795	790	795	772	nd
802	807	802	807	784	nd
804	809	804	809	786	GDC/GDA-sa
800	-	800	-	782	nd
814	-	814	-	796	nd
822	-	-	-	804	GDC-sa
858	863	858	863	840	nd

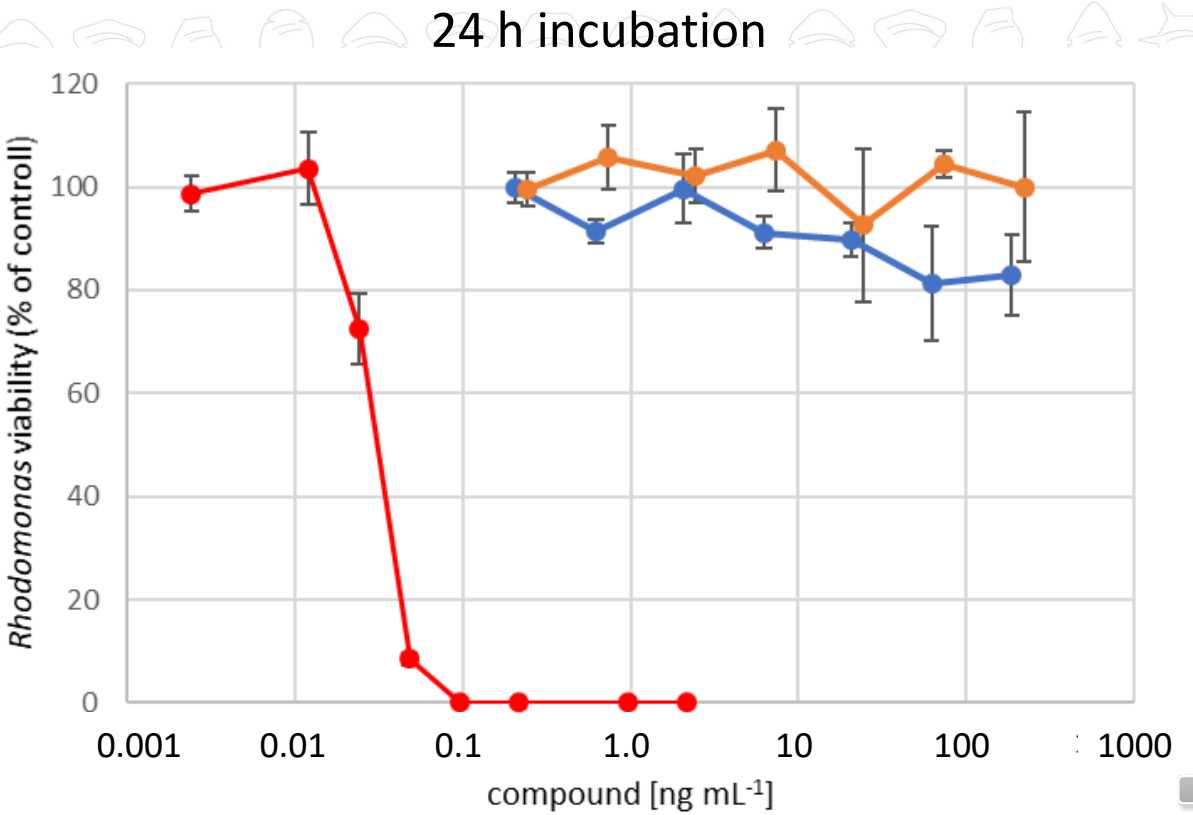
nd = not determined

Are goniodomins lytic (as proxy for ichthyotoxicity)?

GDA

GDB

A. monilatum supernatant



Conclusions

1) Goniodomin A (GDA) easily converts in the presence of water, but is reasonably stable in aprotic organic solvents

2) GDA conversion is rapid and can already been observed after 3 min under chromatographic conditions

3) GDA is relatively stable under alkaline conditions in the chromatographic time scale

4) In the aquatic environment, GDA is almost completely hydrolyzed to seco acids

5) The structural variability of goniodomins is high and not yet fully explored

6) Preliminary results suggest that goniodomins are not responsible for protist lysis and thus probably also not responsible for ichthyotoxicity of GD-producing species


Thanks for your attention!