

Supplementary Information

Improved Isolation Procedure for Azaspiracids from Shellfish, Structural Elucidation of Azaspiracid-6 and Stability studies

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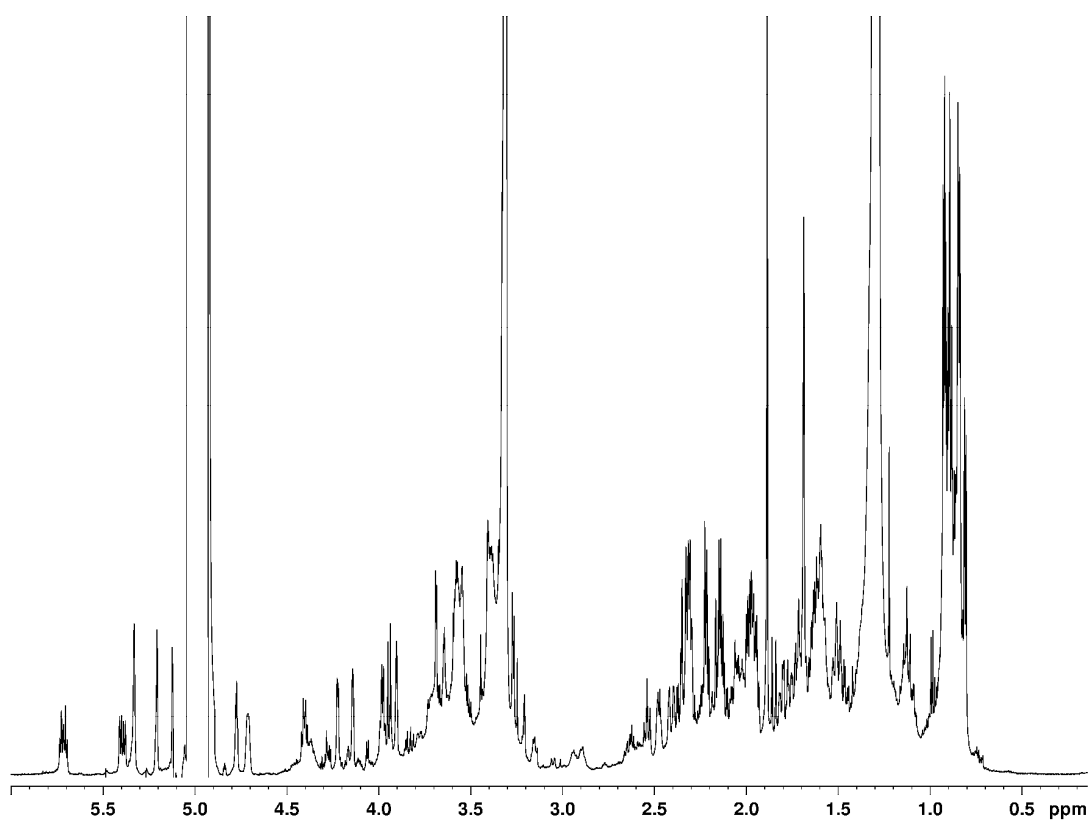


Figure S1. ^1H NMR spectrum of azaspiracid-6 (**6**).

Figure S2. Structure of azaspiracid-6 (**6**) showing ^1H and ^{13}C chemical shifts and COSY correlations.

Figure S3. Structure of azaspiracid-6 (**6**) showing ^1H and ^{13}C chemical shifts and HMBC correlations.

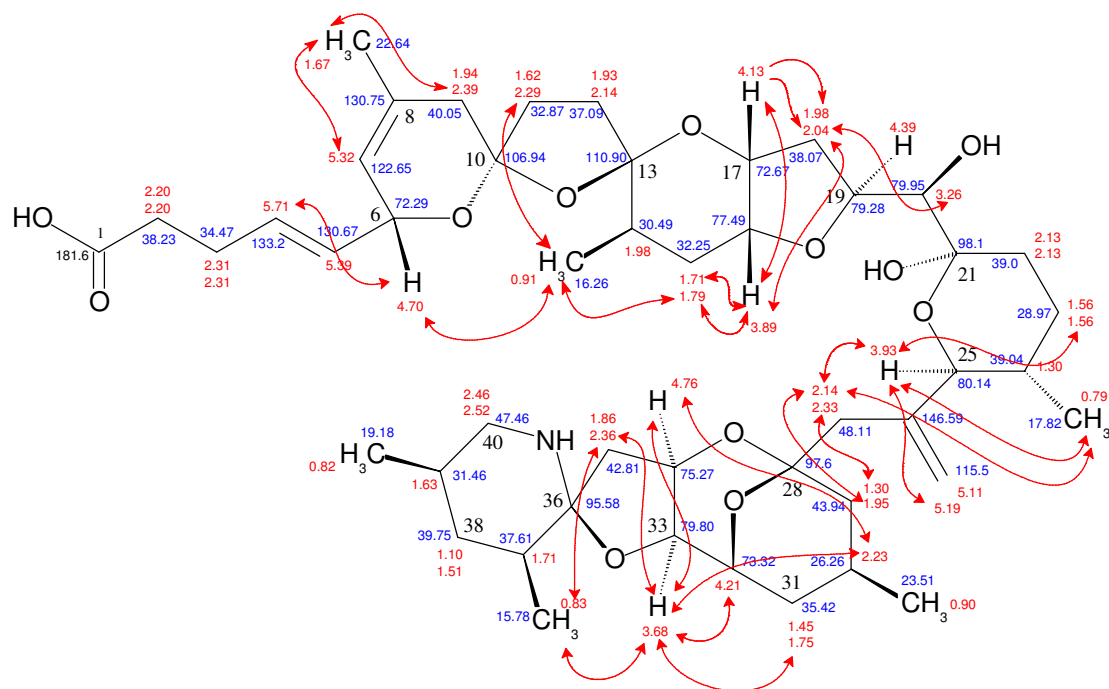


Figure S4. Structure of azaspiracid-6 (**6**) showing ^1H and ^{13}C chemical shifts and ROESY correlations.

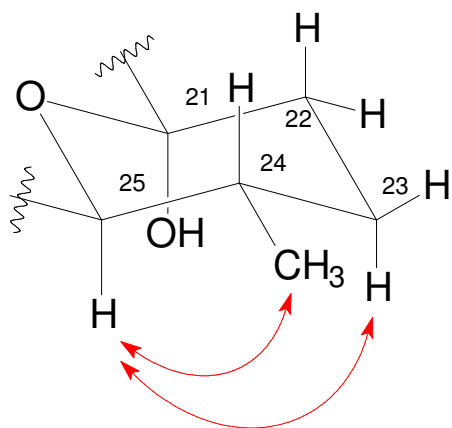


Figure S5. Structure of ring E from C-21 to C-25 showing ROESY correlations.

Figure S6. Structure of fused rings F, G and H from C-28 to C-36 showing ROESY correlations.

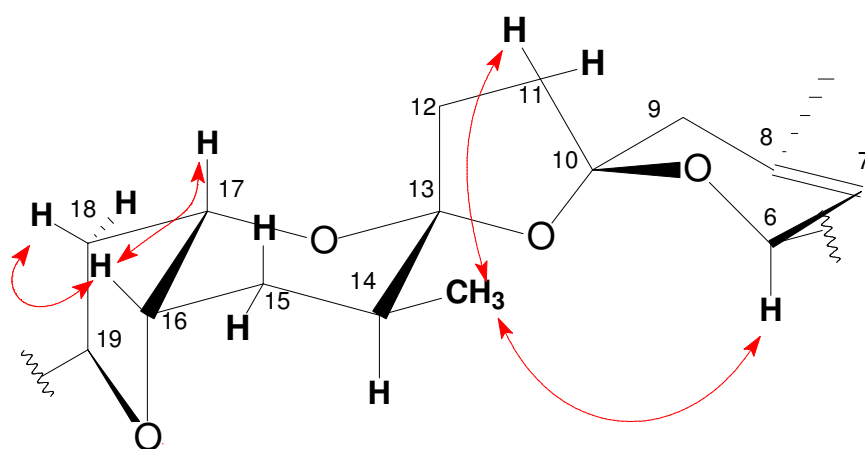


Figure S7. Structure of rings A, B, C and D from C-6 to C-19 showing ROESY correlations.

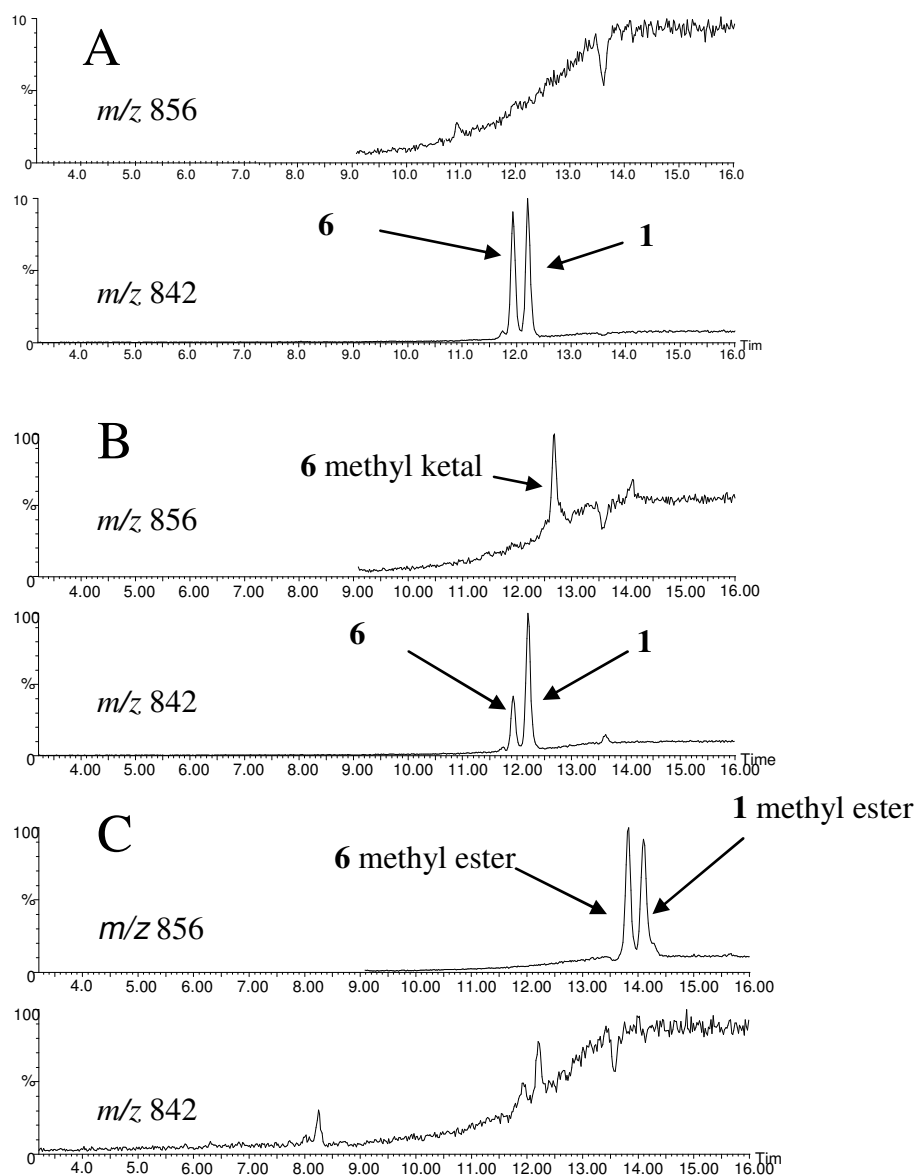


Figure S8. QToF analysis of A) an azaspiracid-1 (1) and azaspiracid-6 (6) sample stored in methanol, B) at 40 °C for 4 weeks and C) after treatment with diazomethane.

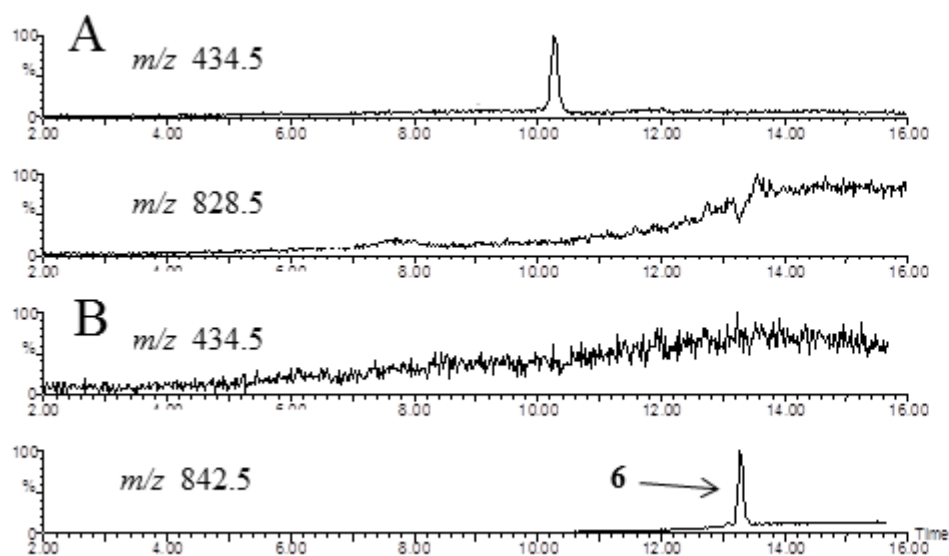


Figure S9. QToF analysis of A) an azaspiracid-6 (**6**) sample after treatment with periodate showing the periodate cleavage product peak in the m/z 434 trace and B) the azaspiracid-6 (**6**) sample prior to reaction with periodate.

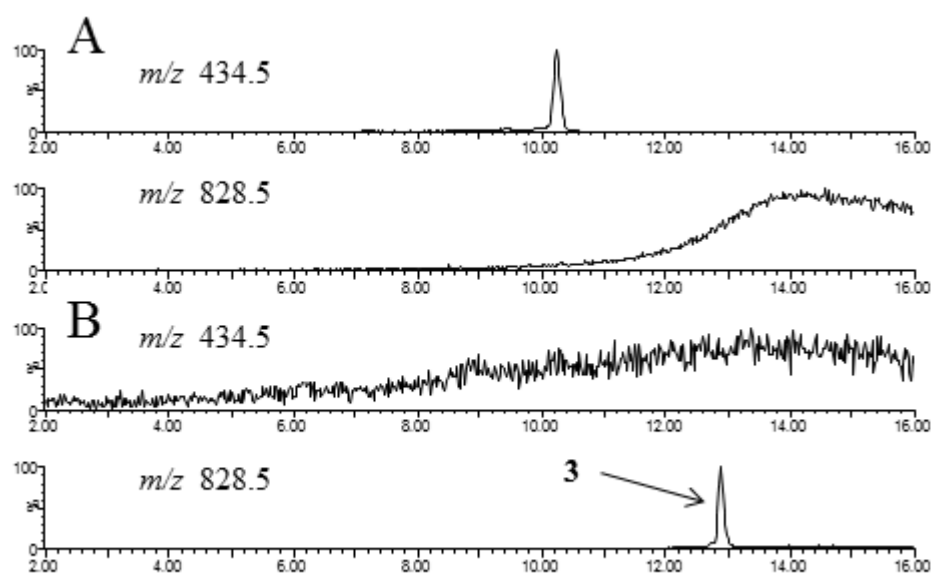


Figure S10. QToF analysis of A) an azaspiracid-3 (**3**) sample after treatment with periodate showing the periodate cleavage product peak in the m/z 434 trace and B) the azaspiracid-3 (**3**) sample prior to reaction with periodate.

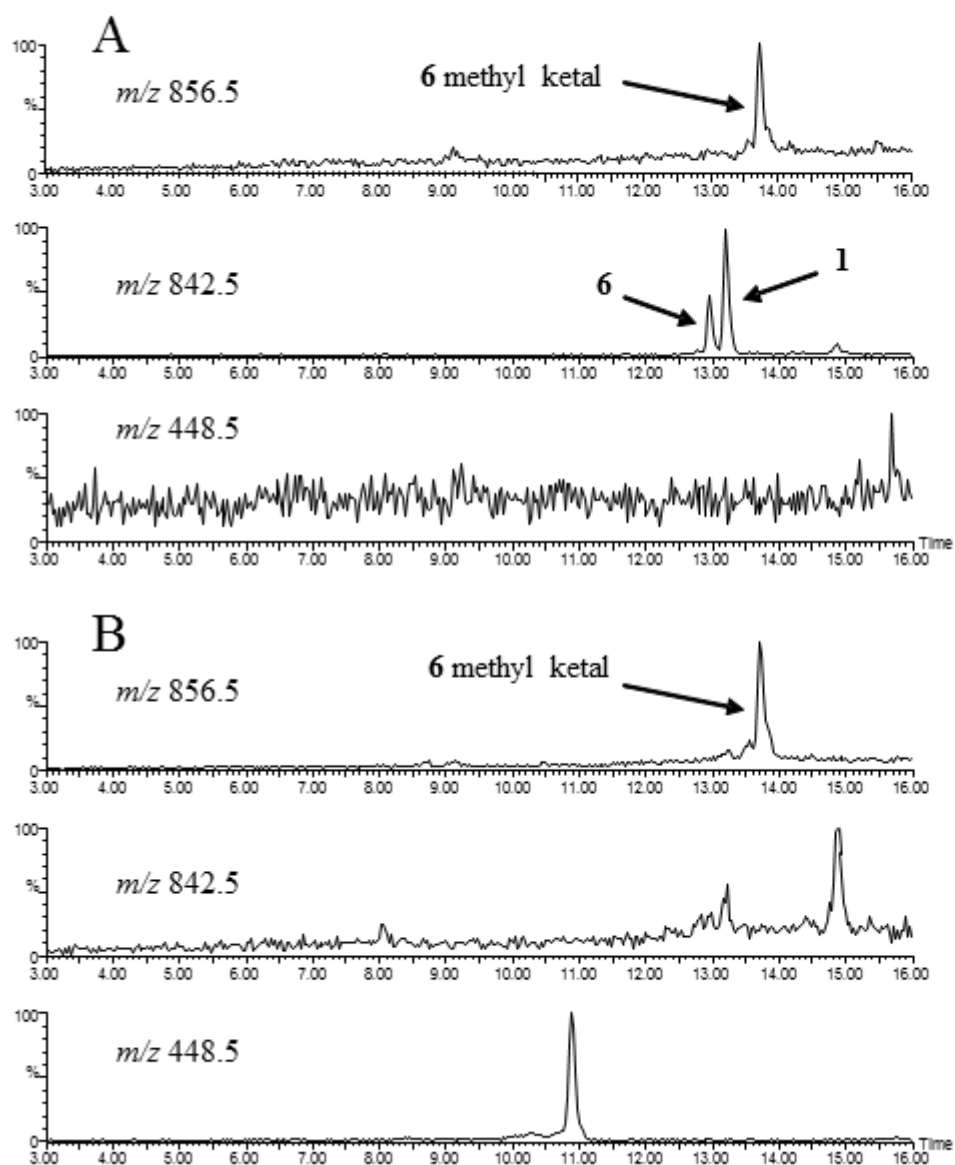


Figure S11. QToF analysis of A) an azaspiracid-1 (**1**) and azaspiracid-6 (**6**) sample stored in methanol at 40 °C for 4 weeks with the formation of azaspiracid-6 (**6**) methyl ketal in the 856.5 trace and B) after treatment with periodate.