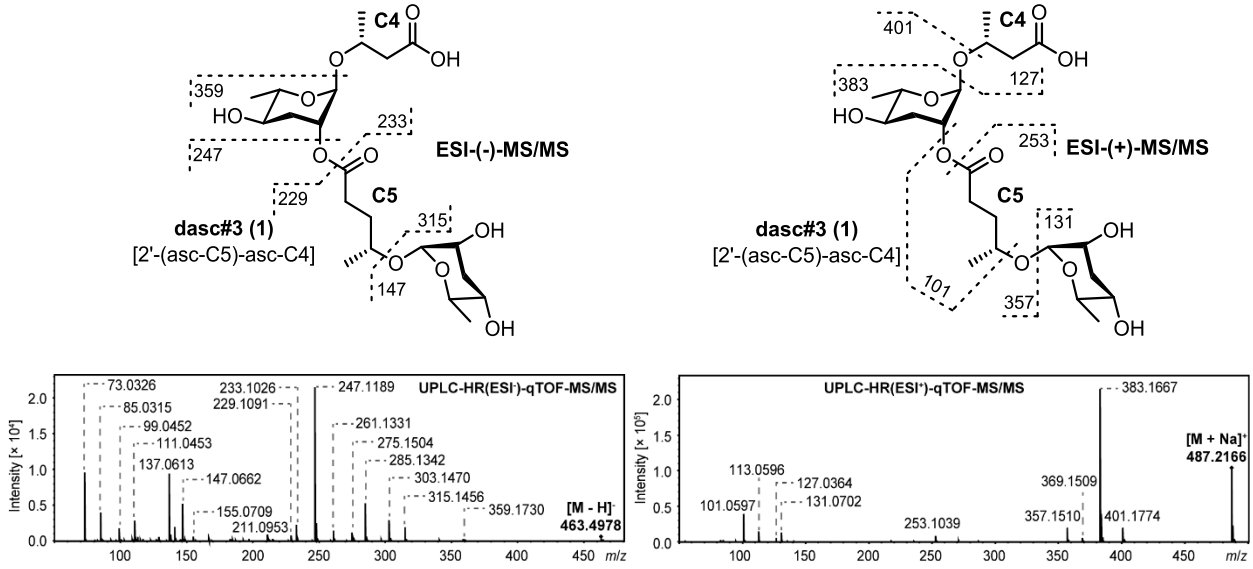
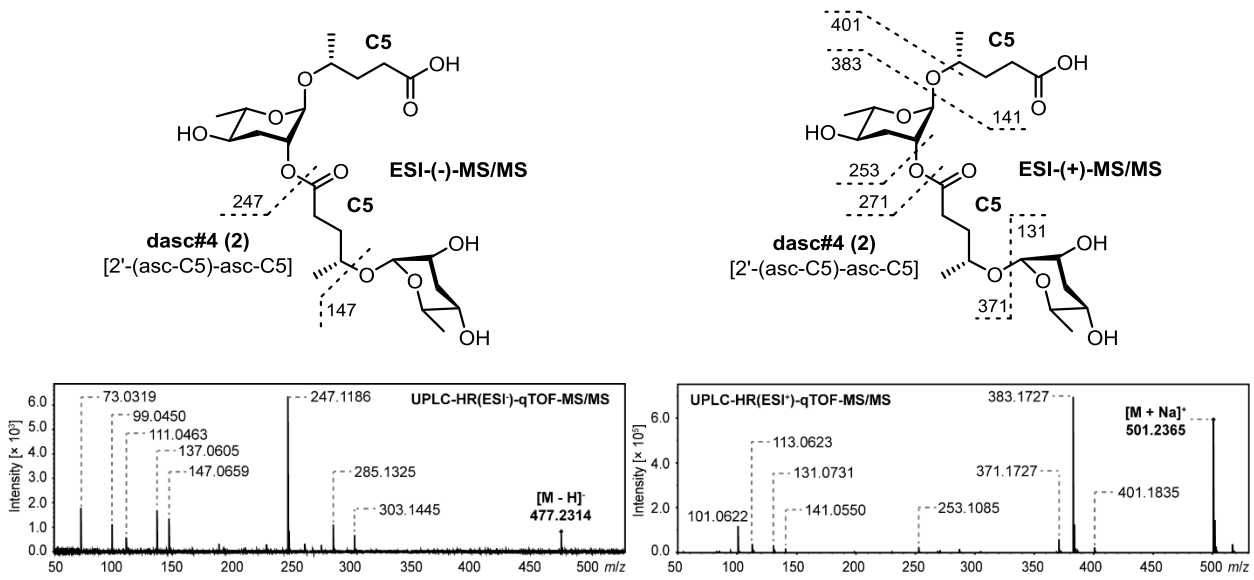
supplementary file 2a: MS/MS spectral data of DASC chemicals Pages



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
463.2178	463.2185	1.4	$C_{21}H_{35}O_{11}^-$
359.1730	359.1711	-5.2	$C_{17}H_{27}O_8^-$
315.1456	315.1449	-2.1	$C_{15}H_{23}O_7^-$
303.1470	303.1449	-6.8	$C_{14}H_{23}O_7^-$
285.1342	285.1344	0.5	$C_{14}H_{21}O_6^-$
275.1504	275.1500	-1.3	$C_{13}H_{23}O_6^-$
261.1331	261.1344	4.8	$C_{12}H_{21}O_6^-$
247.1189	247.1187	-0.6	$C_{11}H_{19}O_6^-$
233.1026	233.1031	2.2	$C_{10}H_{17}O_6^-$
229.1091	229.1081	-4.2	$C_{11}H_{17}O_5^-$
211.0953	211.0976	11.0	$C_{11}H_{15}O_4^-$
155.0709	155.0714	2.8	$C_8H_{11}O_3^-$
147.0662	147.0663	0.9	$C_6H_{11}O_4^-$
137.0613	137.0608	-3.3	$C_8H_9O_2^-$
111.0453	111.0452	-1.6	$C_6H_7O_2^-$
99.0452	99.0452	-0.7	$C_5H_7O_2^-$
85.0315	85.0295	-	$C_4H_5O_2^-$
73.0326	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+Na]^+$
487.2137	487.2150	2.6	$C_{21}H_{36}NaO_{11}^+$
401.1774	401.1782	2.1	$C_{17}H_{30}NaO_9^+$
383.1667	383.1676	2.4	$C_{17}H_{28}NaO_8^+$
369.1509	369.1520	2.8	$C_{16}H_{26}NaO_8^+$
357.1510	357.1520	2.9	$C_{15}H_{26}NaO_8^+$
253.1039	253.1046	3.1	$C_{11}H_{18}NaO_5^+$
131.0702	131.0703	0.9	$C_6H_{11}O_3^+$
127.0364	127.0366	0.9	$C_4H_8NaO_3^+$
113.0596	113.0573	-	$C_4H_{10}NaO_2^+$
101.0597	101.0597	0.5	$C_5H_9O_2^+$

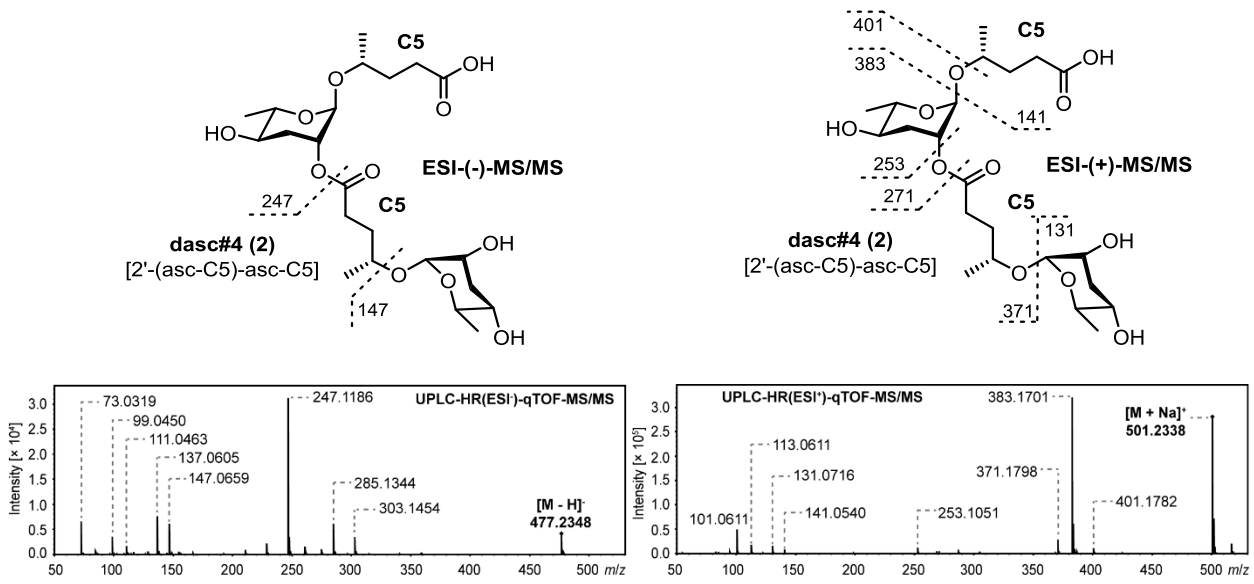
Figure 1. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#3 [2'-(asc-C5)-asc-C4, **1**] in both negative and positive ion modes. MS/MS fragmentation in positive ion mode produced an intensive ion signal of $C_{17}H_{28}NaO_8^+$ (*m/z* = 383.1667) suggesting that the first ascaroside (LC-MS/MS fragmentation pattern of dimeric ascarosides were described in ***Figure 4 – figure supplement 1C***) in dasc#3 [2'-(asc-C5)-asc-C4, **1**] should be ascr#9 [asc-C5] or oasc#9 [asc-ωC5] (***von Reuss et al., 2012***). *dqf*-COSY spectrum of an HPLC enriched sample containg dasc#3 [2'-(asc-C5)-asc-C4, **1**] confirmed that a unit of ascr#9 [asc-C5] was linked the 2'-position of ascr#11 [asc-C4] (***supplementary file 1b – Figure 1***).



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M − H]$^-$
477.2314	477.2341	2.8	$C_{22}H_{37}O_{11}^-$
303.1445	303.1449	0.5	$C_{14}H_{23}O_7^-$
285.1325	285.1344	1.8	$C_{14}H_{21}O_6^-$
247.1168	247.1187	1.9	$C_{11}H_{19}O_6^-$
147.0653	147.0663	1.0	$C_6H_{11}O_4^-$
137.0602	137.0608	0.6	$C_8H_9O_2^-$
111.0450	111.0452	0.1	$C_6H_7O_2^-$
99.0451	99.0452	0.1	$C_5H_7O_2^-$
73.0314	73.0295	-1.9	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M + Na]$^+$
501.2365	501.2306	-11.7	$C_{22}H_{38}N_aO_{11}^+$
401.1835	401.1782	-13.2	$C_{17}H_{30}N_aO_9^+$
383.1727	383.1676	-13.1	$C_{17}H_{28}N_aO_8^+$
371.1727	371.1676	-13.5	$C_{16}H_{28}N_aO_8^+$
253.1085	253.1046	-15.4	$C_{11}H_{18}N_aO_5^+$
141.0550	141.0522	-20.1	$C_5H_{10}N_aO_3^+$
131.0731	131.0703	-21.7	$C_6H_{11}O_3^+$
113.0623	113.0597	-23.3	$C_6H_9O_2^+$
101.0622	101.0597	-24.2	$C_5H_9O_2^+$

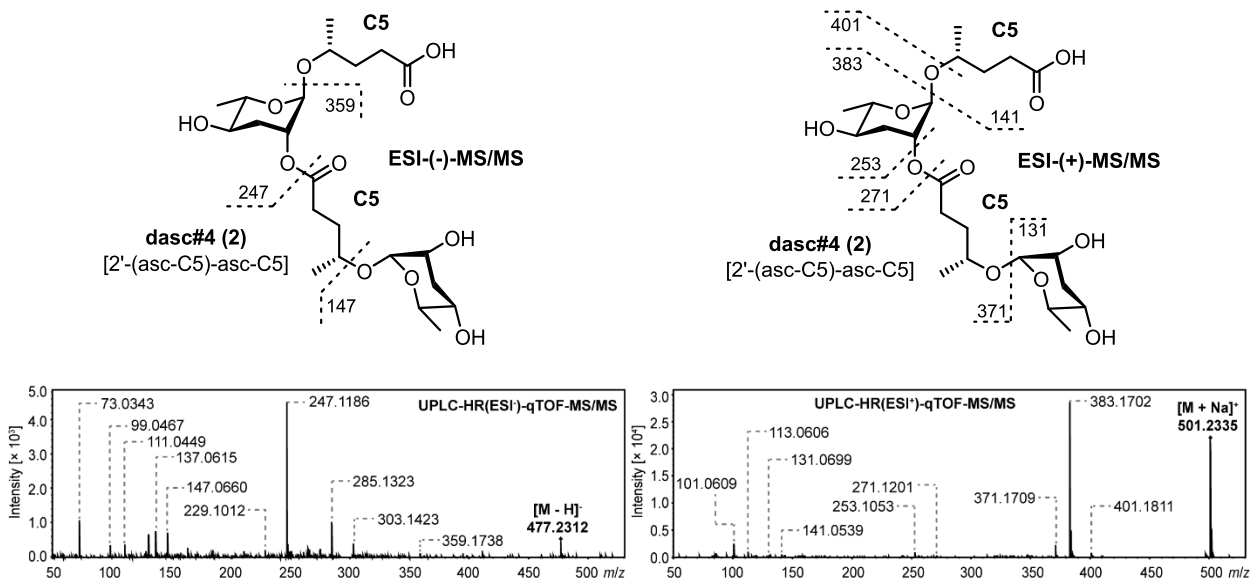
Figure 2. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#4 [2'-(asc-C5)-asc-C5, **2**] from *P. taiwanensis* in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
477.2348	477.2341	-1.5	$C_{22}H_{37}O_{11}^-$
303.1454	303.1449	-1.7	$C_{14}H_{23}O_7^-$
285.1344	285.1344	0.0	$C_{14}H_{21}O_6^-$
247.1186	247.1187	0.3	$C_{11}H_{19}O_6^-$
147.0659	147.0663	2.8	$C_6H_{11}O_4^-$
137.0605	137.0608	2.2	$C_8H_9O_2^-$
111.0463	111.0452	-10.3	$C_6H_7O_2^-$
99.0450	99.0452	1.7	$C_5H_7O_2^-$
73.0319	73.0295	-32.6	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+Na]^+$
501.2338	501.2306	-6.3	$C_{22}H_{38}N_aO_{11}^+$
401.1805	401.1782	-5.9	$C_{17}H_{30}N_aO_9^+$
383.1701	383.1676	-6.5	$C_{17}H_{28}N_aO_8^+$
371.1698	371.1676	-5.7	$C_{16}H_{28}N_aO_8^+$
253.1051	253.1046	-1.7	$C_{11}H_{18}N_aO_5^+$
141.0540	141.0522	-12.7	$C_5H_{10}N_aO_3^+$
131.0716	131.0703	-10.1	$C_6H_{11}O_3^+$
113.0611	113.0597	-12.1	$C_6H_9O_2^+$
101.0611	101.0597	-13.7	$C_5H_9O_2^+$

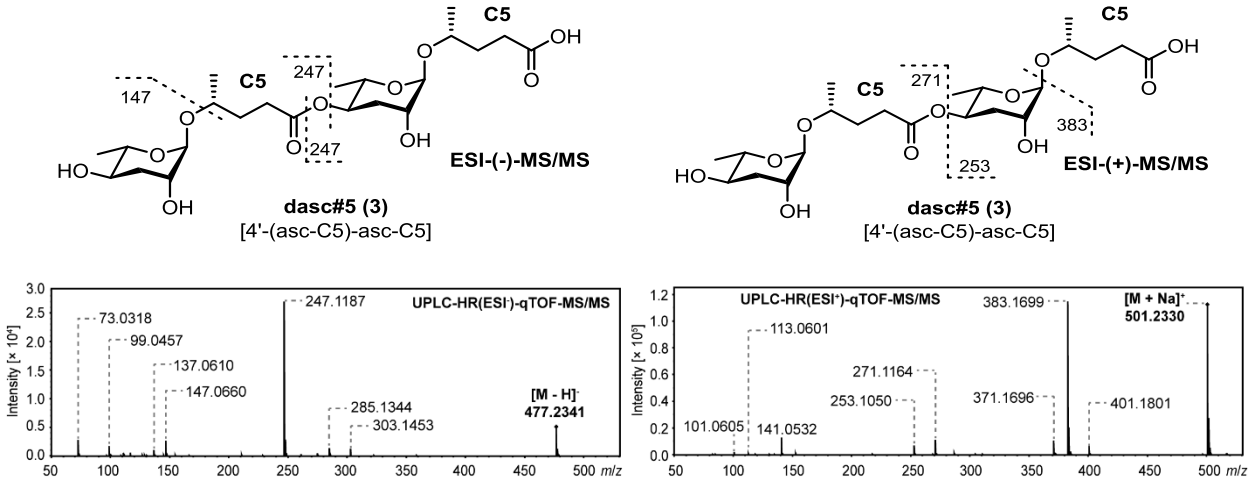
Figure 3. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#4 [2'-(asc-C5)-asc-C5, **2**] from *P. entomophagus* in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
477.2312	477.2341	-6.2	$C_{22}H_{37}O_{11}^-$
359.1738	359.1711	-7.3	$C_{17}H_{27}O_8^-$
303.1423	303.1449	8.7	$C_{14}H_{23}O_7^-$
285.1323	285.1344	7.2	$C_{14}H_{21}O_6^-$
247.1186	247.1187	0.3	$C_{11}H_{19}O_6^-$
229.1012	229.1081	-	$C_{11}H_{17}O_5^-$
147.0660	147.0663	2.3	$C_6H_{11}O_4^-$
137.0615	137.0608	-4.9	$C_8H_9O_2^-$
111.0449	111.0452	2.4	$C_6H_7O_2^-$
99.0467	99.0452	-	$C_5H_7O_2^-$
73.0343	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+Na]^+$
501.2335	501.2306	0.0	$C_{22}H_{38}N_aO_{11}^+$
401.1811	401.1782	-7.1	$C_{17}H_{30}N_aO_9^+$
383.1702	383.1676	-6.8	$C_{17}H_{28}N_aO_8^+$
371.1709	371.1676	-8.7	$C_{16}H_{28}N_aO_8^+$
271.1201	271.1152	-	$C_{11}H_{20}N_aO_6^+$
253.1053	253.1046	-2.7	$C_{11}H_{18}N_aO_5^+$
141.0539	141.0522	-	$C_5H_{10}N_aO_3^+$
131.0699	131.0703	2.5	$C_6H_{11}O_3^+$
113.0606	113.0597	-7.8	$C_6H_9O_2^+$
101.0609	101.0597	-	$C_5H_9O_2^+$

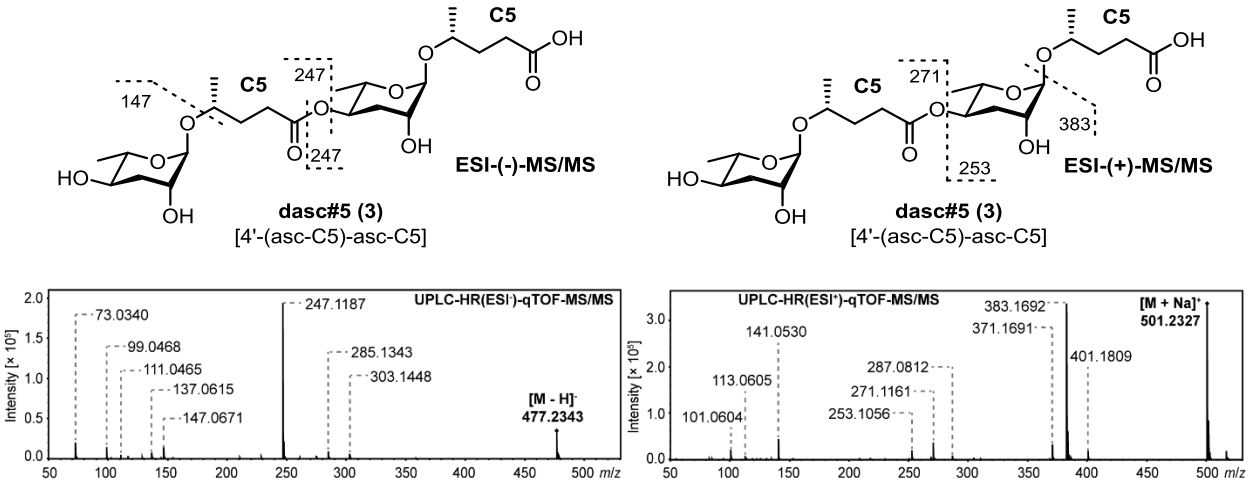
Figure 4. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#4 [2'-(asc-C5)-asc-C5, **2**] from *P. pacificus* RS2333 in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
477.2341	477.2341	0.1	$C_{22}H_{37}O_{11}^-$
303.1453	303.1449	-0.3	$C_{14}H_{23}O_7^-$
285.1344	285.1344	-0.1	$C_{14}H_{21}O_6^-$
247.1187	247.1187	0.0	$C_{11}H_{19}O_6^-$
147.0660	147.0663	0.2	$C_6H_{11}O_4^-$
137.0610	137.0608	-0.2	$C_8H_9O_2^-$
99.0457	99.0452	-0.6	$C_5H_7O_2^-$
73.0318	73.0295	-2.3	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+Na]^+$
501.2330	501.2306	-4.7	$C_{22}H_{38}N_aO_{11}^+$
401.1801	401.1782	-4.8	$C_{17}H_{30}N_aO_9^+$
383.1699	383.1676	-6.0	$C_{17}H_{28}N_aO_8^+$
371.1696	371.1676	-5.3	$C_{16}H_{28}N_aO_8^+$
271.1164	271.1152	-4.2	$C_{11}H_{20}N_aO_6^+$
253.1050	253.1046	-1.4	$C_{11}H_{18}N_aO_5^+$
141.0532	141.0522	-6.7	$C_5H_{10}N_aO_3^+$
113.0601	113.0597	-3.1	$C_6H_9O_2^+$
101.0605	101.0597	-	$C_5H_9O_2^+$

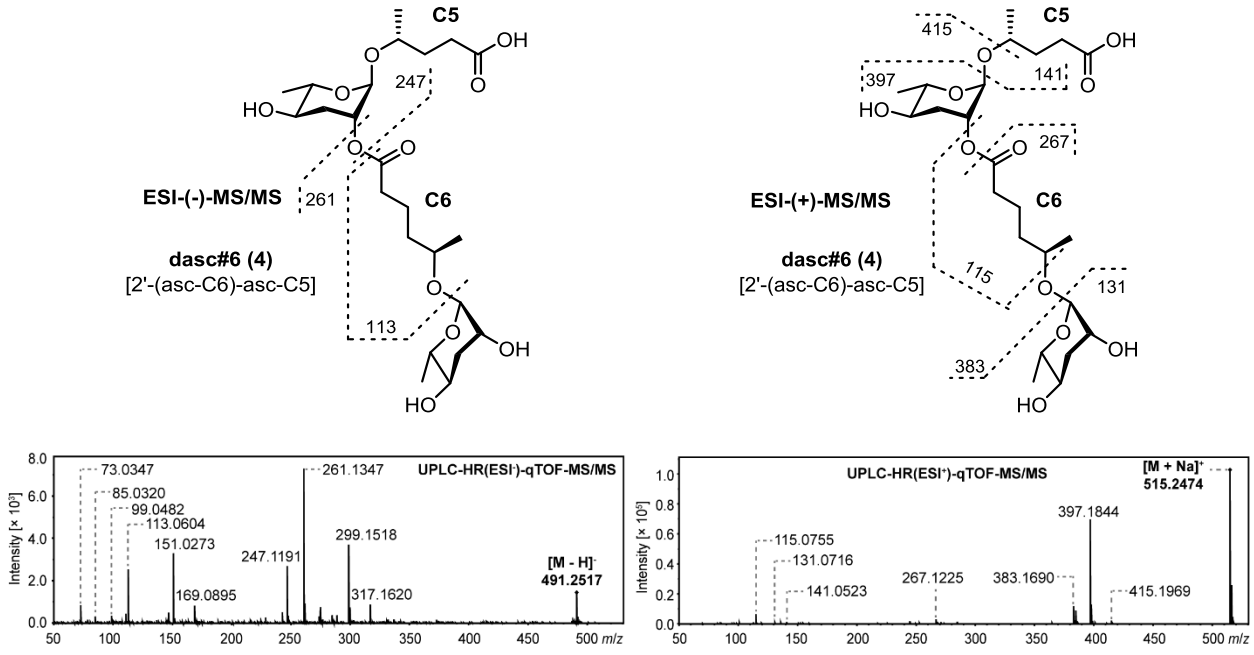
Figure 5. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#5 [4'-(asc-C5)-asc-C5, **3**] from *P. mayeri* in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
477.2343	477.2341	-0.3	$C_{22}H_{37}O_{11}^-$
303.1448	303.1449	0.4	$C_{14}H_{23}O_7^-$
285.1343	285.1344	0.2	$C_{14}H_{21}O_6^-$
247.1187	247.1187	0.2	$C_{11}H_{19}O_6^-$
147.0671	147.0663	-5.4	$C_6H_{11}O_4^-$
137.0615	137.0608	-5.2	$C_8H_9O_2^-$
111.0465	111.0452	-	$C_6H_7O_2^-$
99.0468	99.0452	-	$C_5H_7O_2^-$
73.0340	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+Na]^+$
501.2327	501.2306	-4.1	$C_{22}H_{38}N_aO_{11}^+$
401.1809	401.1782	-6.7	$C_{17}H_{30}N_aO_9^+$
383.1692	383.1676	-4.2	$C_{17}H_{28}N_aO_8^+$
371.1691	371.1676	-4.0	$C_{16}H_{28}N_aO_8^+$
271.1161	271.1152	-3.3	$C_{11}H_{20}N_aO_6^+$
253.1056	253.1046	-3.8	$C_{11}H_{18}N_aO_5^+$
141.0530	141.0522	-5.9	$C_5H_{10}N_aO_3^+$
113.0605	113.0597	-7.4	$C_6H_9O_2^+$
101.0604	101.0597	-6.6	$C_5H_9O_2^+$

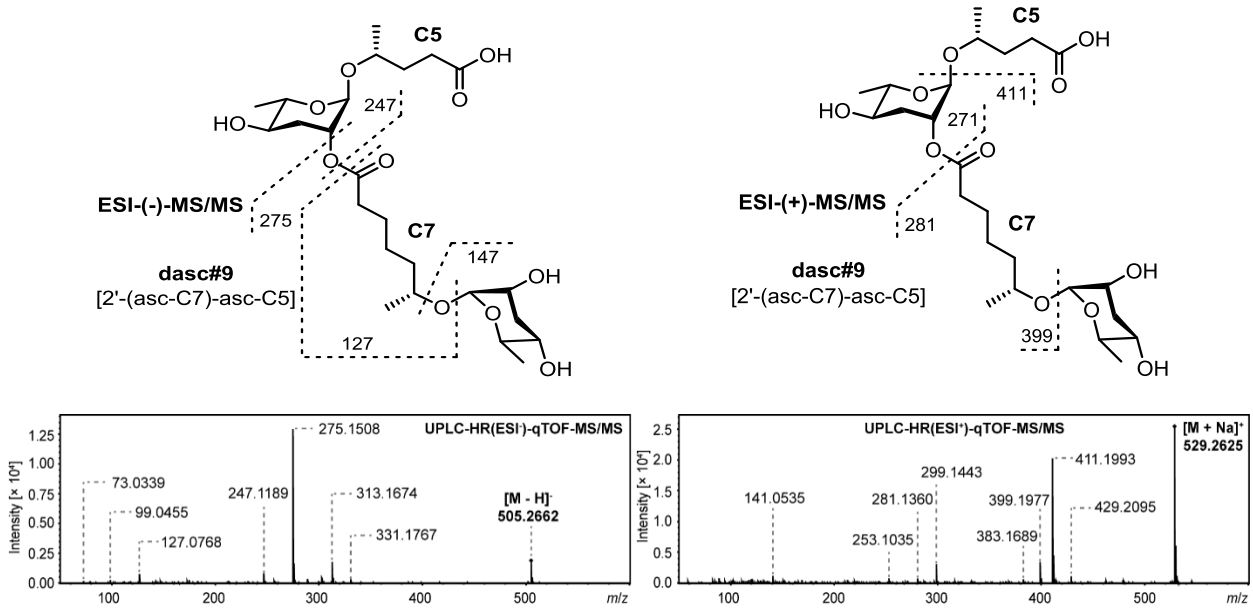
Figure 6. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#5 [4'-(asc-C5)-asc-C5, **3**] from *D. magnus* in both negative and positive ion modes.



UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
491.2517	491.2498	-3.8	$C_{23}H_{39}O_{11}^-$
317.1620	317.1606	-4.5	$C_{15}H_{25}O_7^-$
299.1518	299.1500	-5.8	$C_{15}H_{23}O_6^-$
261.1347	261.1344	-1.2	$C_{12}H_{21}O_6^-$
247.1191	247.1187	-1.5	$C_{11}H_{19}O_6^-$
169.0895	169.0870	-	$C_9H_{13}O_3^-$
151.0273	151.0248	-	$C_4H_7O_6^-$
113.0604	113.0608	3.8	$C_6H_9O_2^-$
99.0482	99.0452	-	$C_5H_7O_2^-$
85.0320	85.0295	-	$C_4H_5O_2^-$
73.0347	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+Na]^+$
515.2474	515.2463	-2.2	$C_{23}H_{40}NaO_{11}^+$
415.1969	415.1939	-7.3	$C_{18}H_{32}NaO_9^+$
397.1844	397.1833	-2.8	$C_{18}H_{30}NaO_8^+$
383.1690	383.1676	-3.5	$C_{17}H_{28}NaO_8^+$
267.1225	267.1203	-	$C_{12}H_{20}NaO_5^+$
141.0523	141.0522	-0.4	$C_5H_{10}NaO_3^+$
131.0716	131.0703	-	$C_6H_{11}O_3^+$
115.0755	115.0754	-1.2	$C_6H_{11}O_2^+$

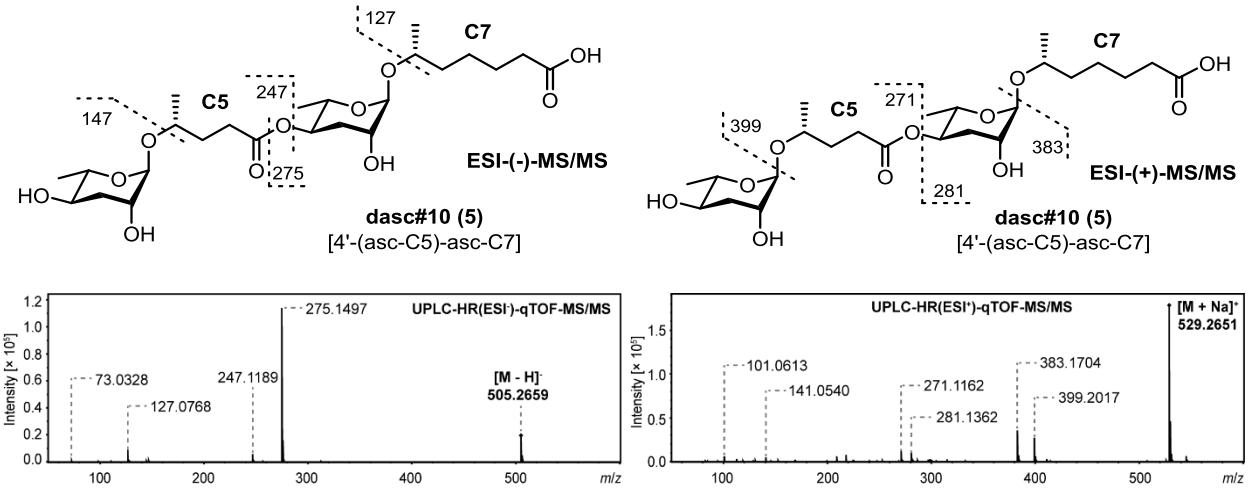
Figure 7. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#6 [2'-(asc-C6)-asc-C5, **4**] in both negative and positive ion modes.



UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
505.2662	505.2654	-1.5	$C_{24}H_{41}O_{11}^-$
331.1767	331.1762	-1.5	$C_{16}H_{27}O_7^-$
313.1674	313.1657	-5.4	$C_{16}H_{25}O_6^-$
275.1508	275.1500	-3.0	$C_{13}H_{23}O_6^-$
247.1189	247.1187	-0.9	$C_{11}H_{19}O_6^-$
127.0768	127.0765	-2.4	$C_7H_{11}O_2^-$
99.0455	99.0452	-3.3	$C_5H_7O_2^-$
73.0339	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+Na]^+$
529.2625	529.2619	-1.0	$C_{24}H_{42}NaO_{11}^+$
429.2095	429.2095	-0.0	$C_{19}H_{34}NaO_9^+$
411.1993	411.1989	-0.8	$C_{19}H_{32}NaO_8^+$
399.1977	399.1989	3.2	$C_{18}H_{32}NaO_8^+$
383.1689	383.1676	-3.4	$C_{17}H_{28}NaO_8^+$
299.1443	299.1465	7.2	$C_{13}H_{24}NaO_6^+$
281.1360	281.1359	-0.2	$C_{13}H_{22}NaO_5^+$
253.1035	253.1046	4.7	$C_{11}H_{18}NaO_5^+$
141.0535	141.0522	-	$C_5H_{10}NaO_3^+$

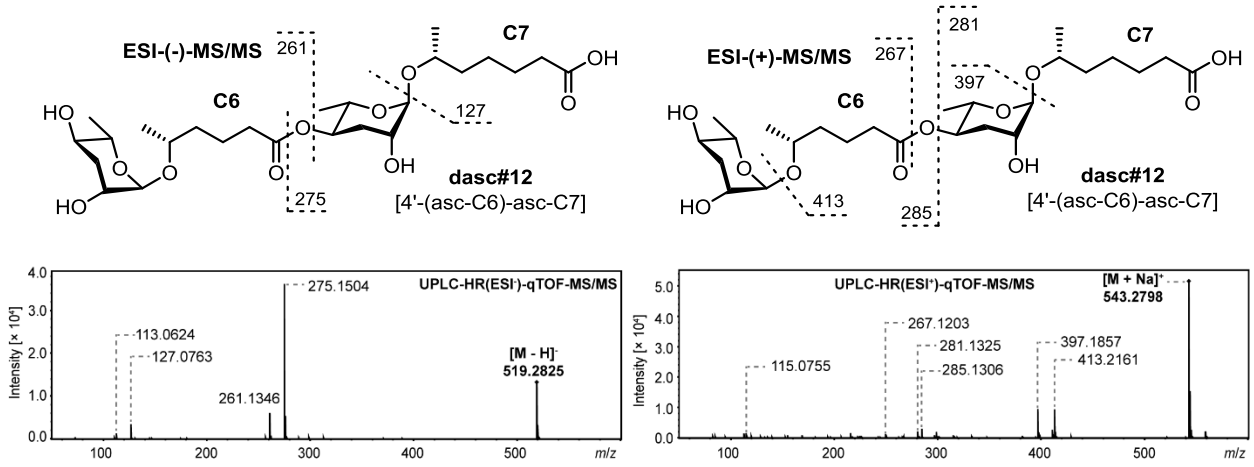
Figure 8. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#9 [2'-(asc-C7)-asc-C5] in both negative and positive ion modes. Note that dasc#9 [2'-(asc-C7)-asc-C5] is tentatively assigned to be linked at the 2'-position, but its final structure has not yet been elucidated.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
505.2659	505.2654	-0.9	$C_{24}H_{41}O_{11}^-$
275.1497	275.1500	1.0	$C_{13}H_{23}O_6^-$
247.1189	247.1187	-0.6	$C_{11}H_{19}O_6^-$
127.0768	127.0765	-2.8	$C_7H_{11}O_2^-$
73.0328	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+Na]^+$
529.2651	529.2619	-6.0	$C_{24}H_{42}NaO_{11}^+$
399.2017	399.1989	-6.8	$C_{18}H_{32}NaO_8^+$
383.1704	383.1676	-7.1	$C_{17}H_{28}NaO_8^+$
281.1362	281.1359	-1.0	$C_{13}H_{22}NaO_5^+$
271.1162	271.1152	-3.7	$C_{11}H_{20}NaO_6^+$
141.0540	141.0522	-	$C_5H_{10}NaO_3^+$
101.0613	101.0597	-	$C_5H_9O_2^+$

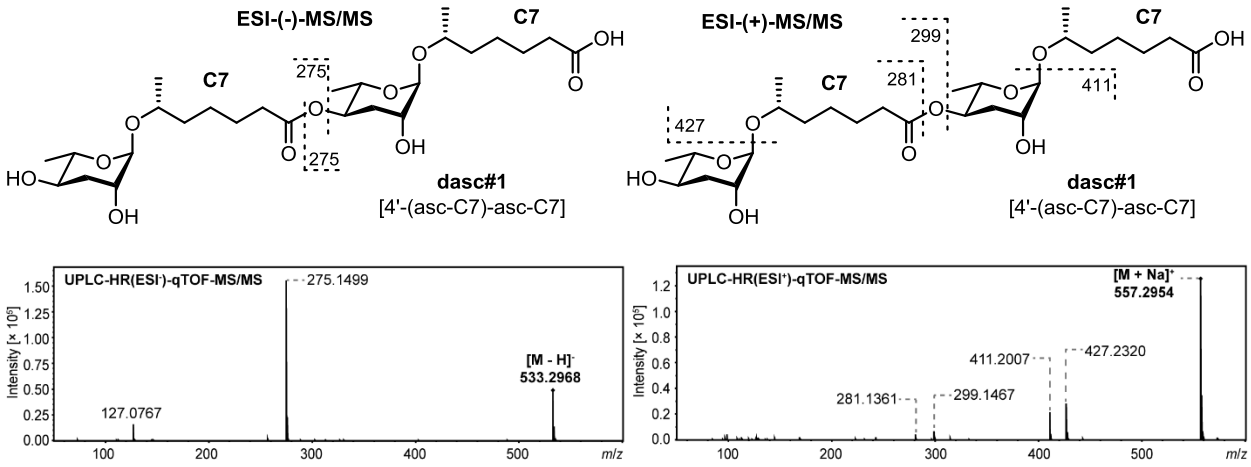
Figure 9. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#10 [4'-(asc-C5)-asc-C7, **5**] in both negative and positive ion modes.



UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
519.2825	519.2811	-2.8	$C_{25}H_{43}O_{11}^-$
275.1504	275.1500	-1.3	$C_{13}H_{23}O_6^-$
261.1346	261.1344	-0.8	$C_{12}H_{21}O_6^-$
127.0763	127.0765	1.0	$C_7H_{11}O_2^-$
113.0624	113.0608	-	$C_6H_9O_2^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+Na]^+$
543.2798	543.2776	-4.1	$C_{25}H_{44}NaO_{11}^+$
413.2161	413.2146	-3.7	$C_{19}H_{34}NaO_8^+$
397.1857	397.1833	-6.1	$C_{18}H_{30}NaO_8^+$
285.1306	285.1309	0.9	$C_{12}H_{22}NaO_6^+$
281.1325	281.1359	12.2	$C_{13}H_{22}NaO_5^+$
267.1203	267.1203	0.0	$C_{12}H_{20}NaO_5^+$
115.0755	115.0754	-1.6	$C_6H_{11}O_2^+$

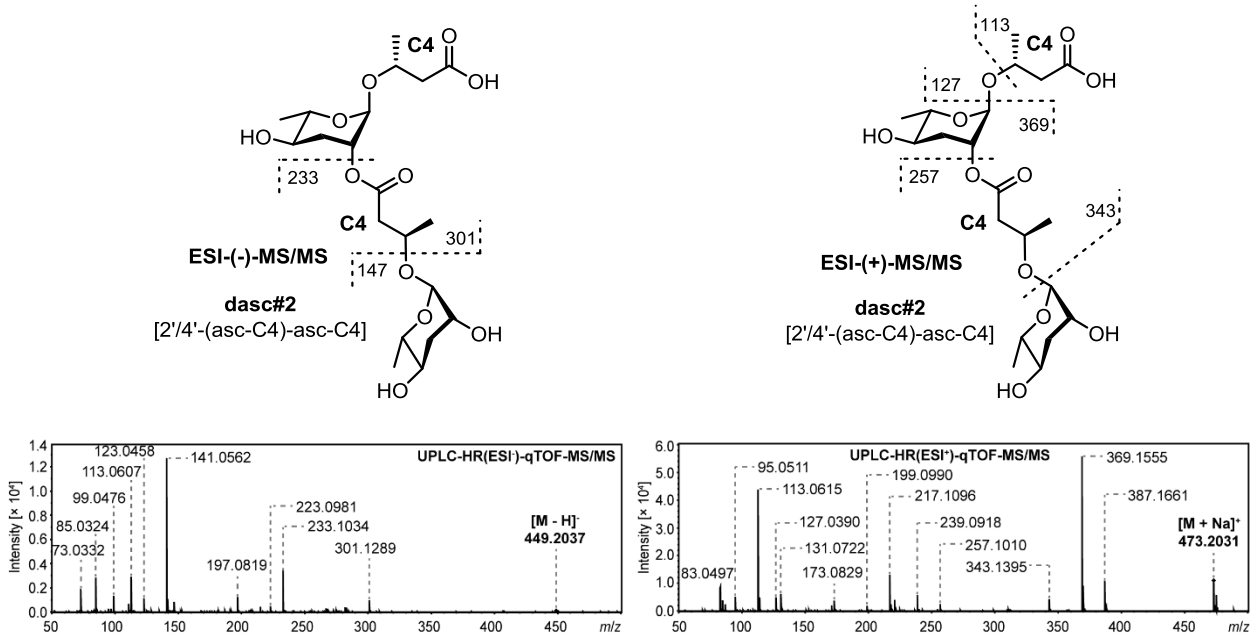
Figure 10. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#12 [4'-(asc-C6)-asc-C7] in both negative and positive ion modes. Note that dasc#12 [4'-(asc-C6)-asc-C7] is tentatively assigned to be linked at the 4'-position, but its absolute structure has not yet been elucidated.



UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
533.2968	533.2967	-0.1	$C_{26}H_{45}O_{11}^-$
275.1499	275.1500	0.4	$C_{13}H_{23}O_6^-$
127.0767	127.0765	-2.2	$C_7H_{11}O_6^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+Na]^+$
557.2954	557.2932	-3.9	$C_{26}H_{46}NaO_{11}^+$
427.2320	427.2302	-4.2	$C_{20}H_{36}NaO_8^+$
411.2007	411.1989	-4.3	$C_{19}H_{32}NaO_8^+$
299.1467	299.1465	-0.6	$C_{13}H_{24}NaO_6^+$
281.1361	281.1359	-0.4	$C_{13}H_{22}NaO_5^+$

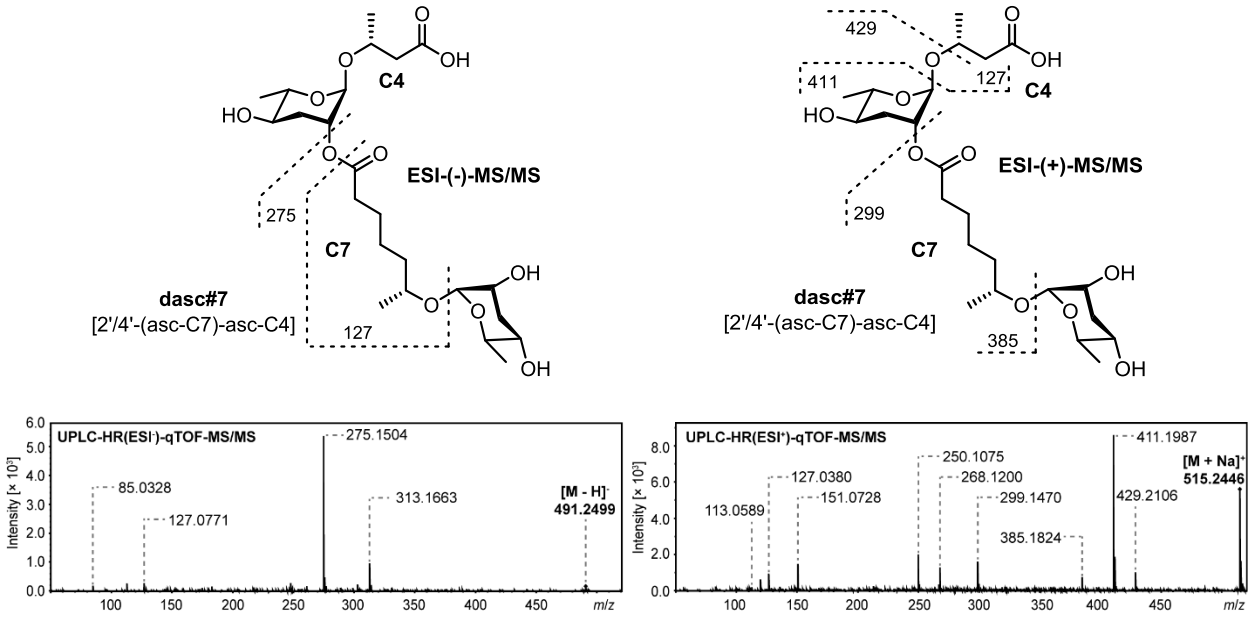
Figure 11. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of known dasc#1 [4'-(asc-C7)-asc-C7] (***Bose et al., 2012***) in both negative and positive ion modes.



UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
449.2037	449.2028	-1.8	$C_{20}H_{33}O_{11}^-$
301.1289	301.1293	1.3	$C_{14}H_{21}O_7^-$
233.1034	233.1031	-1.6	$C_{10}H_{17}O_6^-$
223.0981	223.0976	-2.2	$C_{12}H_{15}O_4^-$
197.0819	197.0819	0.3	$C_{10}H_{13}O_4^-$
141.0562	141.0557	-3.2	$C_7H_9O_3^-$
123.0458	123.0452	-5.2	$C_7H_7O_2^-$
113.0607	113.0608	2.6	$C_6H_9O_2^-$
99.0476	99.0452	-	$C_5H_7O_2^-$
85.0324	85.0295	-	$C_4H_5O_2^-$
73.0332	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+Na]^+$
473.2031	473.1993	-8.1	$C_{20}H_{34}NaO_{11}^+$
387.1661	387.1626	-9.2	$C_{16}H_{28}NaO_9^+$
369.1555	369.1520	-9.4	$C_{16}H_{26}NaO_8^+$
343.1395	343.1363	-9.2	$C_{14}H_{24}NaO_8^+$
257.1010	257.0996	-5.7	$C_{10}H_{18}NaO_6^+$
239.0918	239.0890	-	$C_{10}H_{16}NaO_5^+$
217.1096	217.1046	-	$C_8H_{18}NaO_5^+$
199.0990	199.0841	-	$C_8H_{16}NaO_4^+$
131.0722	131.0703	-	$C_6H_{11}O_3^+$
127.0390	127.0366	-	$C_4H_8NaO_3^+$
113.0615	113.0573	-	$C_4H_{10}NaO_2^+$
95.0511	95.0467	-	$C_4H_8NaO^+$
83.0497	83.0467	-	$C_3H_8NaO^+$

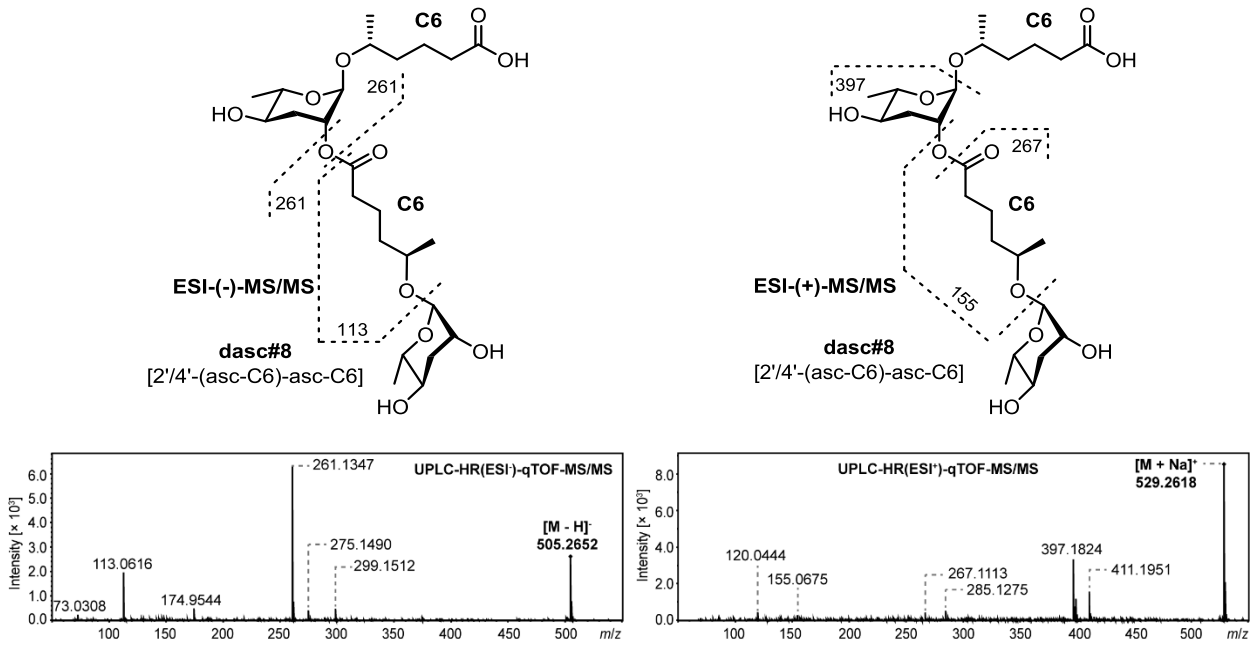
Figure 12. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#2 [2'/4'-(asc-C4)-asc-C4] in both negative and positive ion modes. Note that dasc#2 [2'/4'-(asc-C4)-asc-C4] is proposed and illustrated to be modified at the 2'-position, but its absolute structure has not yet been elucidated.



UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
491.2499	491.2498	-0.2	$C_{23}H_{39}O_{11}^-$
313.1663	313.1657	-2.0	$C_{16}H_{25}O_6^-$
275.1504	275.1500	-1.5	$C_{13}H_{23}O_6^-$
127.0771	127.0765	-4.9	$C_7H_{11}O_2^-$
85.0328	85.0295	-	$C_4H_5O_2^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+Na]^+$
515.2446	515.2463	3.3	$C_{23}H_{40}NaO_{11}^+$
429.2106	429.2095	-2.6	$C_{19}H_{34}NaO_9^+$
411.1987	411.1989	0.6	$C_{19}H_{32}NaO_8^+$
385.1824	385.1833	2.3	$C_{17}H_{30}NaO_8^+$
299.1470	299.1465	-1.6	$C_{13}H_{24}NaO_6^+$
268.1200	268.1179	-7.5	$C_{13}H_{18}NO_5^+$
250.1075	250.1074	-0.6	$C_{13}H_{16}NO_4^+$
151.0728	151.0730	1.1	$C_7H_{12}NaO_2^+$
127.0380	127.0366	-	$C_4H_8NaO_3^+$
113.0589	113.0573	-	$C_4H_{10}NaO_2^+$

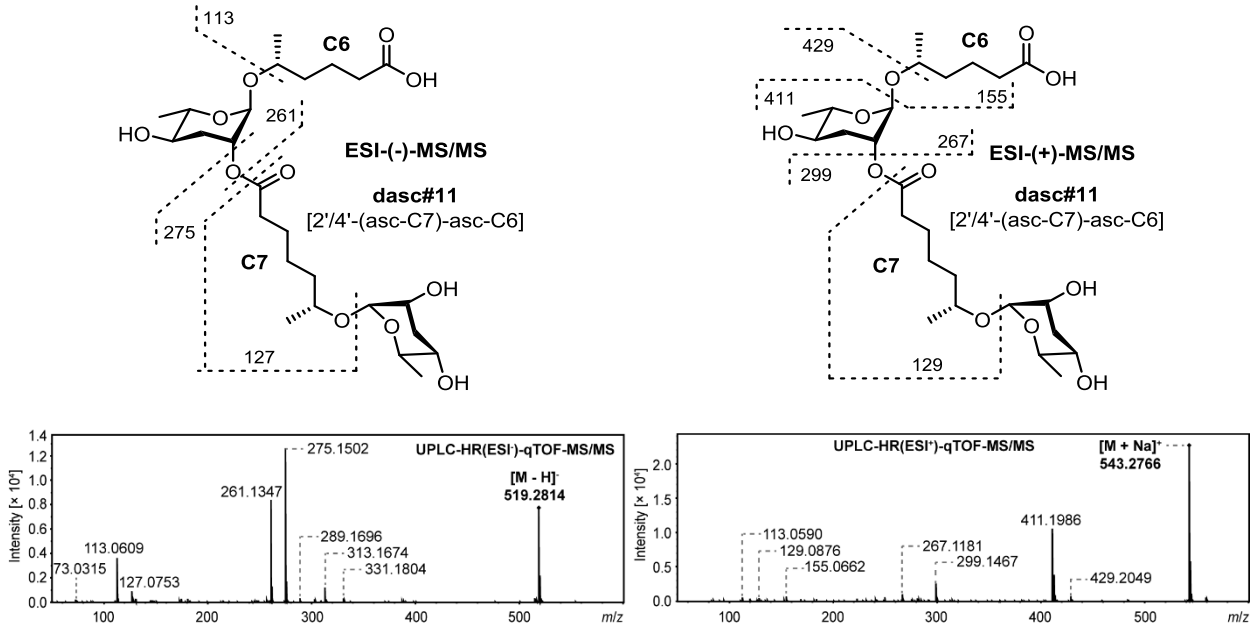
Figure 13. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#7 [2'/4'-(asc-C7)-asc-C4] in both negative and positive ion modes. Note that dasc#7 [2'/4'-(asc-C7)-asc-C4] is tentatively assigned to be linked at the 2'-position, but its absolute structure has not yet been elucidated.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
505.2652	505.2654	0.4	$C_{24}H_{41}O_{11}^-$
299.1512	299.1500	-4.1	$C_{15}H_{23}O_6^-$
275.1490	275.1500	3.6	$C_{13}H_{23}O_6^-$
261.1347	261.1344	-1.5	$C_{12}H_{21}O_6^-$
113.0616	113.0608	-	$C_6H_9O_2^-$
73.0308	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+Na]^+$
529.2618	529.2619	0.2	$C_{24}H_{42}NaO_{11}^+$
411.1951	411.1989	-	$C_{19}H_{32}NaO_8^+$
397.1824	397.1833	2.2	$C_{18}H_{30}NaO_8^+$
285.1275	285.1309	-	$C_{12}H_{22}NaO_6^+$
267.1113	267.1203	-	$C_{12}H_{20}NaO_5^+$
155.0675	155.0679	2.3	$C_6H_{12}NaO_3^+$

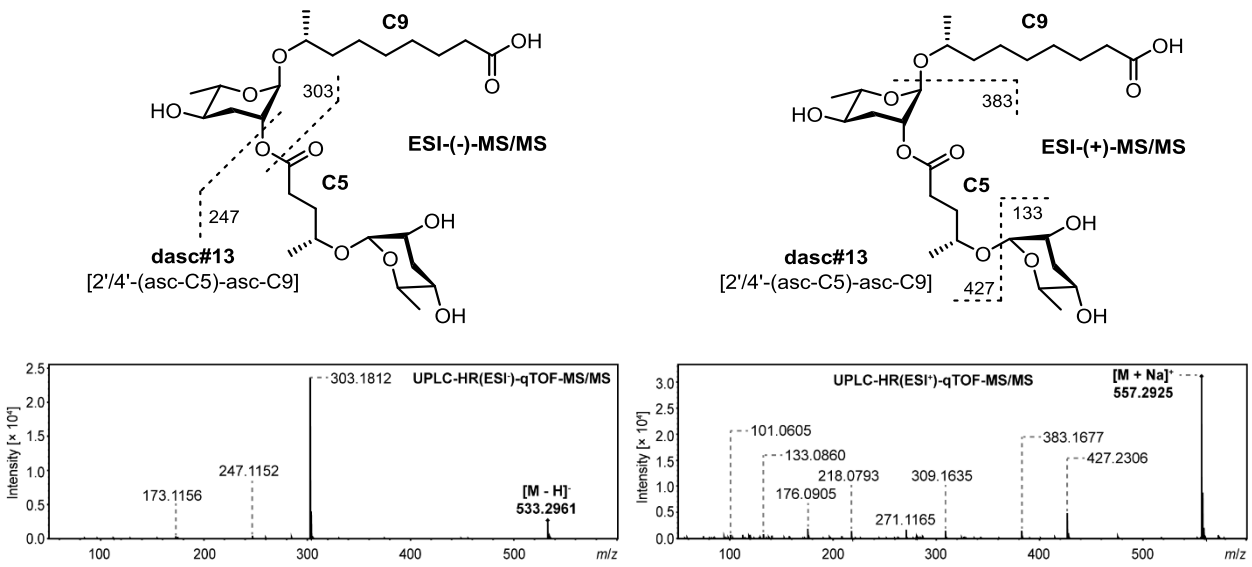
Figure 14. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#8 [2'/4'-(asc-C6)-asc-C6] in both negative and positive ion modes. Note that dasc#8 [2'/4'-(asc-C6)-asc-C6] is tentatively assigned to be linked at the 2'-position, but its absolute structure has not yet been elucidated.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
519.2814	519.2811	-0.6	$C_{25}H_{43}O_{11}^-$
331.1804	331.1762	-	$C_{16}H_{27}O_7^-$
313.1674	313.1657	-5.4	$C_{16}H_{25}O_6^-$
289.1696	289.1657	-	$C_{14}H_{25}O_6^-$
275.1502	275.1500	-0.7	$C_{13}H_{23}O_6^-$
261.1347	261.1344	-1.4	$C_{12}H_{21}O_6^-$
127.0753	127.0765	8.8	$C_7H_{11}O_2^-$
113.0609	113.0608	-1.3	$C_6H_9O_2^-$
73.0315	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+Na]^+$
543.2766	543.2776	1.7	$C_{25}H_{44}NaO_{11}^+$
429.2049	429.2095	-	$C_{19}H_{34}NaO_9^+$
411.1986	411.1989	0.7	$C_{19}H_{32}NaO_8^+$
299.1467	299.1465	-0.6	$C_{13}H_{24}NaO_6^+$
281.1377	281.1359	-6.1	$C_{13}H_{22}NaO_5^+$
267.1181	267.1203	-	$C_{12}H_{20}NaO_5^+$
155.0662	155.0679	-	$C_6H_{12}NaO_3^+$
129.0876	129.0910	-	$C_7H_{13}O_2^+$
113.0590	113.0597	-	$C_6H_9O_2^+$

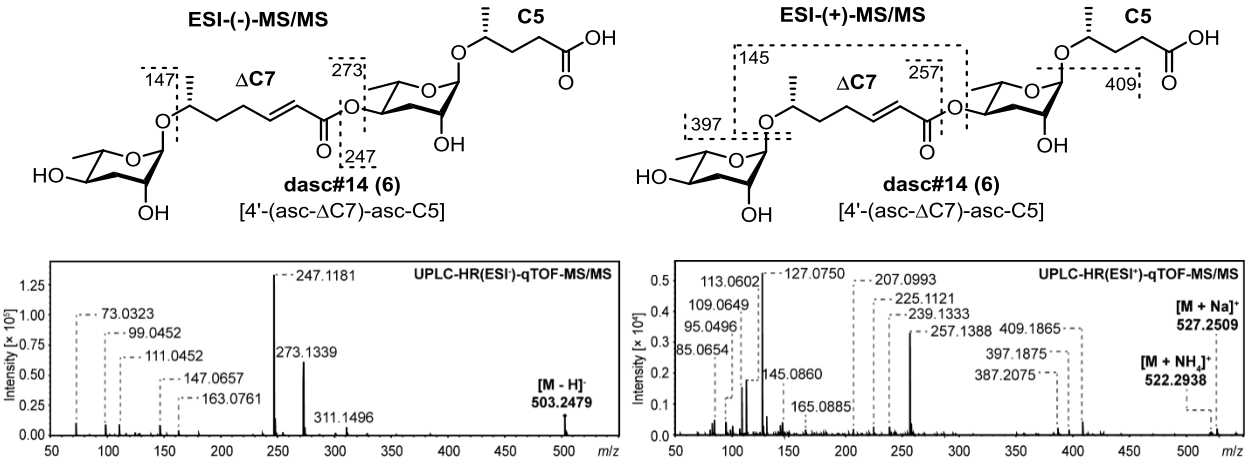
Figure 15. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#11 [2'/4'-(asc-C7)-asc-C6] in both negative and positive ion modes. Note that dasc#11 [2'/4'-(asc-C7)-asc-C6] is tentatively assigned to be linked at the 2'-position, but its absolute structure has not yet been elucidated.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
533.2961	533.2967	1.3	$C_{26}H_{45}O_{11}^-$
303.1812	303.1813	0.3	$C_{15}H_{27}O_6^-$
247.1152	247.1187	-	$C_{11}H_{19}O_6^-$
173.1156	173.1183	-	$C_9H_{17}O_3^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+Na]^+$
557.2925	557.2932	1.4	$C_{26}H_{46}N_aO_{11}^+$
427.2306	427.2302	-0.9	$C_{20}H_{36}N_aO_8^+$
383.1677	383.1676	-0.2	$C_{17}H_{28}N_aO_8^+$
309.1635	309.1672	-	$C_{15}H_{26}N_aO_5^+$
271.1165	271.1152	-4.7	$C_{11}H_{20}N_aO_6^+$
133.0860	133.0859	-0.4	$C_6H_{13}O_3^+$
113.0597	113.0597	-0.2	$C_6H_9O_2^+$

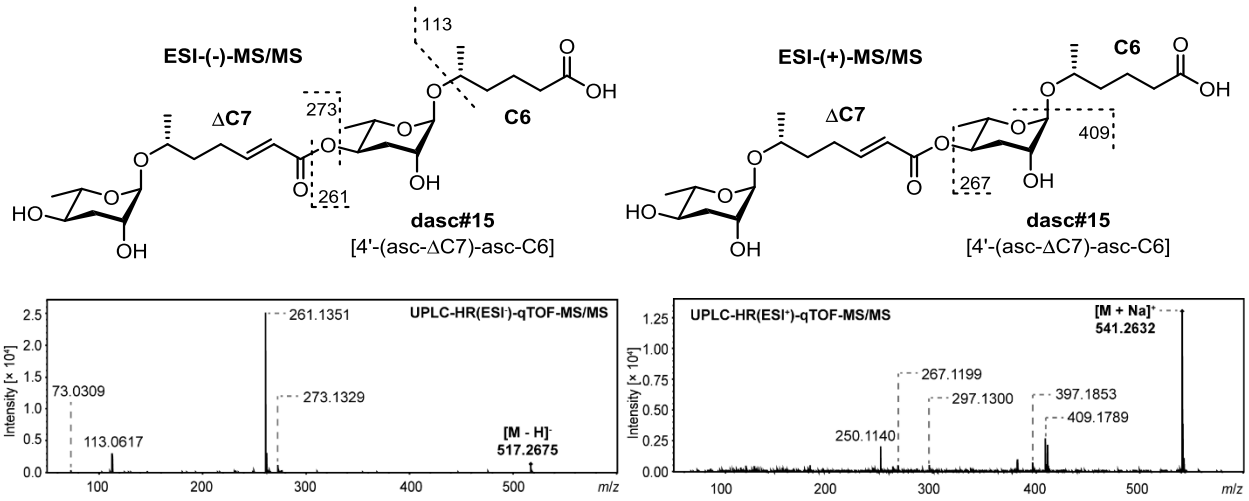
Figure 16. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#13 [2'/4'-(asc-C5)-asc-C9] in both negative and positive ion modes. Note that dasc#13 [2'/4'-(asc-C5)-asc-C9] is tentatively assigned to be linked at the 2'-position, but its absolute structure has not yet been elucidated.



UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
503.2479	503.2498	3.8	$C_{24}H_{39}O_{11}^-$
311.1496	311.1500	1.3	$C_{16}H_{23}O_6^-$
273.1339	273.1344	1.7	$C_{13}H_{21}O_6^-$
247.1181	247.1187	2.4	$C_{11}H_{19}O_6^-$
163.0761	163.0765	2.4	$C_{10}H_{11}O_2^-$
147.0657	147.0663	4.2	$C_6H_{11}O_4^-$
111.0452	111.0452	0.0	$C_6H_7O_2^-$
99.0452	99.0452	-0.1	$C_5H_7O_2^-$
73.0323	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+NH_4]^+$
522.2938	522.2909	-5.5	$C_{24}H_{44}NO_{11}^+$
409.1865	409.1833	-7.9	$C_{19}H_{30}NaO_8^+$
397.1875	397.1833	-	$C_{18}H_{30}NaO_8^+$
387.2075	387.2126	-	$C_{19}H_{31}O_8^+$
257.1388	257.1384	-1.6	$C_{13}H_{21}O_5^+$
239.1333	239.1278	-	$C_{13}H_{19}O_4^+$
225.1121	225.1121	0.1	$C_{10}H_{18}NaO_4^+$
207.0993	207.0992	-0.7	$C_{10}H_{16}NaO_3^+$
165.0885	165.0886	0.4	$C_8H_{14}NaO_2^+$
145.0860	145.0859	-0.8	$C_7H_{13}O_3^+$
127.0750	127.0754	2.9	$C_7H_{11}O_2^+$
113.0602	113.0597	-4.5	$C_6H_9O_2^+$
109.0649	109.0648	-1.1	$C_7H_9O^+$
95.0496	95.0491	-	$C_6H_7O^+$
85.0654	85.0648	-	$C_5H_9O^+$

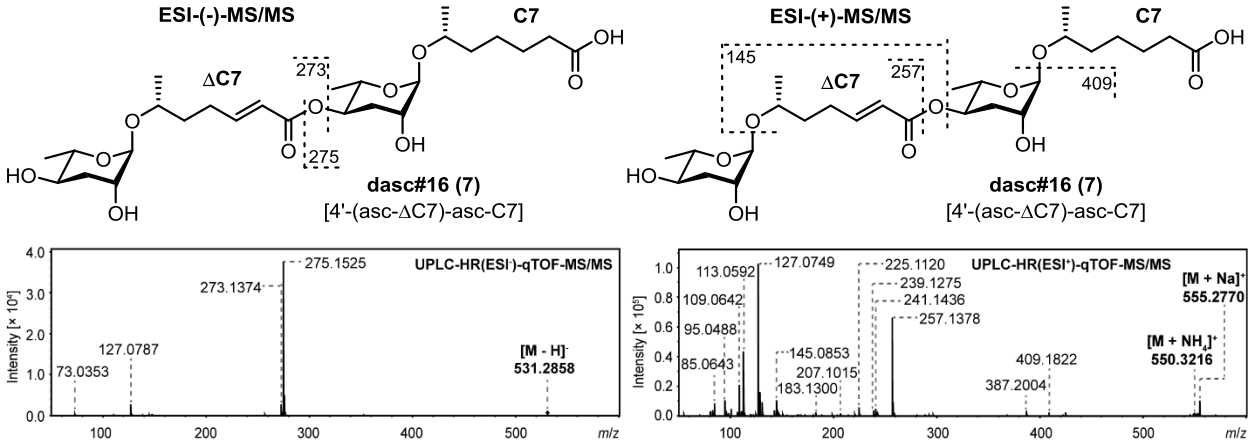
Figure 17. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#14 [4'-(asc-ΔC7)-asc-C5, **6**] in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M − H]$^-$
517.2675	517.2654	-4.1	$C_{25}H_{41}O_{11}^-$
273.1329	273.1344	5.4	$C_{13}H_{21}O_6^-$
261.1351	261.1344	-2.9	$C_{12}H_{21}O_6^-$
113.0617	113.0608	-	$C_6H_9O_2^-$
73.0309	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M + Na]$^+$
541.2632	541.2619	-2.3	$C_{25}H_{42}NaO_{11}^+$
409.1789	409.1833	-	$C_{19}H_{30}NaO_8^+$
397.1853	397.1833	-5.2	$C_{18}H_{30}NaO_8^+$
297.1300	297.1309	2.9	$C_{13}H_{22}NaO_6^+$
267.1199	267.1203	1.4	$C_{12}H_{20}NaO_5^+$

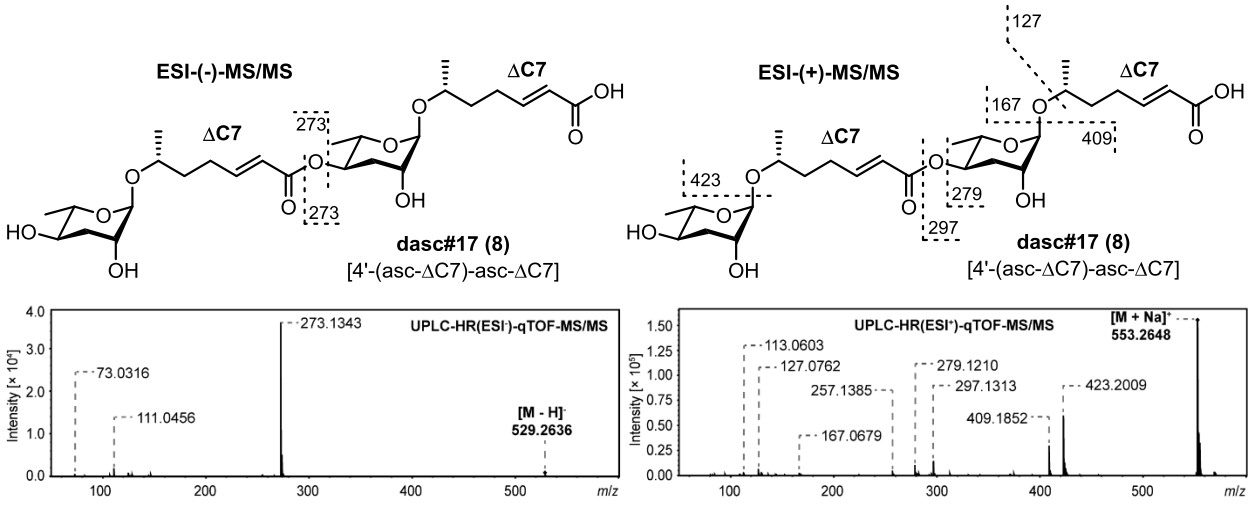
Figure 18. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#15 [4'-(asc-ΔC7)-asc-C6] in both negative and positive ion modes. Note that dasc#15 [4'-(asc-ΔC7)-asc-C6] is proposed to be linked at the 4'-position, but its absolute structure has not yet been elucidated.



UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
531.2858	531.2811	-8.8	$C_{26}H_{43}O_{11}^-$
275.1525	275.1500	-9.0	$C_{13}H_{23}O_6^-$
273.1374	273.1344	-	$C_{13}H_{21}O_6^-$
127.0787	127.0765	-	$C_7H_{11}O_2^-$
73.0353	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+NH_4]^+$
550.3216	550.3222	1.0	$C_{26}H_{48}NO_{11}^+$
555.2770	555.2776	1.0	$C_{26}H_{44}NaO_{11}^+$
409.1822	409.1833	2.6	$C_{19}H_{30}NaO_8^+$
387.2004	387.2013	2.4	$C_{19}H_{31}O_8^+$
257.1378	257.1384	2.1	$C_{13}H_{21}O_5^+$
241.1436	241.1434	-0.7	$C_{13}H_{21}O_4^+$
239.1275	239.1278	1.0	$C_{13}H_{19}O_4^+$
225.1120	225.1121	0.7	$C_{12}H_{17}O_4^+$
207.1015	207.0992	0.5	$C_{12}H_{15}O_3^+$
145.0853	145.0859	4.2	$C_7H_{13}O_3^+$
127.0749	127.0754	4.0	$C_7H_{11}O_2^+$
113.0592	113.0597	4.5	$C_6H_9O_2^+$
109.0642	109.0648	5.9	$C_7H_9O^+$
95.0488	95.0491	3.3	$C_6H_7O^+$
85.0643	85.0648	5.3	$C_5H_9O^+$

Figure 19. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#16 [4'-(asc-ΔC7)-asc-C7, **7**] in both negative and positive ion modes.

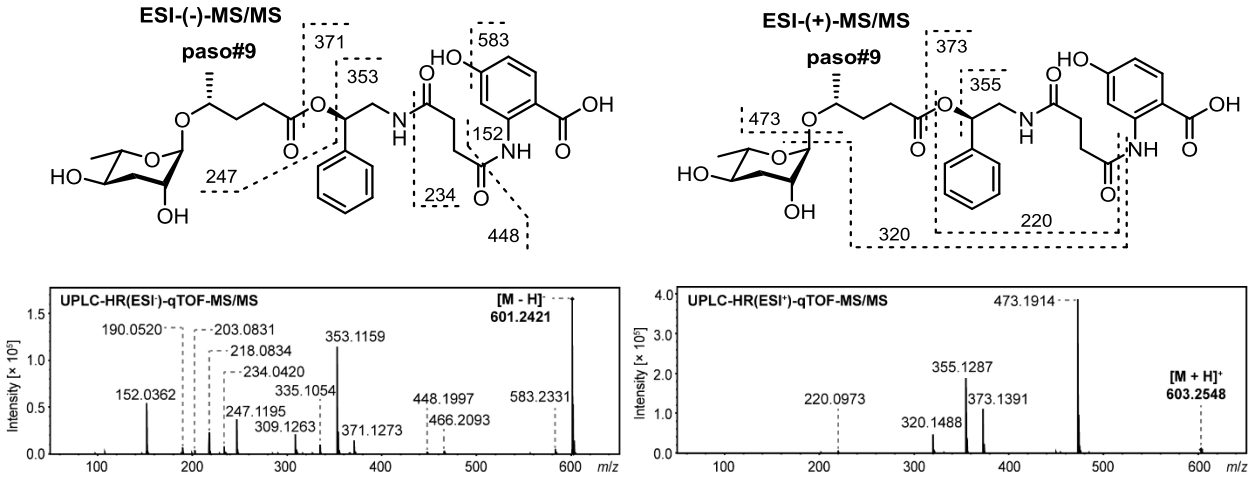


UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
529.2636	529.2654	3.5	$C_{26}H_{41}O_{11}^-$
273.1343	273.1344	0.3	$C_{13}H_{21}O_6^-$
111.0456	111.0452	-4.2	$C_6H_7O_2^-$
73.0316	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+Na]^+$
553.2648	552.2619	-5.2	$C_{26}H_{42}NaO_{11}^+$
423.2009	423.2013	-4.6	$C_{20}H_{32}NaO_8^+$
409.1852	409.1833	-4.7	$C_{19}H_{30}NaO_8^+$
297.1313	297.1309	-1.5	$C_{13}H_{22}NaO_6^+$
279.1210	279.1203	-2.5	$C_{13}H_{20}NaO_5^+$
257.1385	257.1384	-0.6	$C_{13}H_{21}O_5^+$
167.0679	167.0679	-0.2	$C_7H_{13}NaO_3^+$
127.0762	127.0754	-6.4	$C_7H_{11}O_2^+$
113.0603	113.0597	-5.4	$C_6H_9O_2^+$

Figure 20. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of dasc#17 [4'-(asc-ΔC7)-asc-ΔC7, **8**] in both negative and positive ion modes.

supplementary file 2b: MS/MS spectral data of paso#9 Pages

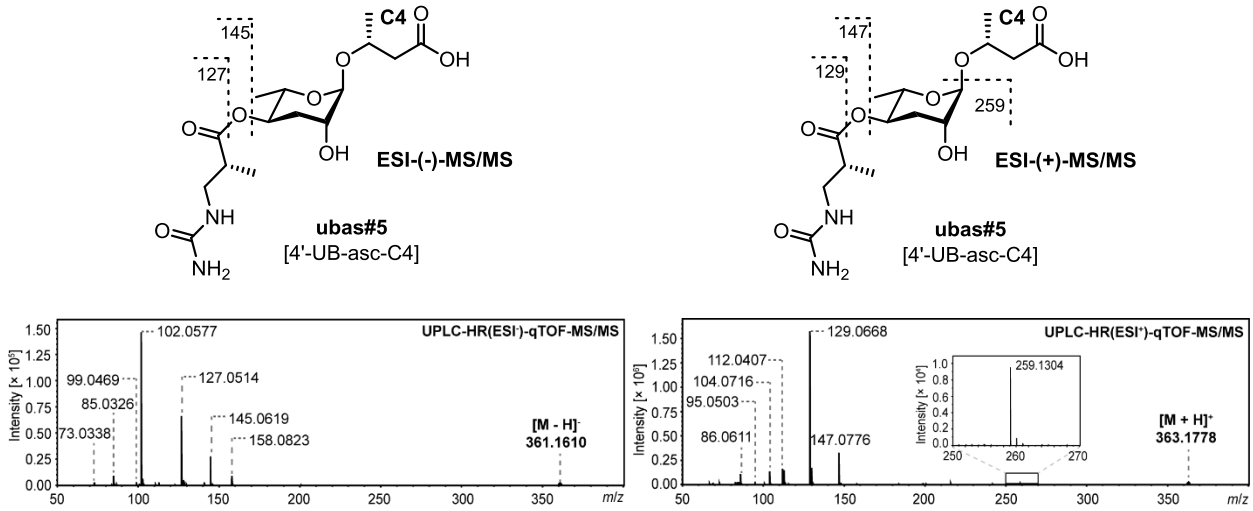


UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
601.2421	601.2403	-1.9	$C_{30}H_{37}N_2O_{11}^-$
583.2331	583.2297	-3.3	$C_{30}H_{35}N_2O_{10}^-$
466.2093	466.2083	-1.0	$C_{23}H_{32}NO_9^-$
448.1997	448.1977	-2.0	$C_{23}H_{30}NO_8^-$
371.1273	371.1249	-2.5	$C_{19}H_{19}N_2O_6^-$
353.1159	353.1143	-1.6	$C_{19}H_{17}N_2O_5^-$
335.1054	335.1037	-1.7	$C_{19}H_{15}N_2O_4^-$
309.1263	309.1245	-1.8	$C_{18}H_{17}N_2O_3^-$
247.1195	247.1187	-0.8	$C_{11}H_{19}O_6^-$
234.0420	234.0408	-1.2	$C_{11}H_8NO_5^-$
218.0834	218.0823	-1.2	$C_{12}H_{12}NO_3^-$
203.0831	203.0826	-0.5	$C_{11}H_{11}N_2O_2^-$
190.0520	190.0510	-1.1	$C_{10}H_8NO_3^-$
152.0362	152.0353	-0.9	$C_7H_6NO_3^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+H]^+$
603.2548	603.2548	0.1	$C_{30}H_{39}N_2O_{11}^+$
473.1914	473.1918	0.4	$C_{24}H_{29}N_2O_8^+$
373.1391	373.1394	0.4	$C_{19}H_{21}N_2O_6^+$
355.1287	355.1288	0.2	$C_{19}H_{19}N_2O_5^+$
320.1488	320.1492	0.5	$C_{17}H_{22}NO_5^+$
220.0973	220.0968	-0.5	$C_{12}H_{14}NO_3^+$

Figure 1. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of paso#9 in both negative and positive ion modes. Analysis of NMR data of paso#9 suggests a 4-hydroxyanthranilic acid moiety in paso#9 (***supplementary file 1c – Figures 5-13*** and ***supplementary file 3 – Table 14***).

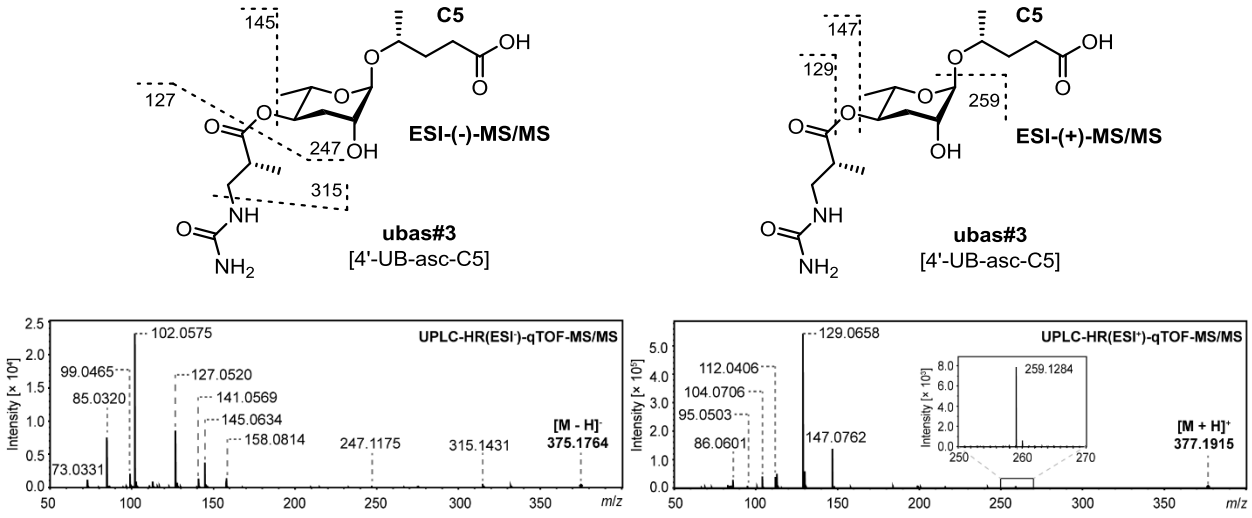
supplementary file 2c: MS/MS spectral data of UBAS chemicals Pages



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M − H]$^-$
361.1610	361.1616	1.9	$C_{15}H_{25}N_2O_8^-$
158.0823	158.0823	-0.2	$C_7H_{12}NO_3^-$
145.0619	145.0619	-0.2	$C_5H_9N_2O_3^-$
127.0514	127.0513	-0.5	$C_5H_7N_2O_2^-$
102.0577	102.0561	-	$C_4H_8NO_2^-$
99.0469	99.0452	-	$C_5H_7O_2^-$
85.0326	85.0295	-	$C_4H_5O_2^-$
73.0338	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M + H]$^+$
363.1778	363.1762	-4.4	$C_{15}H_{27}N_2O_8^+$
259.1304	259.1288	-6.1	$C_{11}H_{19}N_2O_5^+$
147.0776	147.0764	-8.3	$C_5H_{11}N_2O_3^+$
129.0668	129.0659	-7.5	$C_5H_9N_2O_2^+$
112.0407	112.0393	-	$C_5H_6NO_2^+$
104.0716	104.0706	-	$C_4H_{10}NO_2^+$
95.0503	95.0491	-	$C_6H_7O^+$
86.0611	86.0600	-	$C_4H_8NO^+$

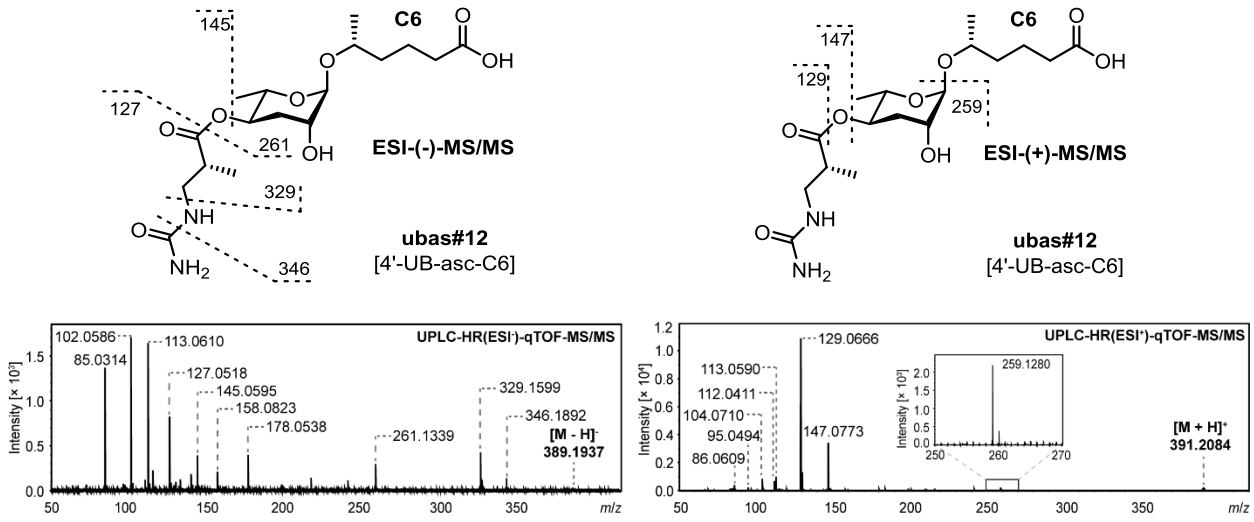
Figure 1. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of known ubas#5 [4'-UB-asc-C4] (***Falcke et al., 2018***) from *P. pacificus* in both negative and positive ion modes. Characteristic ion signal for *m*/*z* 259.1304 containing an ureidoisobutyric acid moiety and an ascarylose unit was used for targeted MS/MS screening. *P. triformis* also produced large amounts of ubas#5 [4'-UB-asc-C4] (***supplementary file 1d – Figures 30-35***).



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M − H]$^-$
375.1764	375.1773	2.3	$C_{16}H_{27}N_2O_8^-$
315.1431	315.1449	5.8	$C_{15}H_{23}O_7^-$
247.1175	247.1187	4.8	$C_{11}H_{19}O_6^-$
158.0814	158.0823	5.3	$C_7H_{12}NO_3^-$
145.0634	145.0619	-	$C_5H_9N_2O_3^-$
141.0569	141.0557	-	$C_7H_9O_3^-$
127.0520	127.0513	-5.8	$C_5H_7N_2O_2^-$
102.0575	102.0561	-	$C_4H_8NO_2^-$
99.0465	99.0452	-	$C_5H_7O_2^-$
85.0320	85.0295	-	$C_4H_5O_2^-$
73.0331	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M + H]$^+$
377.1915	377.1918	0.8	$C_{16}H_{29}N_2O_8^+$
259.1284	259.1288	1.6	$C_{11}H_{19}N_2O_5^+$
147.0762	147.0764	1.5	$C_5H_{11}N_2O_3^+$
129.0658	129.0659	0.6	$C_5H_9N_2O_2^+$
112.0406	112.0393	-	$C_5H_6NO_2^+$
104.0706	104.0706	-0.4	$C_4H_{10}NO_2^+$
95.0503	95.0491	-	$C_6H_7O^+$
86.0601	86.0600	-0.3	$C_4H_8NO^+$

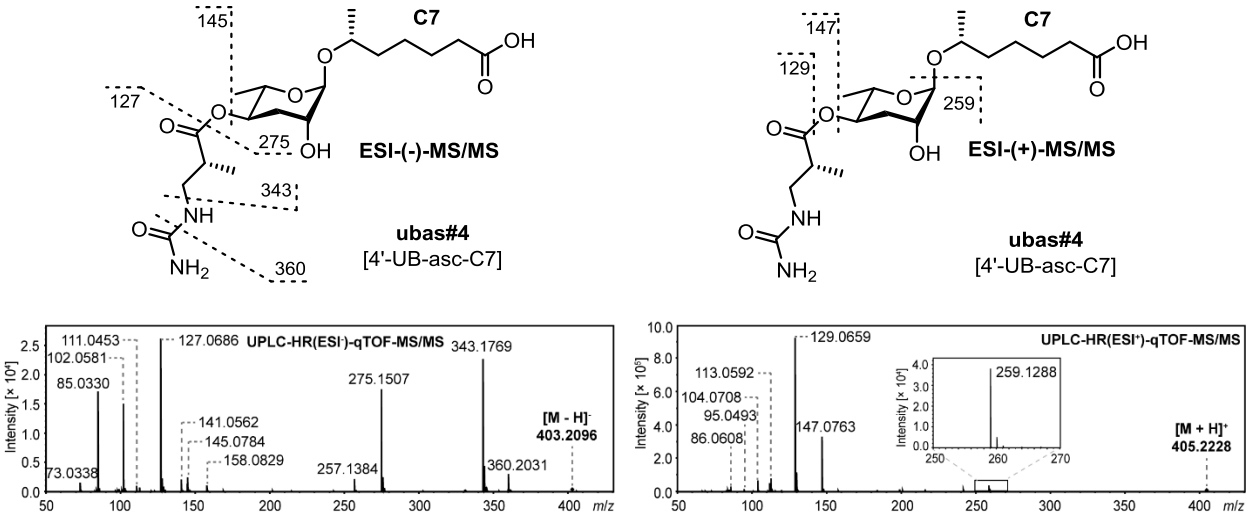
Figure 2. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of known ubas#3 [4'-UB-asc-C5] (***Falcke et al., 2018***) from *P. pacificus* in both negative and positive ion modes. Characteristic ion signal for *m*/*z* 259.1304 containing an ureidoisobutyric acid moiety and an ascarylose unit was used for targeted MS/MS screening.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
389.1937	389.1929	-2.0	$C_{17}H_{29}N_2O_8^-$
346.1892	346.1871	-6.0	$C_{16}H_{28}NO_7^-$
329.1599	329.1606	2.0	$C_{16}H_{25}O_7^-$
261.1339	261.1344	1.6	$C_{12}H_{21}O_6^-$
178.0538	178.0510	-	$C_9H_8NO_3^-$
158.0823	158.0823	0.0	$C_7H_{12}NO_3^-$
145.0595	145.0619	-	$C_5H_9N_2O_3^-$
127.0518	127.0513	-4.3	$C_5H_7N_2O_2^-$
113.0610	113.0608	-1.3	$C_6H_9O_2^-$
102.0586	102.0561	-	$C_4H_8NO_2^-$
85.0314	85.0295	-	$C_4H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+H]^+$
391.2084	391.2075	-2.3	$C_{17}H_{31}N_2O_8^+$
259.1280	259.1288	3.1	$C_{11}H_{19}N_2O_5^+$
147.0773	147.0764	-6.2	$C_5H_{11}N_2O_3^+$
129.0666	129.0659	-5.8	$C_5H_9N_2O_2^+$
113.0590	113.0597	6.0	$C_6H_9O_2^+$
112.0411	112.0393	-	$C_5H_6NO_2^+$
104.0710	104.0706	-3.5	$C_4H_{10}NO_2^+$
95.0494	95.0491	-2.3	$C_6H_7O^+$
86.0609	86.0600	-	$C_4H_8NO^+$

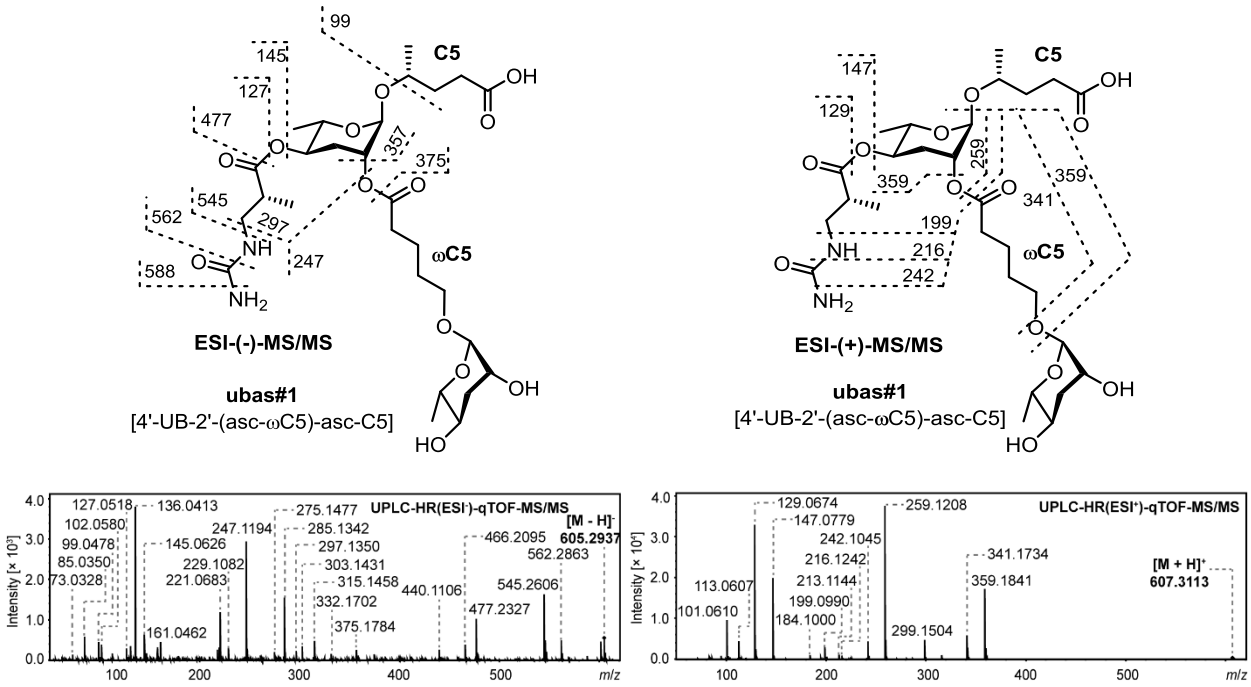
Figure 3. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of known ubas#12 [4'-UB-asc-C6] (***Falcke et al., 2018***) from *P. pacificus* in both negative and positive ion modes. Characteristic ion signal for *m*/*z* 259.1304 containing an ureidoisobutyric acid moiety and an ascarylose unit was used for targeted MS/MS screening.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
403.2096	403.2086	0.0	$C_{18}H_{31}N_2O_8^-$
360.2031	360.2028	-0.8	$C_{17}H_{30}NO_7^-$
343.1769	343.1762	-2.0	$C_{17}H_{27}O_7^-$
275.1507	275.1500	-2.6	$C_{13}H_{23}O_6^-$
257.1384	257.1394	3.9	$C_{13}H_{21}O_5^-$
158.0829	158.0823	-3.7	$C_7H_{12}NO_3^-$
145.0784	145.0619	-	$C_5H_9N_2O_3^-$
141.0562	141.0557	-3.4	$C_7H_9O_3^-$
127.0686	127.0513	-	$C_5H_7N_2O_2^-$
111.0453	111.0452	-1.5	$C_6H_7O_2^-$
102.0581	102.0561	-	$C_4H_8NO_2^-$
85.0330	85.0295	-	$C_4H_5O_2^-$
73.0338	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+H]^+$
405.2228	405.2231	0.8	$C_{18}H_{33}N_2O_8^+$
259.1288	259.1288	0.3	$C_{11}H_{19}N_2O_5^+$
147.0763	147.0764	0.7	$C_5H_{11}N_2O_3^+$
129.0659	129.0659	0.0	$C_5H_9N_2O_2^+$
113.0592	113.0597	4.1	$C_6H_9O_2^+$
104.0708	104.0706	-1.8	$C_4H_{10}NO_2^+$
95.0493	95.0491	-1.2	$C_6H_7O^+$
86.0608	86.0600	-	$C_4H_8NO^+$

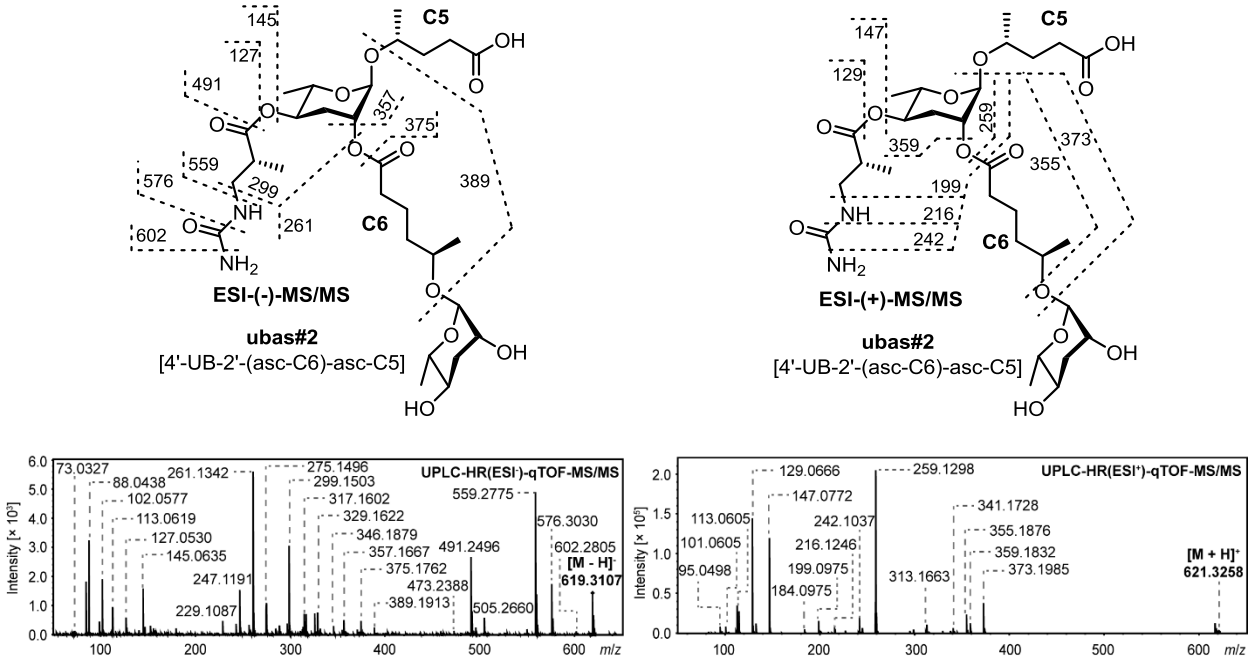
Figure 4. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of known ubas#4 [4'-UB-asc-C7] (***Falcke et al., 2018***) from *P. pacificus* in both negative and positive ion modes. Characteristic ion signal for *m*/*z* 259.1304 containing an ureidoisobutyric acid moiety and an ascarylose unit was used for targeted MS/MS screening.



UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula [M − H]⁻
605.2937	605.2927	-1.7	$C_{27}H_{45}N_2O_{13}^-$
588.2668	588.2662	-1.2	$C_{27}H_{42}NO_{13}^-$
562.2863	562.2869	-5.1	$C_{26}H_{44}NO_{12}^-$
545.2606	545.2604	-0.4	$C_{26}H_{41}O_{12}^-$
477.2327	477.2341	2.9	$C_{22}H_{37}O_{11}^-$
466.2095	466.2083	-2.6	$C_{23}H_{32}NO_9^-$
440.1106	440.1198	20.9	$C_{19}H_{22}NO_{11}^-$
375.1784	375.1773	-3.1	$C_{16}H_{27}N_2O_8^-$
357.1662	357.1667	1.5	$C_{16}H_{25}N_2O_7^-$
332.1702	332.1715	3.7	$C_{15}H_{26}NO_7^-$
315.1458	315.1449	-2.8	$C_{15}H_{23}O_7^-$
303.1431	303.1449	6.1	$C_{14}H_{23}O_7^-$
297.1350	297.1344	-2.2	$C_{15}H_{21}O_6^-$
285.1342	285.1344	0.7	$C_{14}H_{21}O_6^-$
275.1477	275.1500	8.3	$C_{13}H_{23}O_6^-$
247.1194	247.1187	-2.8	$C_{11}H_{19}O_6^-$
229.1082	229.1081	-0.2	$C_{11}H_{17}O_5^-$
221.0683	221.0667	-7.5	$C_8H_{13}O_7^-$
161.0462	161.0455	-4.2	$C_6H_9O_5^-$
145.0626	145.0619	-5.0	$C_5H_9N_2O_3^-$
127.0518	127.0513	-3.9	$C_5H_7N_2O_2^-$
102.0580	102.0561	-	$C_4H_8NO_2^-$
99.0478	99.0452	-	$C_5H_7O_2^-$
85.0350	85.0295	-	$C_4H_5O_2^-$
73.0328	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula [M + H]⁺
607.3113	607.3073	-6.7	$C_{27}H_{47}N_2O_{13}^+$
359.1841	359.1813	-7.9	$C_{16}H_{27}N_2O_7^+$
341.1734	341.1707	-7.8	$C_{16}H_{25}N_2O_6^+$
316.1771	316.1755	-5.1	$C_{16}H_{26}NO_6^+$
299.1504	299.1489	-5.0	$C_{15}H_{23}O_6^+$
259.1208	259.1288	-7.6	$C_{11}H_{19}N_2O_5^+$
242.1045	242.1023	-9.3	$C_{11}H_{16}NO_5^+$
216.1242	216.1230	-5.5	$C_{10}H_{18}NO_4^+$
213.1144	213.1234	-	$C_{10}H_{17}N_2O_3^+$
199.0990	199.0965	-	$C_{10}H_{15}O_4^+$
184.1000	184.0968	-	$C_9H_{14}NO_3^+$
147.0779	147.0764	-	$C_5H_{11}N_2O_3^+$
129.0674	129.0659	-3.5	$C_5H_9N_2O_2^+$
113.0607	113.0597	-4.0	$C_6H_9O_2^+$
101.0610	101.0597	-	$C_5H_9O_2^+$

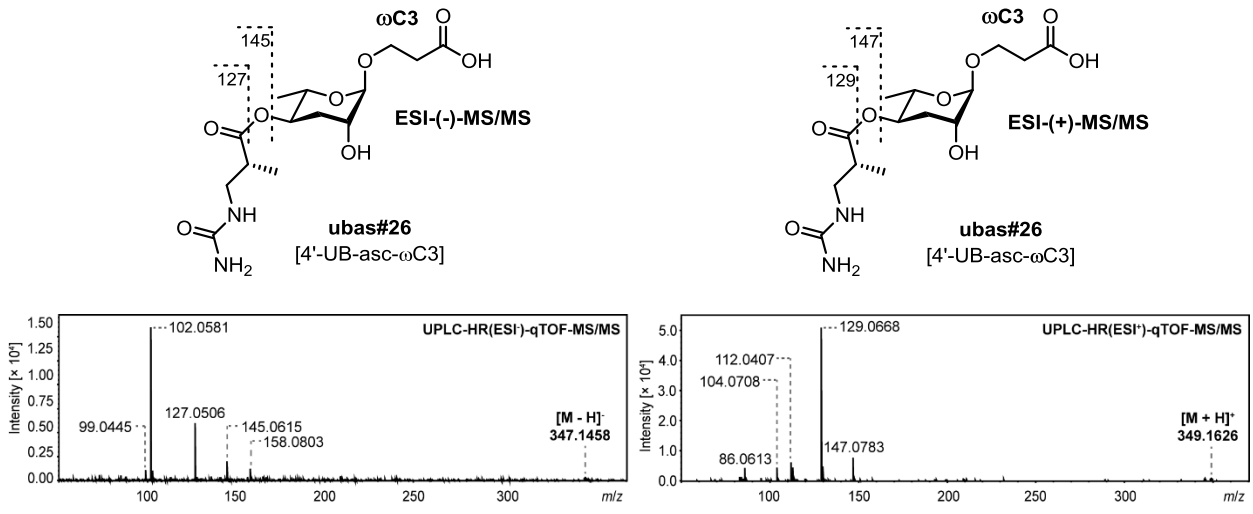
Figure 5. UPLC-HR(ESI⁻/⁺)-qTOF-MS/MS mass spectral data of known ubas#1 [4'-UB-2'-(asc-ωC5)-asc-C5) (***supplementary file 1d – Figures 9-10***) (***Bose et al., 2012***) from *P. pacificus*.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M − H]$^-$
619.3107	619.3084	-3.8	$C_{28}H_{47}N_2O_{13}^-$
602.2805	602.2818	2.2	$C_{28}H_{44}NO_{13}^-$
576.3030	576.3025	-0.7	$C_{27}H_{46}NO_{12}^-$
559.2775	559.2750	-2.6	$C_{27}H_{43}O_{12}^-$
505.2660	505.2654	-1.2	$C_{24}H_{41}O_{11}^-$
491.2496	491.2498	0.4	$C_{23}H_{39}O_{11}^-$
473.2388	473.2392	0.9	$C_{23}H_{37}O_{10}^-$
389.1913	389.1929	4.3	$C_{17}H_{29}N_2O_8^-$
375.1762	375.1773	2.9	$C_{16}H_{27}N_2O_8^-$
357.1667	357.1667	0.1	$C_{16}H_{25}N_2O_7^-$
346.1879	346.1871	-2.4	$C_{16}H_{28}NO_7^-$
329.1622	329.1606	-4.9	$C_{16}H_{25}O_7^-$
317.1602	317.1606	1.2	$C_{15}H_{25}O_7^-$
299.1503	299.1500	-1.1	$C_{15}H_{23}O_6^-$
275.1496	275.1500	1.4	$C_{13}H_{23}O_6^-$
261.1342	261.1344	0.5	$C_{12}H_{21}O_6^-$
247.1191	247.1187	-1.4	$C_{11}H_{19}O_6^-$
229.1087	229.1081	-2.6	$C_{11}H_{17}O_5^-$
145.0635	145.0619	-	$C_5H_9N_2O_3^-$
127.0530	127.0513	-	$C_5H_7N_2O_2^-$
113.0619	113.0608	-	$C_6H_9O_2^-$
102.0577	102.0561	-	$C_4H_8NO_2^-$
88.0438	88.0404	-	$C_3H_6NO_2^-$
73.0327	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M + H]$^+$
621.3258	621.3229	-4.7	$C_{28}H_{49}N_2O_{13}^+$
373.1985	373.1969	-4.2	$C_{17}H_{29}N_2O_7^+$
359.1832	359.1813	-5.3	$C_{16}H_{27}N_2O_7^+$
355.1876	355.1864	-3.6	$C_{17}H_{27}N_2O_6^+$
341.1728	341.1707	-6.1	$C_{16}H_{25}N_2O_6^+$
313.1663	313.1646	-5.7	$C_{16}H_{25}O_6^+$
259.1298	259.1288	-3.6	$C_{11}H_{19}N_2O_5^+$
242.1037	242.1023	-5.6	$C_{11}H_{16}NO_5^+$
216.1246	216.1230	-7.5	$C_{10}H_{18}NO_4^+$
199.0975	199.0965	-5.2	$C_{10}H_{15}O_4^+$
184.0975	184.0968	-3.8	$C_9H_{14}NO_3^+$
147.0772	147.0764	-5.4	$C_5H_{11}N_2O_3^+$
129.0666	129.0659	-6.1	$C_5H_9N_2O_2^+$
113.0605	113.0597	-6.8	$C_6H_9O_2^+$
101.0605	101.0597	-8.2	$C_5H_9O_2^+$
95.0498	95.0491	-6.6	$C_6H_7O^+$

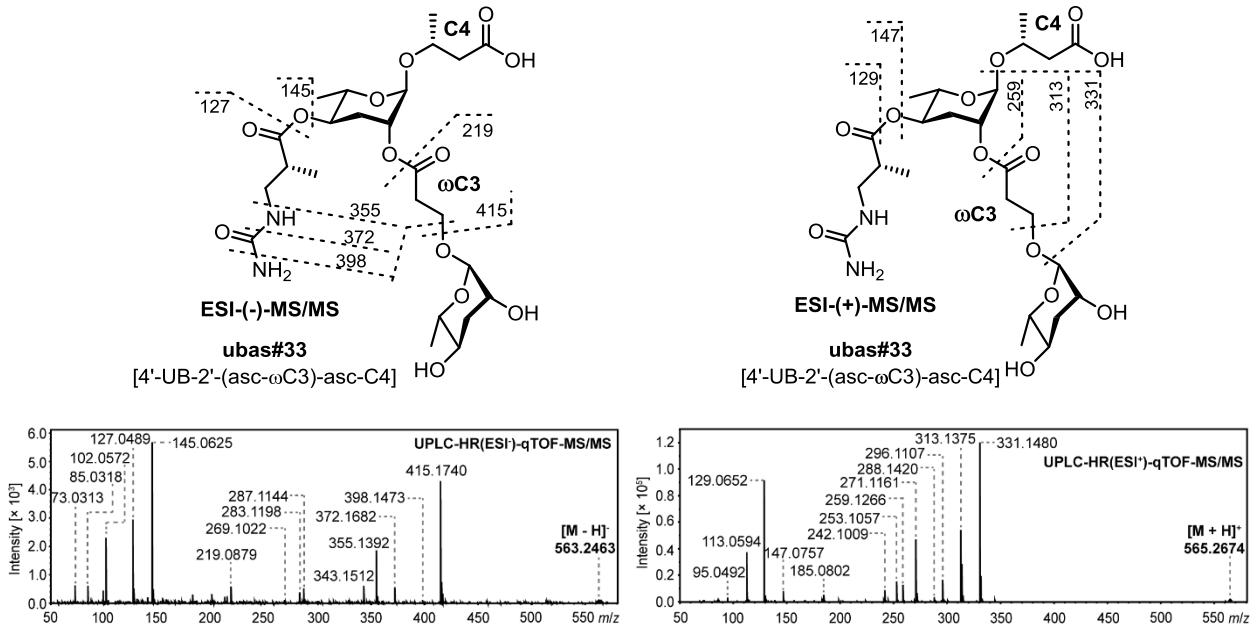
Figure 6. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of known ubas#2 [4'-UB-2'-(asc-C6)-asc-C5) (***Bose et al., 2012***) from *P. pacificus* in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
347.1458	347.1460	0.6	$C_{14}H_{23}N_2O_8^-$
158.0803	158.0823	12.1	$C_7H_{12}NO_3^-$
145.0615	145.0619	2.2	$C_5H_9N_2O_3^-$
127.0506	127.0513	5.6	$C_5H_7N_2O_2^-$
102.0581	102.0561	-	$C_4H_8NO_2^-$
99.0445	99.0452	-	$C_5H_7O_2^-$
85.0307	85.0295	-	$C_4H_5O_2^-$
73.0347	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+H]^+$
349.1626	349.1605	-5.8	$C_{14}H_{25}N_2O_8^+$
147.0783	147.0764	-12.7	$C_5H_{11}N_2O_3^+$
129.0668	129.0659	-7.7	$C_5H_9N_2O_2^+$
112.0407	112.0393	-12.2	$C_5H_6NO_2^+$
104.0708	104.0706	-2.3	$C_4H_{10}NO_2^+$
86.0613	86.0600	-	$C_4H_8NO^+$

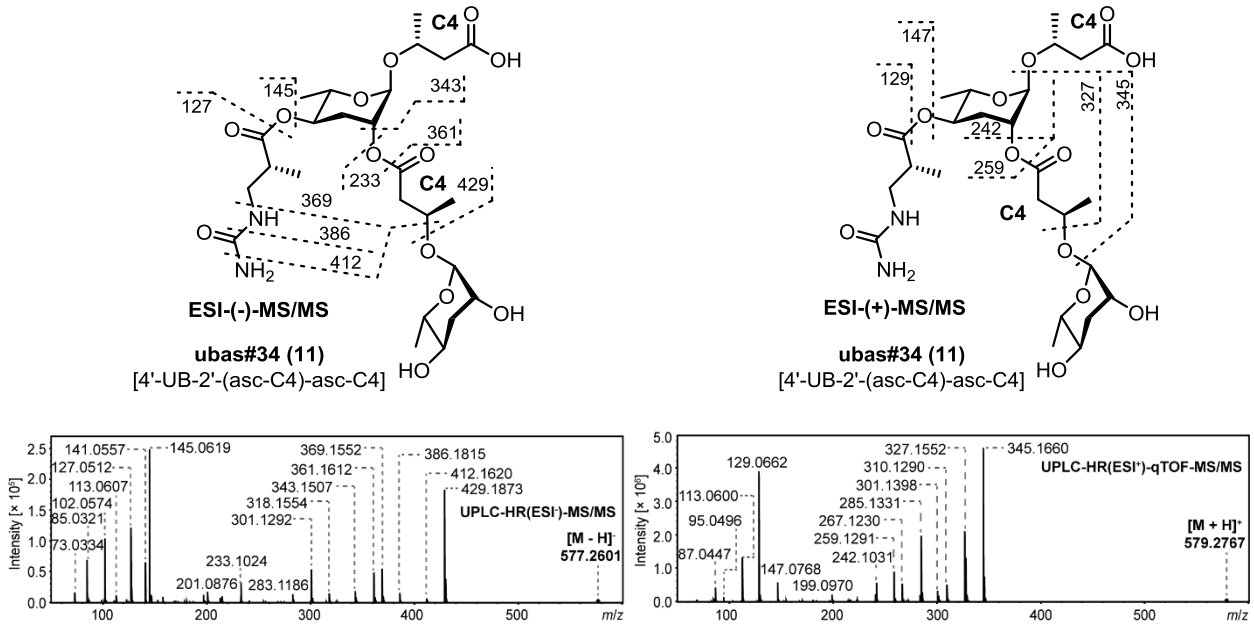
Figure 7. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of newly identified ubas#26 [4'-UB-asc-ωC3] in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
563.2463	563.2458	-1.0	$C_{24}H_{39}N_2O_{13}^-$
415.1740	415.1722	-4.3	$C_{18}H_{27}N_2O_9^-$
398.1473	398.1457	-4.1	$C_{18}H_{23}NO_9^-$
372.1682	372.1664	-4.9	$C_{17}H_{26}NO_8^-$
355.1392	355.1398	1.7	$C_{17}H_{23}O_8^-$
343.1512	347.1511	-0.3	$C_{15}H_{23}N_2O_7^-$
287.1144	287.1136	-2.8	$C_{13}H_{19}O_7^-$
283.1198	283.1187	-3.8	$C_{14}H_{19}O_6^-$
269.1022	269.1031	3.2	$C_{13}H_{17}O_6^-$
219.0879	219.0874	-2.1	$C_9H_{15}O_6^-$
145.0625	145.0619	-4.2	$C_5H_9N_2O_3^-$
127.0489	127.0513	-	$C_5H_7N_2O_2^-$
102.0572	102.0561	-	$C_4H_8NO_2^-$
85.0318	85.0295	-	$C_4H_5O_2^-$
73.0313	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+H]^+$
565.2674	565.2603	5.1	$C_{24}H_{41}N_2O_{13}^+$
331.1480	331.1500	6.0	$C_{14}H_{23}N_2O_7^+$
313.1375	313.1394	6.2	$C_{14}H_{21}N_2O_6^+$
296.1107	296.1129	7.2	$C_{14}H_{18}NO_6^+$
288.1420	288.1442	7.4	$C_{13}H_{22}NO_6^+$
271.1161	271.1176	5.5	$C_{13}H_{19}O_6^+$
259.1266	259.1288	8.7	$C_{11}H_{19}N_2O_5^+$
253.1057	253.1071	5.5	$C_{13}H_{17}O_5^+$
242.1009	242.1023	5.6	$C_{11}H_{16}NO_5^+$
185.0802	185.0808	3.5	$C_9H_{13}O_4^+$
147.0757	147.0764	5.2	$C_5H_{11}N_2O_3^+$
129.0652	129.0659	5.1	$C_5H_9N_2O_2^+$
113.0594	113.0597	3.0	$C_6H_9O_2^+$
95.0492	95.0491	-0.9	$C_6H_7O^+$

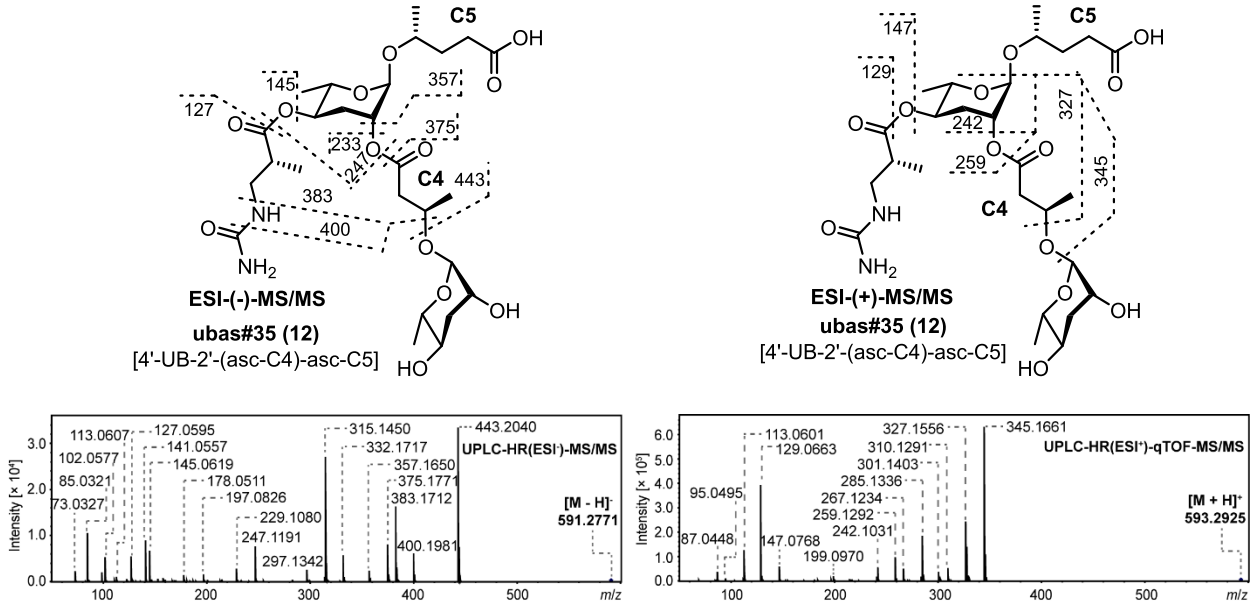
Figure 8. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#33 [4'-UB-2'-(asc-ωC3)-asc-C4] in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
577.2601	577.2614	-2.3	$C_{25}H_{41}N_2O_{13}^-$
429.1873	429.1879	1.3	$C_{19}H_{29}N_2O_9^-$
412.1620	412.1613	-1.7	$C_{19}H_{26}NO_9^-$
386.1815	386.1820	1.3	$C_{18}H_{28}NO_8^-$
369.1552	369.1555	0.8	$C_{18}H_{25}O_8^-$
361.1612	361.1616	1.2	$C_{15}H_{25}N_2O_8^-$
343.1507	343.1511	1.0	$C_{15}H_{23}N_2O_7^-$
318.1554	318.1558	1.2	$C_{14}H_{24}NO_7^-$
301.1292	301.1293	0.1	$C_{14}H_{21}O_7^-$
283.1186	283.1187	0.5	$C_{14}H_{19}O_6^-$
233.1024	233.1031	2.7	$C_{10}H_{17}O_6^-$
201.0876	201.0881	2.4	$C_8H_{13}N_2O_4^-$
145.0619	145.0619	0.0	$C_5H_9N_2O_3^-$
141.0557	141.0557	0.0	$C_5H_9O_3^-$
127.0512	127.0513	0.6	$C_5H_7N_2O_2^-$
113.0607	113.0608	0.9	$C_6H_9O_2^-$
102.0574	102.0561	-	$C_4H_8NO_2^-$
85.0321	85.0295	-	$C_4H_5O_2^-$
73.0334	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+H]^+$
579.2767	579.2760	-1.2	$C_{25}H_{43}N_2O_{13}^+$
345.1660	345.1656	-1.0	$C_{15}H_{25}N_2O_7^+$
327.1552	327.1551	-0.4	$C_{15}H_{23}N_2O_6^+$
310.1290	310.1285	-1.4	$C_{15}H_{20}NO_6^+$
301.1398	301.1394	-1.3	$C_{13}H_{21}N_2O_6^+$
285.1331	285.1333	0.5	$C_{14}H_{21}O_6^+$
267.1230	267.1227	-1.0	$C_{14}H_{19}O_5^+$
259.1291	259.1288	-0.8	$C_{11}H_{19}N_2O_5^+$
242.1031	242.1023	-3.4	$C_{11}H_{16}NO_5^+$
199.0970	199.0965	-2.5	$C_{10}H_{15}O_4^+$
147.0768	147.0764	-2.5	$C_5H_{11}N_2O_3^+$
129.0662	129.0659	-2.4	$C_5H_9N_2O_2^+$
113.0600	113.0597	-3.0	$C_6H_9O_2^+$
95.0496	95.0491	-5.3	$C_6H_7O^+$
87.0447	87.0441	-	$C_4H_7O_2^+$

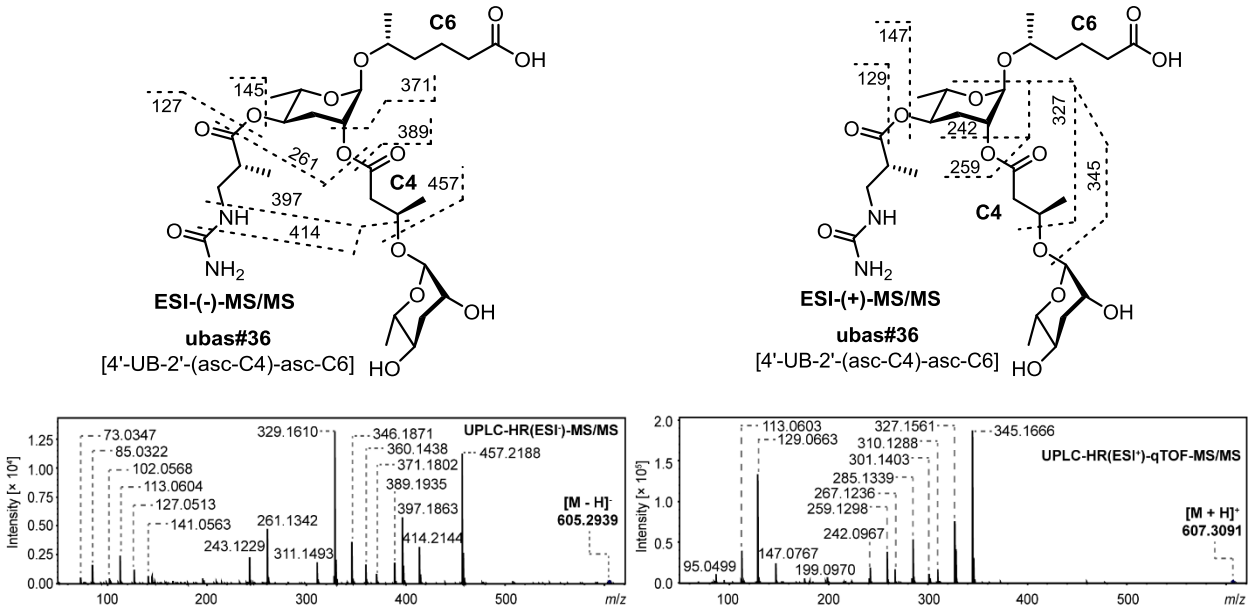
Figure 9. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#34 [4'-UB-2'-(asc-C4)-asc-C4, **11**] in both negative and positive ion modes. UPLC-HR(ESI$^+$)-qTOF-MS/MS fragmentation produced a fragment ion signal for $C_{15}H_{25}N_2O_7^+$ (*m/z* 345.1660 $[M+H]^+$, Δ -1.0 ppm) (***Figure 5 – figure supplement 3***), indicating that ascr#11 [asc-C4] represents the first ascaroside in ubas#34 [4'-UB-2'-(asc-C4)-asc-C4, **11**].



UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
591.2771	591.2771	0.0	$C_{26}H_{43}N_2O_{13}^-$
443.2040	443.2035	-1.2	$C_{20}H_{31}N_2O_9^-$
400.1981	400.1977	-0.9	$C_{19}H_{30}NO_8^-$
383.1712	383.1711	-0.3	$C_{19}H_{27}O_8^-$
375.1771	375.1773	0.5	$C_{16}H_{27}N_2O_8^-$
357.1650	357.1667	4.7	$C_{16}H_{25}N_2O_7^-$
332.1717	332.1715	-0.8	$C_{15}H_{26}NO_7^-$
315.1450	315.1449	-0.2	$C_{15}H_{23}O_7^-$
297.1342	297.1344	0.6	$C_{15}H_{21}O_6^-$
247.1191	247.1187	-1.5	$C_{11}H_{19}O_6^-$
229.1080	229.1081	0.5	$C_{11}H_{17}O_5^-$
197.0826	197.0819	-3.1	$C_{10}H_{13}O_4^-$
178.0511	178.0510	-0.8	$C_9H_8NO_3^-$
145.0619	145.0619	-0.1	$C_5H_9N_2O_3^-$
141.0557	141.0557	0.3	$C_7H_9O_3^-$
127.0595	127.0608	-0.8	$C_5H_7N_2O_2^-$
113.0607	113.0608	-	$C_6H_9O_2^-$
102.0577	102.0561	-	$C_4H_8NO_2^-$
85.0321	85.0295	-	$C_4H_5O_2^-$
73.0327	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+H]^+$
593.2925	593.2916	-1.4	$C_{26}H_{45}N_2O_{13}^+$
345.1661	345.1656	-1.3	$C_{15}H_{25}N_2O_7^+$
327.1556	327.1551	-1.7	$C_{15}H_{23}N_2O_6^+$
310.1291	310.1285	-1.7	$C_{15}H_{20}NO_6^+$
301.1403	301.1394	-3.1	$C_{13}H_{21}N_2O_6^+$
285.1336	285.1333	-1.2	$C_{14}H_{21}O_6^+$
267.1234	267.1227	-2.6	$C_{14}H_{19}O_5^+$
259.1292	259.1288	-1.3	$C_{11}H_{19}N_2O_5^+$
242.1031	242.1023	-3.5	$C_{11}H_{16}NO_5^+$
199.0970	199.0965	-2.5	$C_{10}H_{15}O_4^+$
147.0768	147.0764	-2.8	$C_5H_{11}N_2O_3^+$
129.0663	129.0659	-3.4	$C_5H_9N_2O_2^+$
113.0601	113.0597	-3.3	$C_6H_9O_2^+$
95.0495	95.0491	-5.3	$C_6H_7O^+$
87.0448	87.0441	-	$C_4H_7O_2^+$

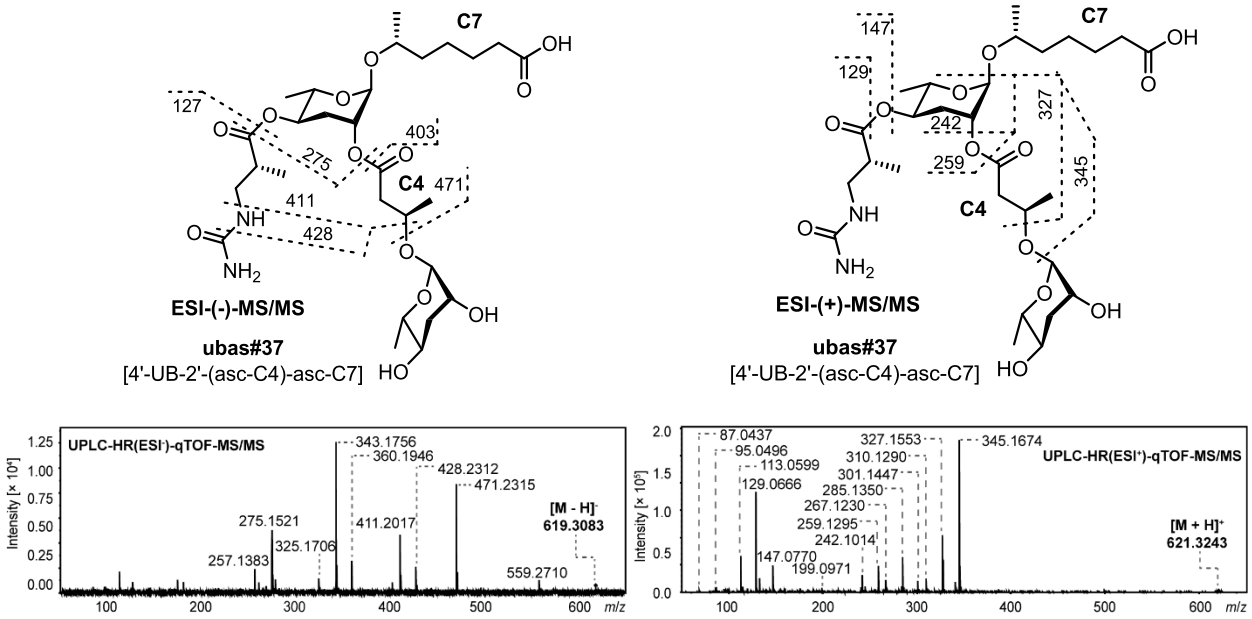
Figure 10. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#35 [4'-UB-2'-(asc-C4)-asc-C5, **12**] in both negative and positive ion modes. UPLC-HR(ESI$^+$)-qTOF-MS/MS fragmentation produced a fragment ion signal for $C_{15}H_{25}N_2O_7^+$ (*m/z* 345.1660 $[M+H]^+$, Δ -1.0 ppm) (***Figure 5 – figure supplement 3***), indicating that ascr#11 [asc-C4] represents the first ascaroside in ubas#35 [4'-UB-2'-(asc-C4)-asc-C5, **12**].



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
605.2939	605.2927	-2.0	$C_{27}H_{45}N_2O_{13}^-$
457.2188	457.2192	0.7	$C_{21}H_{33}N_2O_9^-$
414.2144	414.2133	-2.5	$C_{20}H_{32}NO_8^-$
397.1863	397.1868	1.2	$C_{20}H_{29}O_8^-$
389.1935	389.1929	-1.3	$C_{17}H_{29}N_2O_8^-$
371.1802	371.1824	5.7	$C_{17}H_{27}N_2O_7^-$
360.1438	360.1453	4.2	$C_{19}H_{22}NO_6^-$
346.1871	346.1871	0.2	$C_{16}H_{28}NO_7^-$
329.1610	329.1606	-1.3	$C_{16}H_{25}O_7^-$
311.1493	311.1500	2.4	$C_{16}H_{23}O_6^-$
261.1342	261.1344	0.6	$C_{12}H_{21}O_6^-$
243.1229	243.1238	3.8	$C_{12}H_{19}O_5^-$
141.0563	141.0557	-4.2	$C_7H_9O_3^-$
127.0513	127.0513	0.4	$C_5H_7N_2O_2^-$
113.0604	113.0608	3.1	$C_6H_9O_2^-$
102.0568	102.0561	-	$C_4H_8NO_2^-$
85.0322	85.0295	-	$C_4H_5O_2^-$
73.0347	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+H]^+$
607.3091	607.3073	-3.0	$C_{27}H_{47}N_2O_{13}^+$
345.1666	345.1656	-2.8	$C_{15}H_{25}N_2O_7^+$
327.1561	327.1551	-3.1	$C_{15}H_{23}N_2O_6^+$
310.1288	310.1285	-1.0	$C_{15}H_{20}NO_6^+$
301.1403	301.1394	-2.8	$C_{13}H_{21}N_2O_6^+$
285.1339	285.1333	-2.1	$C_{14}H_{21}O_6^+$
267.1236	267.1227	-2.6	$C_{14}H_{19}O_5^+$
259.1298	259.1288	-1.3	$C_{11}H_{19}N_2O_5^+$
242.0967	242.1023	23.3	$C_{11}H_{16}NO_5^+$
199.0970	199.0965	-2.6	$C_{10}H_{15}O_4^+$
147.0767	147.0764	-2.1	$C_5H_{11}N_2O_3^+$
129.0663	129.0659	-3.4	$C_5H_9N_2O_2^+$
113.0603	113.0597	-5.1	$C_6H_9O_2^+$
95.0499	95.0491	-	$C_6H_7O^+$

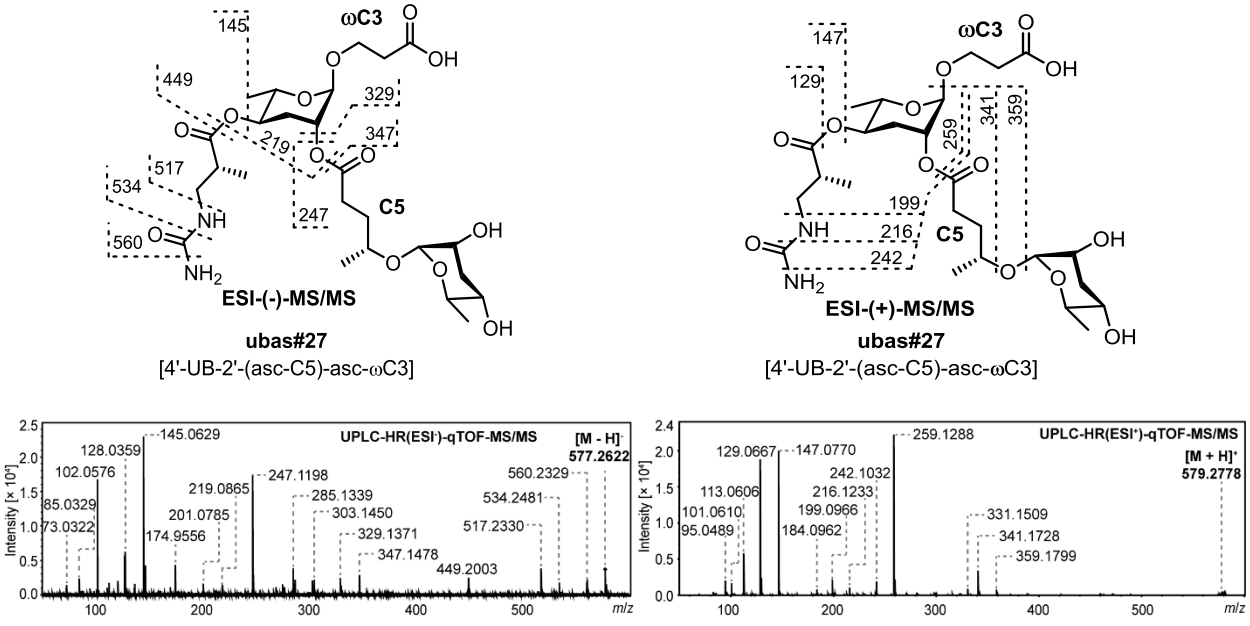
Figure 11. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#36 [4'-UB-2'-(asc-C4)-asc-C6] in both negative and positive ion modes. UPLC-HR(ESI$^+$)-qTOF-MS/MS fragmentation produced a fragment ion signal for $C_{15}H_{25}N_2O_7^+$ (*m/z* 345.1660 $[M+H]^+$, Δ -1.0 ppm) (***Figure 5 – figure supplement 3***), indicating that ascr#11 [asc-C4] represents the first ascaroside in ubas#36 [4'-UB-2'-(asc-C4)-asc-C6].



UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
619.3083	619.3084	0.2	$C_{28}H_{47}N_2O_{13}^-$
471.2315	471.2348	7.1	$C_{22}H_{35}N_2O_9^-$
428.2312	428.2290	-5.2	$C_{21}H_{34}NO_8^-$
411.2017	411.2024	1.7	$C_{21}H_{31}O_8^-$
343.1756	343.1762	1.7	$C_{17}H_{27}O_7^-$
325.1706	325.1657	-	$C_{17}H_{25}O_6^-$
275.1521	275.1500	-7.4	$C_{13}H_{23}O_6^-$
257.1383	257.1394	4.3	$C_{13}H_{21}O_5^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+H]^+$
621.3243	621.3229	-2.2	$C_{28}H_{49}N_2O_{13}^+$
345.1674	345.1656	-5.1	$C_{15}H_{25}N_2O_7^+$
327.1553	327.1551	-0.8	$C_{15}H_{23}N_2O_6^+$
310.1290	310.1285	-1.6	$C_{15}H_{20}NO_6^+$
301.1447	301.1394	-17.4	$C_{13}H_{21}N_2O_6^+$
285.1350	285.1333	-6.0	$C_{14}H_{21}O_6^+$
267.1230	267.1227	-1.1	$C_{14}H_{19}O_5^+$
259.1295	259.1288	-2.6	$C_{11}H_{19}N_2O_5^+$
242.1014	242.1023	3.6	$C_{11}H_{16}NO_5^+$
199.0971	199.0965	-3.0	$C_{10}H_{15}O_4^+$
147.0770	147.0764	-3.7	$C_5H_{11}N_2O_3^+$
129.0666	129.0659	-5.6	$C_5H_9N_2O_2^+$
113.0599	113.0597	-2.1	$C_6H_9O_2^+$
95.0496	95.0491	-4.6	$C_6H_7O^+$
87.0437	87.0441	-3.9	$C_4H_7O_2^+$

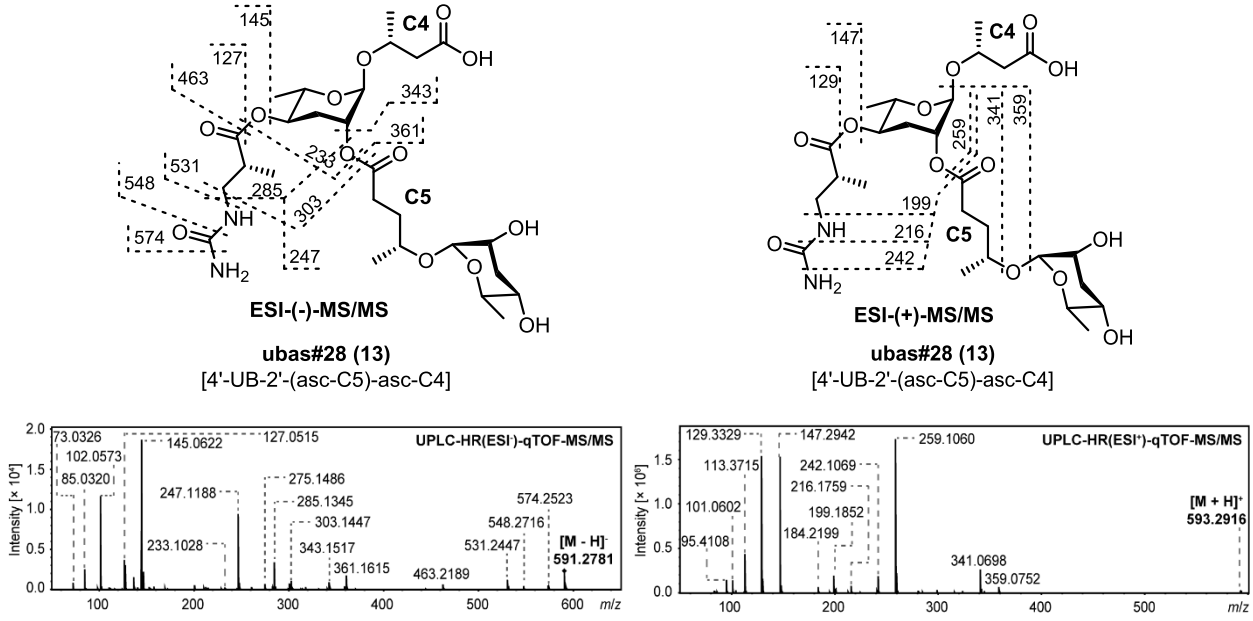
Figure 12. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#37 [4'-UB-2'-(asc-C4)-asc-C7] in both negative and positive ion modes. UPLC-HR(ESI$^+$)-qTOF-MS/MS fragmentation produced a fragment ion signal for $C_{15}H_{25}N_2O_7^+$ (*m/z* 345.1660 $[M+H]^+$, Δ -1.0 ppm) (***Figure 5 – figure supplement 3***), indicating that ascr#11 [asc-C4] represents the first ascaroside in ubas#37 [4'-UB-2'-(asc-C4)-asc-C7].



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
577.2622	577.2614	-1.3	$C_{25}H_{41}N_2O_{13}^-$
560.2329	560.2349	3.5	$C_{25}H_{38}NO_{13}^-$
534.2481	534.2556	14.0	$C_{24}H_{40}NO_{12}^-$
517.2330	517.2291	-7.7	$C_{24}H_{37}O_{12}^-$
449.2003	449.2028	5.6	$C_{20}H_{33}O_{11}^-$
347.1478	347.1460	-5.3	$C_{14}H_{23}N_2O_8^-$
329.1371	329.1354	-5.0	$C_{14}H_{21}N_2O_7^-$
303.1450	303.1449	-0.3	$C_{14}H_{23}O_7^-$
285.1339	285.1344	1.5	$C_{14}H_{21}O_6^-$
247.1198	247.1187	-4.5	$C_{11}H_{19}O_6^-$
219.0865	219.0874	4.2	$C_9H_{15}O_6^-$
201.0785	201.0768	-8.4	$C_9H_{13}O_5^-$
145.0629	145.0619	-7.1	$C_5H_9N_2O_3^-$
128.0359	128.0353	-4.8	$C_5H_6NO_3^-$
102.0576	102.1561	-	$C_4H_8NO_2^-$
85.0329	85.0407	-	$C_4H_5O_2^-$
73.0322	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+H]^+$
579.2778	579.2760	-3.1	$C_{25}H_{43}N_2O_{13}^+$
359.1799	359.1813	3.8	$C_{16}H_{27}N_2O_7^+$
341.1728	341.1707	-6.1	$C_{16}H_{25}N_2O_6^+$
331.1509	331.1500	-2.7	$C_{14}H_{23}N_2O_7^+$
259.1296	259.1288	-3.0	$C_{11}H_{19}N_2O_5^+$
242.1032	242.1023	-3.9	$C_{11}H_{16}NO_5^+$
216.1233	216.1230	-1.0	$C_{10}H_{18}NO_4^+$
199.0966	199.0965	-0.5	$C_{10}H_{15}O_4^+$
184.0962	184.0968	3.5	$C_9H_{14}NO_3^+$
147.0770	147.0764	-3.9	$C_5H_{11}N_2O_3^+$
129.0667	129.0659	-	$C_5H_9N_2O_2^+$
113.0606	113.0597	-	$C_6H_9O_2^+$
101.0610	101.0597	-	$C_5H_9O_2^+$
95.0489	95.0491	2.3	$C_6H_7O^+$

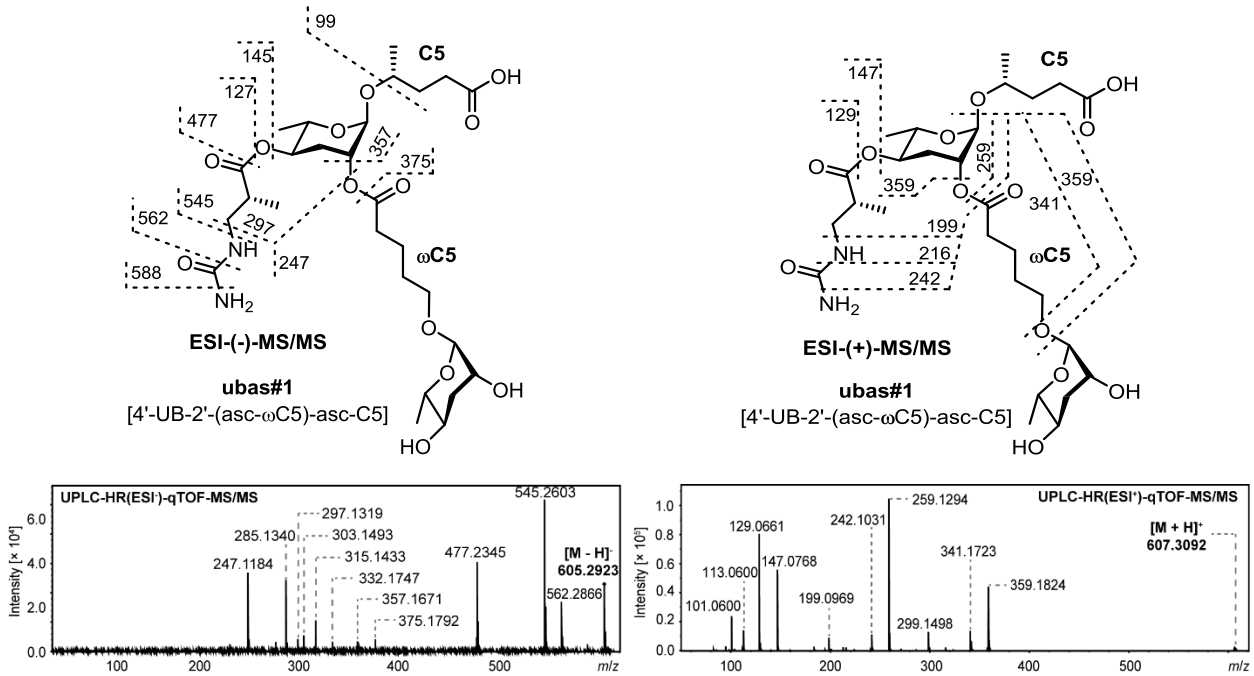
Figure 13. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#27 [4'-UB-2'-(asc-C5)-asc-ωC3] in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M − H]$^-$
591.2781	591.2771	-1.7	$C_{26}H_{43}N_2O_{13}^-$
574.2523	574.2505	-3.1	$C_{26}H_{40}NO_{13}^-$
548.2716	548.2712	-0.6	$C_{25}H_{42}NO_{12}^-$
531.2447	531.2447	0.0	$C_{25}H_{39}O_{12}^-$
463.2189	463.2185	-0.9	$C_{21}H_{35}O_{11}^-$
361.1615	361.1616	0.5	$C_{15}H_{25}N_2O_8^-$
343.1517	343.1511	-1.9	$C_{15}H_{23}N_2O_7^-$
303.1447	303.1449	0.7	$C_{14}H_{23}O_7^-$
285.1345	285.1344	-0.3	$C_{14}H_{21}O_6^-$
275.1486	275.1500	5.0	$C_{13}H_{23}O_6^-$
247.1188	247.1187	-0.2	$C_{11}H_{19}O_6^-$
233.1028	233.1030	1.1	$C_{10}H_{17}O_6^-$
213.0881	213.0881	0.1	$C_9H_{13}N_2O_4^-$
145.0622	145.0619	-2.5	$C_5H_9N_2O_3^-$
127.0515	127.0513	-1.9	$C_5H_7N_2O_2^-$
102.0573	102.0561	-	$C_4H_8NO_2^-$
85.0320	85.0295	-	$C_4H_5O_2^-$
73.0326	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M + H]$^+$
593.2916	593.1916	0.1	$C_{26}H_{45}N_2O_{13}^+$
359.1818	359.1813	-1.5	$C_{16}H_{27}N_2O_7^+$
341.1710	341.1707	-0.7	$C_{16}H_{25}N_2O_6^+$
259.1290	259.1288	-0.5	$C_{11}H_{19}N_2O_5^+$
242.1028	242.1023	-2.1	$C_{11}H_{16}NO_5^+$
216.1234	216.1230	-1.8	$C_{10}H_{18}NO_4^+$
199.0967	199.0965	-1.0	$C_{10}H_{15}O_4^+$
184.0971	184.0968	-1.5	$C_9H_{14}NO_3^+$
147.0766	147.0780	-1.5	$C_5H_{11}N_2O_3^+$
129.0662	129.0659	-2.3	$C_5H_9N_2O_2^+$
113.0600	113.0597	-3.0	$C_6H_9O_2^+$
101.0602	101.0597	-5.4	$C_5H_9O_2^+$
95.0496	95.0491	-4.8	$C_6H_7O^+$

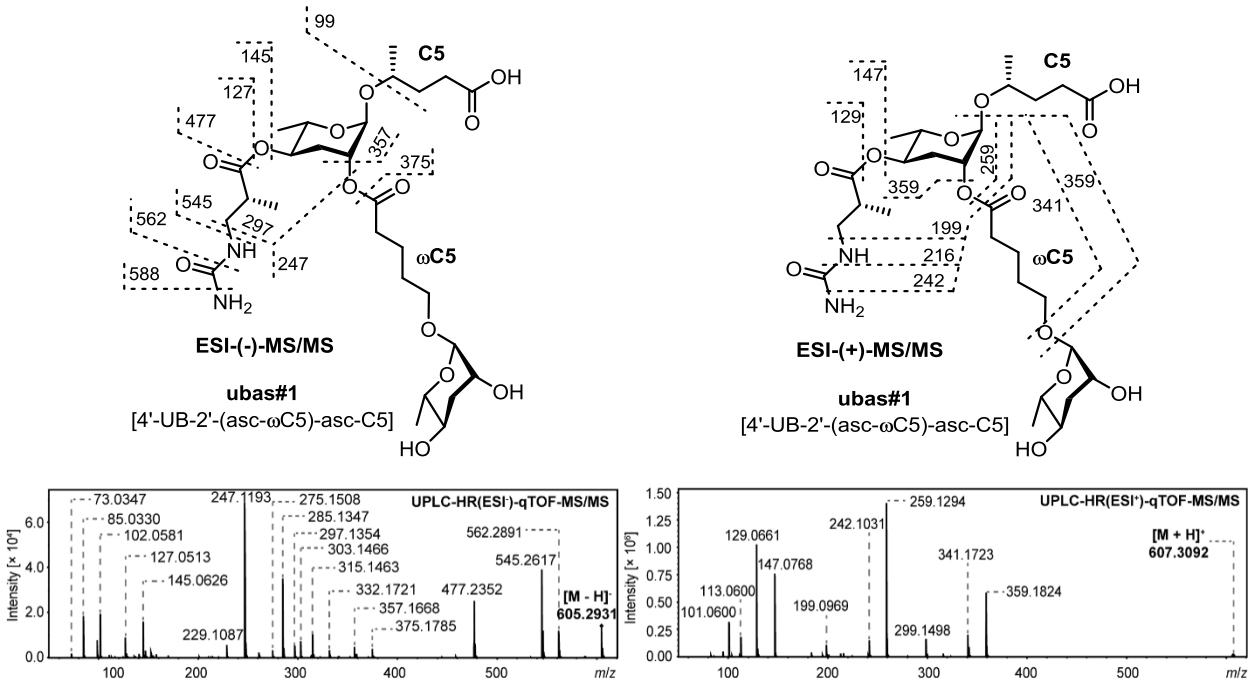
Figure 14. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#28 [4'-UB-2'-(asc-C5)-asc-C4, **13**] in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Obs. [*m/z*]
605.2923	605.2927	0.5	$C_{27}H_{45}N_2O_{13}^-$
562.2866	562.2869	0.3	$C_{26}H_{44}NO_{12}^-$
545.2603	545.2604	0.0	$C_{26}H_{41}O_{12}^-$
477.2345	477.2341	-0.3	$C_{22}H_{37}O_{11}^-$
375.1792	375.1773	-1.9	$C_{16}H_{27}N_2O_8^-$
357.1671	357.1667	-0.4	$C_{16}H_{25}N_2O_7^-$
332.1747	332.1715	-3.3	$C_{15}H_{26}NO_7^-$
315.1433	315.1449	1.6	$C_{15}H_{23}O_7^-$
303.1593	303.1449	0.9	$C_{14}H_{23}O_7^-$
297.1319	297.1370	2.5	$C_{15}H_{21}O_6^-$
285.1340	285.1344	0.4	$C_{14}H_{21}O_6^-$
275.1537	275.1500	-3.7	$C_{13}H_{23}O_6^-$
247.1184	247.1088	0.3	$C_{11}H_{19}O_6^-$
229.1101	229.1081	-2.0	$C_{11}H_{17}O_5^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Error [ppm]	Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]
607.3040	607.3073	5.3	$C_{27}H_{47}N_2O_{13}^+$
359.1801	359.1813	3.4	$C_{16}H_{27}N_2O_7^+$
341.1701	341.1707	1.7	$C_{16}H_{25}N_2O_6^+$
316.1749	316.1755	1.9	$C_{15}H_{26}NO_6^+$
299.1483	299.1489	2.1	$C_{15}H_{23}O_6^+$
259.1284	259.1288	-3.1	$C_{11}H_{19}N_2O_5^+$
242.1024	242.1023	-0.4	$C_{11}H_{16}NO_5^+$
199.0968	199.0965	-1.4	$C_{10}H_{15}O_4^+$
184.0965	184.0968	1.5	$C_9H_{14}NO_3^+$
147.0769	147.0764	-3.2	$C_5H_{11}N_2O_3^+$
129.0664	129.0659	-4.4	$C_5H_9N_2O_2^+$
113.0602	113.0597	-4.4	$C_6H_9O_2^+$
101.0606	101.0597	-8.7	$C_5H_9O_2^+$
95.0500	95.0491	-8.7	$C_6H_7O^+$

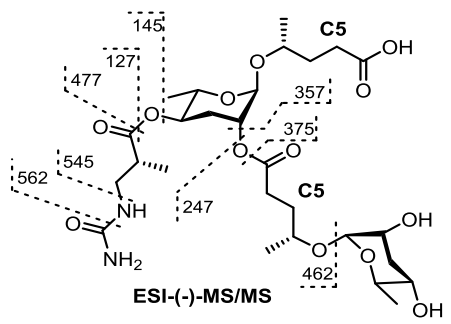
Figure 15. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#1 [4'-UB-2'-(asc-ωC5)-asc-C5] (from *P. taiwanensis*) in both negative and positive ion modes. Analysis of NMR data of ubas#1 isolated from the *exo*-metabolome of *P. taiwanensis* has confirmed its chemical identity (***supplementary file 1d – Figures 12-15***).



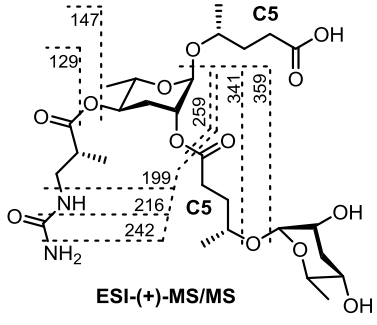
UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula [M − H]$^-$
605.2931	605.2927	-0.7	$C_{27}H_{45}N_2O_{13}^-$
562.2891	562.2869	-3.8	$C_{26}H_{44}NO_{12}^-$
545.2617	545.2604	-2.4	$C_{26}H_{41}O_{12}^-$
477.2352	477.2341	-2.2	$C_{22}H_{37}O_{11}^-$
375.1785	375.1773	-3.2	$C_{16}H_{27}N_2O_8^-$
357.1668	357.1667	-0.3	$C_{16}H_{25}N_2O_7^-$
332.1721	332.1715	-1.9	$C_{15}H_{26}NO_7^-$
315.1463	315.1449	-4.4	$C_{15}H_{23}O_7^-$
303.1466	303.1449	-5.6	$C_{14}H_{23}O_7^-$
297.1354	297.1370	-3.3	$C_{15}H_{21}O_6^-$
285.1347	285.1344	-1.1	$C_{14}H_{21}O_6^-$
275.1508	275.1500	-2.8	$C_{13}H_{23}O_6^-$
247.1193	247.1088	-2.5	$C_{11}H_{19}O_6^-$
229.1087	229.1081	-2.3	$C_{11}H_{17}O_5^-$
145.0626	145.0619	-5.1	$C_5H_9N_2O_3^-$
127.0513	127.0513	-0.3	$C_5H_7N_2O_2^-$
102.0581	102.0561	-19.7	$C_4H_8NO_2^-$
85.0330	85.0295	-41.2	$C_4H_5O_2^-$
73.0347	73.0295	-70.8	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula [M + H]$^+$
607.3092	607.3073	-3.1	$C_{27}H_{47}N_2O_{13}^+$
359.1824	359.1813	-4.7	$C_{16}H_{27}N_2O_7^+$
341.1723	341.1707	-1.8	$C_{16}H_{25}N_2O_6^+$
316.1771	316.1755	-5.0	$C_{15}H_{26}NO_6^+$
299.1500	299.1489	-3.5	$C_{15}H_{23}O_6^+$
259.1294	259.1288	-2.0	$C_{11}H_{19}N_2O_5^+$
242.1031	242.1023	-3.3	$C_{11}H_{16}NO_5^+$
199.0969	199.0965	-2.1	$C_{10}H_{15}O_4^+$
147.0768	147.0764	-2.3	$C_5H_{11}N_2O_3^+$
129.0661	129.0659	-1.9	$C_5H_9N_2O_2^+$
113.0600	113.0597	-3.0	$C_6H_9O_2^+$
101.0600	101.0597	-3.0	$C_5H_9O_2^+$
95.0493	95.0491	-1.8	$C_6H_7O^+$

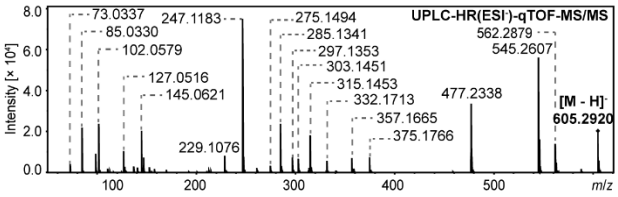
Figure 16. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#1 [4'-UB-2'-(asc-ωC5)-asc-C5] (from *P. laevicollis*) in both negative and positive ion modes. Analysis of NMR data of ubas#1 isolated from the *exo*-metabolome of *P. laevicollis* confirmed its chemical identity (***supplementary file 1d – Figures 16-19***).

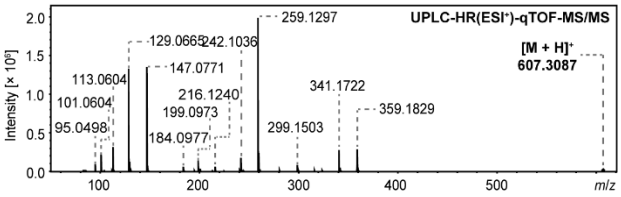


ubas#30 (9)
[4'-UB-2'-(asc-C5)-asc-C5]



ubas#30 (9)
[4'-UB-2'-(asc-C5)-asc-C5]

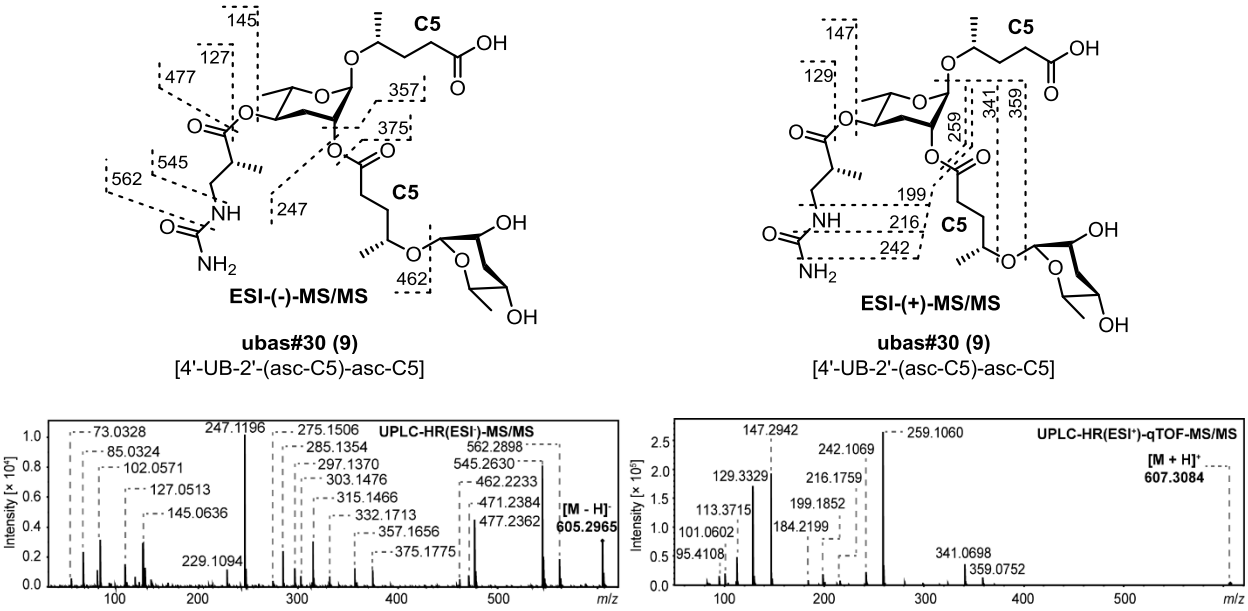




UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
605.2920	605.2927	1.2	$C_{27}H_{45}N_2O_{13}^-$
562.2879	562.2869	-1.8	$C_{26}H_{44}NO_{12}^-$
545.2607	545.2604	-0.6	$C_{26}H_{41}O_{12}^-$
477.2338	477.2341	0.7	$C_{22}H_{37}O_{11}^-$
375.1766	375.1773	2.0	$C_{16}H_{27}N_2O_8^-$
357.1665	357.1667	0.6	$C_{16}H_{25}N_2O_7^-$
332.1713	332.1715	0.6	$C_{15}H_{26}NO_7^-$
315.1453	315.1449	-1.3	$C_{15}H_{23}O_7^-$
303.1451	303.1449	-0.4	$C_{14}H_{23}O_7^-$
297.1353	297.1370	-3.1	$C_{15}H_{21}O_6^-$
285.1341	285.1344	-0.8	$C_{14}H_{21}O_6^-$
275.1494	275.1500	2.1	$C_{13}H_{23}O_6^-$
247.1183	247.1088	1.5	$C_{11}H_{19}O_6^-$
229.1076	229.1081	2.4	$C_{11}H_{17}O_5^-$
145.0621	145.0619	-1.9	$C_5H_9N_2O_3^-$
127.0516	127.0513	-2.6	$C_5H_7N_2O_2^-$
102.0579	102.0561	-18.2	$C_4H_8NO_2^-$
85.0330	85.0295	-40.6	$C_4H_5O_2^-$
73.0337	73.0295	-57.2	$C_3H_5O_2^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+H]^+$
607.3087	607.3073	-2.3	$C_{27}H_{47}N_2O_{13}^+$
359.1829	359.1813	-4.7	$C_{16}H_{27}N_2O_7^+$
341.1722	341.1707	-4.3	$C_{16}H_{25}N_2O_6^+$
299.1503	299.1489	-4.6	$C_{15}H_{23}O_6^+$
259.1297	259.1288	-3.1	$C_{11}H_{19}N_2O_5^+$
242.1036	242.1023	-5.5	$C_{11}H_{16}NO_5^+$
216.1240	216.1230	-4.3	$C_{10}H_{18}NO_4^+$
199.0973	199.0965	-4.3	$C_{10}H_{15}O_4^+$
184.0977	184.0968	-4.6	$C_{14}H_{14}NO_3^+$
147.0771	147.0764	-4.6	$C_5H_{11}N_2O_3^+$
129.0665	129.0659	-5.1	$C_5H_9N_2O_2^+$
113.0604	113.0597	-6.1	$C_6H_9O_2^+$
101.0604	101.0597	-6.9	$C_5H_9O_2^+$
95.0498	95.0491	-7.2	$C_6H_7O^+$

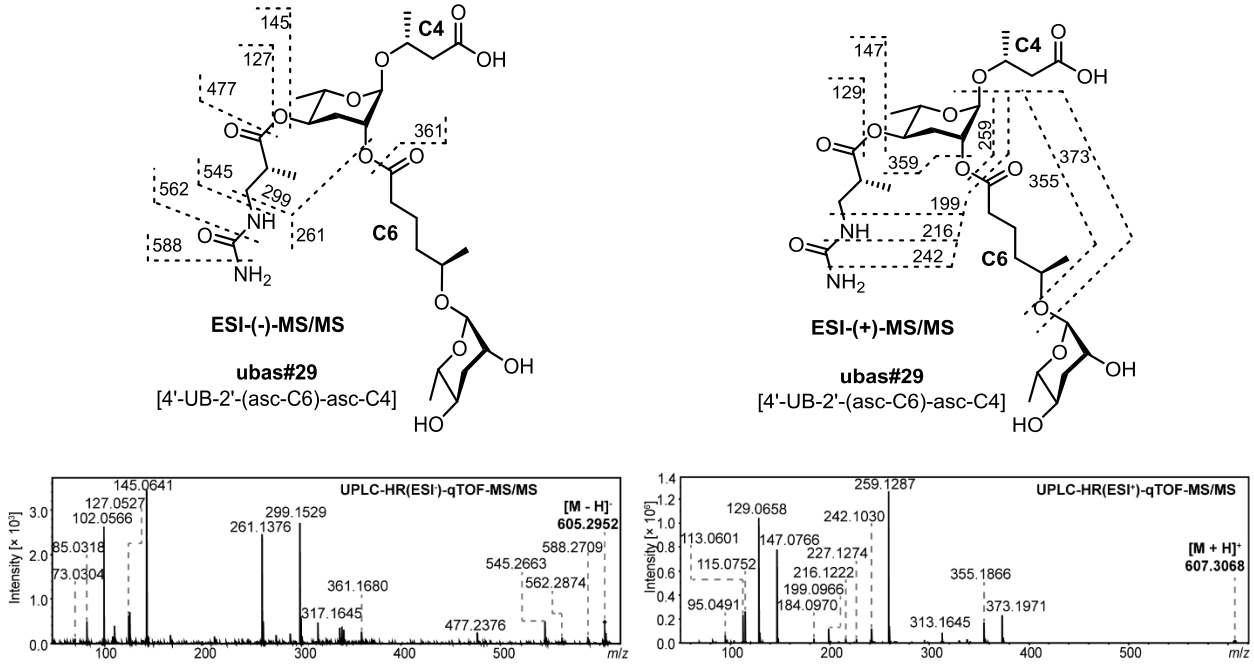
Figure 17. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#30 [4'-UB-2'-(asc-C5)-asc-C5, **9**] (from *P. maxplancki*) in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
605.2954	605.2927	-4.5	$C_{27}H_{45}N_2O_{13}^-$
562.2898	562.2869	-5.1	$C_{26}H_{44}NO_{12}^-$
545.2630	545.2604	-4.9	$C_{26}H_{41}O_{12}^-$
477.2362	477.2341	-4.4	$C_{22}H_{37}O_{11}^-$
471.2384	471.2348	-7.6	$C_{22}H_{35}N_2O_9^-$
462.2233	462.2345	24.1	$C_{21}H_{36}NO_{10}^-$
375.1775	375.1773	-0.5	$C_{16}H_{27}N_2O_8^-$
357.1656	357.1667	3.0	$C_{16}H_{25}N_2O_7^-$
332.1713	332.1715	0.4	$C_{15}H_{26}NO_7^-$
315.1466	15.1449	-5.5	$C_{15}H_{23}O_7^-$
303.1476	303.1449	-8.8	$C_{14}H_{23}O_7^-$
297.1370	297.1370	-9.0	$C_{15}H_{21}O_6^-$
285.1354	285.1344	-3.8	$C_{14}H_{21}O_6^-$
275.1506	275.1500	-2.2	$C_{13}H_{23}O_6^-$
247.1196	247.1088	-3.4	$C_{11}H_{19}O_6^-$
229.1094	229.1081	-5.3	$C_{11}H_{17}O_5^-$
145.0636	145.0619	-	$C_5H_9N_2O_3^-$
127.0513	127.0513	0.0	$C_5H_7N_2O_2^-$
102.0571	102.0561	-	$C_4H_8NO_2^-$
85.0324	85.0295	-	$C_4H_5O_2^-$
73.0328	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+H]^+$
607.3084	607.3073	-1.9	$C_{27}H_{47}N_2O_{13}^+$
359.1827	359.1813	-3.9	$C_{16}H_{27}N_2O_7^+$
341.1713	341.1707	-1.8	$C_{16}H_{25}N_2O_6^+$
259.1293	259.1288	-1.8	$C_{11}H_{19}N_2O_5^+$
242.1024	242.1023	-0.3	$C_{11}H_{16}NO_5^+$
216.1239	216.1230	-3.9	$C_{10}H_{18}NO_4^+$
199.0969	199.0965	-1.9	$C_{10}H_{15}O_4^+$
184.0968	184.0968	0.3	$C_9H_{14}NO_3^+$
147.0768	147.0764	-2.9	$C_5H_{11}N_2O_3^+$
129.0663	129.0659	-3.5	$C_5H_9N_2O_2^+$
113.0602	113.0597	-4.0	$C_6H_9O_2^+$
101.0605	101.0597	-	$C_5H_9O_2^+$
95.0497	95.0491	-	$C_6H_7O^+$

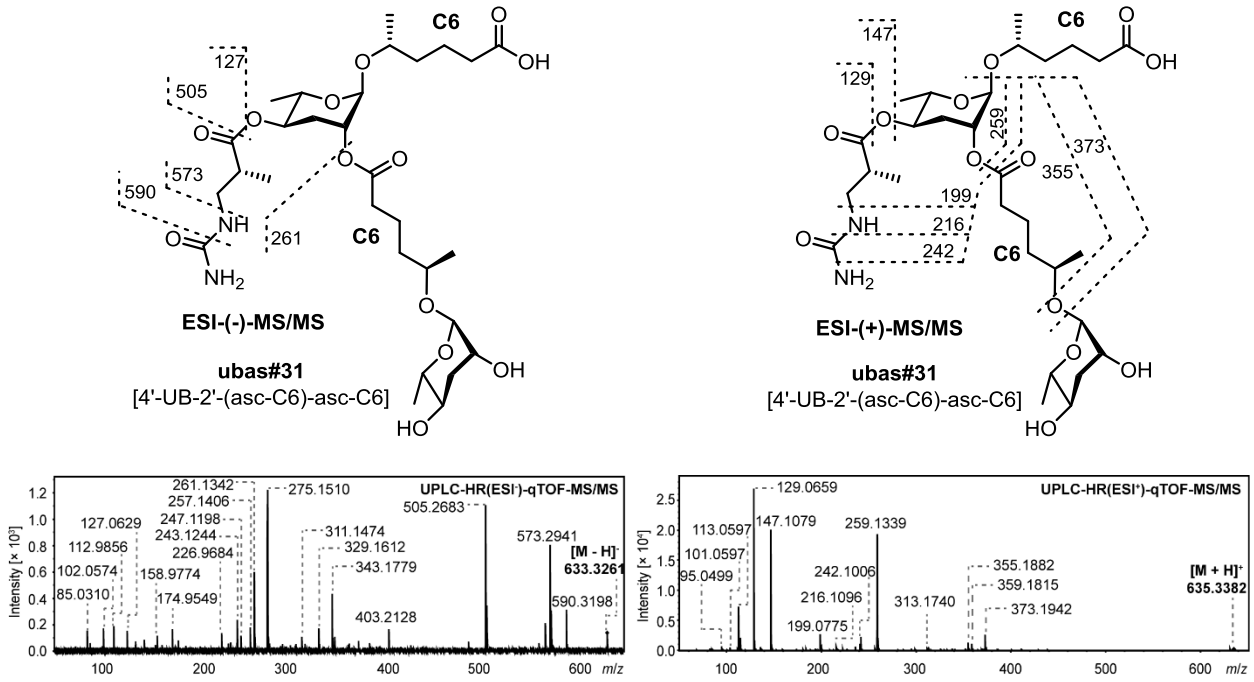
Figure 18. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#30 [4'-UB-2'-(asc-C5)-asc-C5, **9**] (from *P. fukushimae*) in both negative and positive ion modes. Peak at *m*/*z* 605.2954 was tentatively assigned to be ubas#30 [4'-UB-2'-(asc-C5)-asc-C5, **9**].



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
605.2952	605.2927	-4.1	$C_{27}H_{45}N_2O_{13}^-$
588.2709	588.2662	-8.1	$C_{27}H_{42}NO_{13}^-$
562.2874	562.2869	-0.9	$C_{26}H_{44}NO_{12}^-$
545.2663	545.2604	-10.9	$C_{26}H_{41}O_{12}^-$
477.2376	477.2341	-7.3	$C_{22}H_{37}O_{11}^-$
361.1680	361.1616	-17.6	$C_{15}H_{25}N_2O_8^-$
317.1645	317.1718	23.0	$C_{14}H_{25}N_2O_6^-$
299.1529	299.1500	-9.5	$C_{15}H_{23}O_6^-$
261.1376	261.1344	-	$C_{12}H_{21}O_6^-$
145.0641	145.0619	-	$C_5H_9N_2O_3^-$
127.0527	127.0513	-	$C_5H_7N_2O_2^-$
102.0566	102.0561	-	$C_4H_8NO_2^-$
85.0318	85.0295	-	$C_4H_5O_2^-$
73.0304	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+H]^+$
607.3068	607.3073	0.8	$C_{27}H_{47}N_2O_{13}^+$
373.1971	373.1969	-0.5	$C_{17}H_{29}N_2O_7^+$
355.1866	355.1864	-0.8	$C_{17}H_{27}N_2O_6^+$
313.1645	313.1646	0.3	$C_{16}H_{25}O_6^+$
259.1287	259.1288	0.5	$C_{11}H_{19}N_2O_5^+$
242.1030	242.1023	-2.9	$C_{11}H_{16}NO_5^+$
227.1274	227.1278	1.8	$C_{12}H_{19}O_4^+$
216.1222	216.1230	3.7	$C_{10}H_{18}NO_4^+$
199.0966	199.0965	-0.4	$C_{10}H_{15}O_4^+$
184.0970	184.0968	-1.2	$C_9H_{14}NO_3^+$
147.0766	147.0764	-1.0	$C_5H_{11}N_2O_3^+$
129.0658	129.0659	0.2	$C_5H_9N_2O_2^+$
115.0752	115.0754	1.7	$C_6H_{11}O_2^+$
113.0601	113.0597	-3.4	$C_6H_9O_2^+$
95.0491	95.0491	0.4	$C_6H_7O^+$

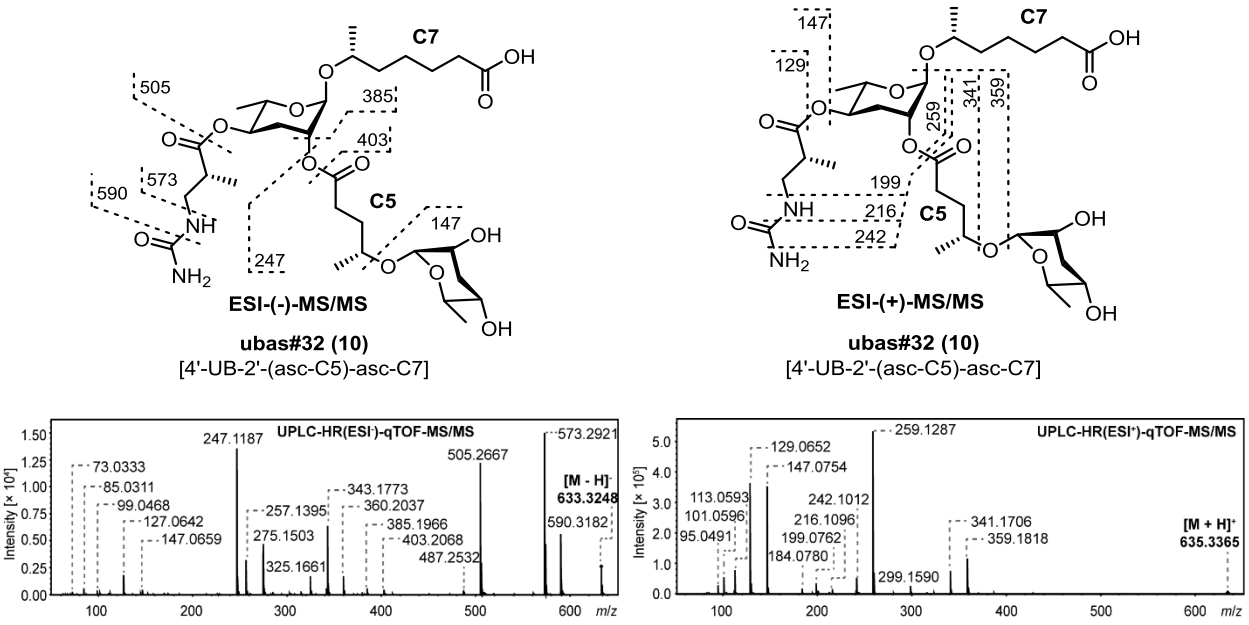
Figure 19. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#29 [4'-UB-2'-(asc-C6)-asc-C4] in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
633.3261	633.3240	-3.4	$C_{29}H_{49}N_2O_{13}^-$
590.3198	590.3182	-2.7	$C_{28}H_{48}NO_{12}^-$
573.2941	573.2917	-4.4	$C_{28}H_{45}O_{12}^-$
505.2683	505.2654	-5.7	$C_{24}H_{41}O_{11}^-$
403.2128	403.2126	-0.4	$C_{23}H_{31}O_6^-$
343.1779	343.1762	-4.8	$C_{27}H_{27}O_7^-$
329.1612	329.1606	-1.9	$C_{16}H_{25}O_7^-$
311.1474	311.1500	9.4	$C_{16}H_{23}O_6^-$
275.1510	275.1500	-3.5	$C_{13}H_{23}O_6^-$
261.1342	261.1344	0.6	$C_{12}H_{21}O_6^-$
257.1406	257.1394	-4.3	$C_{13}H_{21}O_5^-$
247.1198	247.1187	-4.4	$C_{11}H_{19}O_6^-$
243.1244	243.1238	-2.4	$C_{12}H_{19}O_5^-$
127.0629	127.0513	-	$C_5H_7N_2O_2^-$
102.0574	102.0561	-	$C_4H_8NO_2^-$
85.0310	85.0295	-	$C_4H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+H]^+$
635.3382	635.3386	0.4	$C_{29}H_{51}N_2O_{13}^+$
373.1942	373.1969	7.4	$C_{17}H_{29}N_2O_7^+$
359.1815	359.1813	-0.5	$C_{16}H_{27}N_2O_7^+$
355.1882	355.1864	-5.1	$C_{17}H_{27}N_2O_6^+$
313.1740	316.1758	-5.9	$C_{15}H_{25}NO_5^+$
259.1339	259.1288	-	$C_{11}H_{19}N_2O_5^+$
242.1006	242.1023	7.2	$C_{11}H_{16}NO_5^+$
199.0775	199.0965	-	$C_{10}H_{15}O_4^+$
147.1079	147.0764	-	$C_5H_{11}N_2O_3^+$
129.0659		-	$C_5H_9N_2O_2^+$
113.0597		-	$C_6H_9O_2^+$

Figure 20. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#31 [4'-UB-2'-(asc-C6)-asc-C6] in both negative and positive ion modes.

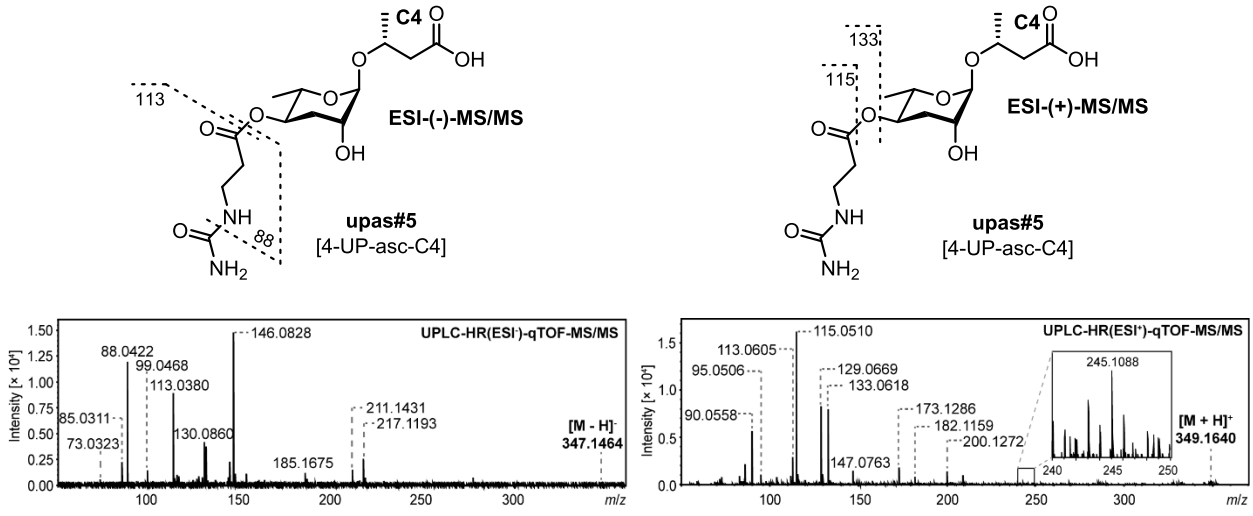


UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula [M − H]$^-$
633.3248	633.3240	-1.3	$C_{29}H_{49}N_2O_{13}^-$
590.3182	590.3182	0.0	$C_{28}H_{48}NO_{12}^-$
573.2921	573.2917	-0.8	$C_{28}H_{45}O_{12}^-$
505.2667	505.2654	-2.6	$C_{24}H_{41}O_{11}^-$
487.2532	487.2549	3.5	$C_{24}H_{39}O_{10}^-$
403.2068	403.2086	4.4	$C_{18}H_{31}N_2O_8^-$
385.1966	385.1980	3.8	$C_{18}H_{29}N_2O_7^-$
360.2037	360.2028	-2.6	$C_{17}H_{30}NO_7^-$
343.1773	343.1762	-3.2	$C_{27}H_{27}O_7^-$
325.1661	325.1657	-1.3	$C_{17}H_{25}O_6^-$
275.1503	275.1500	-1.2	$C_{13}H_{23}O_6^-$
257.1395	257.1394	-0.4	$C_{13}H_{21}O_5^-$
247.1187	247.1187	0.2	$C_{11}H_{19}O_6^-$
147.0659	147.0663	2.4	$C_6H_{11}O_4^-$
99.0468	99.0452	-	$C_5H_7O_2^-$
85.0311	85.0295	-	$C_4H_5O_2^-$
73.0333	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula [M + H]$^+$
635.3365	635.3386	2.1	$C_{29}H_{51}N_2O_{13}^+$
359.1818	359.1813	-1.6	$C_{16}H_{27}N_2O_7^+$
341.1706	341.1707	0.1	$C_{16}H_{27}N_2O_6^+$
299.1590	299.1601	3.9	$C_{14}H_{23}N_2O_5^+$
259.1287	259.1288	0.2	$C_{11}H_{19}N_2O_5^+$
242.1012	242.1023	4.7	$C_{11}H_{16}NO_5^+$
199.0962	199.0965	0.3	$C_{10}H_{15}O_4^+$
147.0754	147.0764	1.1	$C_5H_{11}N_2O_3^+$
129.0652	129.0659	0.5	$C_5H_9N_2O_2^+$
113.0593	113.0597	0.4	$C_6H_9O_2^+$
101.0596	101.0597	0.2	$C_5H_9O_2^+$
95.0491	95.0491	0.0	$C_6H_7O^+$

Figure 21. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of ubas#32 [4'-UB-2'-(asc-C5)-asc-C7, **10**] in both negative and positive ion modes. Analysis of the *dqf*-COSY spectrum of ubas#32 [4'-UB-2'-(asc-C5)-asc-C7, **10**] (800 MHz, CD_3OD) enriched from the *exo*-metabolome of *P. maxplancki* confirmed the presence of one 2'- and 4'-substituted ascarylose sugar, an unsubstituted ascarylose moiety, one (ω-1)-hydroxylated C5 side chain and one (ω-1)-hydroxylated C7 side chain in ubas#32 (***supplementary file 1d – Figure 20***).

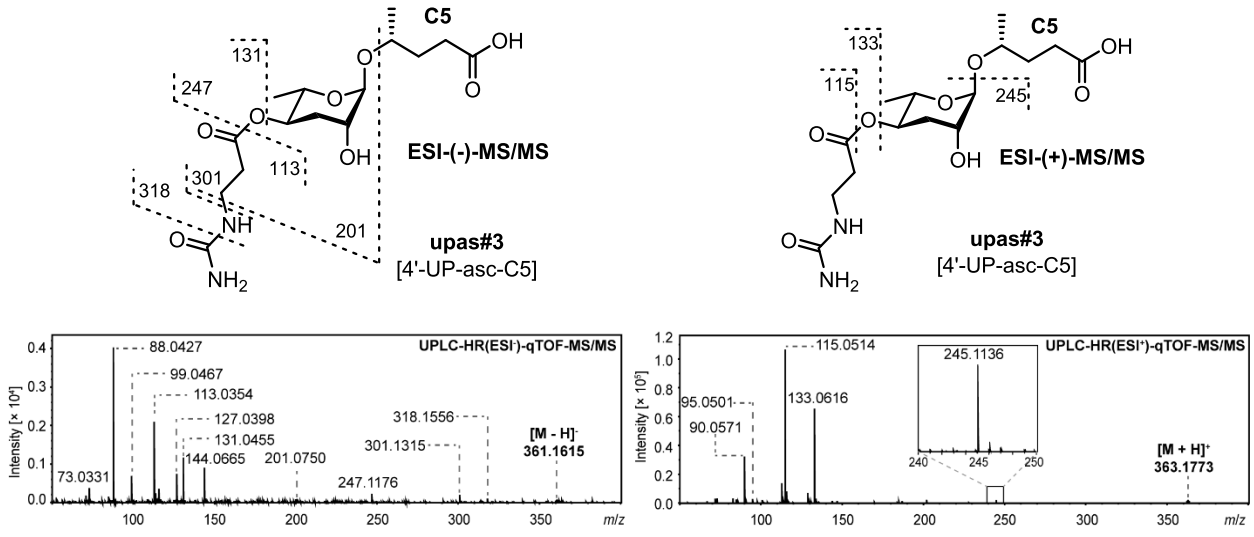
supplementary file 2d: MS/MS spectral data of UPAS chemicals Pages



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
347.1464	347.1460	-1.1	$C_{14}H_{23}N_2O_8^-$
217.1193	217.1194	0.5	$C_9H_{17}N_2O_4^-$
211.1431	211.1452	-	$C_{11}H_{19}N_2O_2^-$
185.1675	185.1659	-8.2	$C_{10}H_{21}N_2O^-$
146.0828	146.0823	-3.5	$C_6H_{12}NO_3^-$
130.0860	130.0874	-	$C_6H_{12}NO_2^-$
113.0380	113.0357	-	$C_4H_5N_2O_2^-$
99.0468	99.0452	-	$C_5H_7O_2^-$
88.0422	88.0404	-	$C_3H_6NO_2^-$
85.0311	85.0295	-	$C_4H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+H]^+$
349.1640	349.1605	-9.8	$C_{14}H_{25}N_2O_8^+$
245.1088	245.1132	-	$C_{10}H_{17}N_2O_5^+$
200.1272	200.1281	4.5	$C_{10}H_{18}NO_3^+$
182.1159	182.1176	8.9	$C_{10}H_{16}NO_2^+$
173.1286	173.1285	-0.9	$C_8H_{17}N_2O_2^+$
147.0763	147.0764	0.6	$C_5H_{11}N_2O_3^+$
133.0618	133.0608	-	$C_4H_9N_2O_3^+$
129.0669	129.0659	-	$C_5H_9N_2O_2^+$
115.0510	115.0502	-	$C_4H_7N_2O_2^+$
113.0605	113.0597	-	$C_6H_9O_2^+$
95.0506	95.0491	-	$C_6H_7O^+$
90.0558	90.0550	-	$C_3H_8NO_2^+$

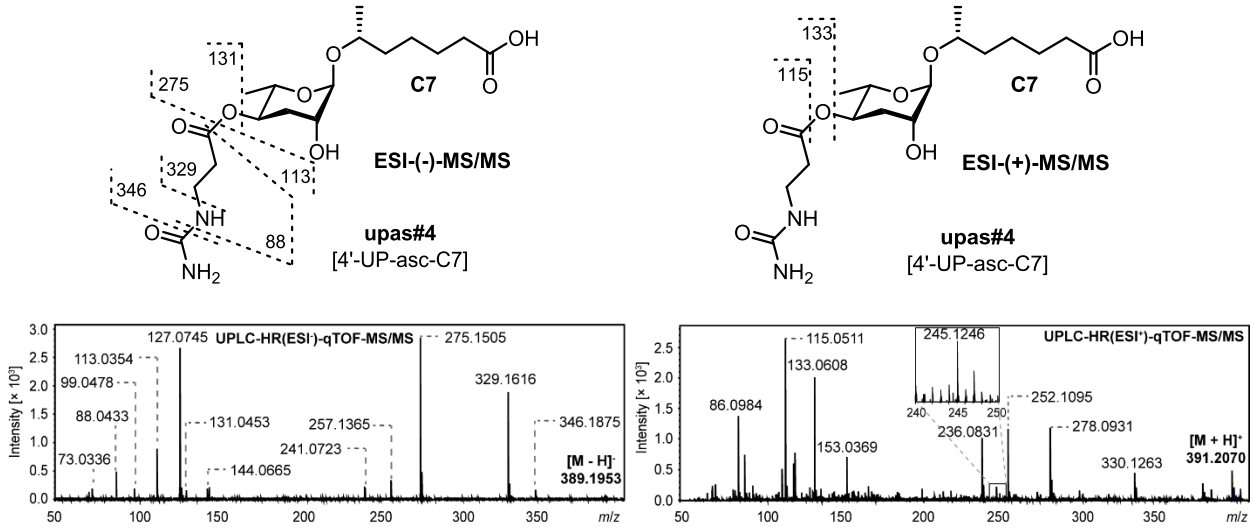
Figure 1. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of upas#5 [4'-UP-asc-C4] in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
361.1615	361.1616	0.4	$C_{15}H_{25}N_2O_8^-$
318.1556	318.1558	0.8	$C_{14}H_{24}NO_7^-$
301.1315	301.1293	-7.5	$C_{14}H_{21}O_7^-$
247.1176	247.1187	4.6	$C_{11}H_{19}O_6^-$
201.0750	201.0768	9.0	$C_9H_{13}O_5^-$
144.0665	144.0666	0.8	$C_6H_{10}N_2O_3^-$
131.0455	131.0462	5.3	$C_4H_7N_2O_3^-$
127.0398	127.0401	1.9	$C_6H_7O_3^-$
113.0354	113.0357	2.0	$C_4H_5N_2O_2^-$
99.0467	99.0452	-	$C_5H_7O_2^-$
88.0427	88.0404	-	$C_3H_6NO_2^-$
73.0331	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+H]^+$
363.1773	363.1762	-3.1	$C_{15}H_{27}N_2O_8^+$
245.1136	245.1132	-1.7	$C_{10}H_{17}N_2O_5^+$
133.0616	133.0608	-6.4	$C_4H_9N_2O_3^+$
115.0514	115.0502	-	$C_4H_7N_2O_2^+$
95.0501	95.0491	-	$C_6H_7O^+$

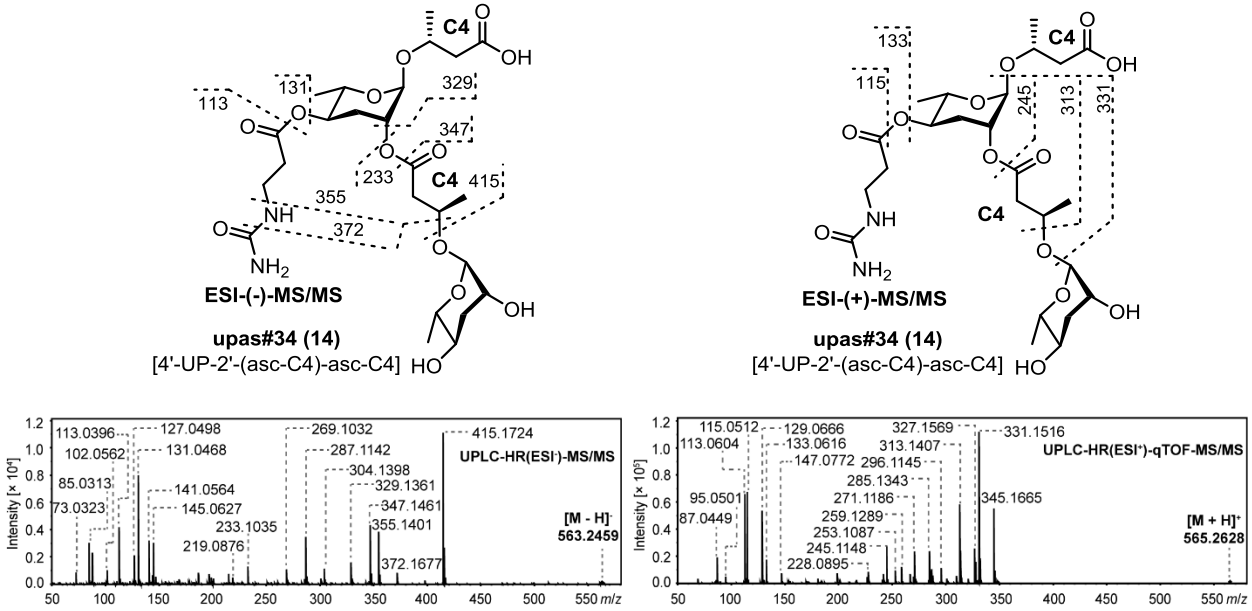
Figure 2. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of upas#3 [4'-UP-asc-C5] in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M − H]$^-$
389.1935	389.1929	-1.4	$C_{17}H_{29}N_2O_8^-$
346.1875	346.1871	-1.0	$C_{16}H_{28}NO_7^-$
329.1616	329.1606	-3.2	$C_{16}H_{25}O_7^-$
275.1505	275.1500	-1.9	$C_{13}H_{23}O_6^-$
257.1365	257.1354	-4.3	$C_8H_{21}N_2O_7^-$
241.0723	241.0718	-2.1	$C_{11}H_{13}O_6^-$
144.0665	144.0666	0.9	$C_6H_{10}NO_3^-$
131.0453	131.0462	7.0	$C_4H_7N_2O_3^-$
127.0745	127.0765	-	$C_7H_{11}O_2^-$
113.0354	113.0357	2.0	$C_4H_5N_2O_2^-$
99.0478	99.0452	-	$C_5H_7O_2^-$
88.0433	88.0404	-	$C_3H_6NO_2^-$
73.0336	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula [M + H]$^+$
391.2070	391.2075	1.2	$C_{17}H_{31}N_2O_8^+$
278.0931	278.0870	-	$C_{10}H_{16}NO_8^+$
252.1095	252.1078	-6.7	$C_9H_{18}NO_7^+$
245.1246	245.1132	-	$C_{10}H_{17}N_2O_5^+$
236.0831	236.0765	-	$C_8H_{14}NO_7^+$
133.0608	133.0608	0.0	$C_4H_9N_2O_3^+$
115.0511	115.0502	-	$C_4H_7N_2O_2^+$

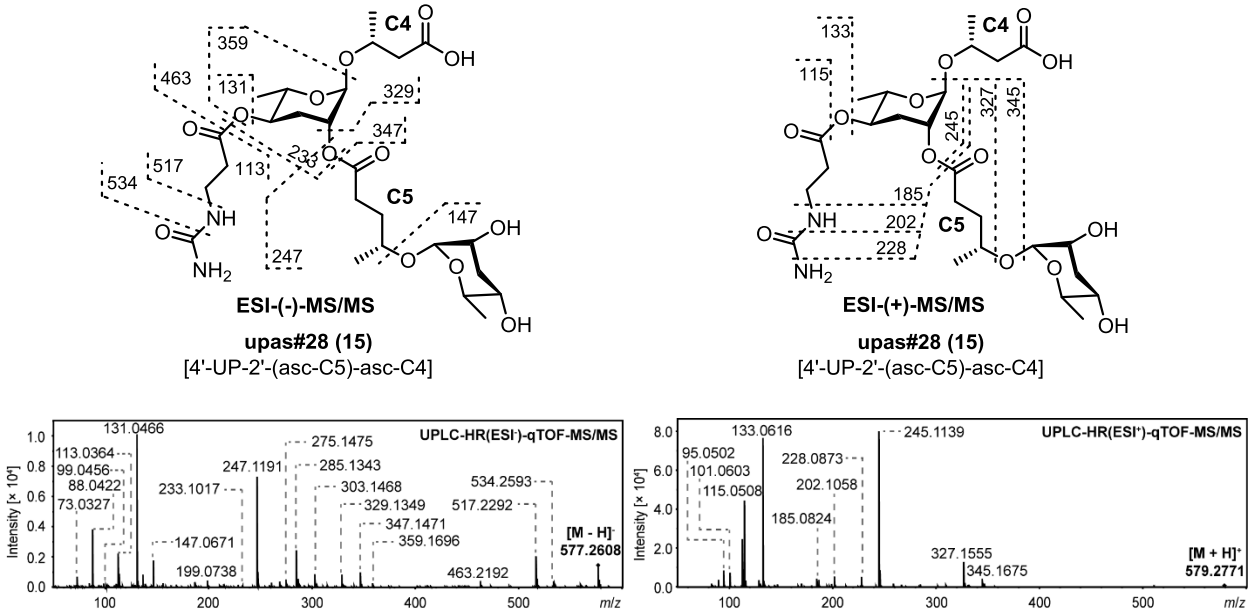
Figure 3. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of upas#4 [4'-UP-asc-C7] in both negative and positive ion modes.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M-H]^-$
563.2459	563.2458	-0.3	$C_{24}H_{39}N_2O_{13}^-$
415.1724	415.1722	-0.5	$C_{18}H_{27}N_2O_9^-$
372.1677	372.1664	-3.4	$C_{17}H_{26}NO_8^-$
355.1401	355.1398	-0.7	$C_{17}H_{23}O_8^-$
347.1461	347.1460	-0.4	$C_{14}H_{23}N_2O_8^-$
329.1361	329.1354	-1.9	$C_{14}H_{21}N_2O_7^-$
304.1398	304.1402	1.1	$C_{13}H_{22}NO_7^-$
287.1142	287.1136	-2.1	$C_{13}H_{19}O_7^-$
269.1032	269.1031	-0.5	$C_{13}H_{17}O_6^-$
233.1035	233.1031	-1.8	$C_{10}H_{17}O_6^-$
219.0876	219.0874	-0.7	$C_9H_{15}O_6^-$
145.0627	145.0619	-5.9	$C_5H_9N_2O_3^-$
141.0564	141.0557	-5.0	$C_5H_9O_3^-$
131.0468	131.0462	-4.7	$C_4H_7N_2O_3^-$
127.0498	127.0513	-	$C_5H_7N_2O_2^-$
113.0392	113.0357	-	$C_4H_5N_2O_2^-$
102.0562	102.0561	-1.7	$C_4H_8NO_2^-$
88.0413	88.0404	-	$C_3H_6NO_2^-$
85.0313	85.0295	-	$C_4H_5O_2^-$
73.0323	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula $[M+H]^+$
565.2628	565.2603	-4.3	$C_{24}H_{41}N_2O_{13}^+$
345.1665	345.1656	-2.4	$C_{15}H_{25}N_2O_7^+$
331.1516	331.1500	-4.8	$C_{14}H_{23}N_2O_7^+$
327.1569	327.1551	-5.5	$C_{15}H_{23}N_2O_6^+$
313.1407	313.1394	-4.1	$C_{14}H_{21}N_2O_6^+$
296.1145	296.1129	-5.6	$C_{14}H_{18}NO_6^+$
285.1343	285.1333	-3.5	$C_{14}H_{21}O_6^+$
271.1186	271.1176	-3.8	$C_{13}H_{19}O_6^+$
259.1289	259.1288	-0.3	$C_{11}H_{19}N_2O_5^+$
253.1087	253.1071	-6.6	$C_{13}H_{17}O_5^+$
245.1148	245.1132	-6.4	$C_{10}H_{17}N_2O_5^+$
228.0895	228.0866	-	$C_{10}H_{14}NO_5^+$
217.1083	217.1071	-5.9	$C_{10}H_{17}O_5^+$
199.0985	199.0965	-	$C_{10}H_{15}O_4^+$
181.0870	181.0859	-6.1	$C_{10}H_{13}O_3^+$
147.0772	147.0764	-5.1	$C_5H_{11}N_2O_3^+$
133.0616	133.0608	-6.0	$C_4H_9N_2O_3^+$
115.0512	115.0502	-	$C_4H_7N_2O_2^+$
113.0604	113.0597	-	$C_6H_9O_2^+$
95.0501	95.0491	-	$C_6H_7O^+$
87.0449	87.0441	-	$C_4H_7O_2^+$

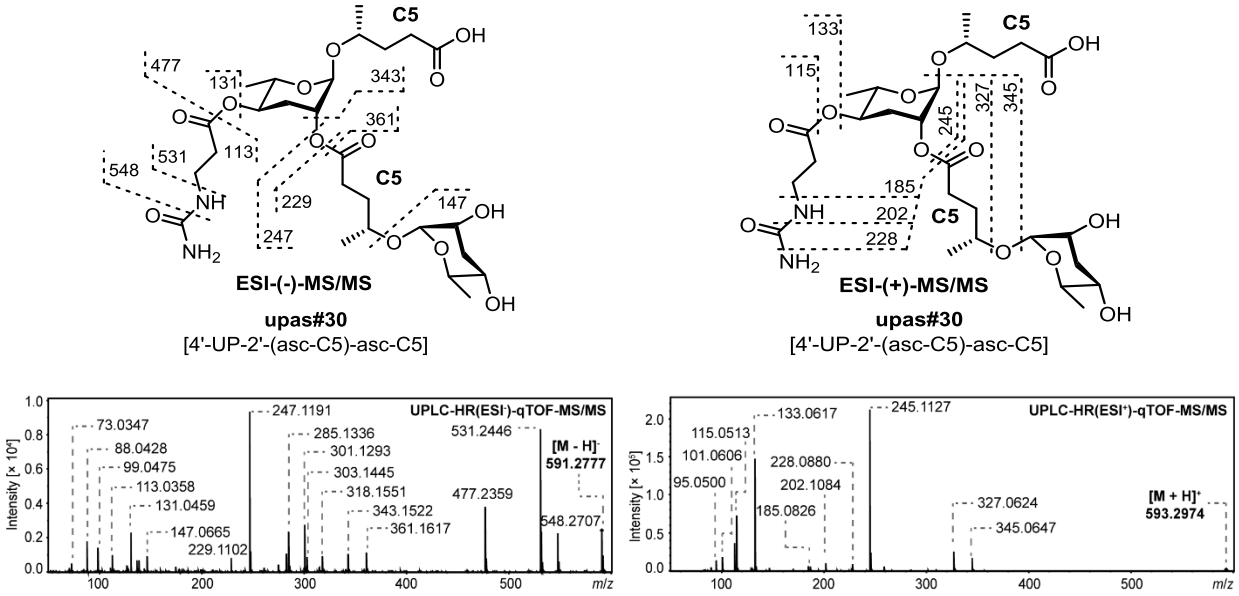
Figure 4. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of upas#34 [4'-UP-2'-(asc-C4)-asc-C4, **14**] in both negative and positive ion modes. Observation of the fragment ion signal for $C_4H_7N_2O_3^-$ (*m/z* 131.0468 [M - H]$^-$) indicated the presence of a ureidopropionic acid group in upas#34 [4'-UP-2'-(asc-C4)-asc-C4, **14**].



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula [M − H]$^-$
577.2608	577.2596	-2.1	$C_{25}H_{41}N_2O_{13}^-$
534.2593	534.2556	-6.9	$C_{24}H_{40}NO_{12}^-$
517.2292	517.2291	-0.2	$C_{24}H_{37}O_{12}^-$
463.2192	463.2185	-1.4	$C_{21}H_{35}O_{11}^-$
359.1696	359.1711	4.2	$C_{17}H_{27}O_8^-$
347.1471	347.1460	-3.2	$C_{14}H_{23}N_2O_8^-$
329.1349	329.1354	-1.5	$C_{14}H_{21}N_2O_7^-$
303.1468	303.1449	-6.3	$C_{14}H_{23}O_7^-$
285.1343	285.1344	0.1	$C_{14}H_{21}O_6^-$
275.1475	275.1500	9.3	$C_{13}H_{23}O_6^-$
247.1191	247.1187	-1.5	$C_{11}H_{19}O_6^-$
233.1017	233.1031	5.9	$C_{10}H_{17}O_6^-$
199.0738	199.0724	-7.0	$C_8H_{11}N_2O_4^-$
147.0671	147.0663	-5.8	$C_6H_{11}O_4^-$
131.0466	131.0462	-3.1	$C_4H_7N_2O_3^-$
113.0364	113.0357	-6.4	$C_4H_5N_2O_2^-$
99.0456	99.0452	-4.8	$C_5H_7O_2^-$
88.0422	88.0404	-	$C_3H_6NO_2^-$
73.0327	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m/z*]	Calc. [*m/z*]	Error [ppm]	Ion Formula [M + H]$^+$
579.2771	579.2760	-2.0	$C_{25}H_{43}N_2O_{13}^+$
345.1675	345.1656	-5.4	$C_{15}H_{25}N_2O_7^+$
327.1555	327.1551	-1.2	$C_{15}H_{23}N_2O_6^+$
245.1139	245.1132	-3.0	$C_{10}H_{17}N_2O_5^+$
228.0873	228.0866	-2.7	$C_{10}H_{14}NO_5^+$
202.1058	202.1074	-7.6	$C_9H_{16}NO_4^+$
185.0824	185.0808	-8.6	$C_9H_{13}O_4^+$
133.0616	133.0608	-5.9	$C_4H_9N_2O_3^+$
115.0508	115.0502	-5.5	$C_4H_7N_2O_2^+$
101.0603	101.0597	-5.9	$C_5H_9O_2^+$
95.0502	95.0491	-	$C_6H_7O^+$

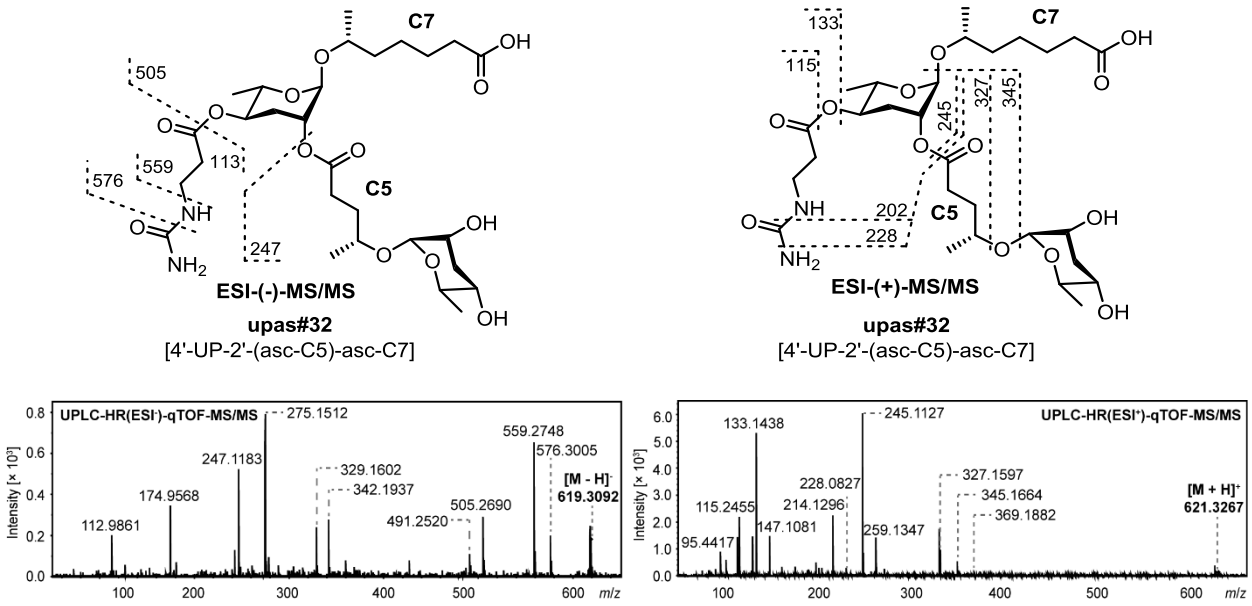
Figure 5. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of upas#28 [4'-UP-2'-(asc-C5)-asc-C4, **15**] in both negative and positive ion modes. Observation of the fragment ion signal for $C_4H_7N_2O_3^-$ (*m/z* 131.0466 [M - H]$^-$) indicated the presence of a ureidopropionic acid group in upas#28 [4'-UP-2'-(asc-C5)-asc-C4, **15**]. Observation of two other ion signals of $C_{15}H_{23}N_2O_6^-$ (*m/z* 327.1555 [M + H]$^+$) and $C_{15}H_{25}N_2O_7^-$ (*m/z* 345.1675 [M + H]$^+$) indicated that the first ascaroside in upas#28 [4'-UP-2'-(asc-C5)-asc-C4, **15**] should carry a C5 side chain.



UPLC-HR(ESI$^-$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
591.2777	591.2771	-1.1	$C_{26}H_{43}N_2O_{13}^-$
548.2707	548.2712	1.0	$C_{25}H_{42}NO_{12}^-$
531.2446	531.2447	0.3	$C_{25}H_{39}O_{12}^-$
477.2359	477.2341	-3.7	$C_{22}H_{37}O_{11}^-$
361.1617	361.1616	-0.3	$C_{15}H_{25}N_2O_8^-$
343.1522	343.1511	-3.4	$C_{15}H_{23}N_2O_7^-$
318.1551	381.1558	2.3	$C_{14}H_{24}NO_7^-$
303.1445	303.1449	1.4	$C_{14}H_{23}O_7^-$
301.1293	301.1293	-0.2	$C_{14}H_{21}O_7^-$
285.1336	285.1344	0.1	$C_{14}H_{21}O_6^-$
247.1191	247.1187	-1.7	$C_{11}H_{19}O_6^-$
229.1102	229.1081	-	$C_{11}H_{17}O_5^-$
147.0665	147.0663	-1.4	$C_6H_{11}O_4^-$
131.0459	131.0462	2.1	$C_4H_7N_2O_3^-$
113.0358	113.0357	-1.7	$C_4H_5N_2O_2^-$
99.0475	99.0452	-	$C_5H_7O_2^-$
88.0428	88.0404	-	$C_3H_6NO_2^-$
73.0347	73.0295	-	$C_3H_5O_2^-$

UPLC-HR(ESI$^+$)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+H]^+$
593.2974	593.2916	-5.2	$C_{26}H_{45}N_2O_{13}^+$
345.0647	345.1656	3.4	$C_{15}H_{25}N_2O_7^+$
327.0624	327.1551	-3.8	$C_{15}H_{23}N_2O_6^+$
245.1127	245.1132	2.0	$C_{10}H_{17}N_2O_5^+$
228.0880	228.0866	-5.9	$C_{10}H_{14}NO_5^+$
202.1084	202.1074	-5.3	$C_9H_{16}NO_4^+$
185.0826	185.0808	-	$C_9H_{13}O_4^+$
133.0617	133.0608	-7.2	$C_4H_9N_2O_3^+$
115.0513	115.0502	-	$C_4H_7N_2O_2^+$
101.0606	101.0597	-	$C_5H_9O_2^+$
95.0500	95.0491	-	$C_6H_7O^+$

Figure 6. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of upas#30 [4'-UP-2'-(asc-C5)-asc-C5] in both negative and positive ion modes**.**



UPLC-HR(ESI⁻)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M-H]^-$
619.3092	619.3084	-1.4	$C_{28}H_{47}N_2O_{13}^-$
576.3005	576.3025	-3.6	$C_{27}H_{46}NO_{12}^-$
559.2748	559.2760	2.1	$C_{27}H_{43}O_{12}^-$
505.2690	505.2654	-7.1	$C_{24}H_{41}O_{11}^-$
491.2520	491.2498	-4.5	$C_{23}H_{39}O_{11}^-$
342.1937	342.1922	-4.5	$C_{27}H_{28}NO_6^-$
329.1602	329.1606	1.1	$C_{16}H_{25}O_7^-$
275.1512	275.1500	-4.3	$C_{13}H_{23}O_6^-$
247.1183	247.1187	1.8	$C_{11}H_{19}O_6^-$
112.9861	112.9880	-	$C_4HO_4^-$

UPLC-HR(ESI⁺)-qTOF-MS/MS			
Obs. [*m*/*z*]	Calc. [*m*/*z*]	Error [ppm]	Ion Formula $[M+H]^+$
621.3267	621.3229	-6.1	$C_{28}H_{49}N_2O_{13}^+$
369.1882	369.1908	-3.9	$C_{14}H_{29}N_2O_9^+$
345.1664	345.1656	-2.2	$C_{15}H_{25}N_2O_7^+$
259.1347	259.1288	-	$C_{11}H_{19}N_2O_5^+$
245.1127	245.1132	1.9	$C_{10}H_{17}N_2O_5^+$
228.0827	228.0866	-	$C_{10}H_{14}NO_5^+$
133.1438		-	$C_4H_9N_2O_3^+$
115.2455		-	$C_4H_7N_2O_2^+$

Figure 7. UPLC-HR(ESI$^{-/+}$)-qTOF-MS/MS mass spectral data of upas#32 [4'-UP-2'-(asc-C5)-asc-C7] in both negative and positive ion modes**.**

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