Supplementary material

Arsenosugar phospholipids and arsenic hydrocarbons in two species of brown macroalgae

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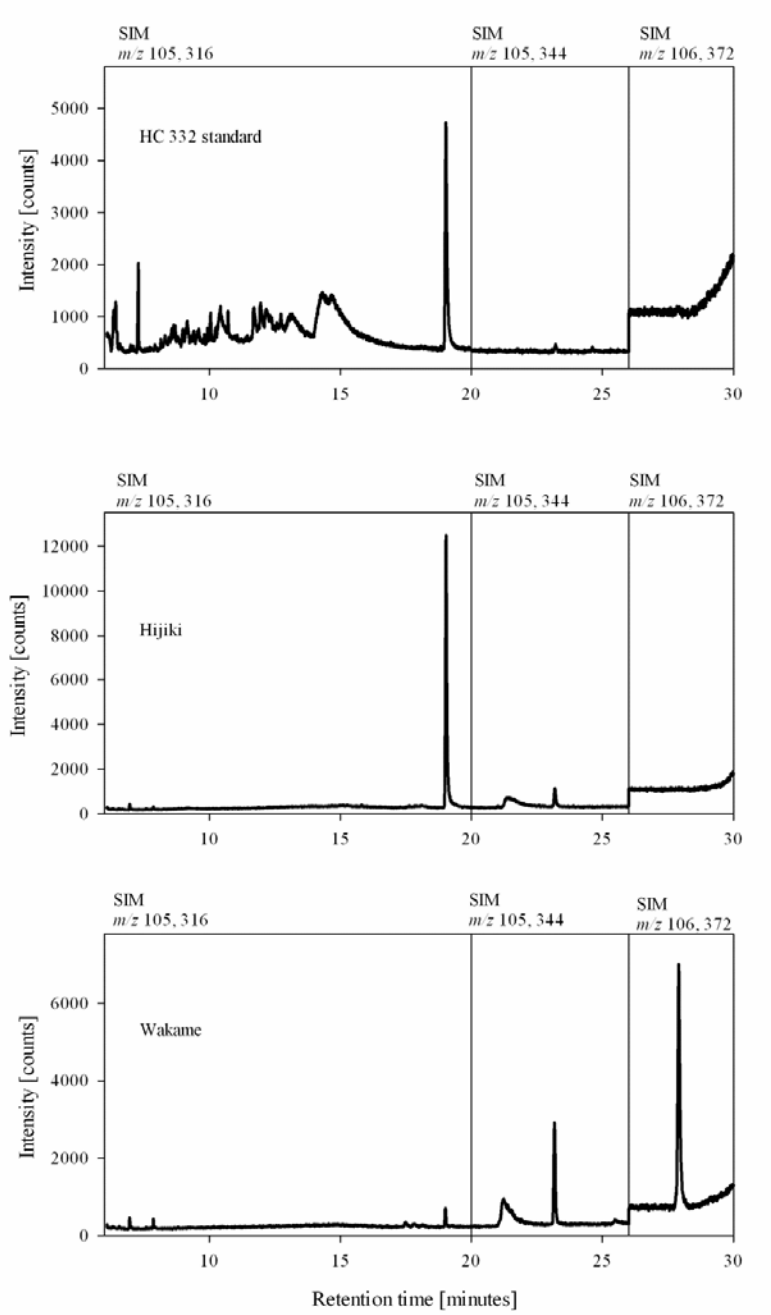
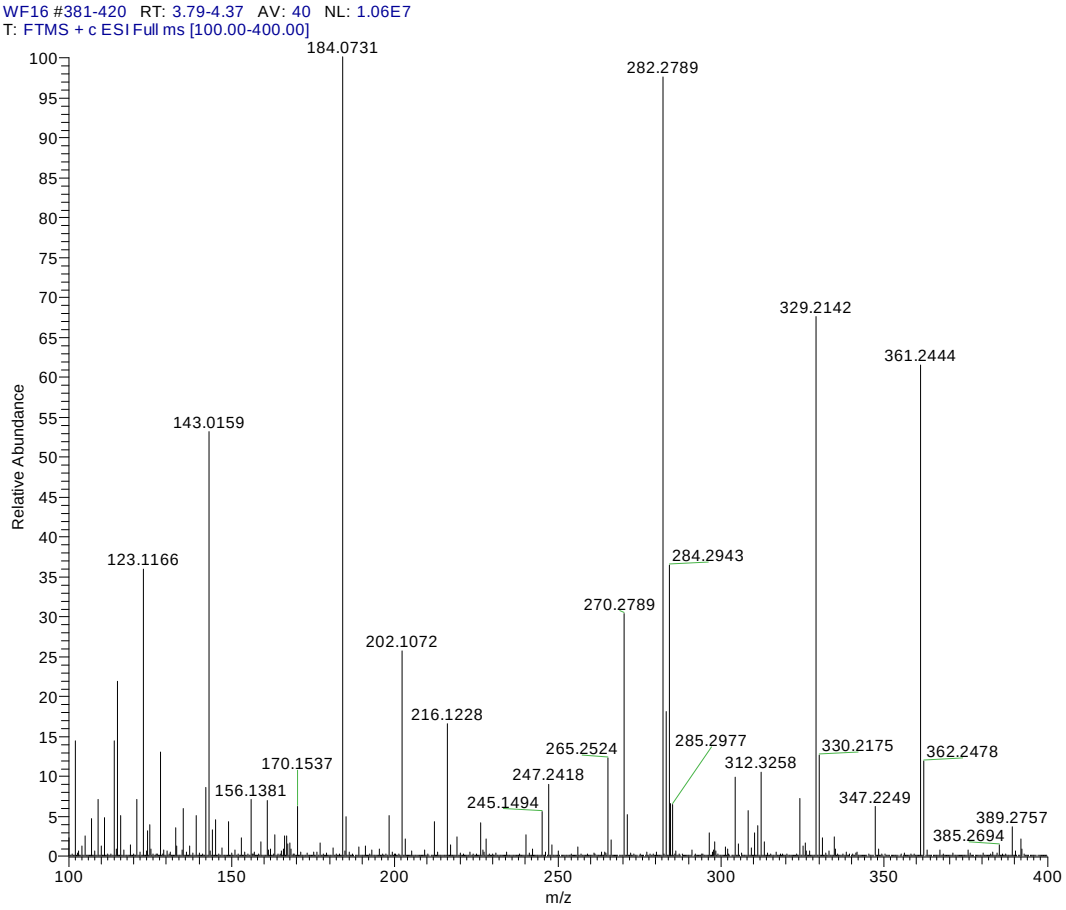


Fig. S1. GC/MS (electron ionisation) of arsenic-hydrocarbons in Wakame and Hijiki, together with standard compound As-HC332. For GC/MS determinations, a system combining a GC 7890A with a quadrupole MS 5975C (Agilent Technologies, Waldbronn, Germany) was used. The injection volume was 1 µL (splitless injection; injection port temperature 280 °C). A (5 %-phenyl)methylpolysiloxane column, 30 m × 0.25-mm internal diameter, 0.25-µm film thickness (DB-5ms from Agilent) was used. Carrier gas was helium. The temperature of the column was started at 50 °C for 1 min, raised to 180 °C at 10 °C min^{-1}, raised to 220 °C at 3 °C min^{-1} and held for 1 min and then raised to 300 °C at 10 °C min^{-1} and held for 4 min. The arsenic-hydrocarbons were detected in scan mode (mass range 20–500), and in selected ion monitoring (SIM) mode at *m/z* 105, 106, 316, 344 and 372 (at 6 min: SIM *m*/*z* 105, 316, dwell time 50 ms; at 20 min: SIM *m*/*z* 105, 344, dwell time 50 ms; at 26 min: SIM *m*/*z* 106, 372, dwell time 50 ms). The arsenic-hydrocarbons lose oxygen (presumably by pyrolysis/reduction) from the dimethylarsinoyl group upon injection, and chromatograph as the respective arsines (M-16), as previously described.[A]

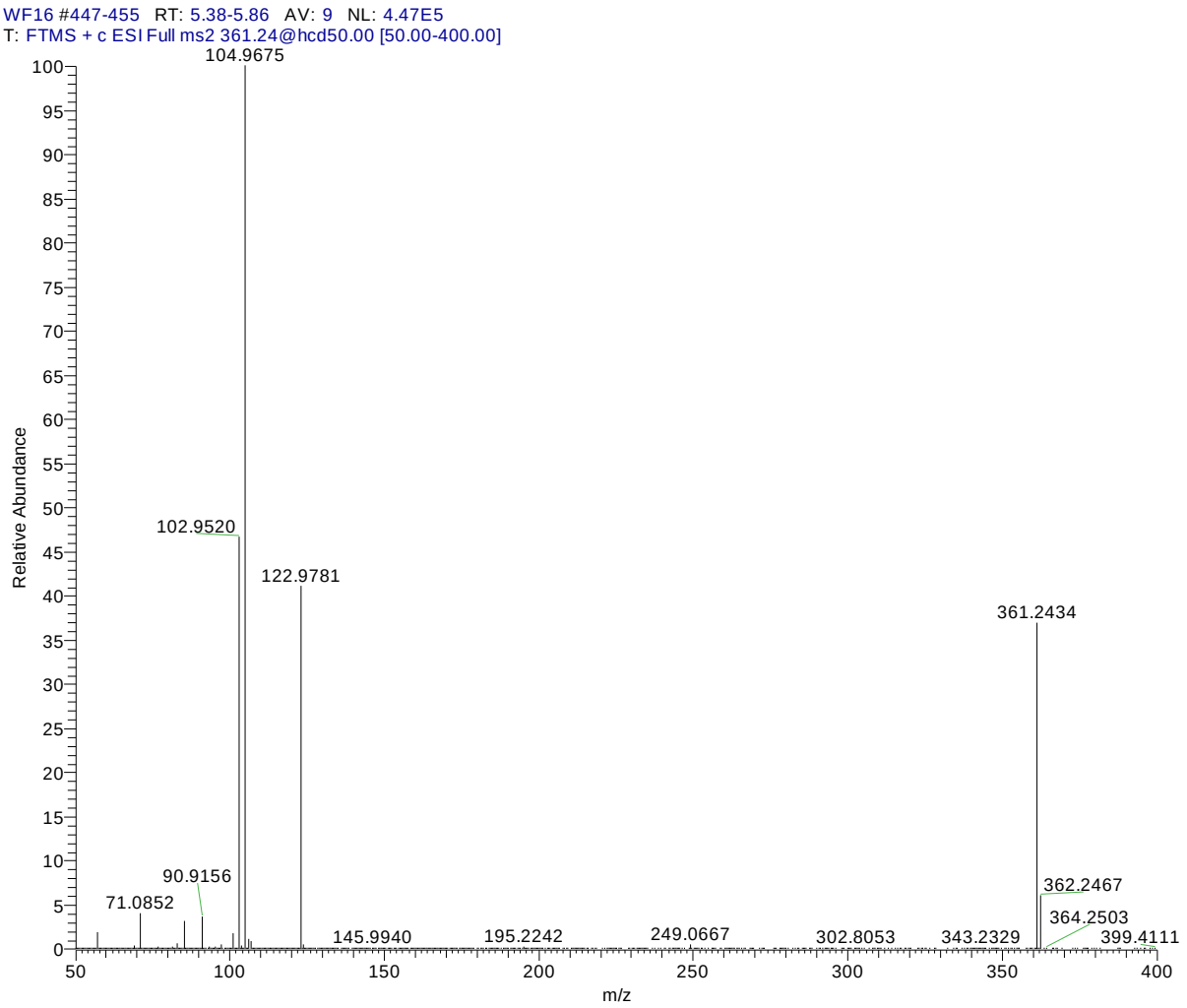
High resolution mass spectra of arsenic-hydrocarbons found in Wakame or Hijiki Wakame fractions

Sample W_F16 *m*/*z* 361



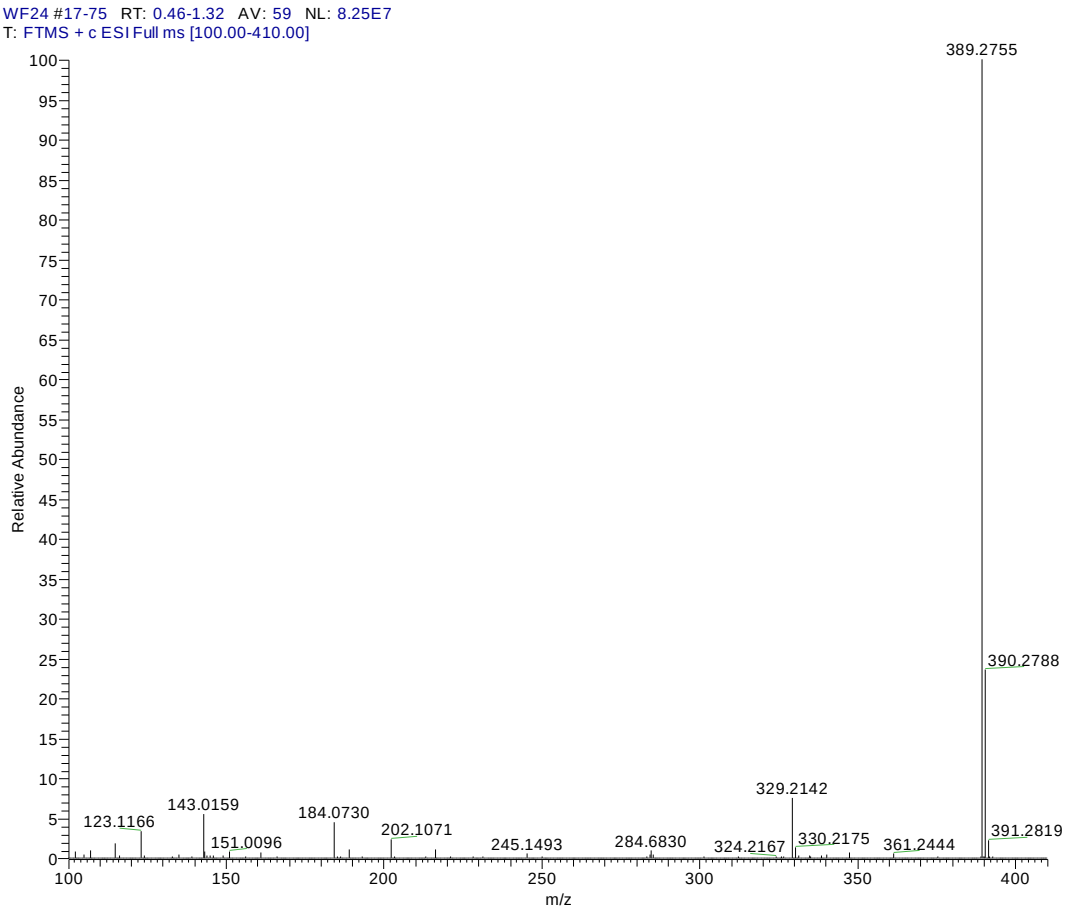
m/*z*	Theoretical mass	Delta (ppm)	Composition
361.2444	361.2446	–0.54	$C_{19}H_{42}OAs$

MS/MS measurements of *m*/*z* 361



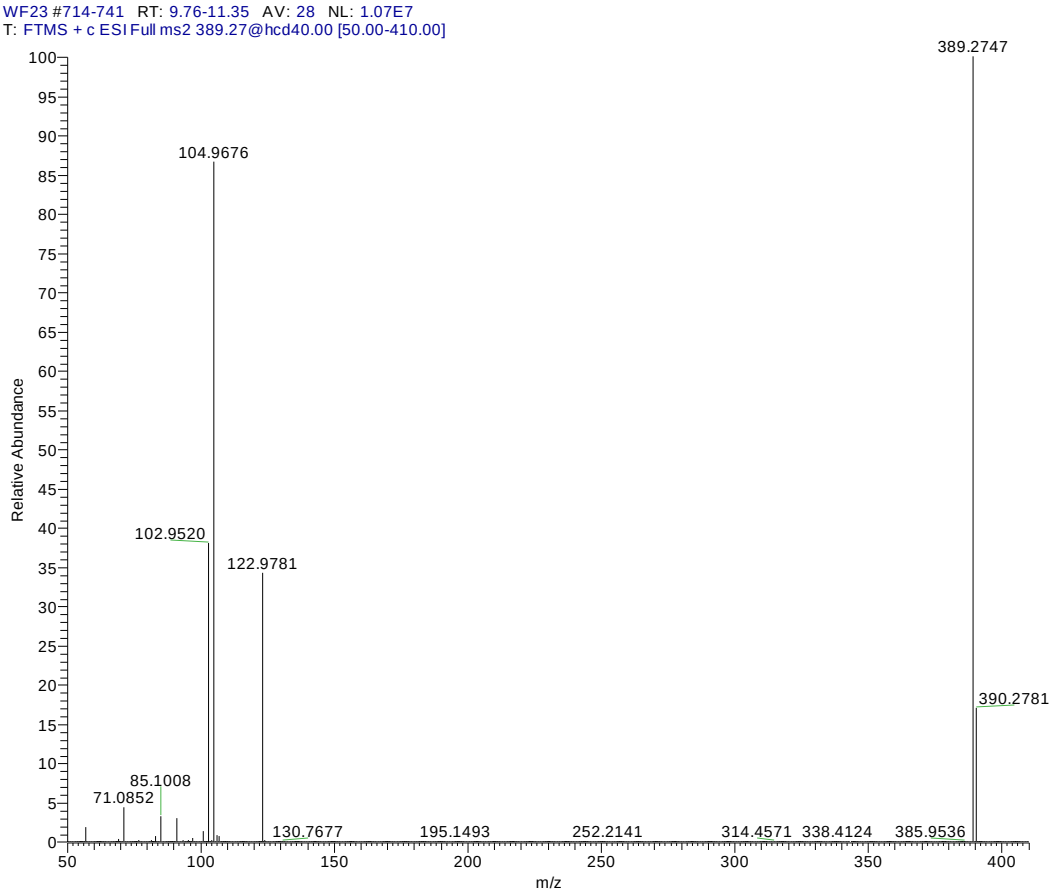
m/*z*	Theoretical mass	Delta (ppm)	Composition
122.9781	122.9786	–3.84	C_2H_8OAs
104.9676	104.9680	–4.27	C_2H_6As
102.9520	102.9523	–3.67	C_2H_4As
90.9156	90.9160	–3.99	OAs

Sample W_F24 *m/z* 389



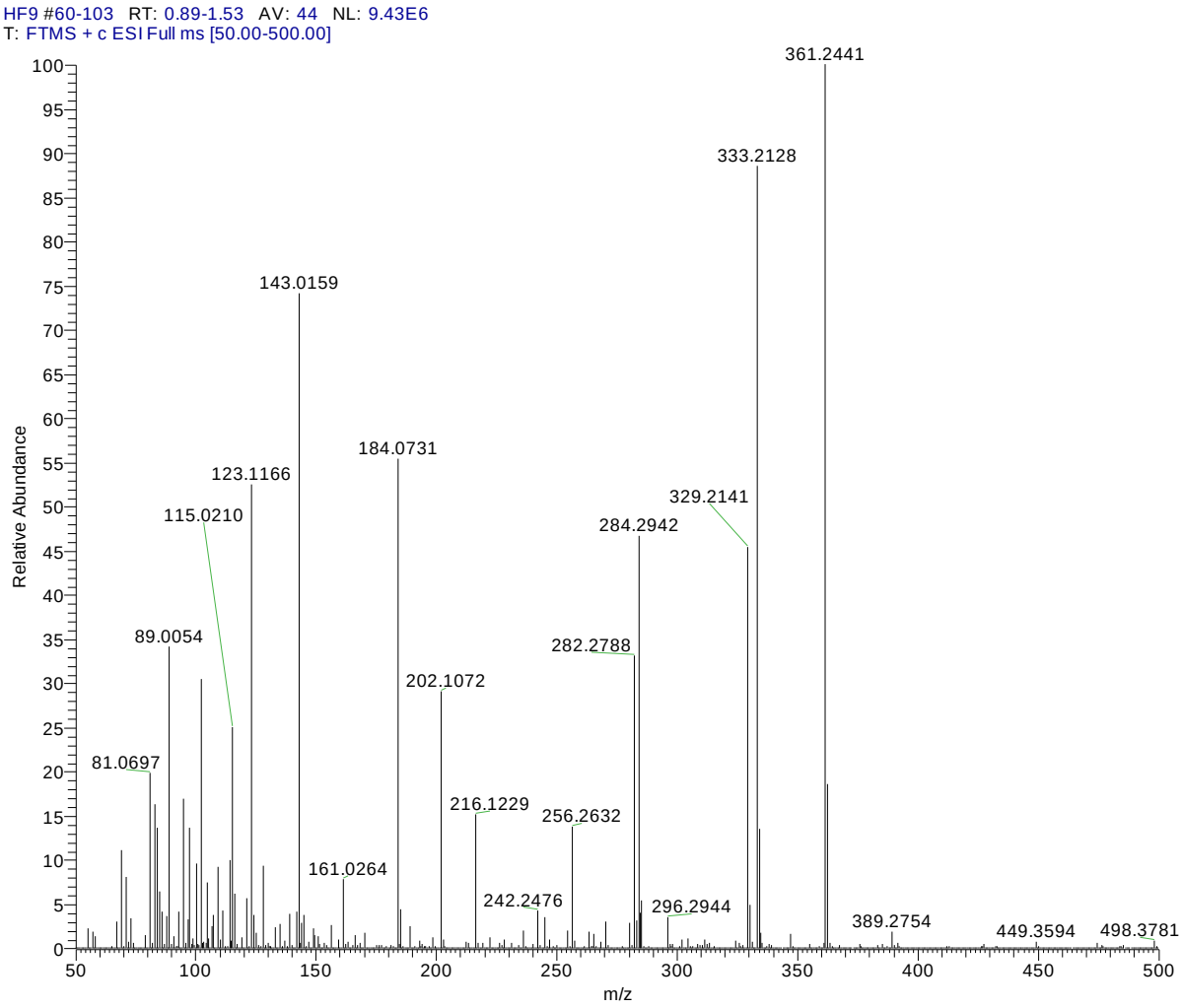
m/z	Theoretical mass	Delta (ppm)	Composition
389.2755	389.2759	–1.04	$C_{21}H_{46}OAs$

MS/MS measurements of *m*/*z* 389



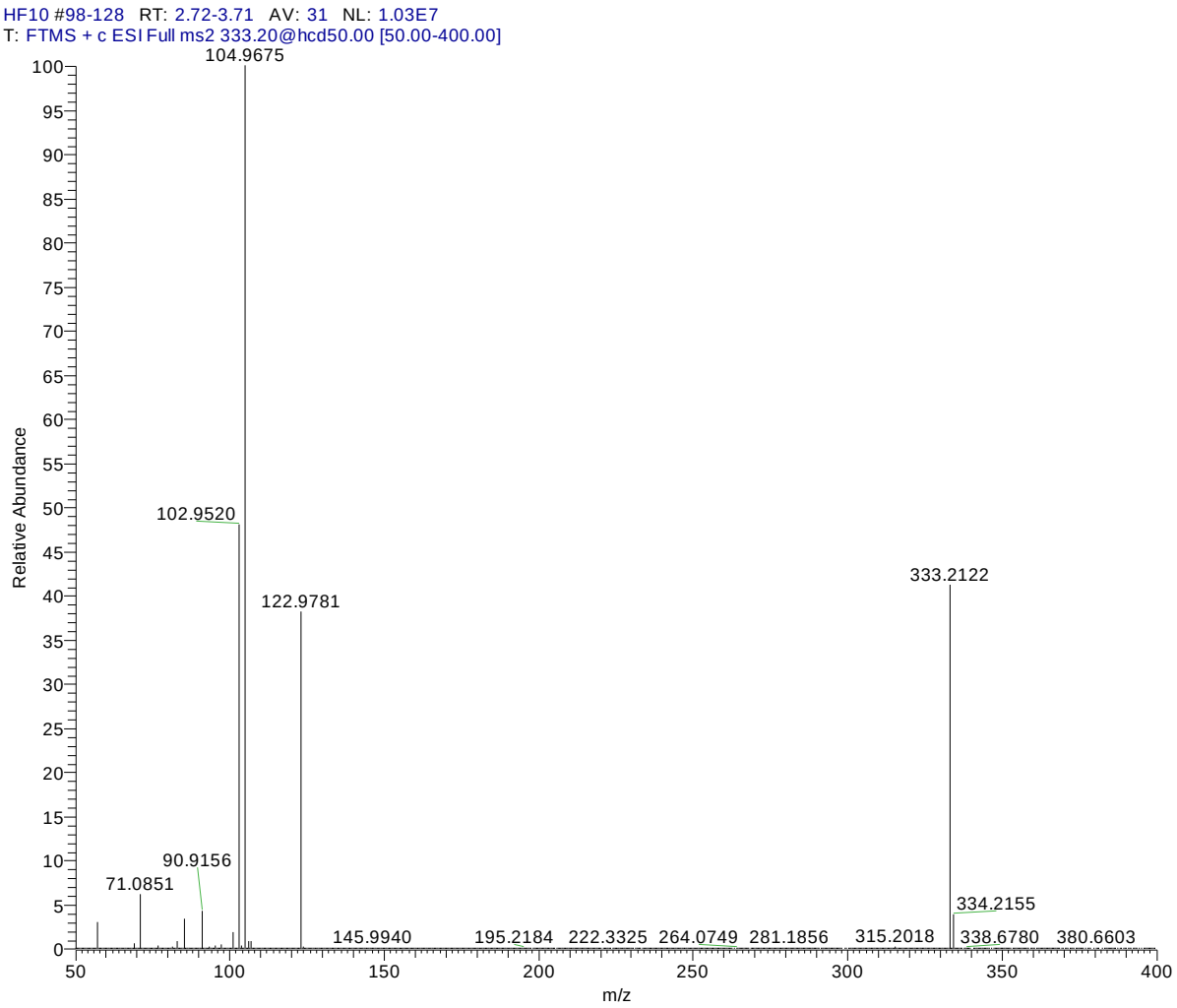
Hijiki fraction 9

Sample H_F09 *m/z* 333



m/z	Theoretical mass	Delta (ppm)	Composition
333.2128	333.2133	–1.63	$C_{17}H_{38}OAs$
361.2441	361.2446	–1.31	$C_{19}H_{42}OAs$

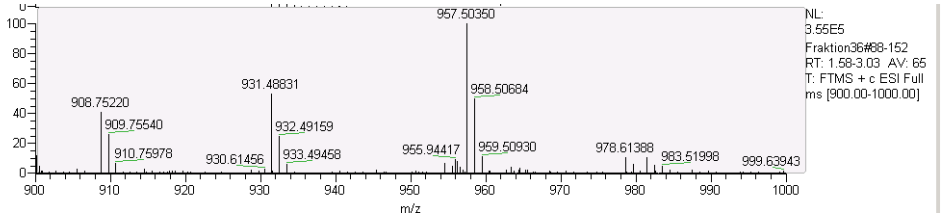
MS/MS of *m/z* 333



ESI source	
Source voltage (kV)	4.01
Sheath gas flow rate (arb)	5.15
Auxillary gas flow rate (arb)	1.03
Typical: capillary voltage (V)	27.98
Capillary temperature (°C)	275.03
Typical: tube lens voltage (V)	154.85
Direct infusion (μL min^{-1})	3
Resolution	60 000
Full scan mode	positive

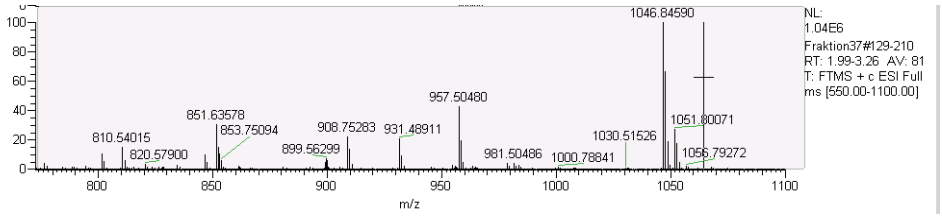
High resolution mass spectra of arsenosugar-phospholipids found in Hijiki

Fraction 37 – As-PL930



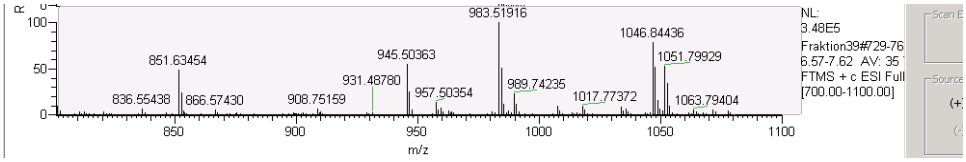
m/z	Theoretical mass	Delta (ppm)	Composition
931.4883	931.4887	–0.46	$C_{43}H_{85}O_{14}AsP$

Fraction 37 – As-PL930



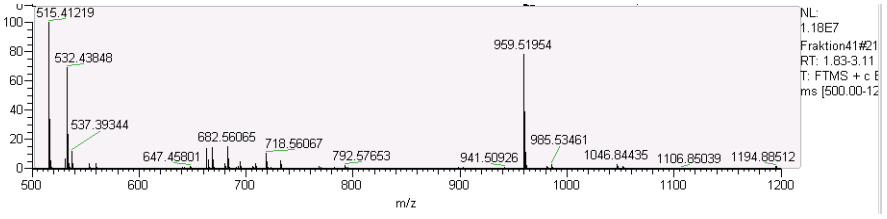
m/z	Theoretical mass	Delta (ppm)	Composition
957.5048	957.5044	0.43	$C_{45}H_{87}O_{14}AsP$

Fraction 39 – As-PL944 and As-PL982



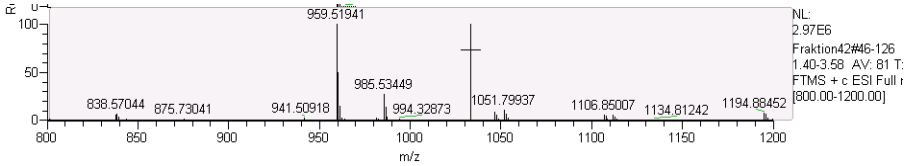
m/z	Theoretical mass	Delta (ppm)	Composition
983.5192	983.5200	–0.90	$C_{47}H_{89}O_{14}AsP$
945.5036	945.5044	–1.26	$C_{44}H_{87}O_{14}AsP$

Fraction 41 – As-PL958



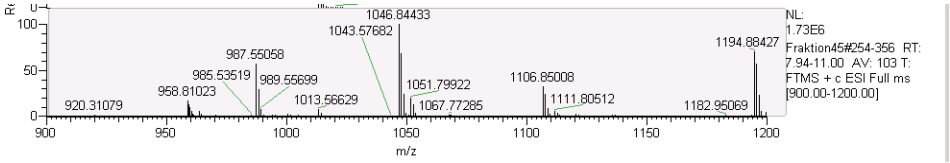
m/z	Theoretical mass	Delta (ppm)	Composition
959.5195	959.5200	–0.52	$C_{45}H_{89}O_{14}AsP$

Fraction 42 – As-PL958 and As-PL984



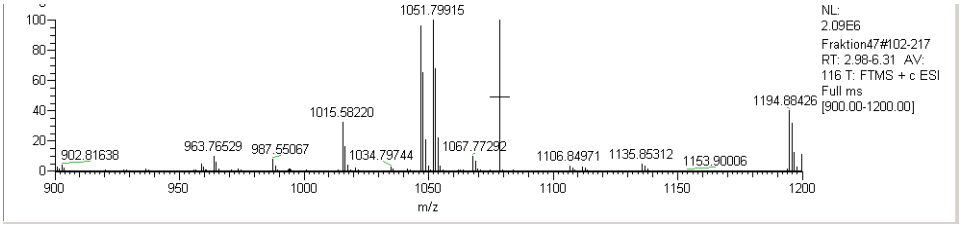
m/z	Theoretical mass	Delta (ppm)	Composition
959.5194	959.5200	–0.66	$C_{45}H_{89}O_{14}AsP$
985.5345	985.5357	–1.22	$C_{47}H_{91}O_{14}AsP$

Fraction 42 – As-PL986 and As-PL1012



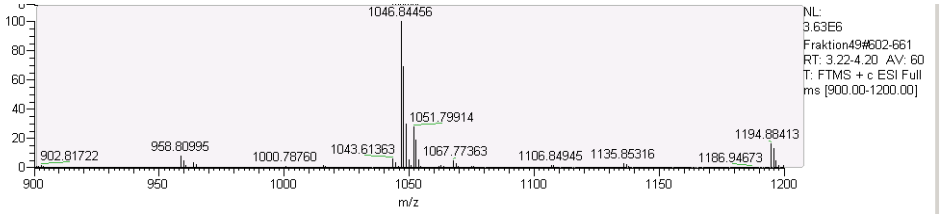
m/z	Theoretical mass	Delta (ppm)	Composition
987.5506	987.5513	–0.80	$C_{47}H_{93}O_{14}AsP$
1013.5663	1013.5670	–0.72	$C_{49}H_{95}O_{14}AsP$

Fraction 47 – As-PL1014



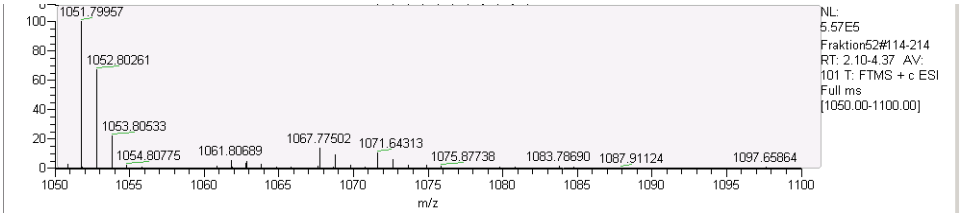
m/z	Theoretical mass	Delta (ppm)	Composition
1015.5822	1015.5826	–0.44	$C_{49}H_{97}O_{14}AsP$

Fraction 49 – As-PL1042



m/z	Theoretical mass	Delta (ppm)	Composition
1043.6136	1043.6139	–0.30	$C_{51}H_{101}O_{14}AsP$

Fraction 52 – As-PL1070



m/*z*	Theoretical mass	Delta (ppm)	Composition
1071.6431	1071.6452	–1.97	$C_{53}H_{105}O_{14}AsP$

[A]*Accurate mass measurements*. In a separate HPLC run, the effluent was split with 10 % going to the ICPMS and the rest collected in 100- or 200-µL fractions. Accurate mass measurements were made on these fractions by direct infusion (5 µL min^{-1}) with a LTQ Orbitrap XL (Thermo Scientific), equipped with a heated electrospray ion source. The system was operated in FTMS high resolution positive scan mode (60 000 resolution) under the following conditions: source voltage, 5.01 kV; vaporiser temperature, 36 °C; sheath gas flow, 20.08 arb; auxiliary gas, 9.98 arb; capillary voltage, 16.02–36 V; capillary temperature, 275 °C; tube lens voltage, 69–124 V.