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Supplementary Material

CHEMICAL COMPOSITION AND MEASURING THE DISTRIBUTION OF HAEMANTHIDINE BY MALDI-TOF MS IMAGING FROM *Crinum scabrum* LEAVES

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General remarks

Solvents of analytical grades with purity higher than 99.5% were purchased from Synth (São Paulo, SP, Brazil). The dehydration oven (Ethik Technology, São Paulo, SP, Brazil) was used. Rotavapor model R-3 (BUCHI, Valinhos, SP, Brazil) connected to a V-100 vacuum pump (BUCHI, Valinhos, SP, Brazil) was used. For open-layer chromatography, 5 × 30 cm and 5 × 28 cm glass columns packed with silica gel stationary phase (particle size of 0.04-0.063 mm and 25-40 μm) in hexane were used. Nuclear magnetic resonance (NMR) spectra were recovered on a Varian 400 MHz instrument (Palo Alto, USA) using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as the internal standard both from Sigma-Aldrich (St. Louis, MO, USA). The chemical shift (δ) is in ppm and J values in hertz (Hz).

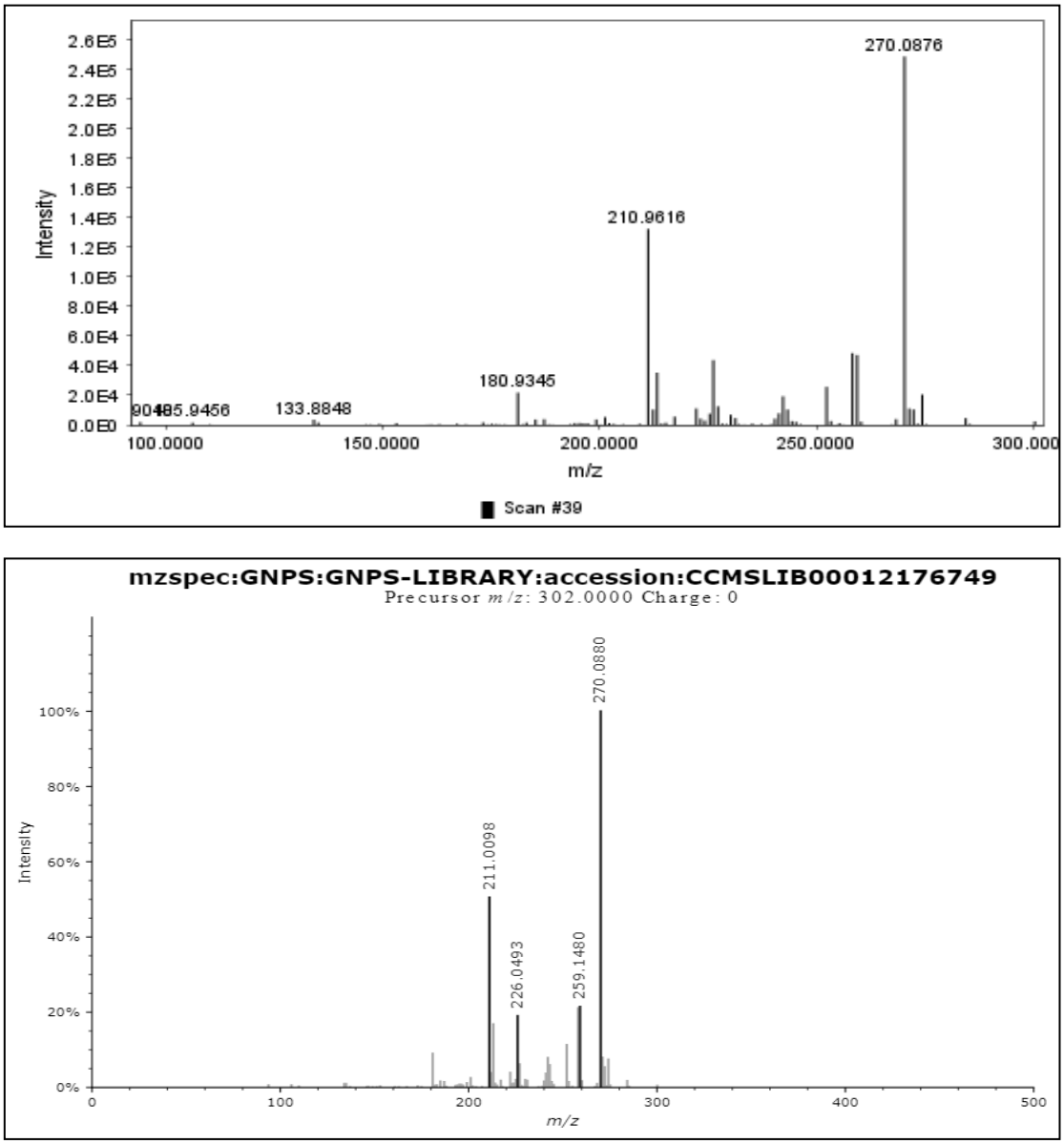
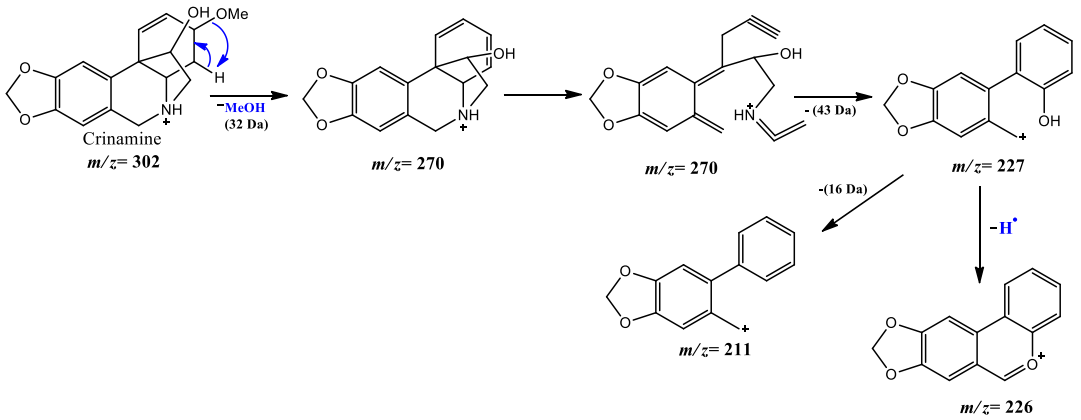
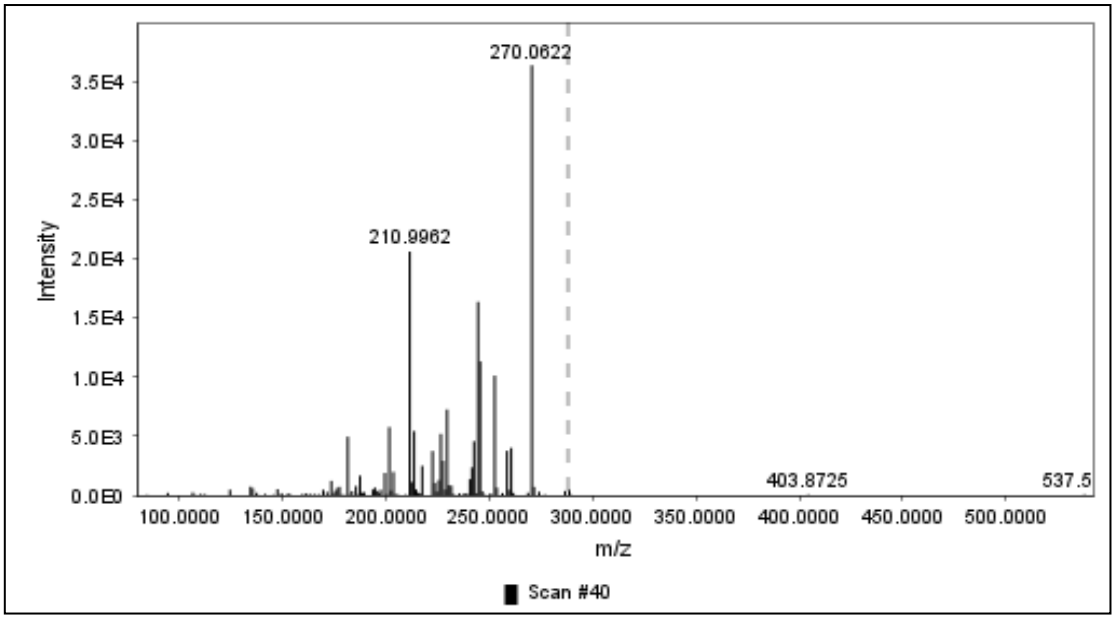


Figure 1S. *Comparison of fragmentation spectra obtained by ESI-LTQ-XL-MS/MS and from GNPS for the alkaloid crinamine*



Scheme 1S. *Proposed fragmentation pathway for crinamine*



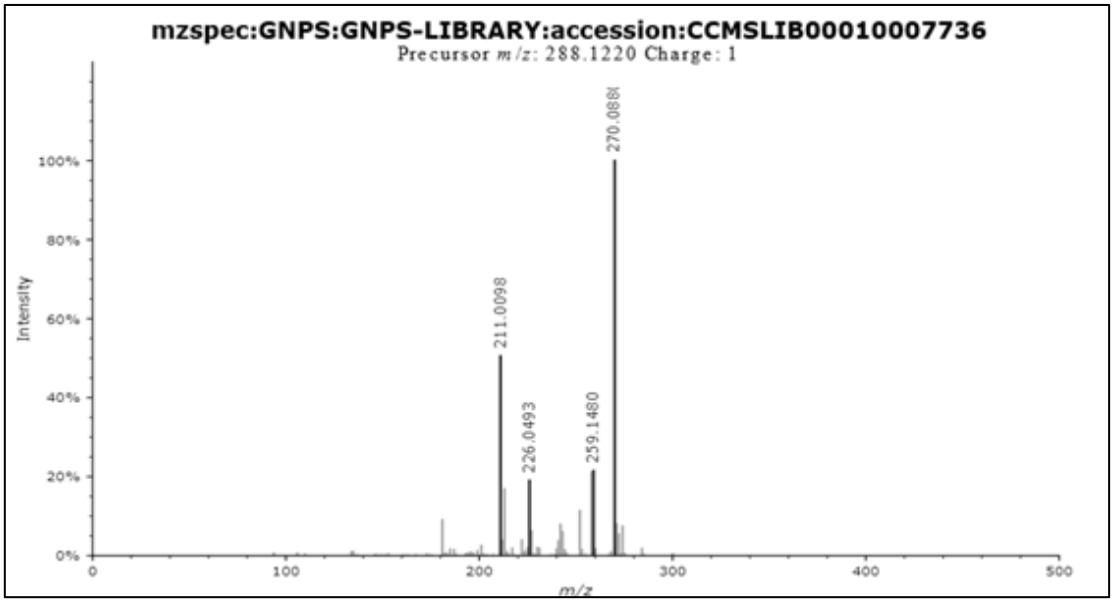
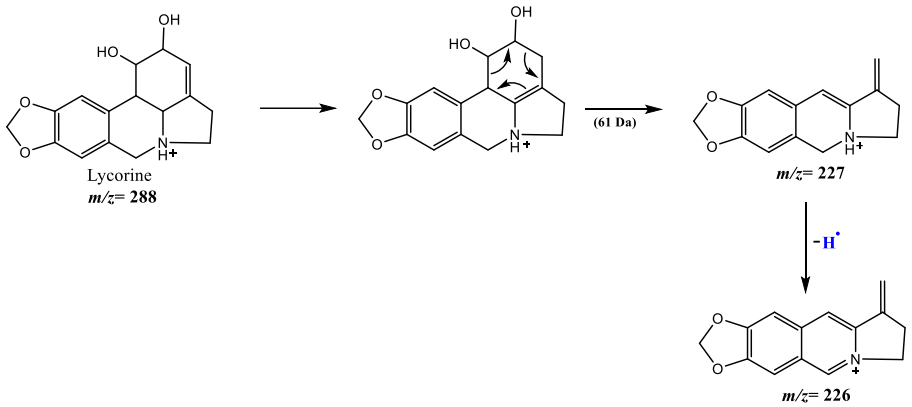


Figure 2S. *Comparison of fragmentation spectra obtained by ESI-LTQ-XL-MS/MS and from GNPS for the alkaloid lycorine*



Scheme 2S. *Proposed fragmentation pathway for lycorine*

Table 1S. ^{1}H NMR (400 MHz, $CDCl_3$) spectroscopic data for compound **1**/**2**, **3** and **4**, compared with literature values

	δ ^{1}H, *J* in Hz					
No.	**1 / 2**	Haemanthidine/ 6-*epi*- haemanthidine (400 MHz, $CDCl_3$)[1]	**3**	Crinamine (400 MHz, CD_3OD)[2]	**4**	Trisphaeridine (400 MHz, CD_3OD)[1]
1	6.20-6.25 m	6.28-6.38 m	6.25 bs	6.10 d (10.5)	8.39 d (9.5)	8.86 dd (8.0, 2.0)
2	6.20-6.25 m	6.28-6.38 m	6.25 bs	6.30 dd (10.5, 2.1)	7.66 m	7.97 td (7.6, 1.6)
3	3.91-3.93 m	3.87 m	3.96-4.02 m	3.99 m	7.71 m	8.01 td (7.6, 1.6)
4	–	–	2.04-2.16 m	2.09 m	8.21 d (9.3)	8.17 dd (8.0, 1.6)
4α	2.17-2.24 m / 2.26-2.33 m	2.38 ddd (13.6, 13.6, 4.4) / 2.27 br dd (12.4, 4.8)	2.08 m	–	–	–
4β	2.09-2.12 m / 2.17-2.24 m	2.20 dd (13.6, 4.4) / 2.07 dd (13.6, 4.8)	2.08 m	–	–	–
4a	3.79 dd (12.0, 6.0) / 3.33-3.37 m	3.73 dd (13.6, 4.8) / 3.28-3.36 m	3.22 dd (4.7, 13.3)	obscured signal	–	–
6	–	–	–	–	9.11 s	9.55 s
6α	– / 5.02 s	– / 5.16 s	3.69 d (16.8)	4.34 d (16.5)	–	
6β	5.62 s / –	5.87 s / –	4.31 d (16.8)	3.81 d (16.5)	–	
7	6.98 s / 6.82 s	6.95 s / 6.80 s	6.47 s	6.56 s	7.36 s	7.83 s
10	6.75 s / 6.77 s	6.76 s / 6.78 s	6.80 s	6.85 s	7.93 s	8.44 s
11	–	–	3.96-4.02 m		–	–

Table 1S. ^{1}H NMR (400 MHz, $CDCl_3$) spectroscopic data for compound **1**/**2**, **3** and **4**, compared with literature values (cont.)

	δ ^{1}H, *J* in Hz					
No.	**1 / 2**	Haemanthidine/ 6-*epi*- haemanthidine (400 MHz, $CDCl_3$)[1]	**3**	Crinamine (400 MHz, CD_3OD)[2]	**4**	Trisphaeridine (400 MHz, CD_3OD)[1]
11 endo	3.91-3.93 m	3.96 m	3.96 m	3.33 (t-like)	–	
12 endo	3.33-3.37 m / 4.21 dd (14.4, 6.8)	4.26 dd (14.0, 6.8) / 3.28-3.36 m	3.31-3.42 m	3.25 (t-like)	–	
12 exo	3.03 dd (17.6, 6.4) / 3.33-3.37 m	3.09 dd (14.4, 2.4) / 3.28-3.36 m	3.38 m	–	–	
OCH_2O	5.90 d (1.4) / 5.93 d (1.4)	5.91 2d (1.6) / 5.93 2d (1.3)	5.89 d (1.5) / 5.90 d (1.5)	5.80 s	6.19 s	6.42 s
OCH_3	3.40 s	3.36 s / 3.34 s	3.40 s	3.41 s	–	–

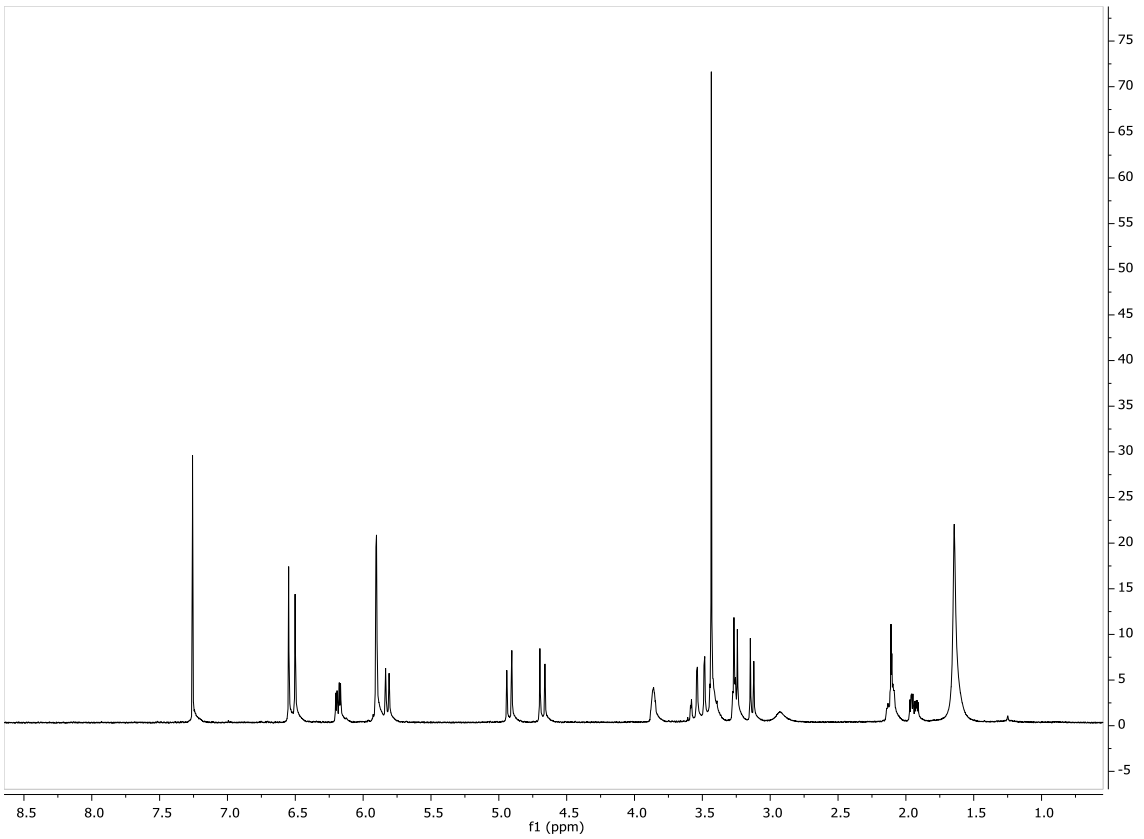


Figure 3S. *^{1}H NMR spectrum of compound **C1/2** in $CDCl_3$ (400 MHz)*

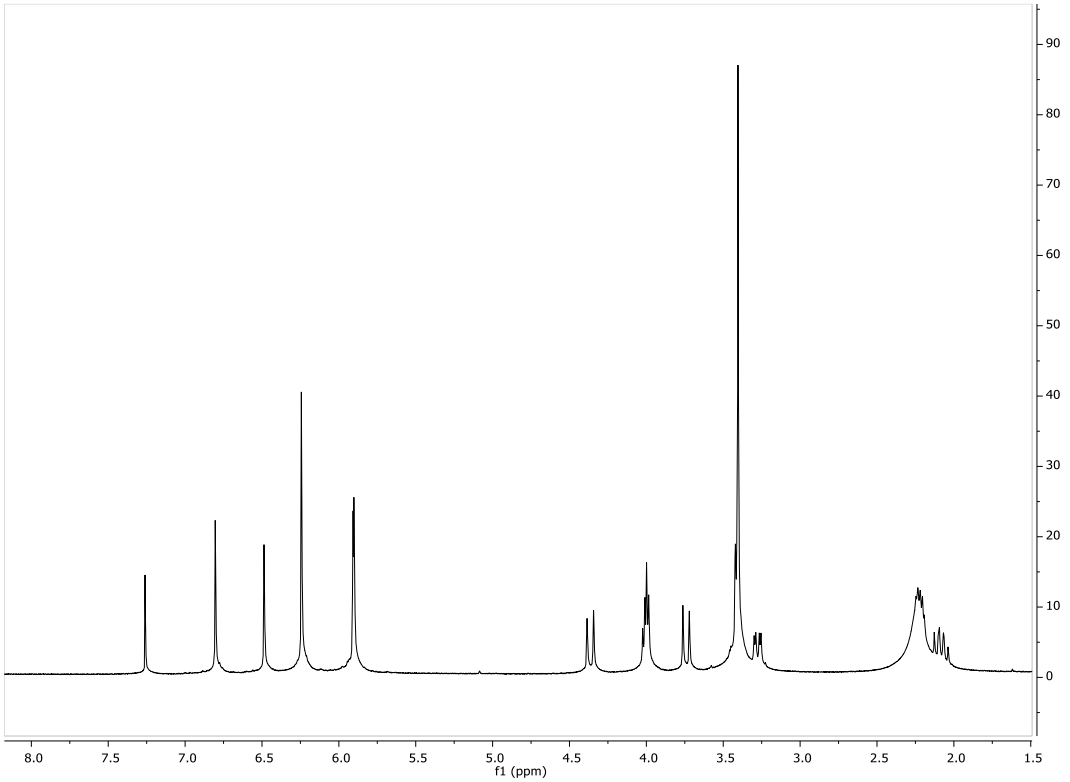


Figure 4S. *^{1}H NMR spectrum of compound **C3** in $CDCl_3$ (400 MHz)*

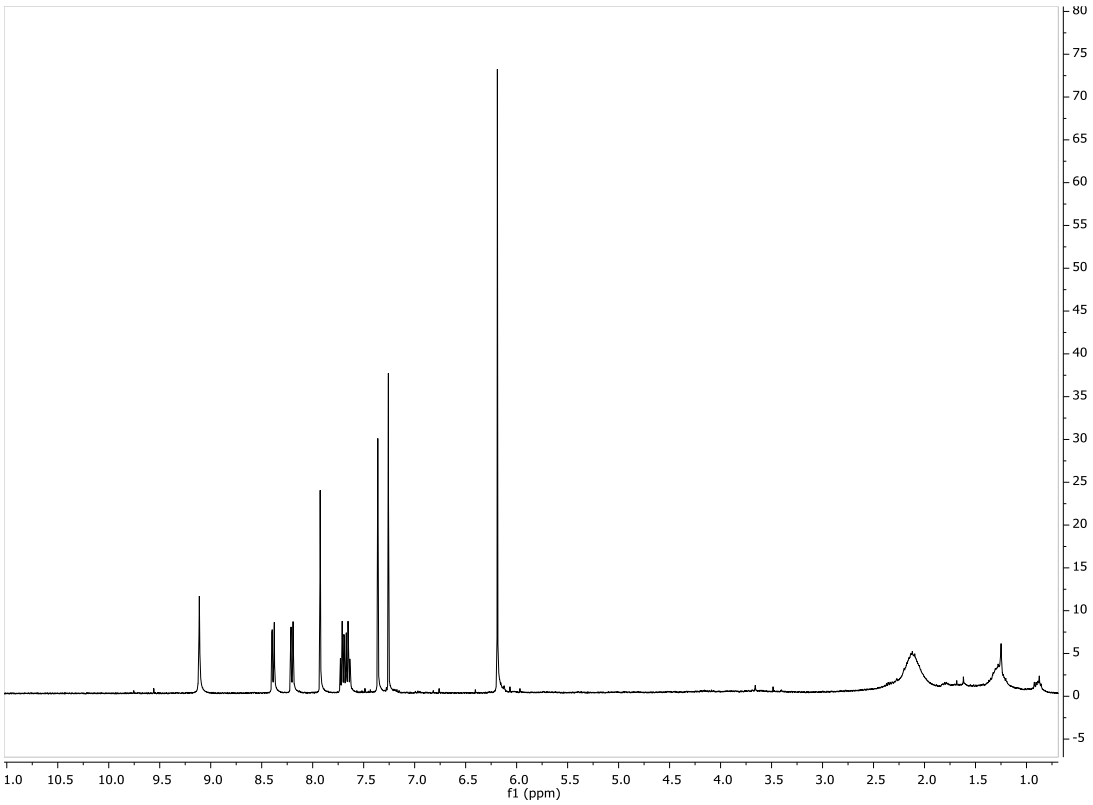


Figure 5S. *^{1}H NMR spectrum of compound **C4** in $CDCl_3$ (400 MHz)*

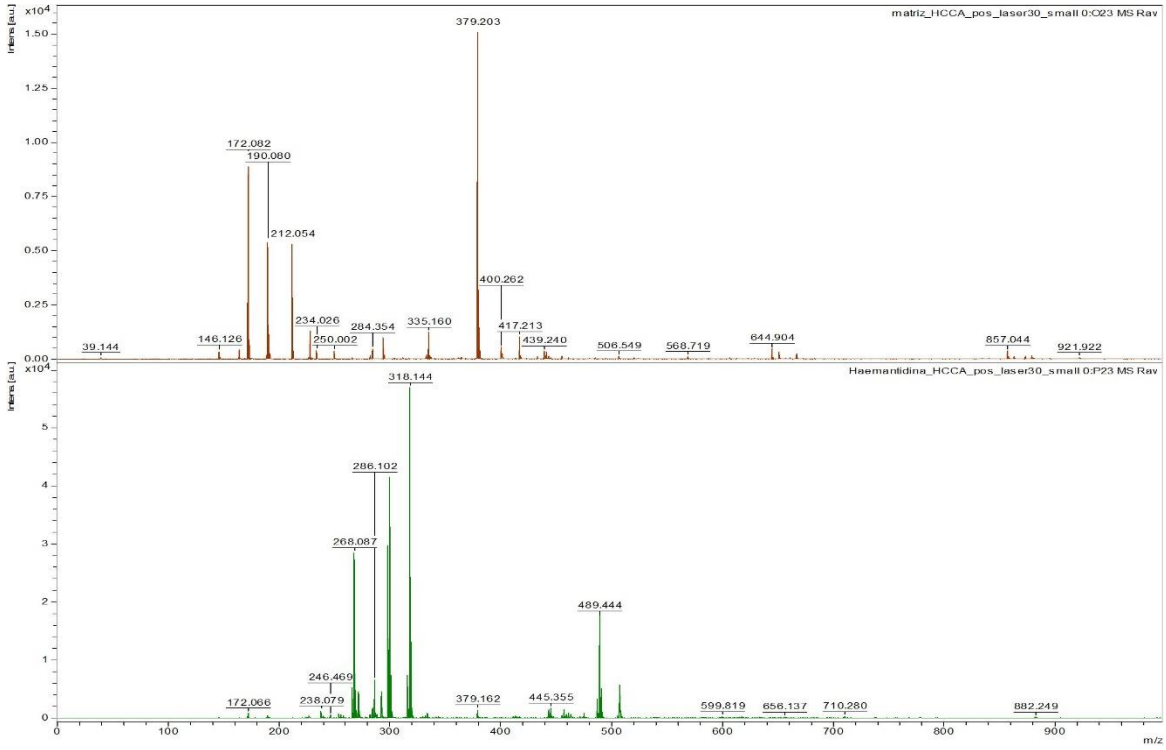


Figure 6S. *Comparison of mass spectrum of the HCCA matrix and that of the detected ion corresponding to haemanthidine*

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