

Occurrence and stability of ptesculentoside, caudatoside and ptaquiloside in surface waters

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Supplementary material

Table S1. Measured concentrations of illudane glycosides and corresponding pterosins in surface water bodies. The empty cells represent no detection (<LOD). High PtrG concentrations (No. 8,11,12,14) clearly correlate with high PTE concentrations, from which PtrG originate.

Site ID	Location name	Country	Water type	pH	Conductivity (µS/cm)	WGS84 coordinates	Distance from bracken (m)	Number of sampling events	(number of sampling events with positive detection): detected range ng/l					
									PTE	PtrG	CAU	PtrA	PTA	PtrB
1	Humleore	Denmark	Stream (3 sites)	7.5	610	55.47542, 11.90639	30	9x3 ¹			(1): trace	(5): trace – 3.4	(1): 5.9	
2	Humleore	Denmark	Pond	7.2	180	55.47487, 11.90836	10	9		(1): 13.7		(1): trace	(1): 21.2	
3	Gribskov	Denmark	Lake	6.4	123	55.99644, 12.3516	5	2				(2): trace – 2.1		
4	Helsingør	Denmark	Lake	6.3	120	56.03350, 12.56145	5	2						
5	Asljunga	Sweden	Stream	6.9	77	56.3063, 13.37894	100	2				(1): trace		
6	Asljunga	Sweden	Lake	7.9	413	56.30315, 13.3743	25	2						
7	Asturias	Spain	Seepage water ²	N.m. ³	N.m.	43.22904, -5.65816	~2	2		(1): 12.6	(1): 6.5	(2): 1.3 – 2.5		
8								1	(1): 5300	(1): 1230				
9								1		(1): 26.8				
10								1		(1): 3.3		(1): 1.4		
11								1	(1): 399	(1): 1190				
12								1	(1): 403	(1): 2280		(1): 7.3		
13								1						
14								1	(1): 399	(1): 1000				

¹ Nine sampling events in three sub-locations remote by 150 m.

² Seepage water in drainage ditches and pits, accessible for drinking to horses and beef cattle.

³ Not measured.

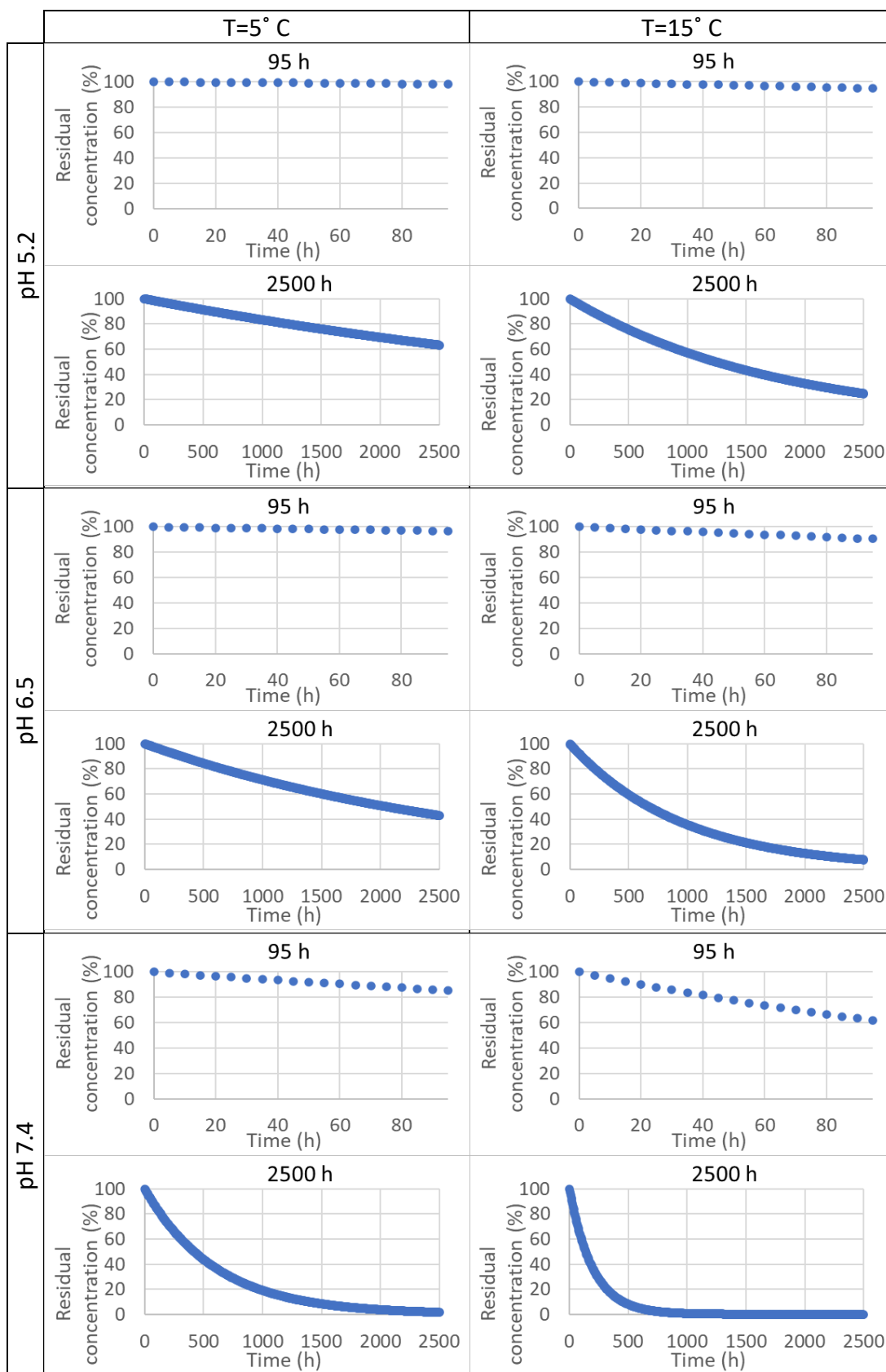


Figure S1. Application of the laboratory-based rate equation (Equation 1) to predict PTA degradation as function of pH and temperature (1 data point corresponds to 5 hours). The equation represents the first order reaction but within relatively short time periods (95 h windows) the degradation rates appear linear.

Formation and degradation of pterosins in stability experiments:

Pterosins G and B were monitored in surface waters in stability experiments after 21 days. The pterosins form from illudane glycosides by hydrolysis following the mechanism presented in Figure 1 of the main text. The formed pterosins are subject to microbial degradation¹. Therefore, besides the pteroin formation we also observe downward trend of their concentration, particularly in the experiments representing non-sterilised and warm conditions (Figure S2).

¹Skourti-Stathaki E., Clauson-Kaas F., Brandt K.K., Rasmussen L.H., Hansen H.C.B. Dissipation of pteroin B in acid soils - tracking the fate of the bracken fern carcinogen ptaquiloside. Chemosphere, vol. 165, pp. 453-459, 2016.

Natural pH

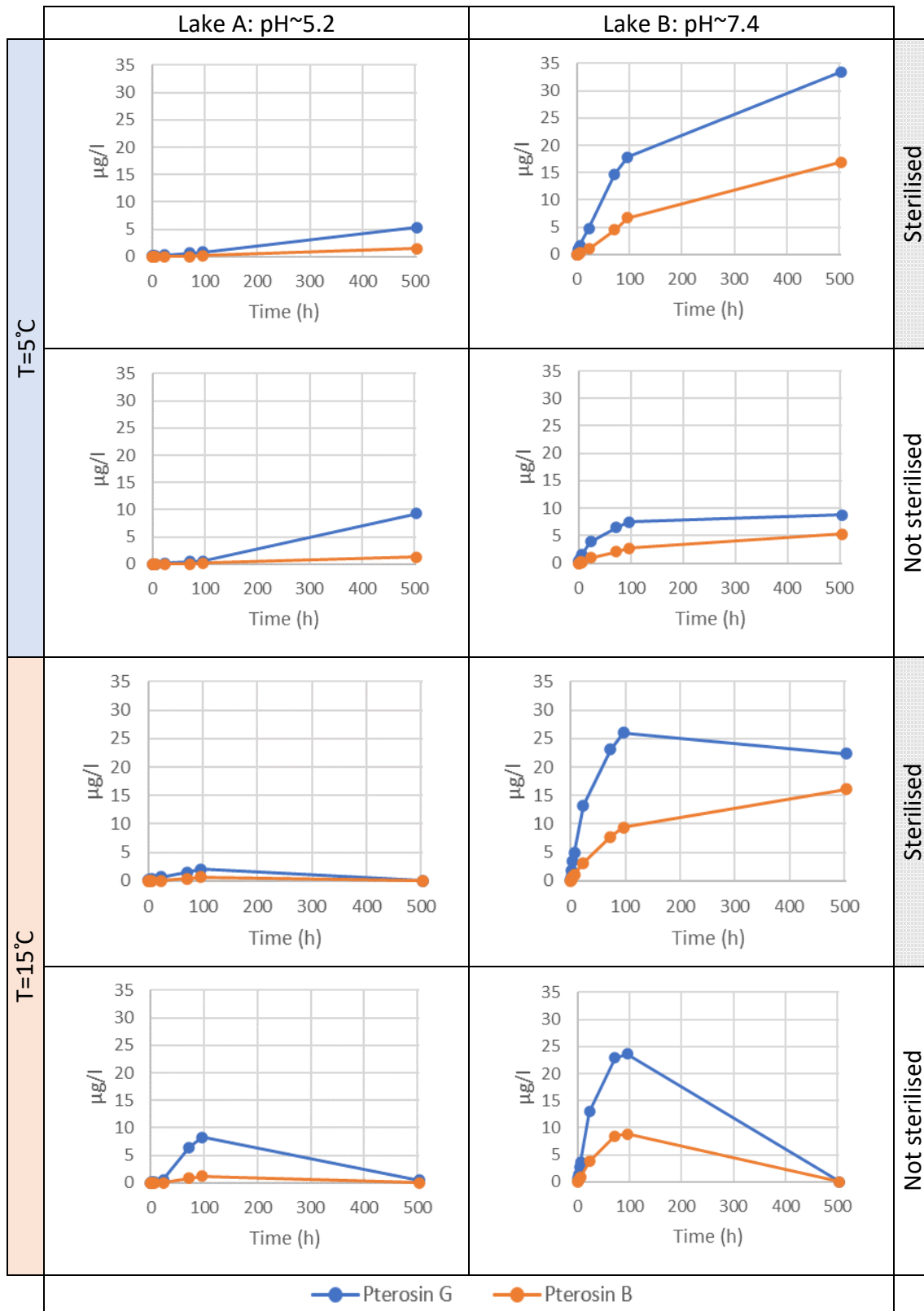


Figure S2. (continues next page)

Controlled pH (~6.5)

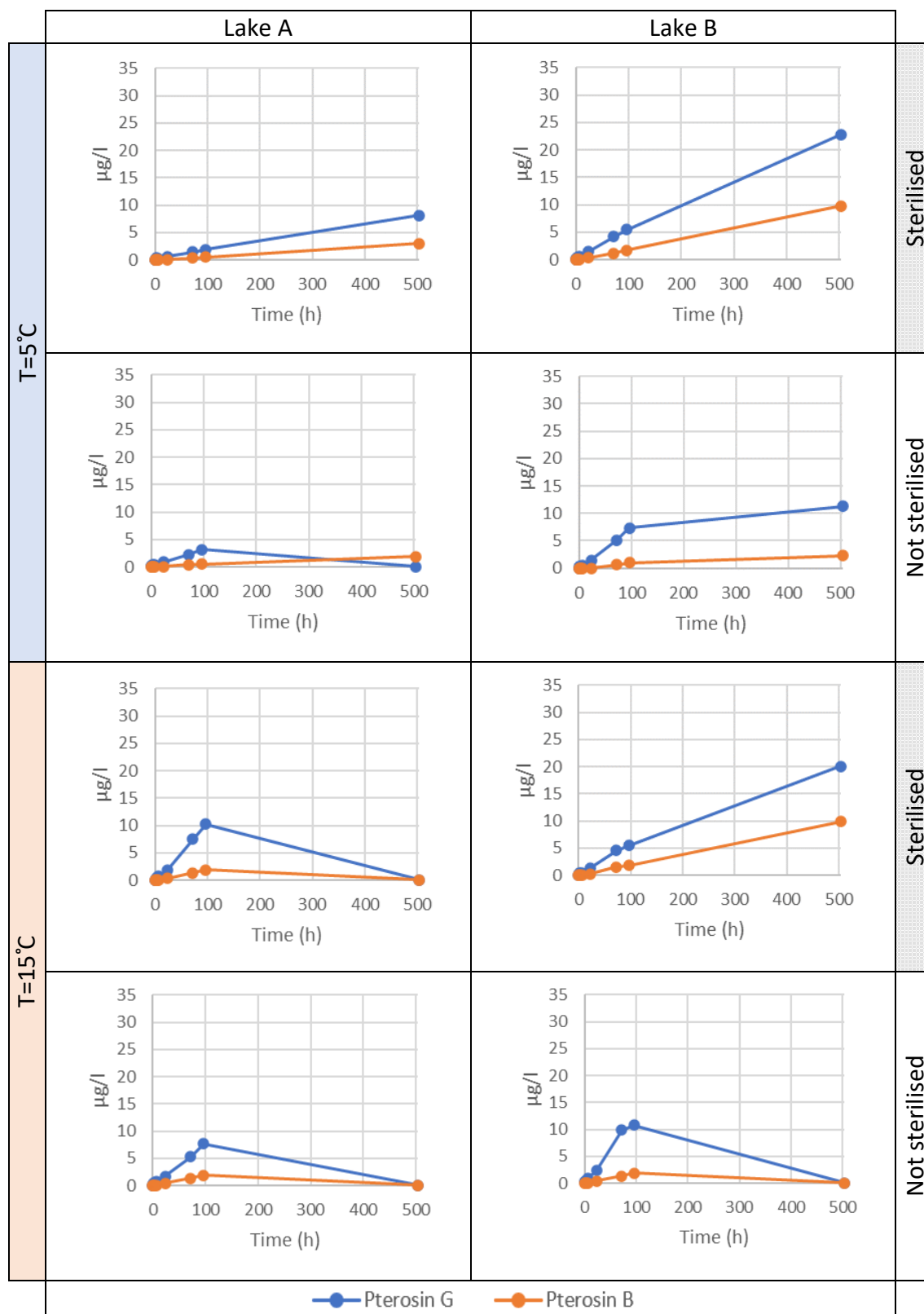


Figure S2. Concentration of pterosins G and B in waters of illudane glycoside stability experiments. (Concentration of CAU hydrolysis product pterosin A was not monitored)

Formation of intermediates in stability experiments:

Controlled pH (~6.5):

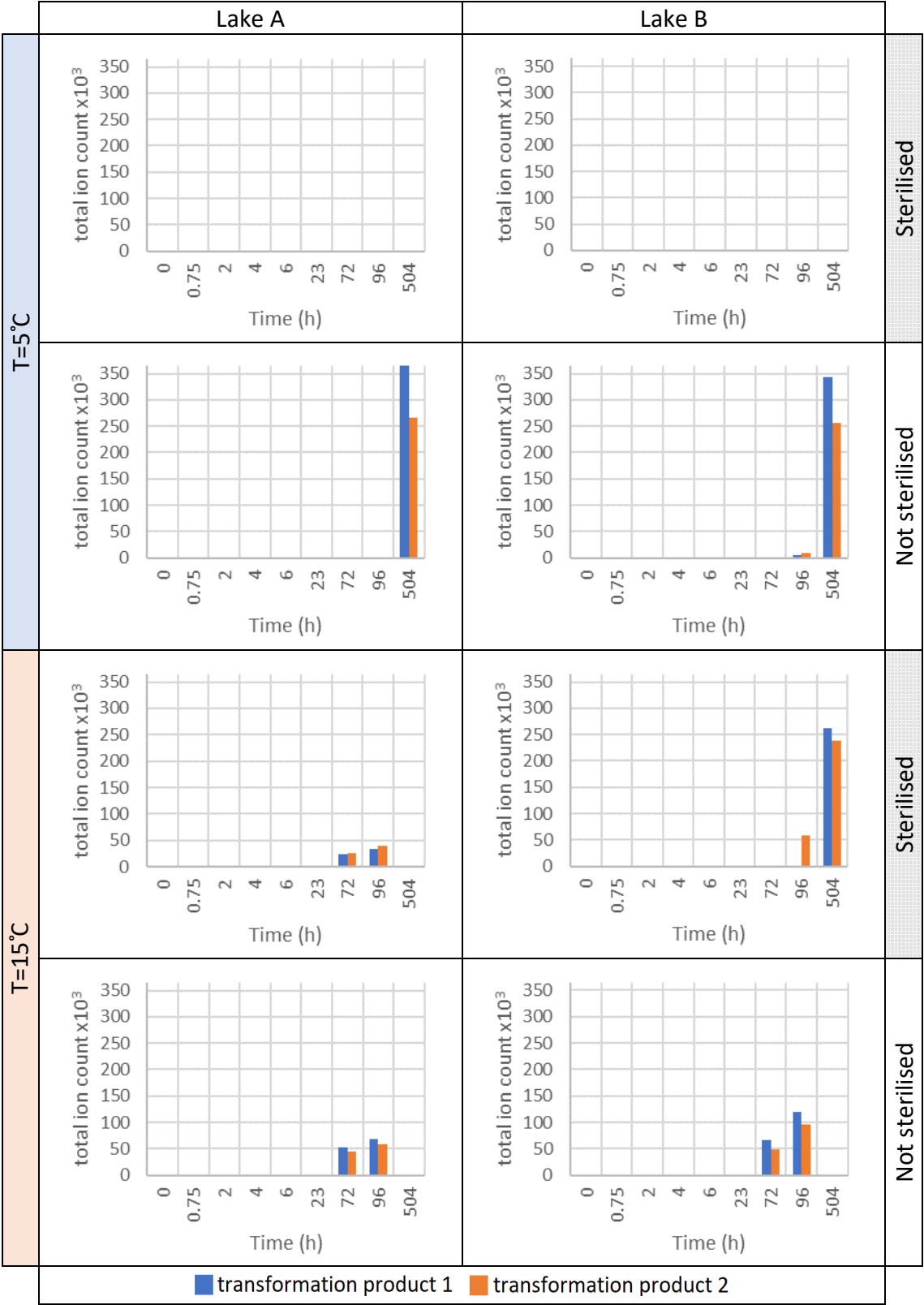


Figure S3. (continues next page)

Natural pH:

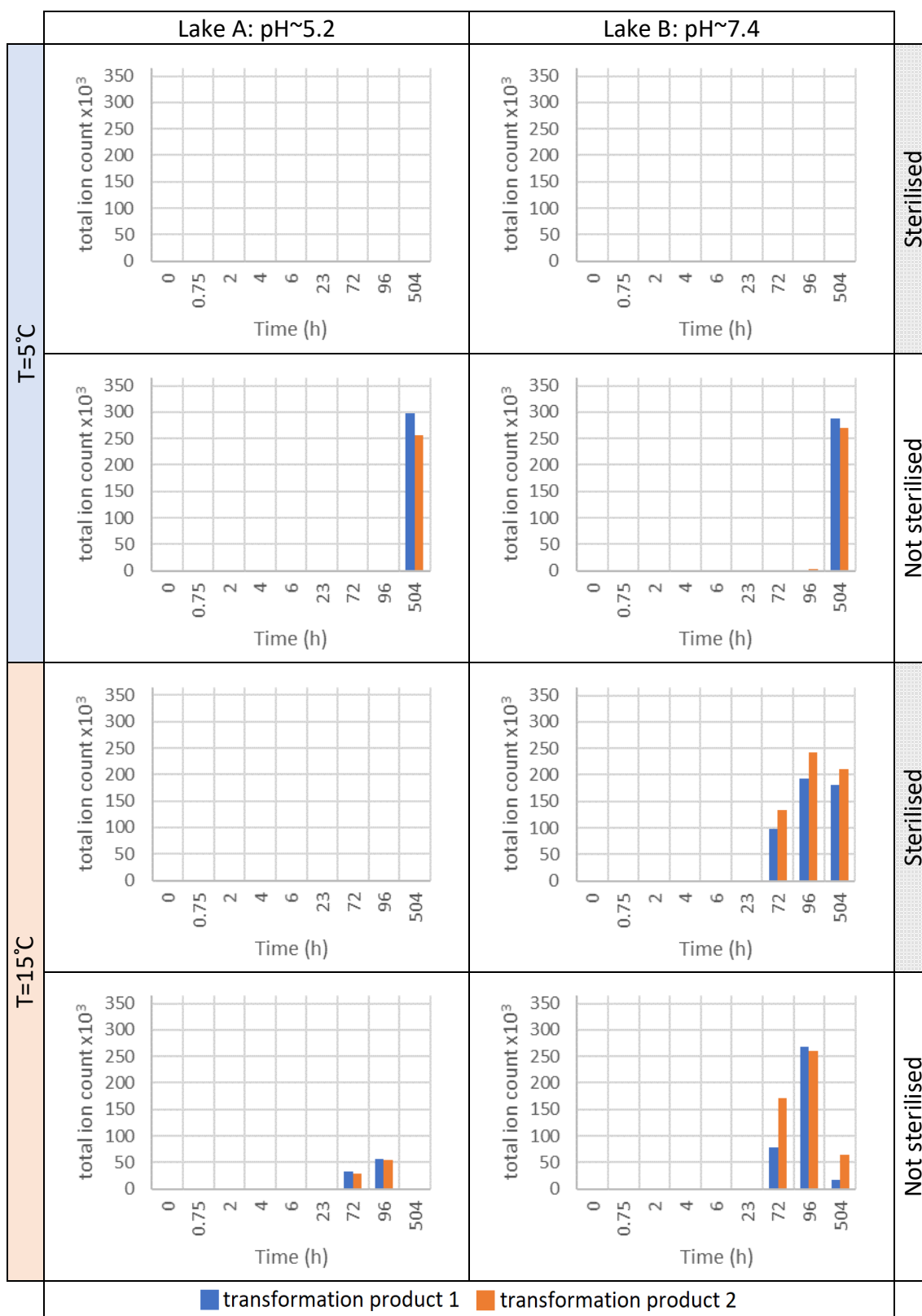


Figure S3. Formation of transformation products (TP) in waters of illudane glycoside stability experiments. TP1 in the stability experiment of PTE; TP2 in the stability experiment of PTA. (Formation of an analogous TP in the stability experiment of CAU was not monitored).

Formation of transformation products in stability experiments:

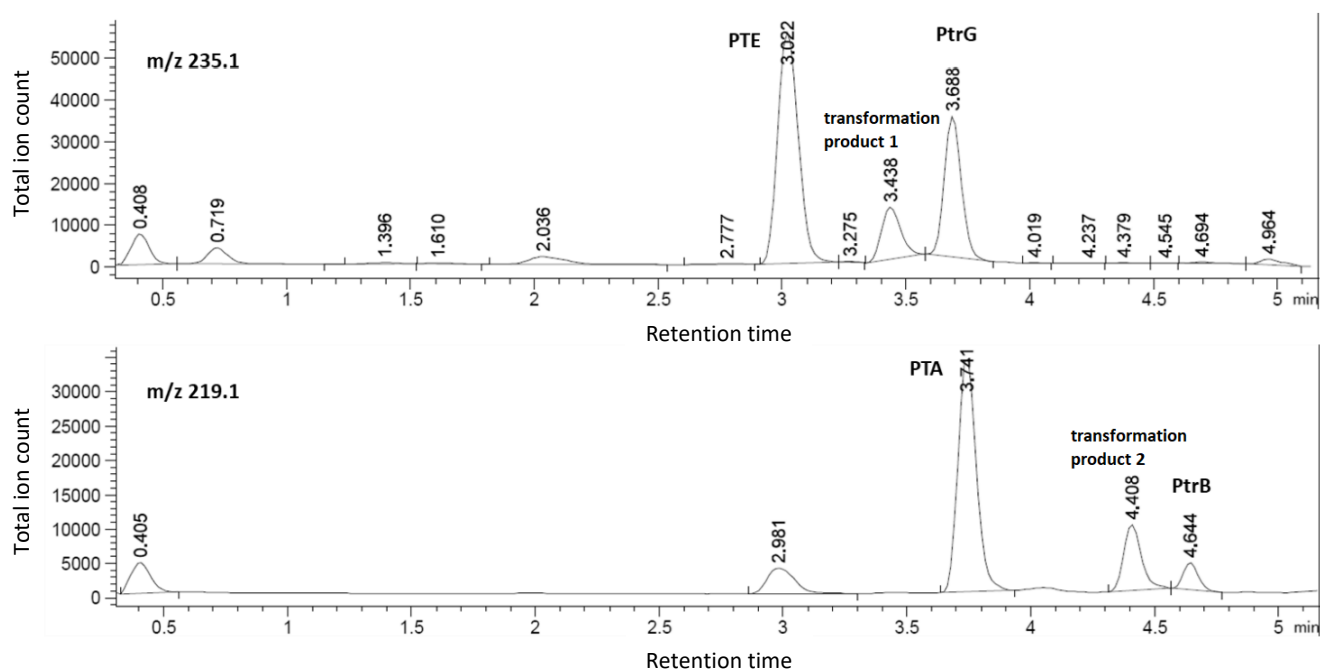


Figure S4. Formation of the unidentified PTE transformation product 1 (top) and PTA transformation product 2 (bottom) in the compound stability experiments.

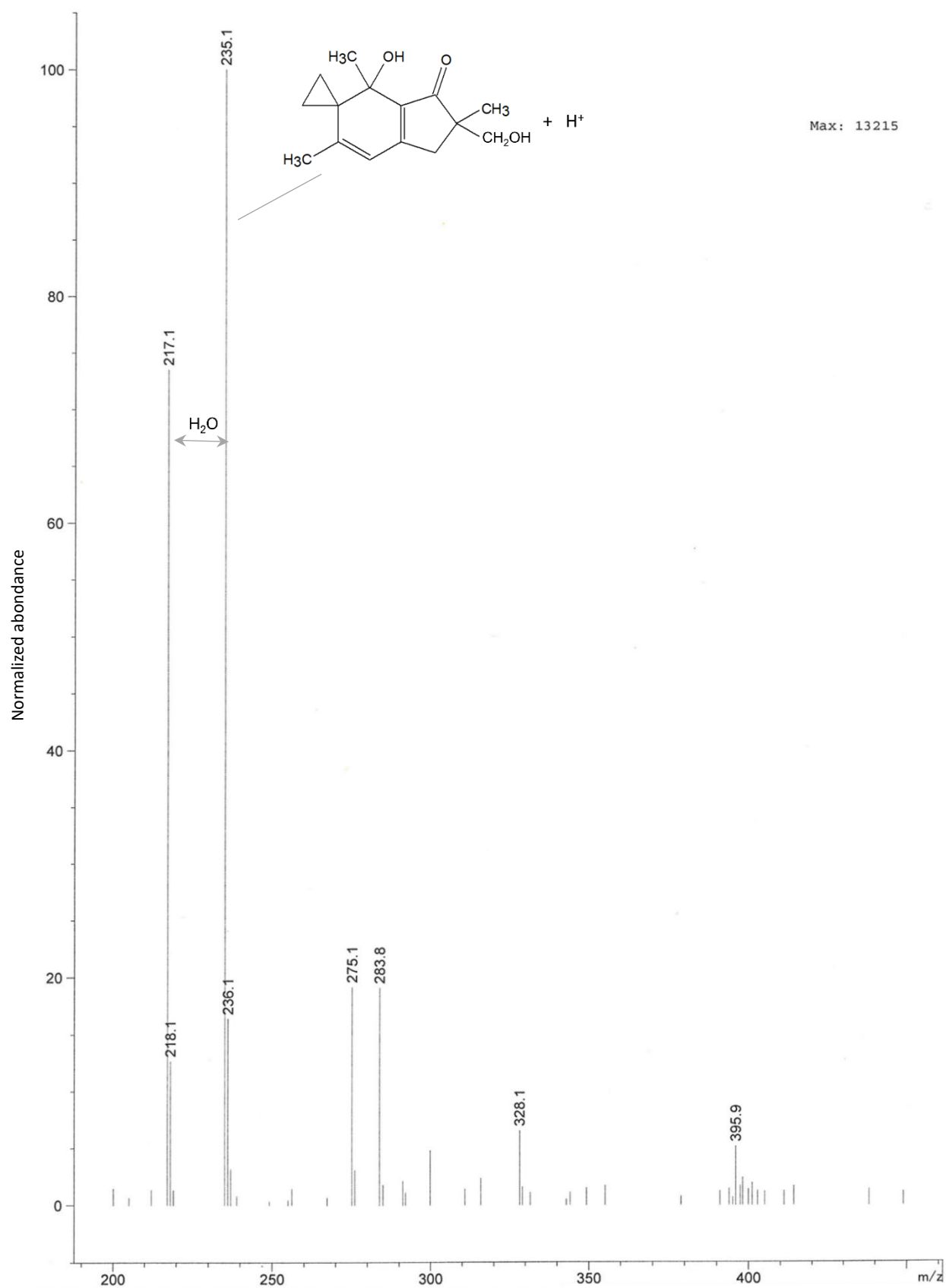


Figure S5. Mass spectral data of unidentified systematically forming PTE transformation product 1 (presumed molecular structure illustrated).

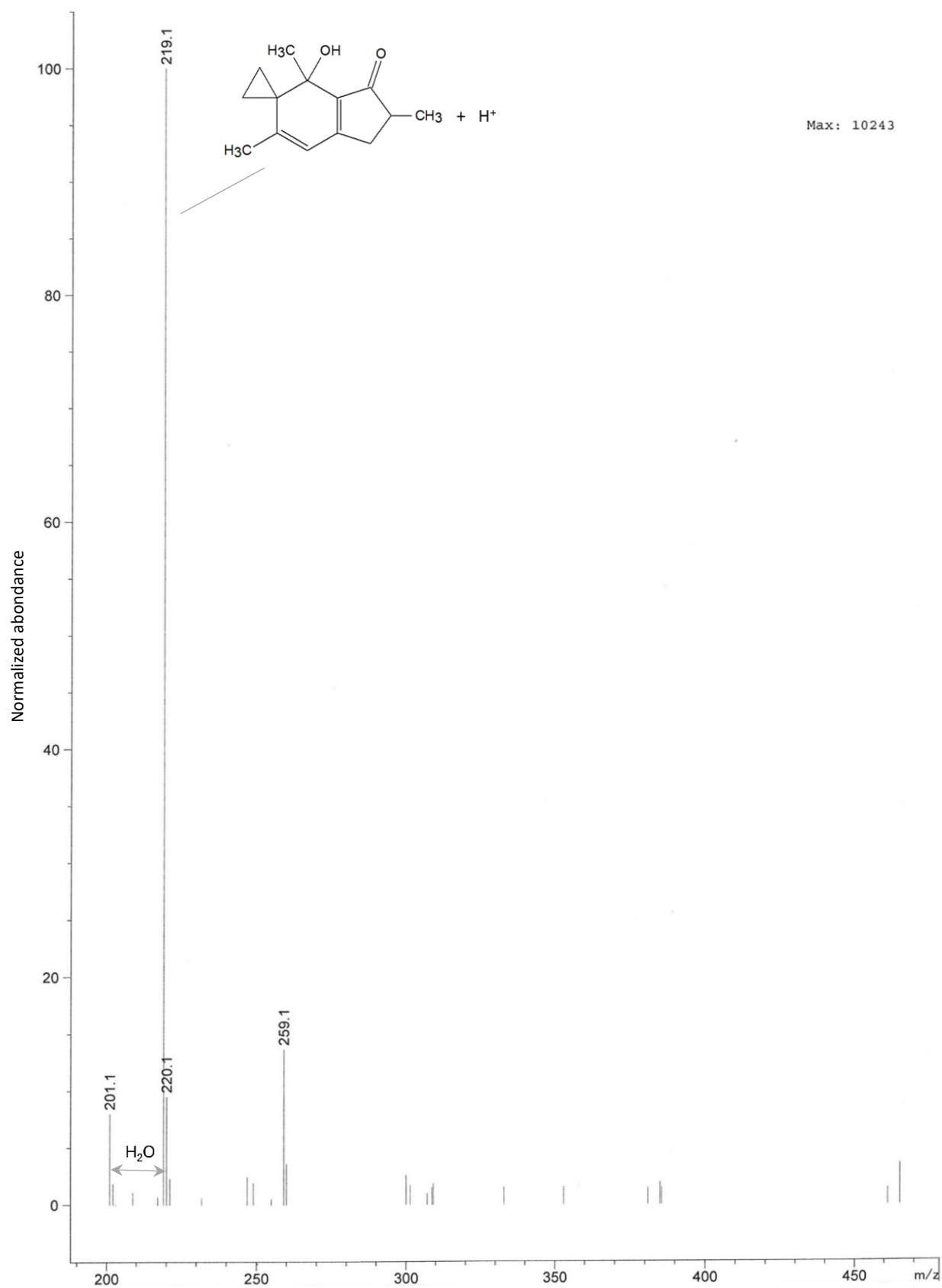


Figure S6. Mass spectral data of unidentified systematically forming PTA transformation product 2 (presumed molecular structure illustrated).