

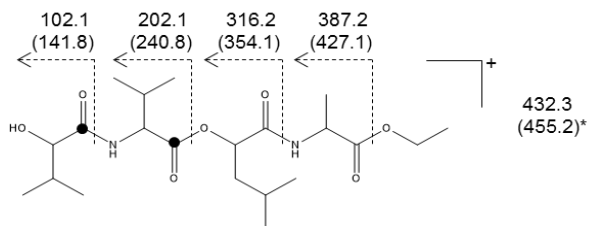
Supplementary Information

Depsipeptide Intermediates Interrogate Proposed Biosynthesis of Cereulide, the Emetic Toxin of *Bacillus cereus*

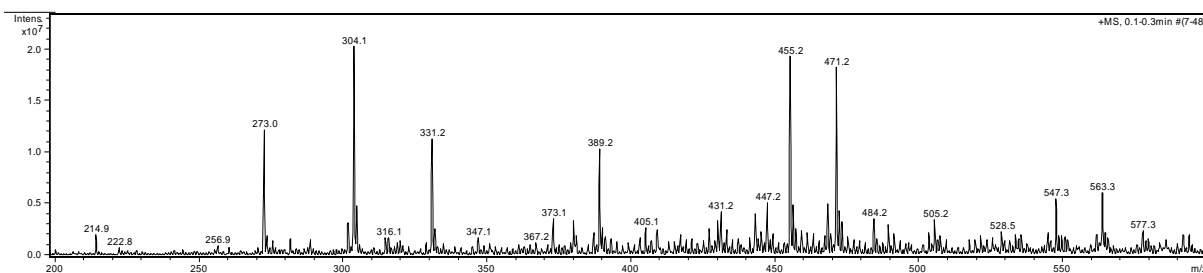
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FRENZEL,³ SIEGFRIED SCHERER^{2,4}, MONIKA EHLING-SCHULZ,³ AND THOMAS
HOFMANN^{1*}

Figure S1 Sequential MSⁿ-spectra of the ethyl esters of (a) tetradepsipeptide (**DP4**), (b) hexadepsipeptide (**DP6a**), (c) hexadepsipeptide (**DP6b**), (d) octadepsipeptide (**DP8**), (e) decadepsipeptide (**DP10a**), (f) decadepsipeptide (**DP10b**), and (g) dodecadepsipeptide (**DP12**) (upper masses: calculated, lower masses given in parenthesis: measured ([M+K]⁺) and ([M+Na]⁺)* ions), ●: ¹³C-labeling of α-hydroxy isovaleric acid and valine.

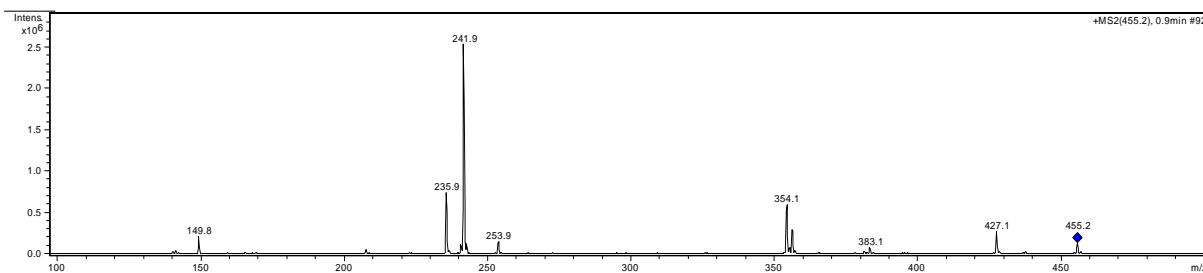
a) Tetrapeptide (DP4)



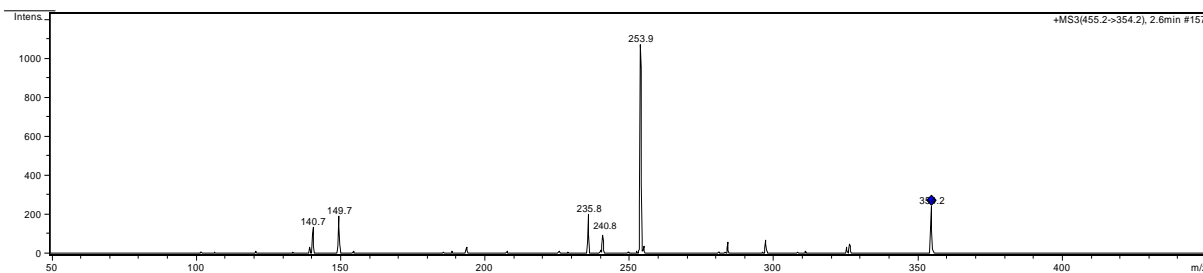
MS



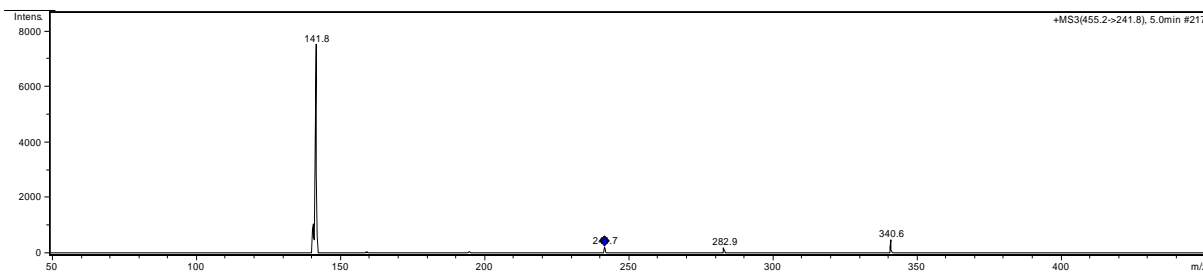
MS² (455.2 \rightarrow x)



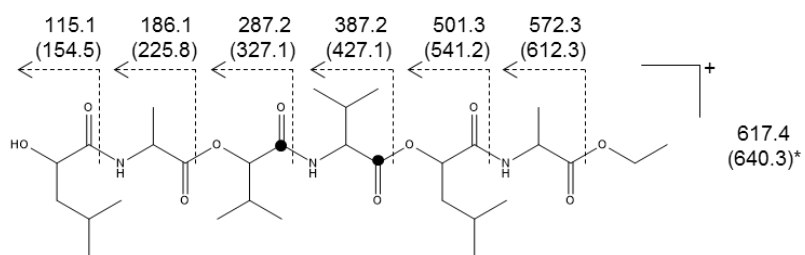
MS³ (354.1 \rightarrow x)



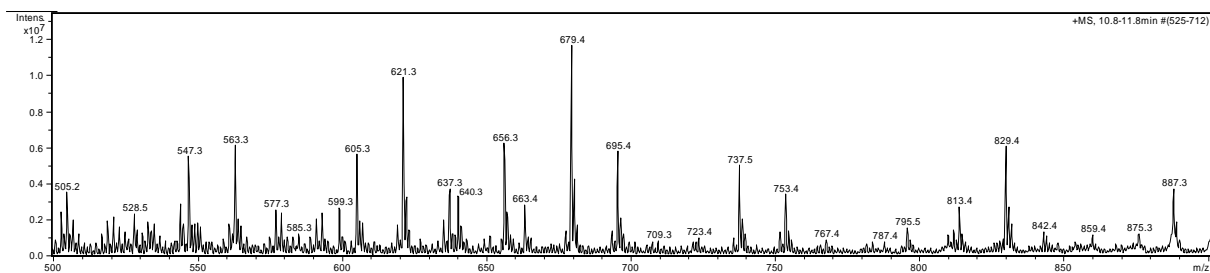
MS⁴ (240.8 \rightarrow x)



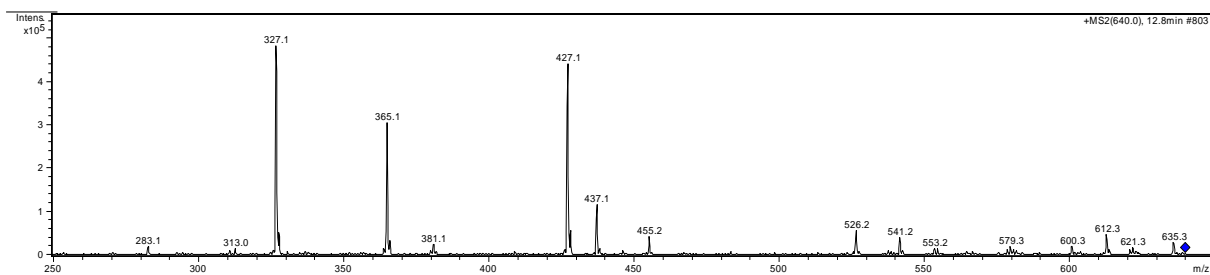
b) Hexadepsipeptide (DP6a)



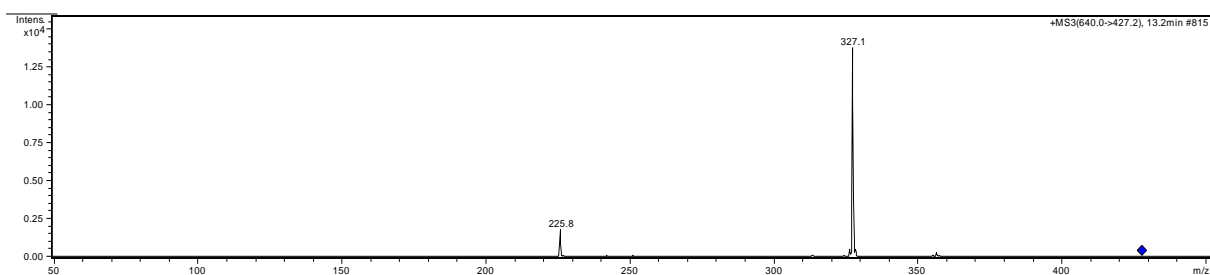
MS



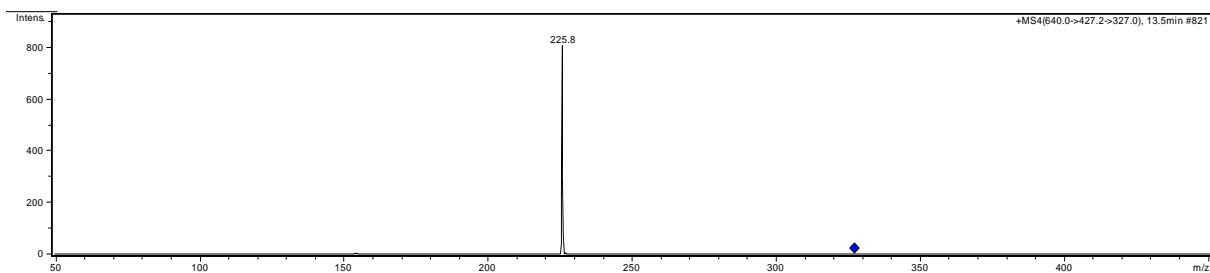
MS² (640.3 → x)



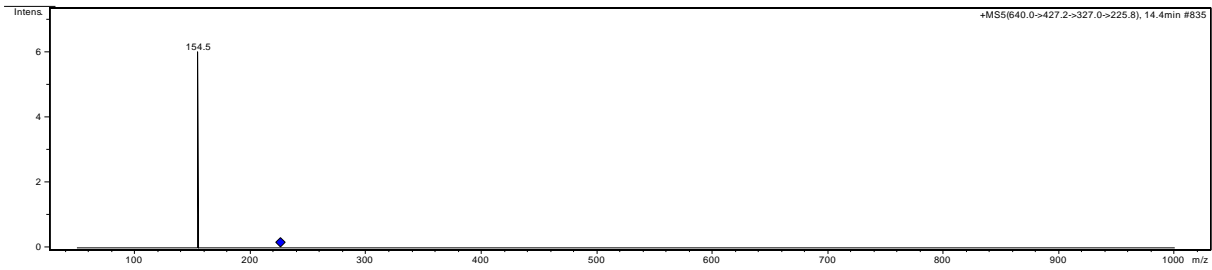
MS³ (427.1 → x)



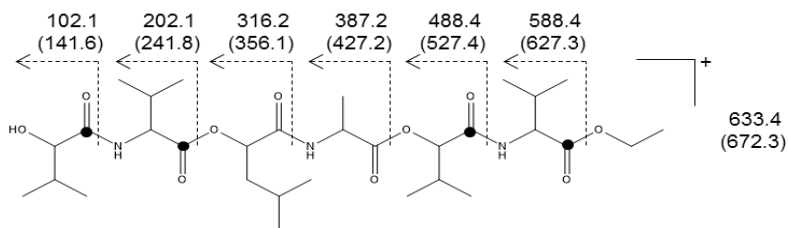
MS⁴ (327.1 → x)



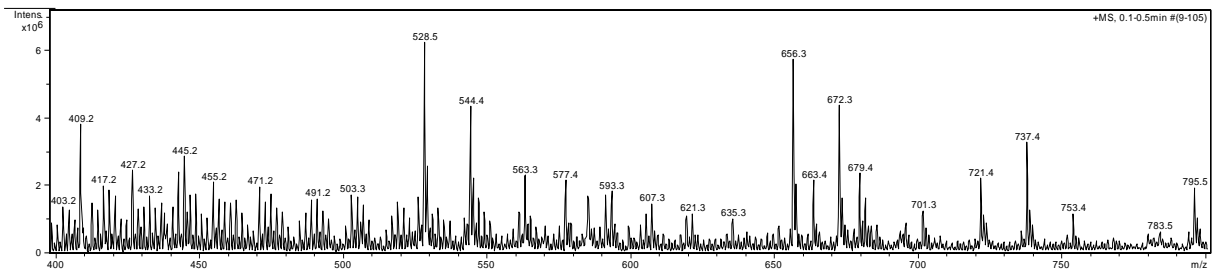
MS⁴ (225.8 → x)



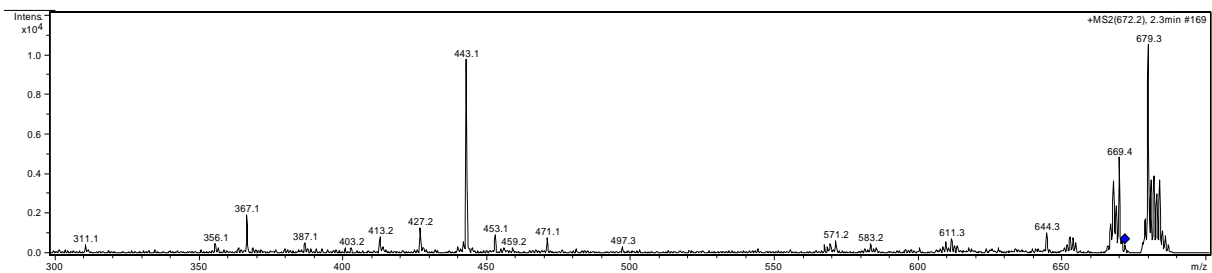
c) Hexadepsipeptide (DP6b)



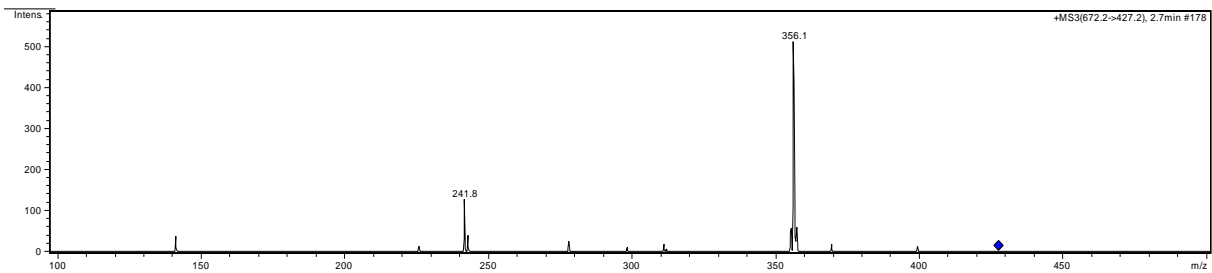
MS



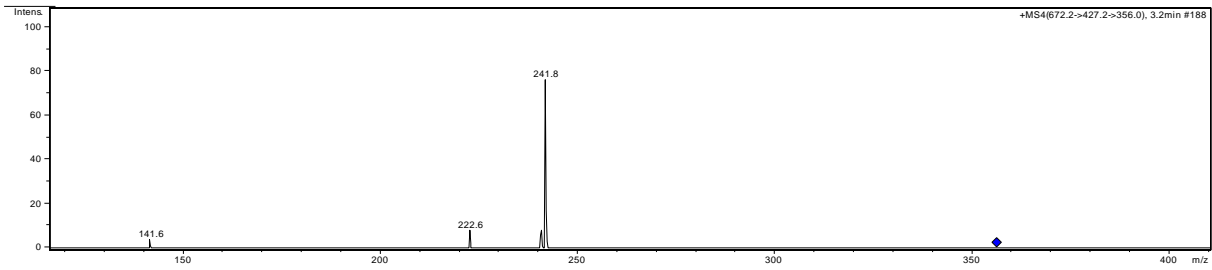
MS² (672.3 → x)



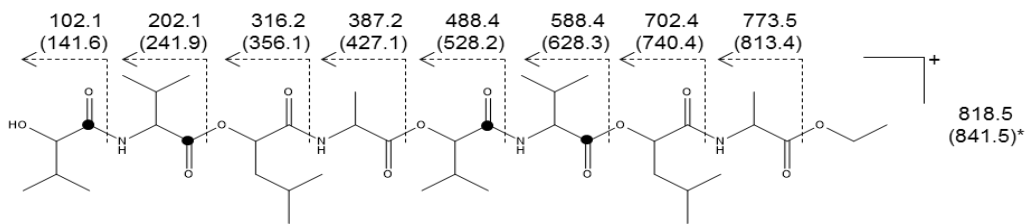
MS³ (427.2 → x)



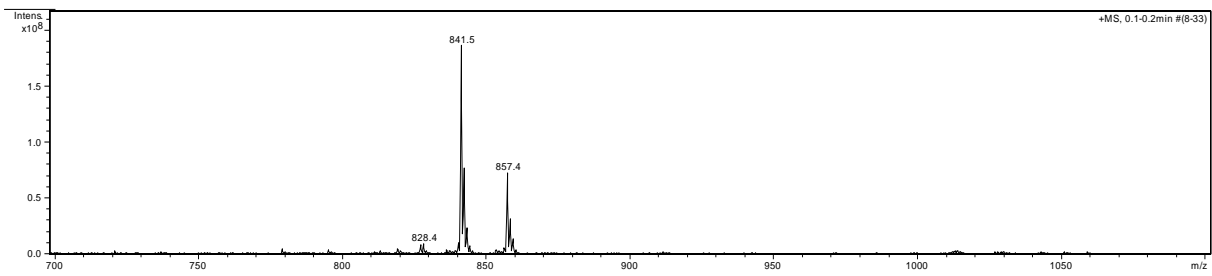
MS⁴ (356.1 → x)



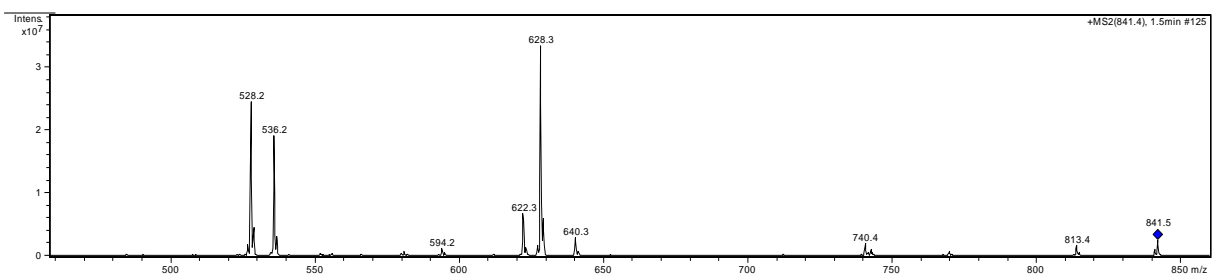
d) Octadepsipeptide (DP8)



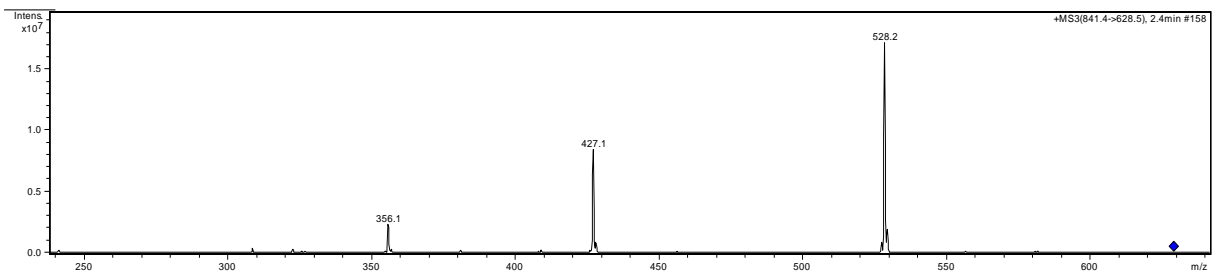
MS



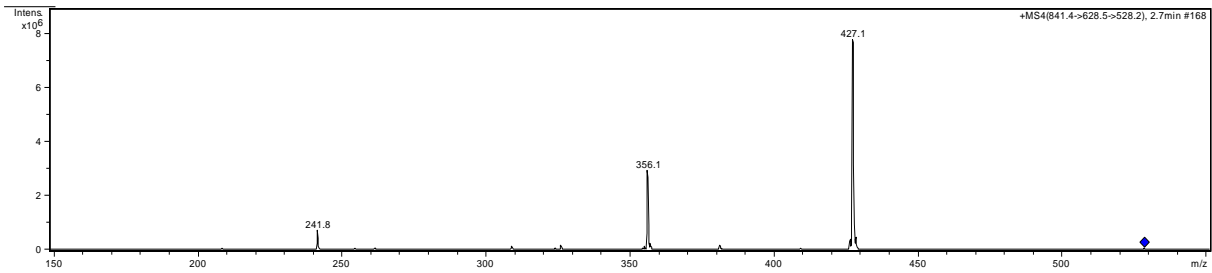
MS² (841.5 → x)



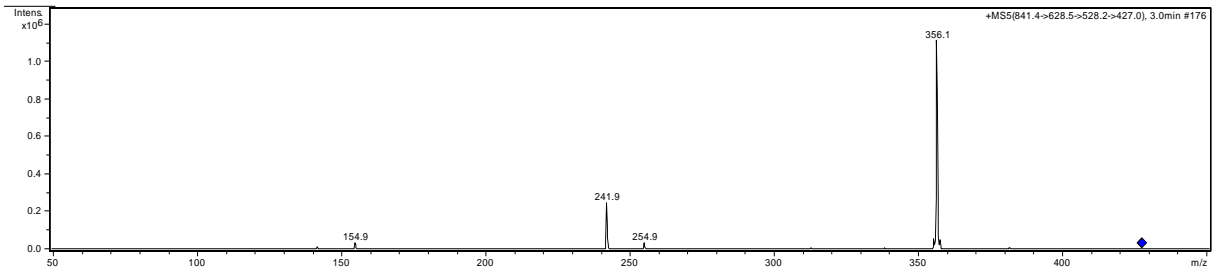
MS³ (628.3 → x)



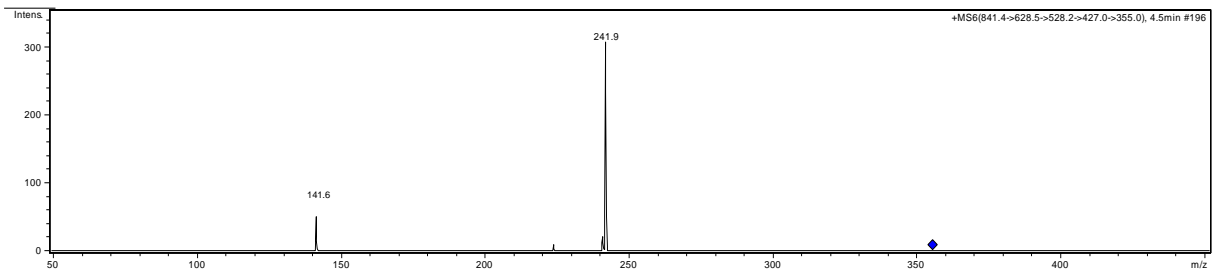
MS⁴ (528.2 → x)



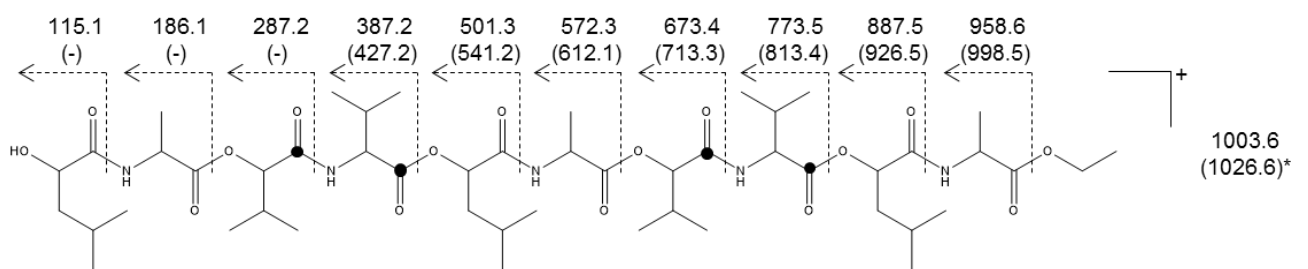
MS⁵ (427.1 → x)



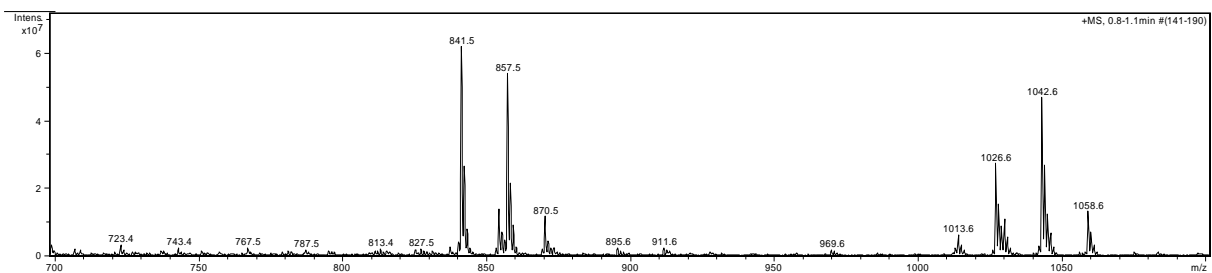
MS⁶ (356.1 → x)



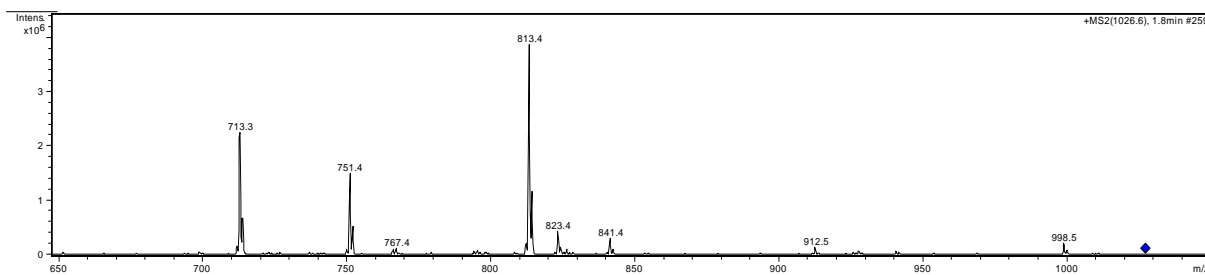
e) Decadepsipeptide (DP10a)



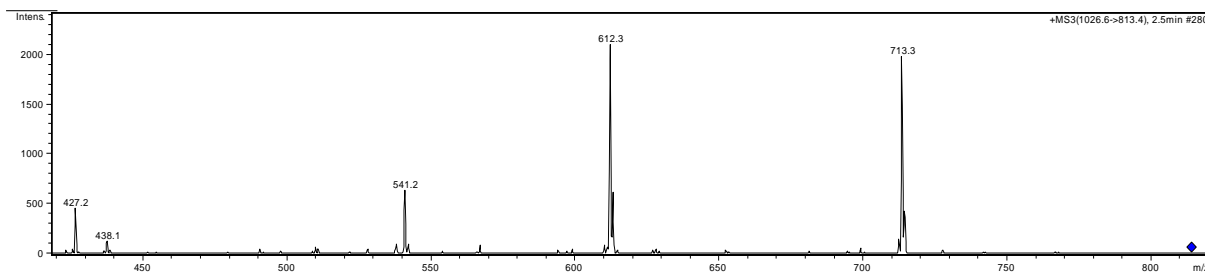
MS



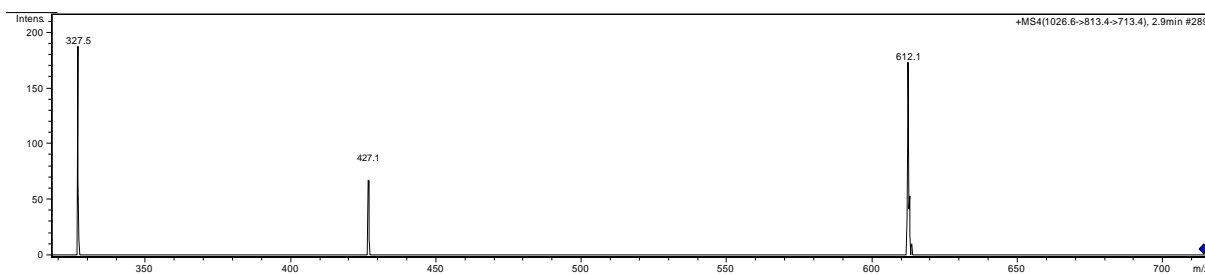
MS² (1026.6 → x)



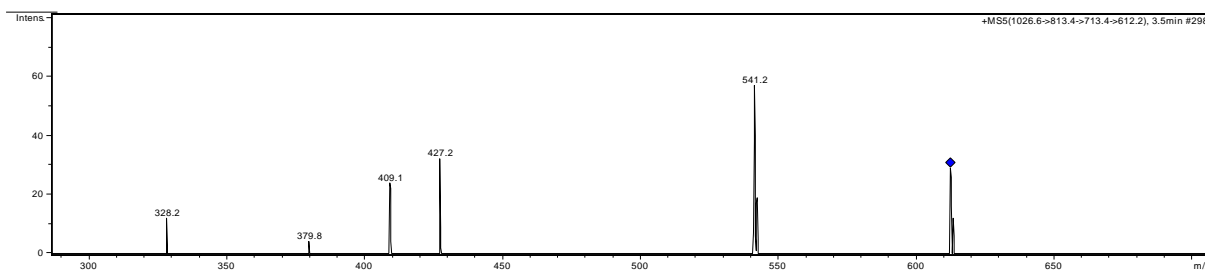
MS³ (813.4 → x)



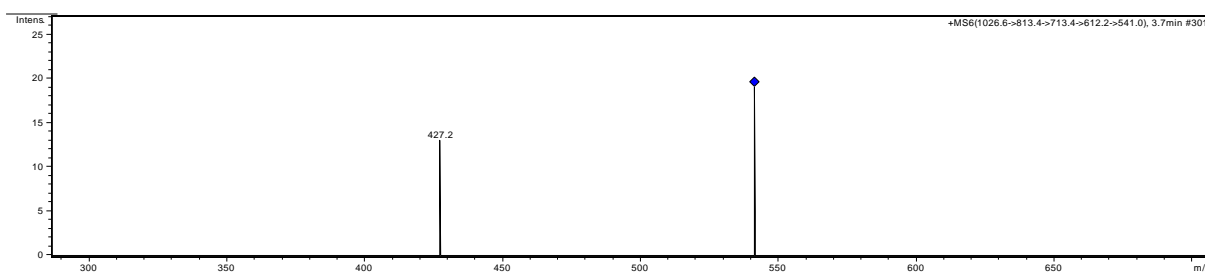
MS⁴ (713.3 → x)



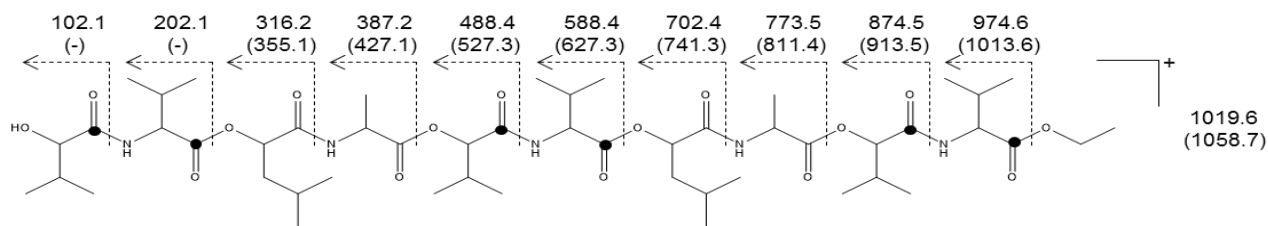
MS⁵ (612.1 → x)



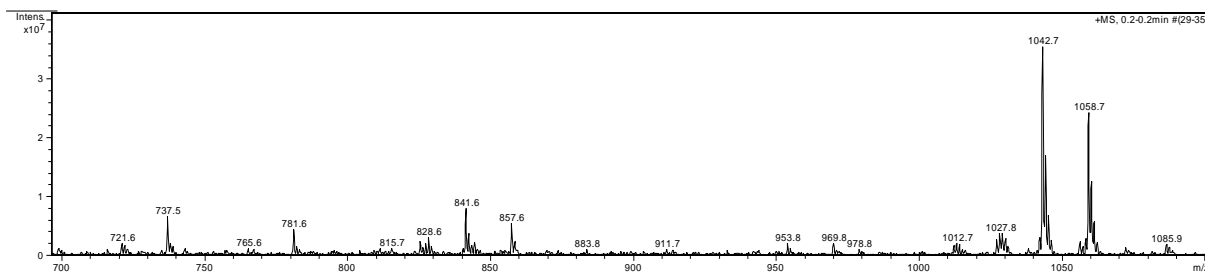
MS⁶ (541.2 → x)



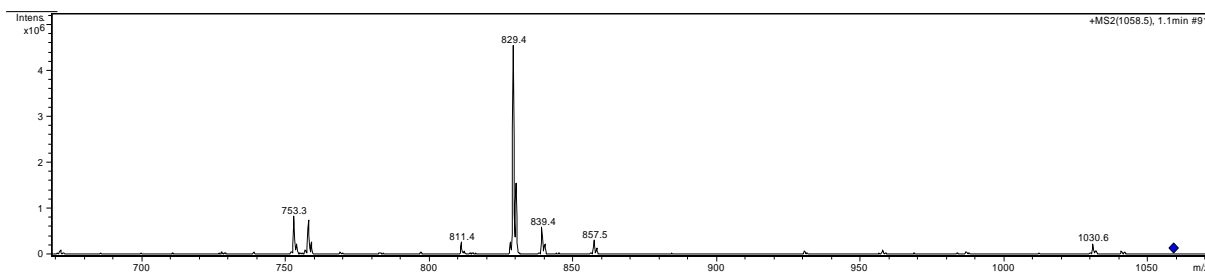
f) Decadepsipeptide (DP10b)



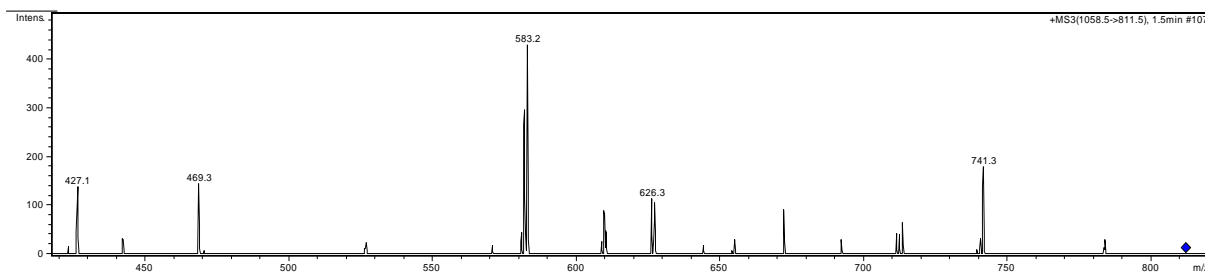
MS



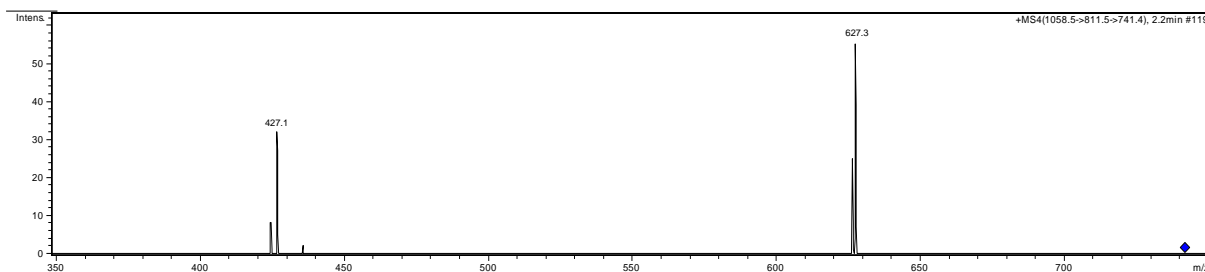
MS² (1058.7 → x)



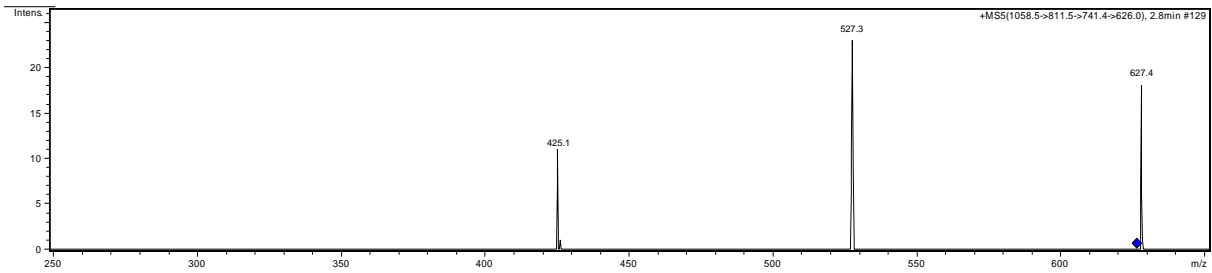
MS³ (811.4 → x)



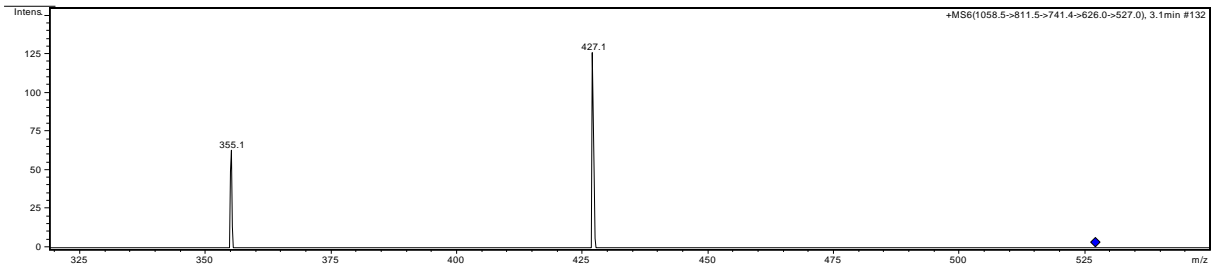
MS⁴ (741.3 → x)



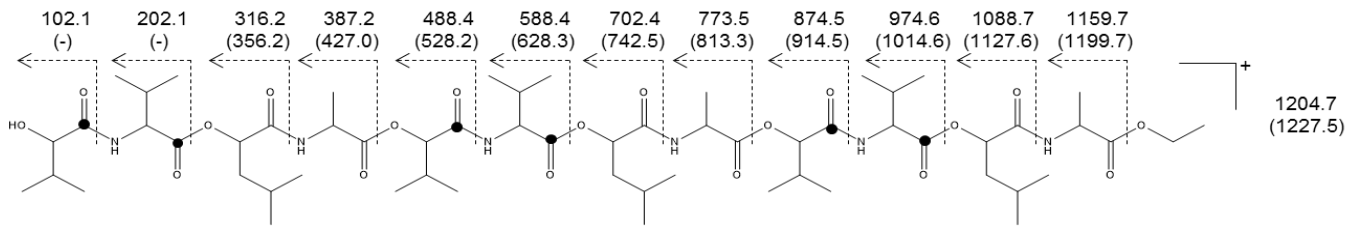
MS⁵ (627.3 → x)



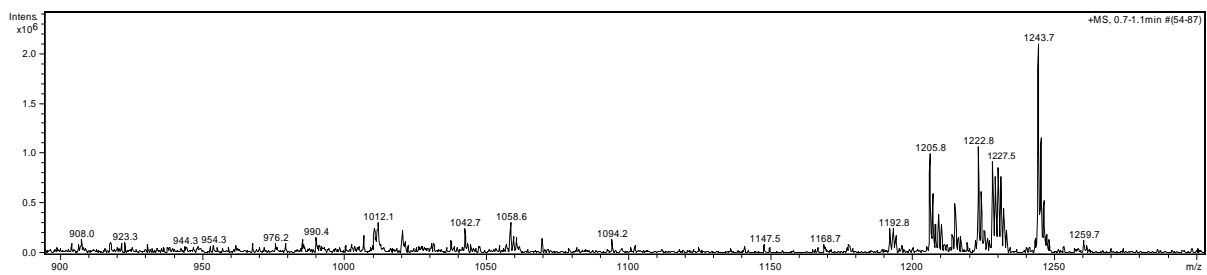
MS⁶ (527.3 → x)



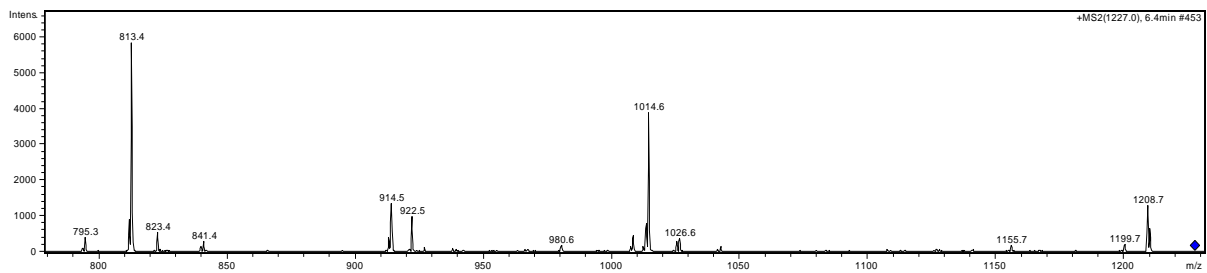
g) Dodecadeptide (DP12)



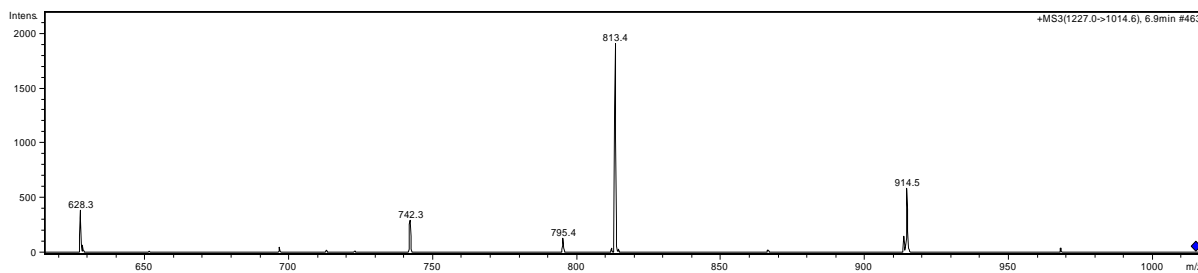
MS



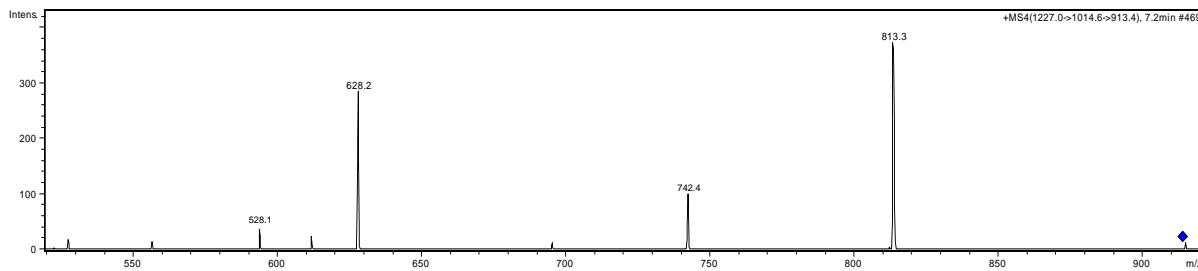
MS² (1227.5 → x)



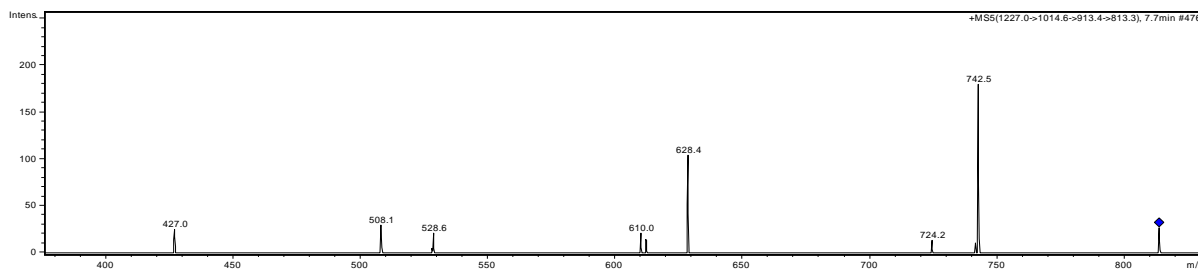
MS³ (1014.6 → x)



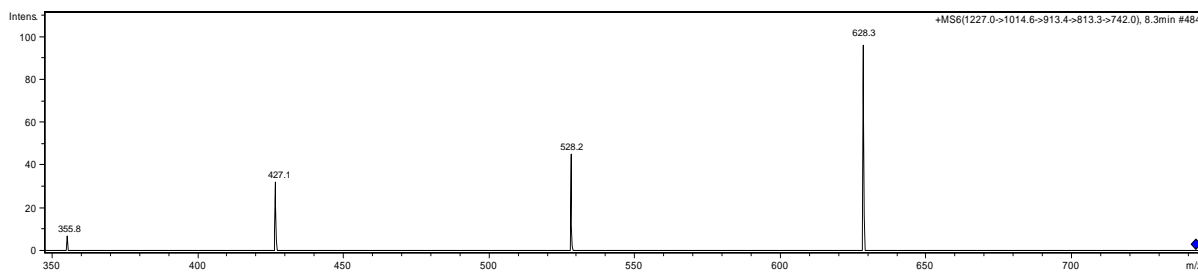
MS⁴ (914.5 → x)



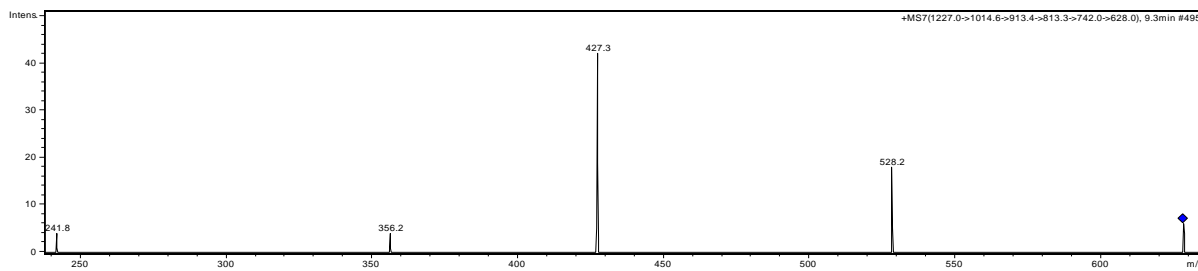
MS⁵ (813.3 → x)



MS⁶ (742.5 → x)



MS⁷ (628.3 → x)



MS⁸ (528.2 → x)

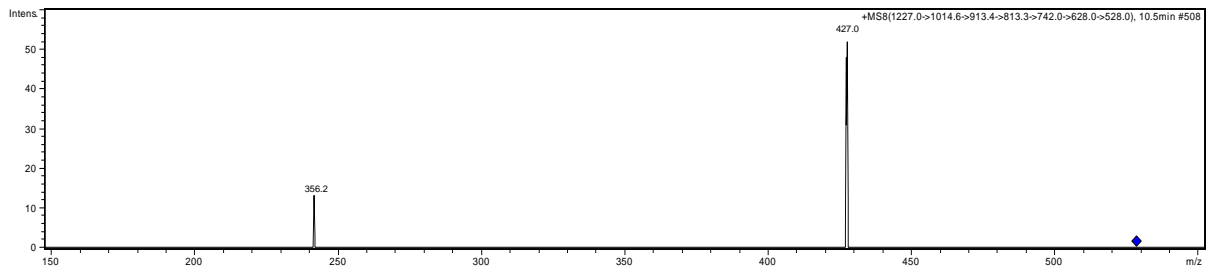


Figure S2 UPLC-TOF MS (ESI⁺) analysis of ¹³C₆-cereulide and cereulide in a *B. cereus* culture (F4810/72) incubated in the presence of synthetic ¹³C₆-cereulide (two biological and three analytical replicates each, ±SD).

