Supporting Infgormation

Elysiapyrones from *Elysia diomedea*. Do such Metabolites Evidence an Enzymatically-Assisted Electrocyclization Cascade for the Biosynthesis of their Bicyclo[4.2.0]octane Core?

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Index:

Table 1. NMR Data of **1** and **2** [500 MHz, δ ppm, (*J*) Hz]

	1			**2**	
nº	δ_H	δ_C	HMBC	δ_H	δ_C
1	---	163.2		---	162.0
2	---	105.4		---	100.9
3	---	182.5		---	181.7
4	---	118.9		---	117.8
5	---	166.1		---	162.3
6	---	44.9		---	44.3
7	2.27 (s)	54.0	C-5, C-6, C-8, C-11, C-17, C-20	2.93 (s)	46.9
8	---	59.2		---	56.2
9	3.18 (s)	61.1	C-10, C-11	3.08 (s)	60.3
10	---	56.7		---	56.7
11	2.39 (s)	62.1	C-7, C-12, C-13	2.82 (s)	57.8
12	---	35.7		---	34.0
13	2.43 q (7.5)	43.8	C-5, C-6, C-11,C-12	2.52 q (6.8)	46.0
14	1.19 d (7.5)	20.3	C-6, C-12, C-13	1.16 d (6.8)	10.0
15	1.93 (s)	7.4	C-1, C-2, C-3	1.86 (s)	7.1
16	1.89 (s)	11.0	C-3, C-4, C-5	2.08 (s)	10.8
17	1.38 (s)	23.4	C-5, C-6, C-7, C-13	1.37 (s)	15.7
18	1.55 (s)	22.0	C-7, C-8, C-9	1.40 (s)	21.4
19	1.20 (s)	11.2	C-9, C-10, C-11	1.58 (s)	21.0
20	1.03 (s)	18.4	C-7, C-11, C-12, C-13	1.17 (s)	26.1
21	3.98 (s)	60.4	C-1	4.03 (s)	57.3

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Experimental

General procedures

Optical rotations were measured on a Perkin-Elmer model 343 Plus polarimeter using a Na lamp at 25 ºC. IR spectra were obtained with a Perkin-Elmer 1650/FTIR spectrometer. ^{1}H NMR and ^{13}C NMR, HSQC, HMBC and COSY spectra were measured employing a Bruker AMX 500 instrument operating at 500 MHz for ^{1}H NMR and at 125 MHz for ^{13}C NMR. Two-dimensional NMR spectra were obtained with the standard Bruker software. EIMS and HRMS data were taken on a Micromass Autospec spectrometer. HPLC separations were performed with a Hewlett Packard 1050 (Jaigel-Sil semipreparative column, 10μ, 20x250 mm) with hexane-EtOAc mixtures. The gel filtration column (Sephadex LH-20) used hexane-MeOH-CH_2Cl_2 (3:1:1) as solvent. The spray reagent for TLC was H_2SO_4-H_2O-AcOH (1:4:20).

Biological Material

One hundred twenty specimens of *Elysia diomedea* were collected by hand off Saboga Island (Panama) at –1.5 m.

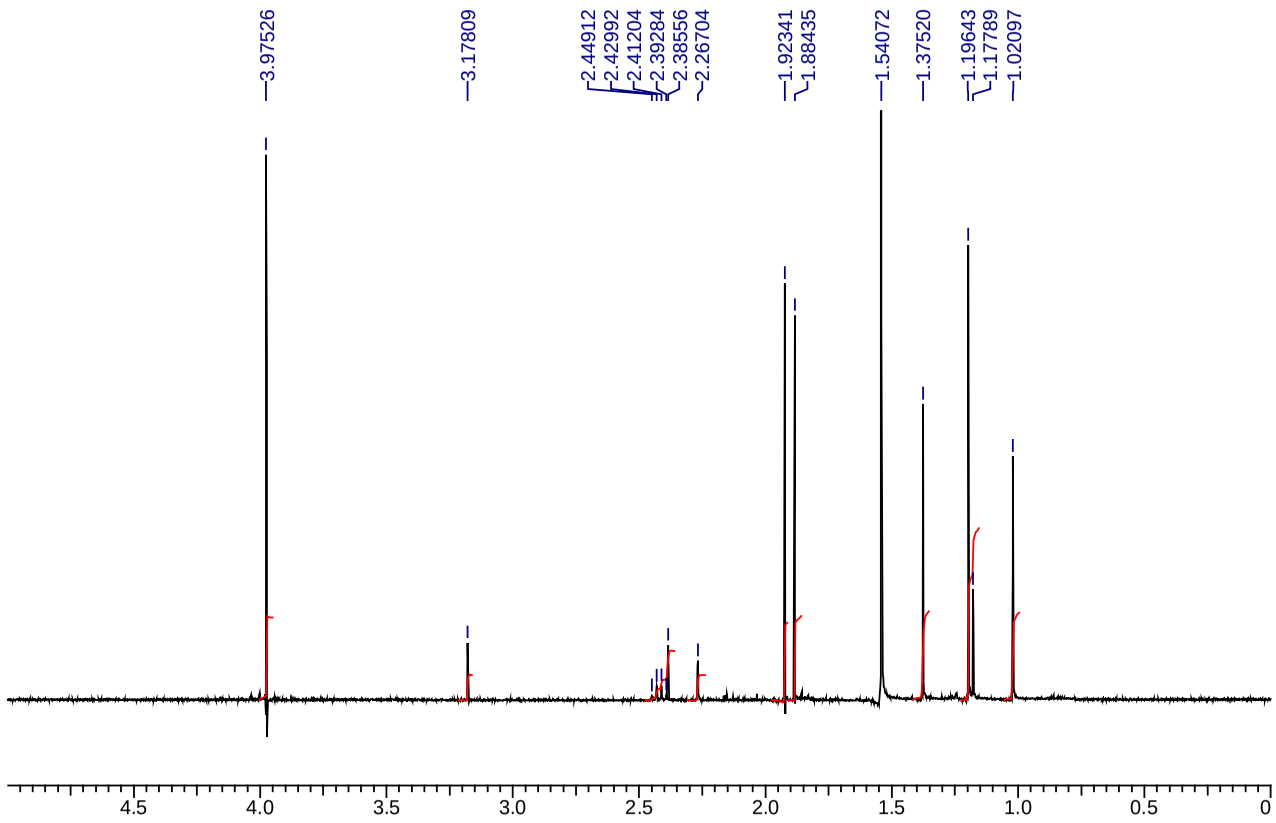
Extraction and Isolation

Wet samples were extracted with methanol at room temperature, and were concentrated to give a dark residue (5.0 g). The extract was partitioned between EtOAc (3x75 ml) and water (75 ml). The EtOAc extracts were combined to obtain a brown oil (643.5 mg) that was chromatographed on a LH-20 column. Fractions containing pyrones, as indicated by their ^{1}H NMR spectra, were further chromatographed on HPLC to give compounds **1** (0.6 mg), and **2** (0.6 mg) and the known compounds tridachione (77.7 mg), 9,10-deoxytridachione (15.2 mg), 15-norphotodeoxytridachione (3.2 mg), and iso-9,10-deoxytridachione (2.2 mg).

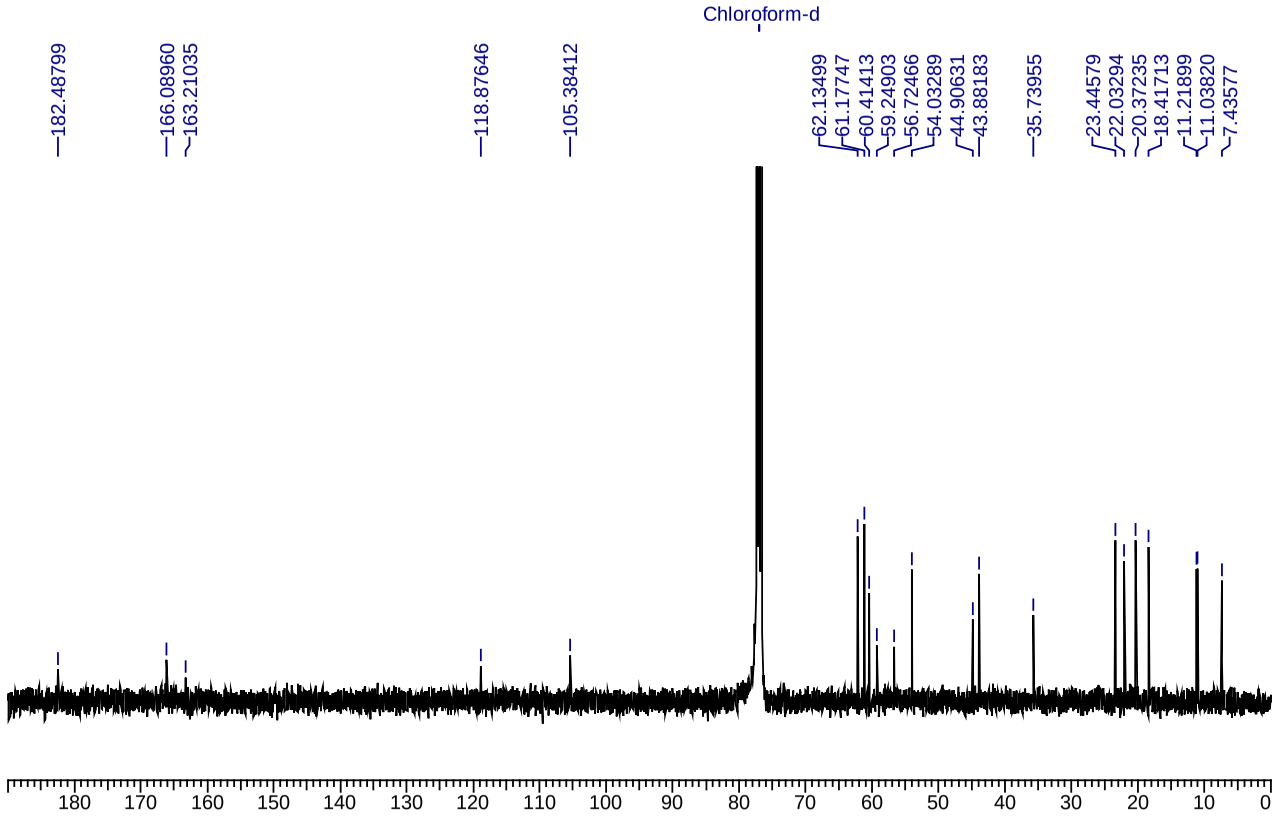
Elysiapyrone A (1). Colorless oil; $[\alpha]_D^{25}$ = +37º (*c* 0.08, $CHCl_3$); IR (film): ν_{max} 1548 cm^{-1}; EIMS (70 eV): *m/z* (%): 360 [M^+] (6), 345 [M^+ –Me] (6), 317 [M^+ – Me –CO] (13), 209 (64), 193 (100); HREIMS 360.1883 (calcd for $C_{21}H_{28}O_5$ 360.1936), 345.1652 (calcd for $C_{20}H_{25}O_5$ 345.17019), 317.1676 (calcd for $C_{19}H_{25}O_4$ 317.1752).

Elysiapyrone B (2). Colorless oil; $[\alpha]_D^{25}$ = +225º (c 0.08, $CHCl_3$); IR (film): ν_{max} 1548 cm^{-1}; EIMS (70 eV): *m/z* (%) 360 [M^+] (20), 345 [M^+ –Me] (4), 317 [M^+ – Me –CO] (14), 209 (63), 193 (100); HREIMS 360.1925 (calcd for $C_{21}H_{28}O_5$ 360.1936), 345.1651 (calcd for $C_{20}H_{25}O_5$ 345.17019), 317.1718 (calcd for $C_{19}H_{25}O_4$ 317.1752).

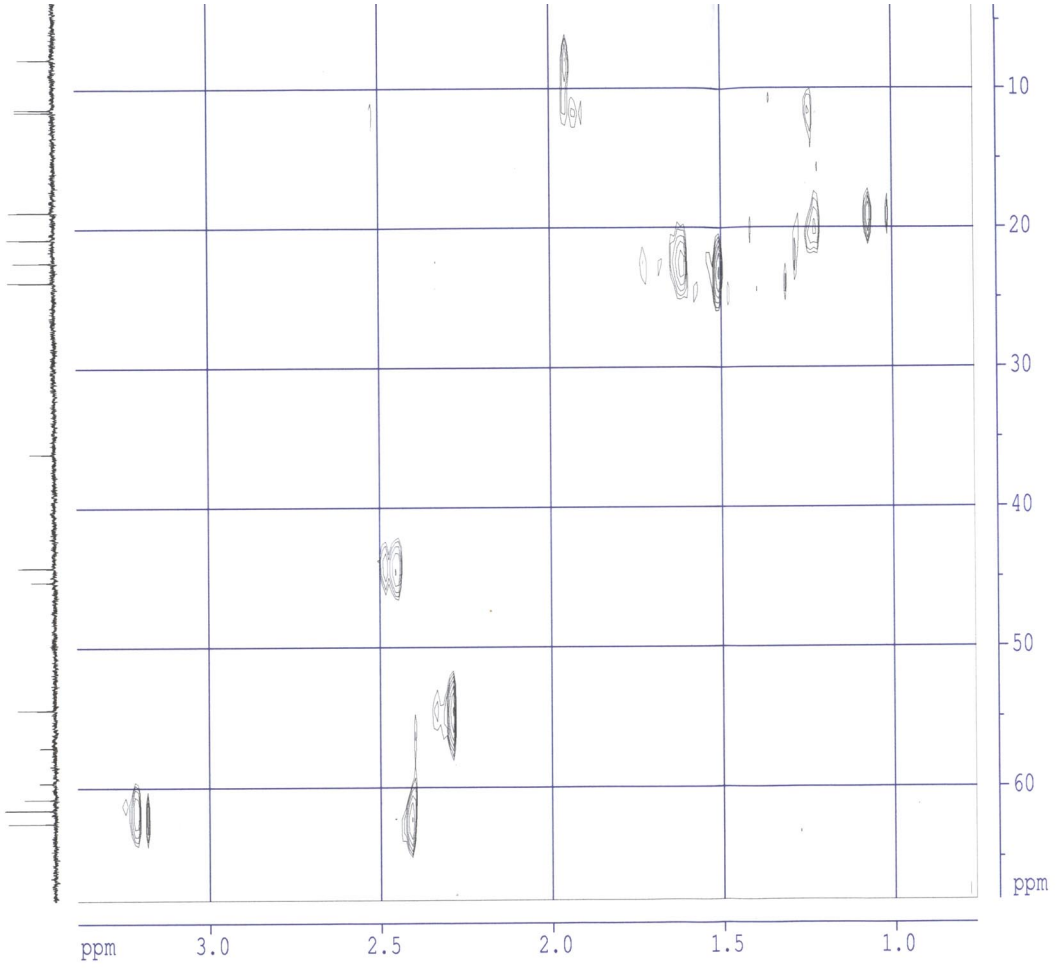
^{1}H NMR of elysiapyrone A (**1**) in $CDCl_3$



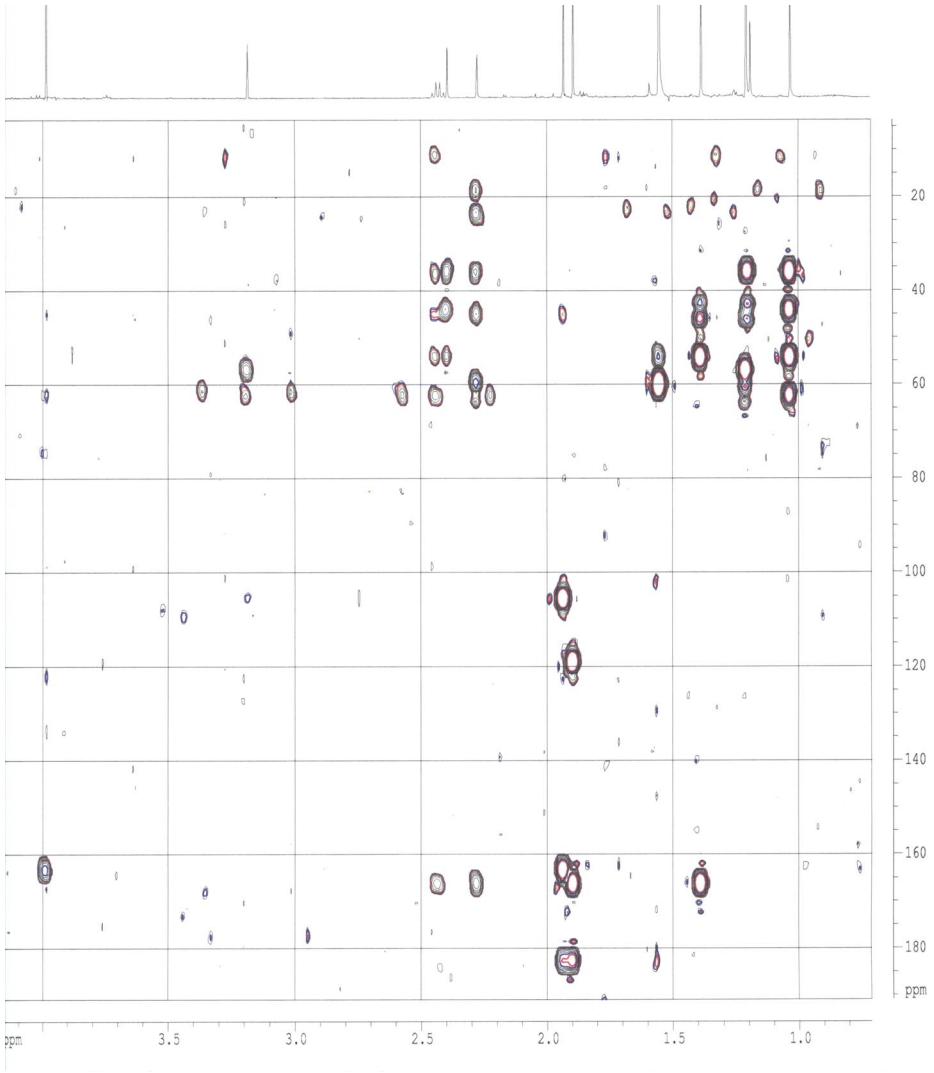
^{13}C NMR of elysiapyrone A (**1**) in $CDCl_3$



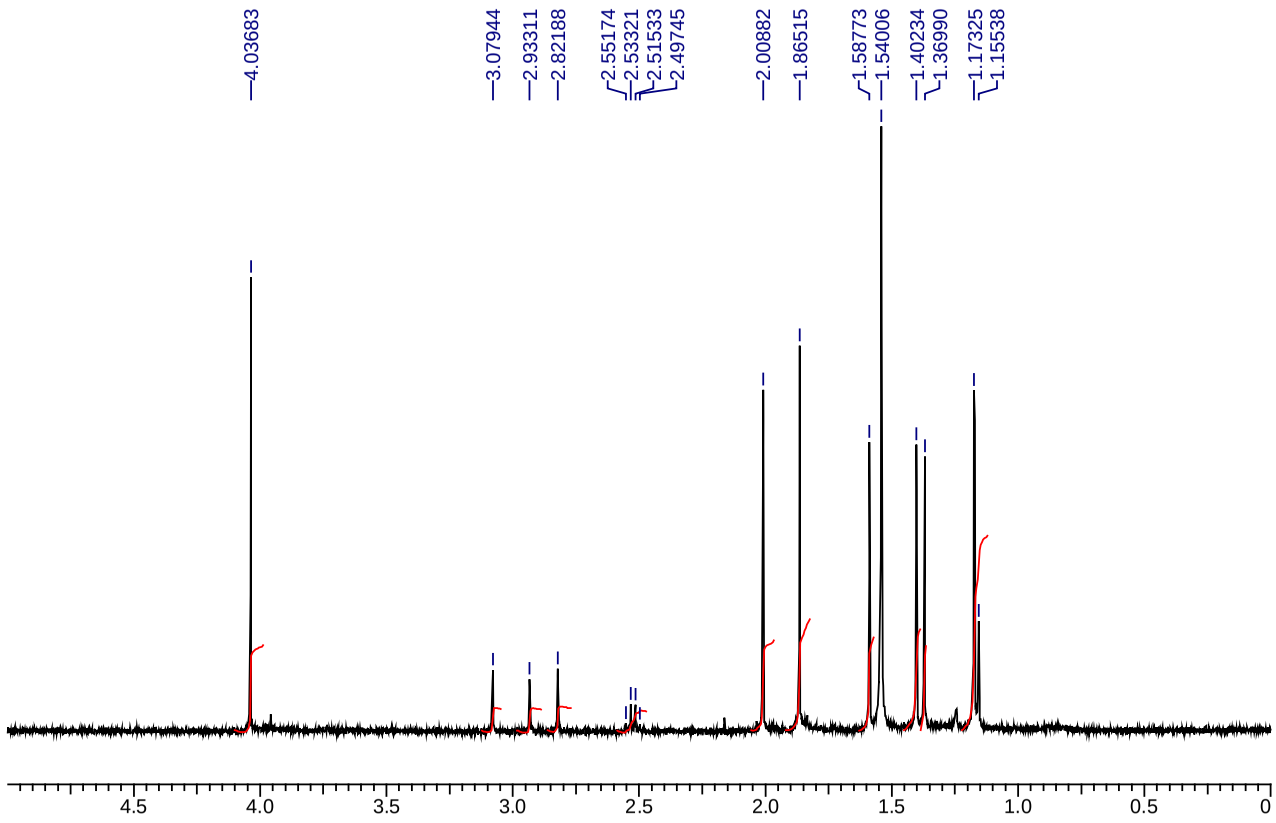
HSQC of elysiapyrone A (**1**) in $CDCl_3$



HMBC of elysiapyrone A (**1**) in $CDCl_3$



^{1}H NMR of elysiapyrone B (**2**) in $CDCl_3$



^{13}C NMR of elysiapyrone B (**2**) in $CDCl_3$