Supplementary Materials: Metabolite profiling of triterpene glycosides of the Far Eastern sea cucumber Eupentacta fraudatrix and their distribution in various body components using LC-ESI QTOF-MS

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Figure S11. Relative quantities of triterpene glycosides grouped by sugar moiety structures detected in *E. fraudatrix* in respiratory trees (RT), gonads (GN), aquapharyngeal bulbs (AB), guts (G) and body walls (BW) (bar plots represent the concentration in μ g/g animal material of metabolites (mean ± SD) scaled by 100%).

т	No	Structure of oligosaccharide chain	<i>m/z</i> -a, b														
Type			b2	b_1	C4	B ₄	$^{1,5}A_4$	^{1,3} A ₄	C ₃	Вз	$^{1,3}A_4/Y_{2\beta}$	B ₃ /Y _{2β}	^{2,5} A ₃	^{3,5} A ₃	C2	B ₂	B 1
Ι	9, 12, 18, 37, 41, 45, 49, 53	$\begin{array}{c} \underbrace{B_{1}}_{H_{3}CO} \underbrace{B_{2}}_{OH} \underbrace{\frac{1,3}{A_{4}}}_{H_{3}CO} \underbrace{B_{2}}_{OH} \underbrace{\frac{2,3}{A_{3}}}_{H_{4}C} \underbrace{B_{3}}_{H_{3}CO} \underbrace{B_{3}}_{O} O C_{3} \underbrace{B_{3}}_{H_{3}} \underbrace{B_{3}}_{O} \underbrace$	893.36	881.36	759.25	741.24	-	669.22	627.21	609.20	537.18	477.16	417.14	389.14	349.11	331.10	169.05
II	43, 44, 47, 48, 51	$\begin{array}{c} \begin{array}{c} \begin{array}{c} 1.3 \\ A_4 \end{array} \\ B_1 \\ H_0 \\ H_0 \\ CO \\ OH \end{array} \\ \begin{array}{c} 0 \\ H_0 \\ H_$	761.32	749.32	627.21	609.20	-	537.18	495.17	477.16	-	-	417.14	389.14	349.11	331.10	169.05
III	34, 39	$\begin{array}{c} \underline{B_1} \\ \underline{B_2} \\ OH \\ H_3CO \\ OH \\ \underline{V_1} \\ HO \\ OH \\ \underline{V_2} \\ \end{array} \begin{array}{c} 1.3 \underline{A_4} \\ \underline{B_4} \\ \underline{C_4} \\ $	923.37	911.37	789.26	771.25	-	699.23	657.22	.639.21	567.19	507.17	447.15	419.15	379.12	361.11	199.06
IV	36, 40	$H_{HO}^{3.5} - H_{HO}^{3.5} - H_{HO}^{2} -$	-	735.30	-	-	-	-	613.19	595.18	523.16	-	-	243.08 (^{3,5} A ₂)	463.14	481.15; 331.10 (B2/Y2β)	-
V	3, 4, 10, 13, 21, 29, 25	$\begin{array}{c} \underline{B_1} \\ \underline{B_2} \\ \underline{A_1 B_2} \\ \underline{A_2 B_3 D_3 S_1 D_1} \\ \underline{A_2 B_3 D_3 S_1 D_1} \\ \underline{A_2 B_3 D_3 S_1 D_1} \\ \underline{A_1 B_2} \\ \underline{A_2 B_3 D_3 S_1 D_1} \\ \underline{A_2 B_3 D_3 S_1 D_1} \\ \underline{A_1 B_2} \\ \underline{A_2 B_3 D_3 S_1 D_1} \\ \underline{A_1 B_2 D_1 D_2 } \\ \underline{A_1 B_2 D_1 D_2 D_1} \\ \underline{A_1 B_2 D_1 D_2 D_1 D_2 D_1} \\ \underline{A_1 B_2 D_1 D_2 D_1 D_2 D_1 } \\ A_1 B_2 D_2 D_2 D_1 D_2 D_1 D_2 D_2 D_2 D_1 \\ \underline{A_1 B_2 D_2 D_2 D_2 D_2 D_2 D_2 D_2 D_2 D_2 D$	-	983.30	861.19; 741.24	723.23	695.24	669.22	627.21	609.20	537.18	477.16	417.14	389.14	-	331.10	169.05

Table S1. Fragmentation of the different types of oligosaccharide chains determined in triterpene glycosides from the ethanol extract of the sea cucumber *E. fraudatrix*

VI	6, 14, 16, 26, 30, 32, 42, 50	$\begin{array}{c} \begin{array}{c} 1.5_{A_4} \\ 1.5_{A_4} \\ B_1 \\ H_0 \\ H_1 \\ CO \\ OH \\ OH \\ OH \\ OH \\ OH \\ OH \\ OH$	-	731.31	729.15; 609.20	591.19	563.19	537.18	495.17	477.16	-	-	417.14	389.14	349.11	331.10	169.05
VII	22, 27	$\begin{array}{c} \underbrace{\begin{array}{c} 1.3_{A_4} \\ B_1 \\ OH \\ H_3CO \\ OH \\ H_3CO \\ OH \\ H_0 \\ \end{array}} \underbrace{\begin{array}{c} 1.3_{A_4} \\ B_2 \\ OH \\ O$	-	893.36	891.20; 771.25	753.24	725.25	699.23	657.22	639.21	-	507.17	447.15	419.15	-	361.11	-
VIII	17, 31, 38, 52	$\begin{array}{c} 1,3_{A_{4}} \\ 1,3_{A_{4}} \\ 1,3_{A_{5}} \\ H_{3}O_{3}SO_{3}O_{3}O_{3}O_{3}O_{3}O_{3}O_{3}O_{3}$	-	-	-	667.17	-	593.14	-	533.12	-	-	-	445.10	-	387.06	-
IX	11, 15, 23, 28	$\begin{array}{c} \begin{array}{c} 1.3 \underline{A}_{4} & \underline{B}_{4} \\ \hline & & & \\ B_{2} & 3.5 \underline{A}_{3} & \underline{B}_{3} \\ \hline & & & \\ & & & \\ H_{0} \\ C \\ OH \end{array} \xrightarrow{(Na O_{3} SO}_{OH} & OH \\ H_{0} \\ \hline & & & \\ H_{0} \\ \hline \\ \hline & \\ H_{0} \\ \hline \\ \hline & \\ H_{0} \\ \hline \\ \hline \\ H_{0} \\ \hline \\ \hline \\ H_{0} \\ \hline \\ \hline \\ \hline \\ H_{0} \\ \hline \\ \hline \\ \hline \\ H_{0} \\ \hline \\ $	-	-	-	799.22	-	725.18	-	665.16	-	533.12	-	445.10	-	387.06	-
X	33	B_{a} $HO + O + O + O + O + O + O + O + O + O +$	-	-	-	-	-	-	-	519.10	_	-	-	-	-	-	-
XI	35	$H_{HO} = O_{OH}^{O}$	-	-	-	-	-	-	-	489.09	-	-	-	-	-	-	-

^a Types I-VII: fragment ions from product ion spectrum of [M + Na]⁺ precursor; types VIII and IX: fragment ions from product ion spectrum of [M – 2Na]^{2–} precursor; types X and XI: fragment ions from product ion spectrum of [M – Na]⁻ precursor;

^b Fragment ions C₄, B₄ and A₄ found in desulfated form are in italics.



Figure 1S. LC-ESI MS base-peak chromatogram of the ethanol extract of sea cucumber *Eupentacta fraudatrix* in negative ion mode.



Figure 2S. Fragment of ESI MS/MS spectrum of $[M + Na]^+$ precursor ion at m/z 1121 of cucumarioside A₁.



Figure 3S. Calibration curve for cucumarioside A₁ (ion $[M - H]^-$ at m/z 1097).



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Figure 5S. Calibration curve for cucumarioside I₂ (ion $[M - 2Na]^{2-}$ at m/z 693).



Figure 6S. ¹³C NMR spectrum of glycoside 39.



Figure 7S. ¹H NMR spectrum of glycoside 39.



Figure 8S. ¹H NMR spectrum of glycoside 34.



Figure 9S. Relative quantities of triterpene glycosides detected in *E. fraudatrix* in body walls (BW), gonads (GN), guts (G), aquapharyngeal bulbs (AB), and respiratory trees (RT) (bar plots represent the concentration in µg/g animal material of metabolites (mean ± SD) scaled by 100%).



Figure 10S. Relative quantities of triterpene glycosides grouped by aglycone structures detected in *E. fraudatrix* in respiratory trees (RT), gonads (GN), aquapharyngeal bulbs (AB), guts (G) and body walls (BW) (bar plots represent the concentration in µg/g animal material of metabolites scaled by 100%).



Figure 11S. Relative quantities of triterpene glycosides grouped by sugar moiety structures detected in *E. fraudatrix* in respiratory trees (RT), gonads (GN), aquapharyngeal bulbs (AB), guts (G) and body walls (BW) (bar plots represent the concentration in µg/g animal material of metabolites scaled by 100%).