

SUPPORTING INFORMATION

Antioxidant and Anti-inflammatory Meroterpenoids from the Brown Alga *Cystoseira usneoides*

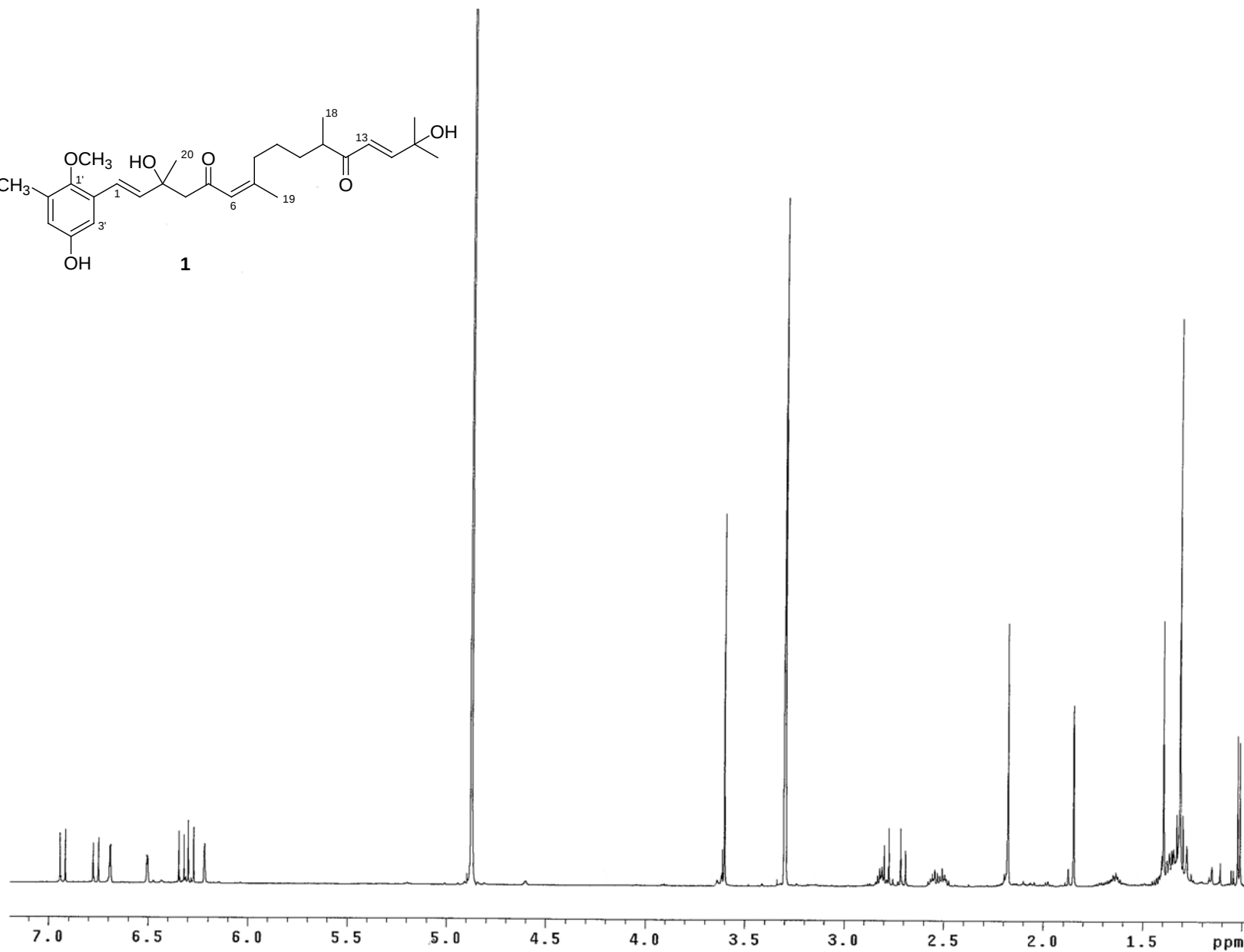
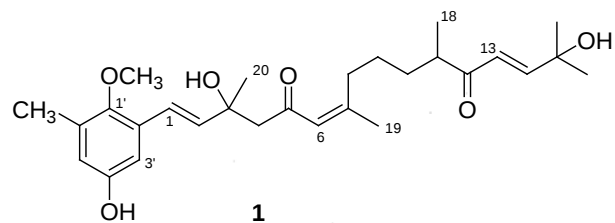
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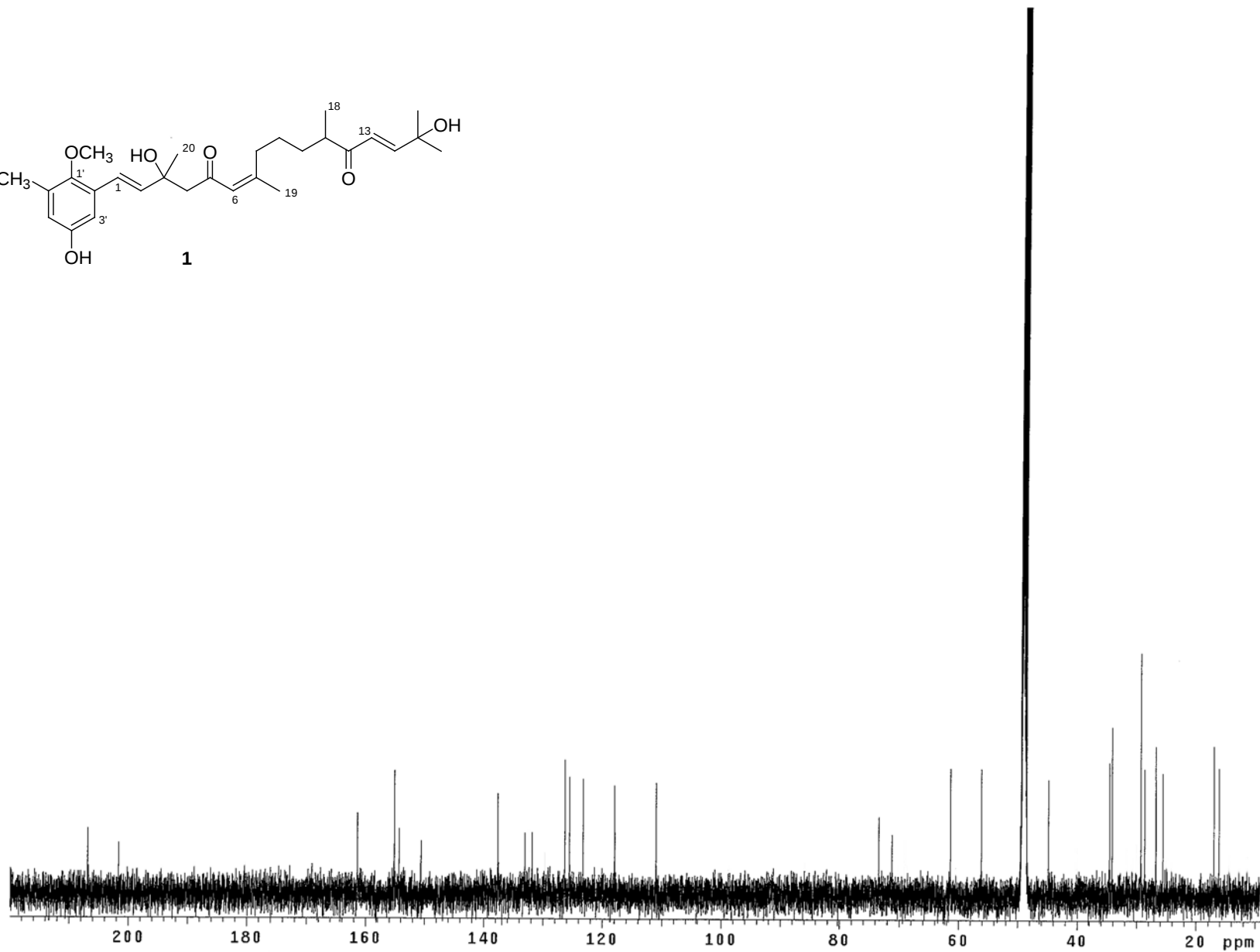
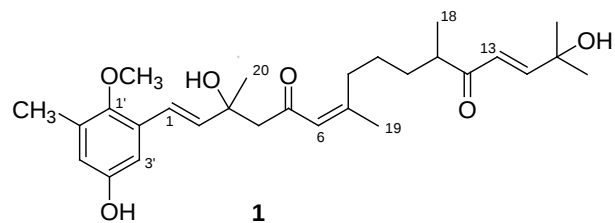
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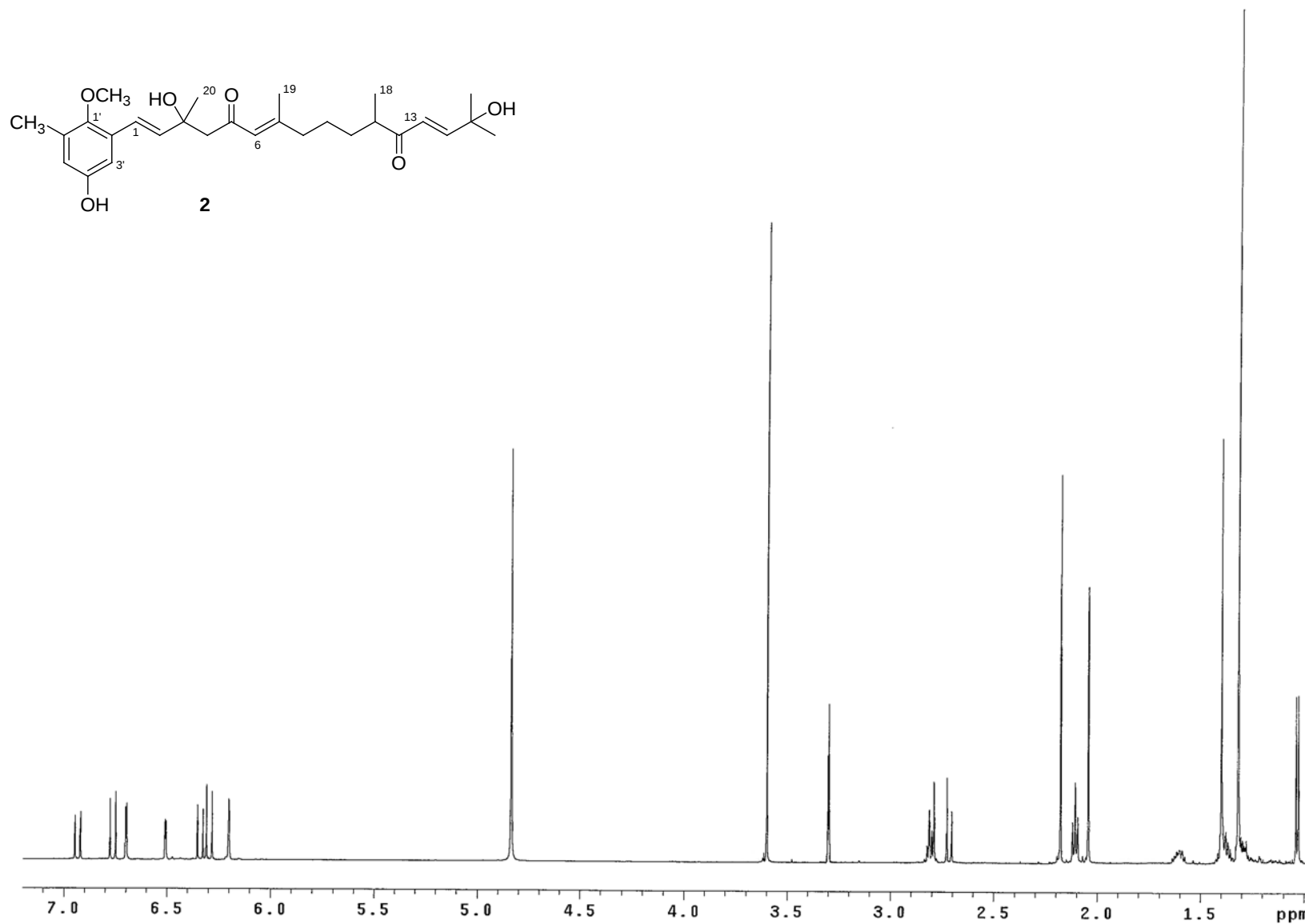
- S1 ¹H NMR spectrum (600 MHz, CD₃OD) of cystodione A (**1**)
- S2 ¹³C NMR spectrum (150 MHz, CD₃OD) of cystodione A (**1**)
- S3 ¹H NMR spectrum (600 MHz, CD₃OD) of cystodione B (**2**)
- S4 ¹³C NMR spectrum (125 MHz, CD₃OD) of cystodione B (**2**)
- S5 ¹H NMR spectrum (600 MHz, CD₃OD) of cystodione C (**3**)
- S6 ¹³C NMR spectrum (150 MHz, CD₃OD) of cystodione C (**3**)
- S7 ¹H NMR spectrum (600 MHz, CD₃OD) of cystodione D (**4**)
- S8 ¹³C NMR spectrum (150 MHz, CD₃OD) of cystodione D (**4**)
- S9 ¹H NMR spectrum (600 MHz, CD₃OD) of cystodione E (**5**)
- S10 ¹³C NMR spectrum (150 MHz, CD₃OD) of cystodione E (**5**)
- S11 ¹H NMR spectrum (500 MHz, CD₃OD) of cystodione F (**6**)
- S12 ¹³C NMR spectrum (125 MHz, CD₃OD) of cystodione F (**6**)
- S13 ¹H NMR spectrum (500 MHz, CDCl₃) of 6-*cis*-amentadione-1'-methyl ether (**7**)
- S14 ¹³C NMR spectrum (125 MHz, CDCl₃) of 6-*cis*-amentadione-1'-methyl ether (**7**)
- S15 ¹H NMR spectrum (500 MHz, CDCl₃) of amentadione-1'-methyl ether (**8**)
- S16 ¹H NMR spectrum (500 MHz, CDCl₃) of amentadione-1'-methyl ether (**8**)
- S17 ¹H NMR spectrum (600 MHz, CD₃OD) of usneoidone Z (**11**)
- S18 ¹³C NMR spectrum (150 MHz, CD₃OD) of usneoidone Z (**11**)
- S19 ¹H NMR spectrum (500 MHz, CDCl₃) of usneoidone Z (**11**)
- S20 ¹³C NMR spectrum (125 MHz, CDCl₃) of usneoidone Z (**11**)
- S21 ¹H NMR spectrum (500 MHz, CD₃OD) of compound **12**
- S22 ¹³C NMR spectrum (125 MHz, CD₃OD) of compound **12**
- S23 ¹H NMR spectrum (500 MHz, CDCl₃) of 11-hydroxyamentadione-1'-methyl ether (**12**)
- S24 ¹³C NMR spectrum (150 MHz, CDCl₃) of 11-hydroxyamentadione-1'-methyl ether (**12**)
- S25 Table T1. HMBC and COSY correlations observed for compounds **1**, **2**, **3**, and **4**
- S26 Table T2. HMBC and COSY correlations observed for compounds **5**, **6**, **11**, and **12**
- S27 Table T3. NMR data reported for usneoidones and NMR data of compounds **11** and **12**



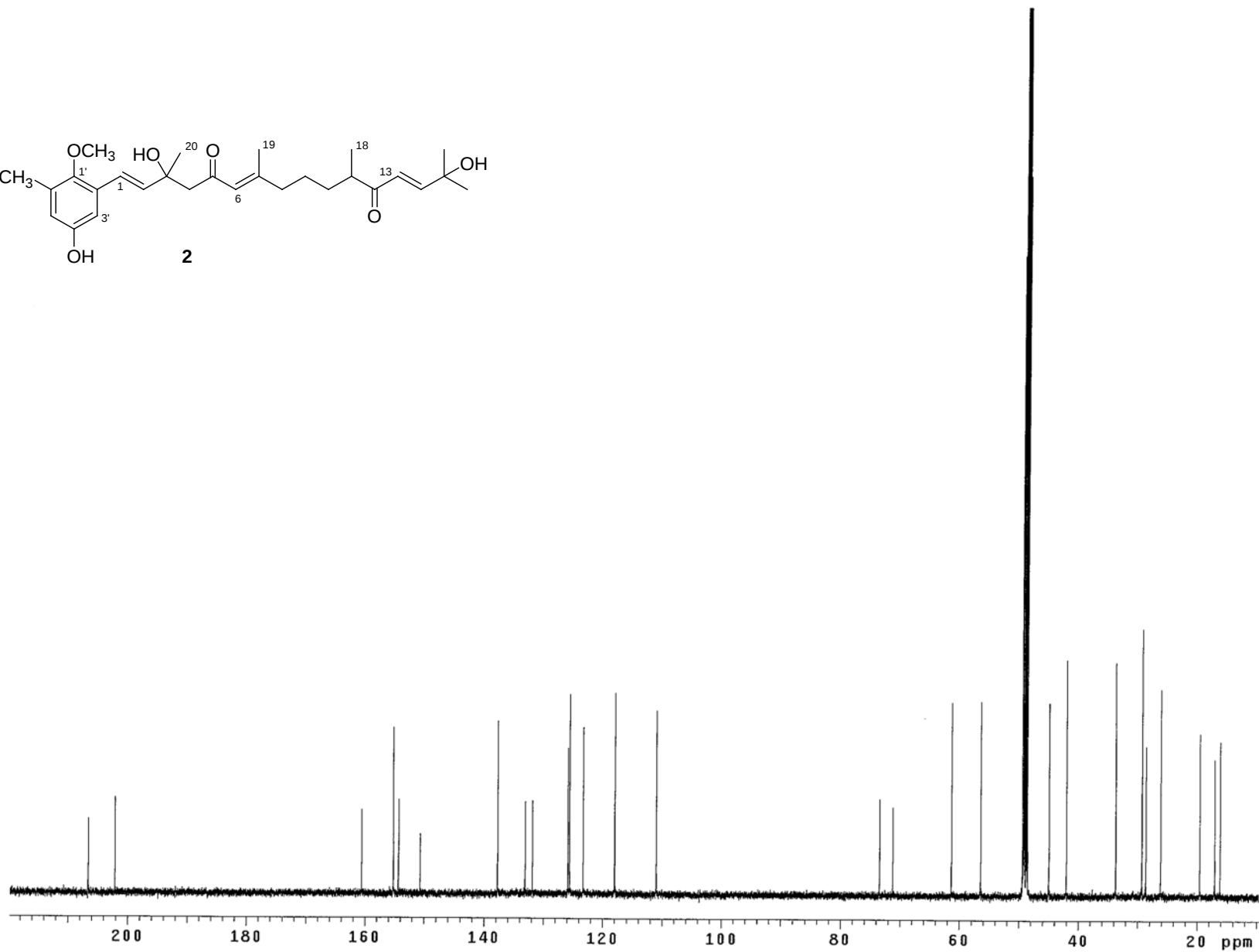
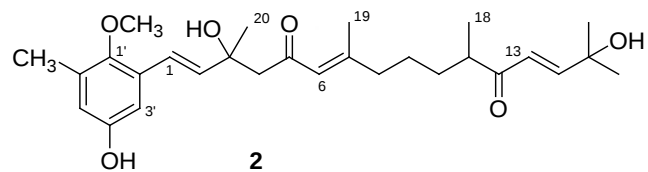
S1.- ¹H NMR spectrum of cystodione A (**1**) in CD₃OD



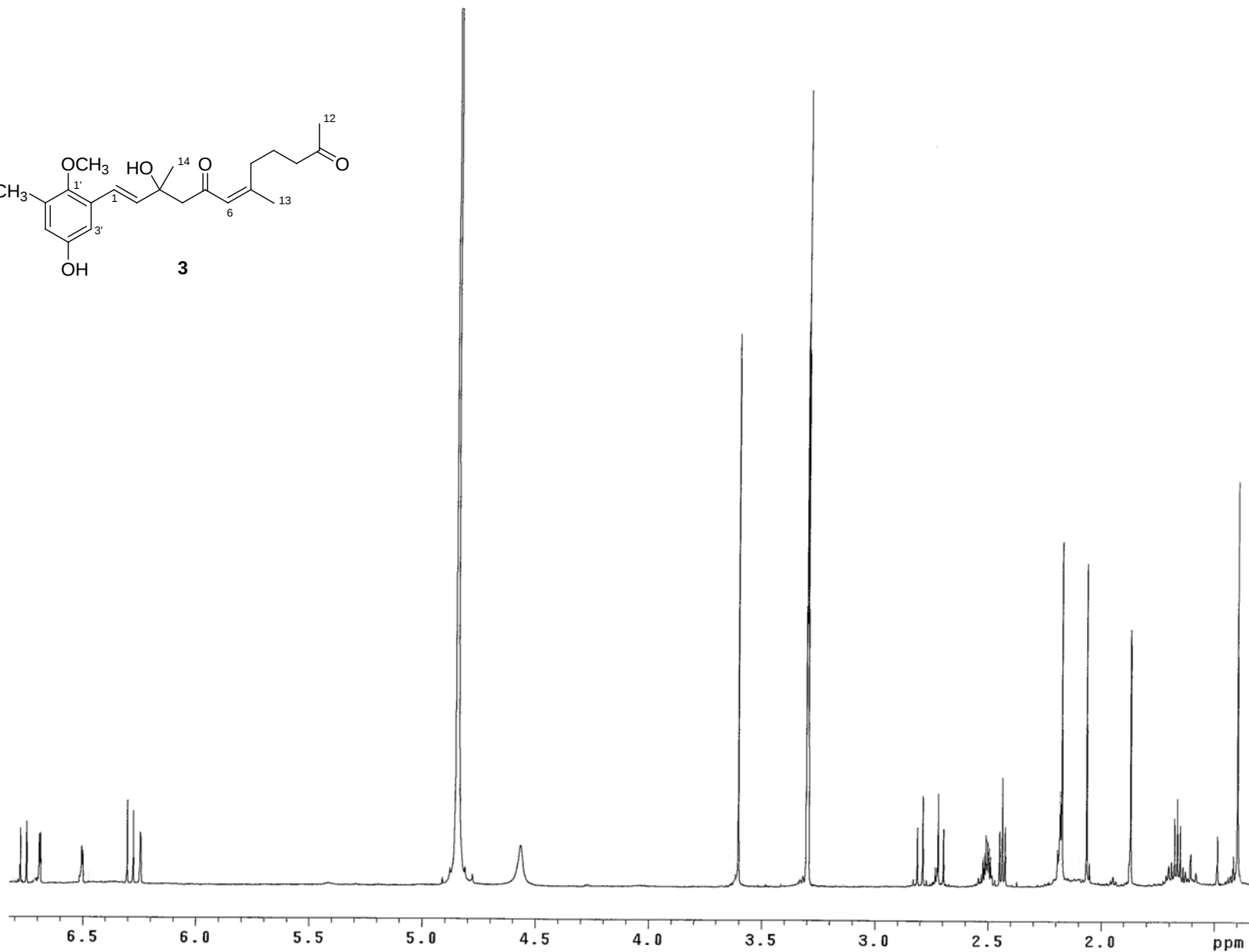
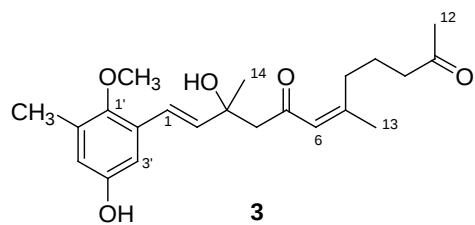
S2.- ¹³C NMR spectrum of cystodione A (**1**) in CD₃OD



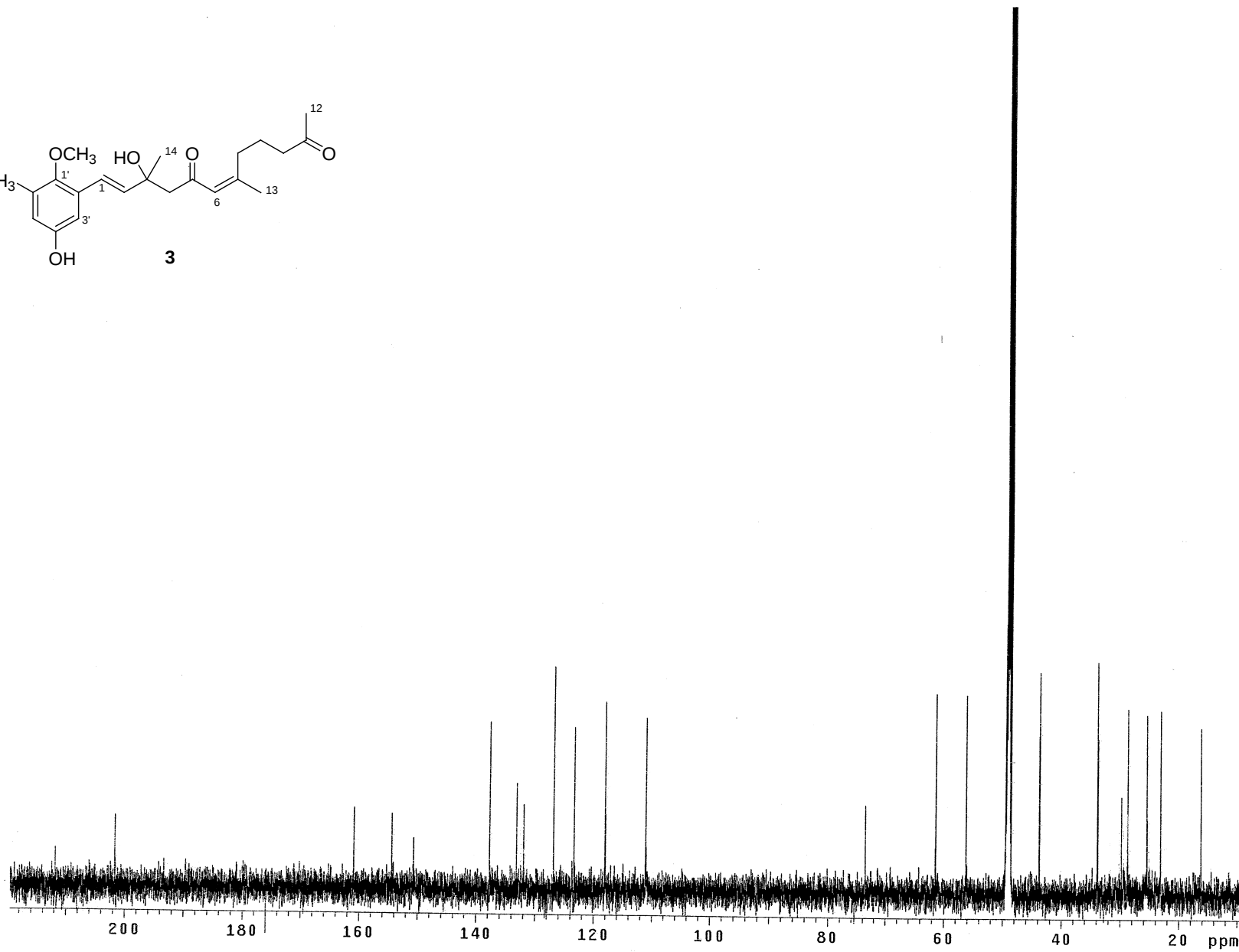
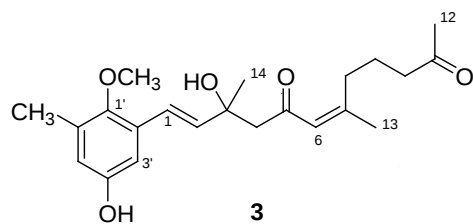
S3.- ^1H NMR spectrum of cystodione B (**2**) in CD_3OD



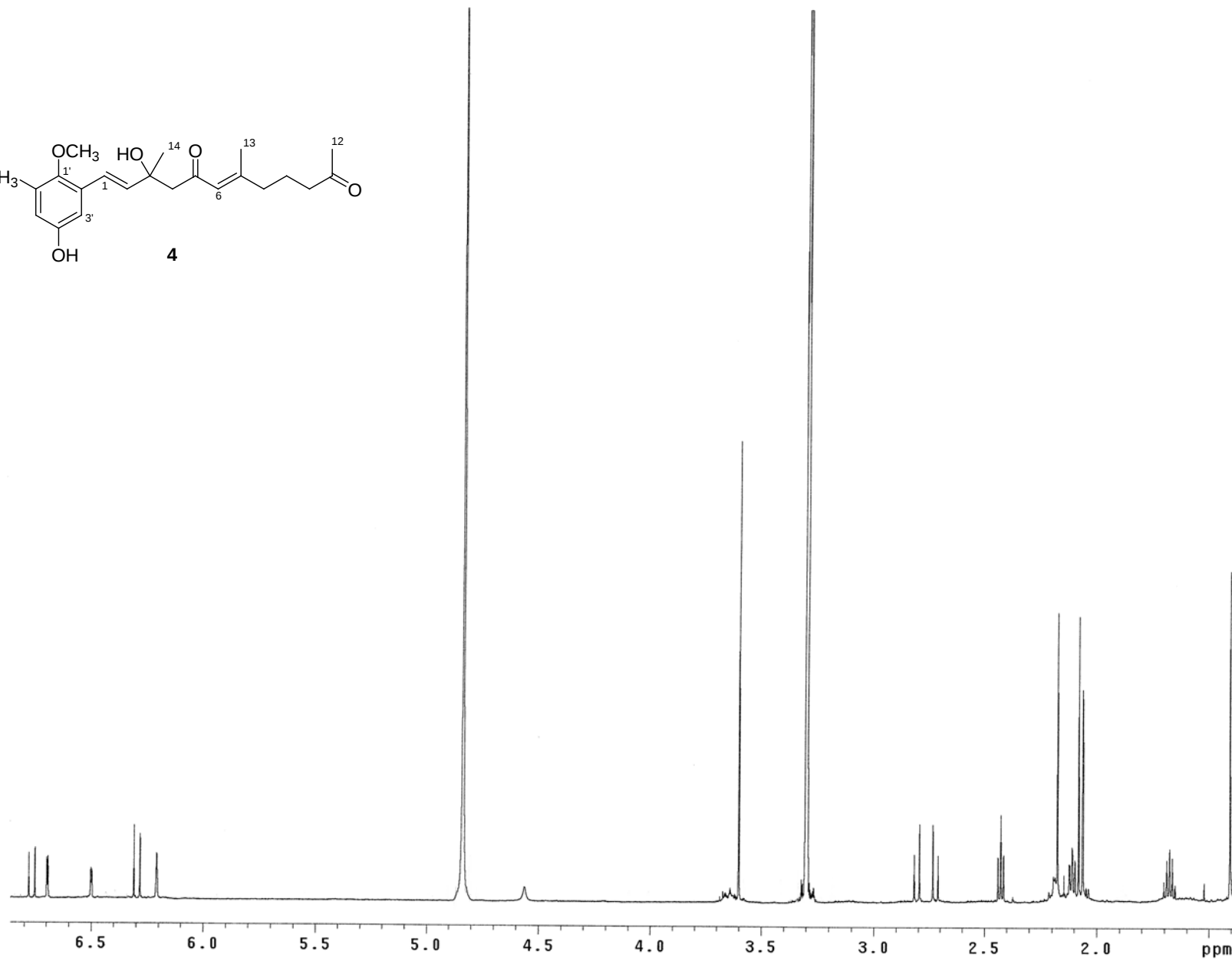
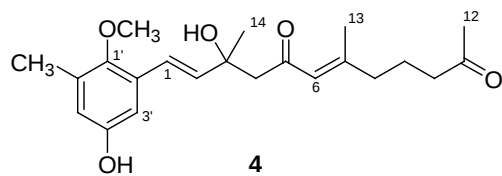
S4.- ^{13}C NMR spectrum of cystodione B (2) in CD_3OD



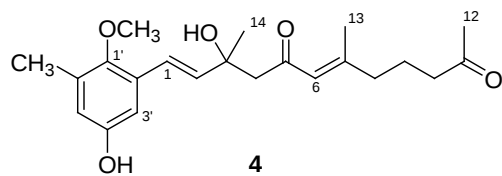
S5.- ^1H NMR spectrum of cystodione C (**3**) in CD_3OD



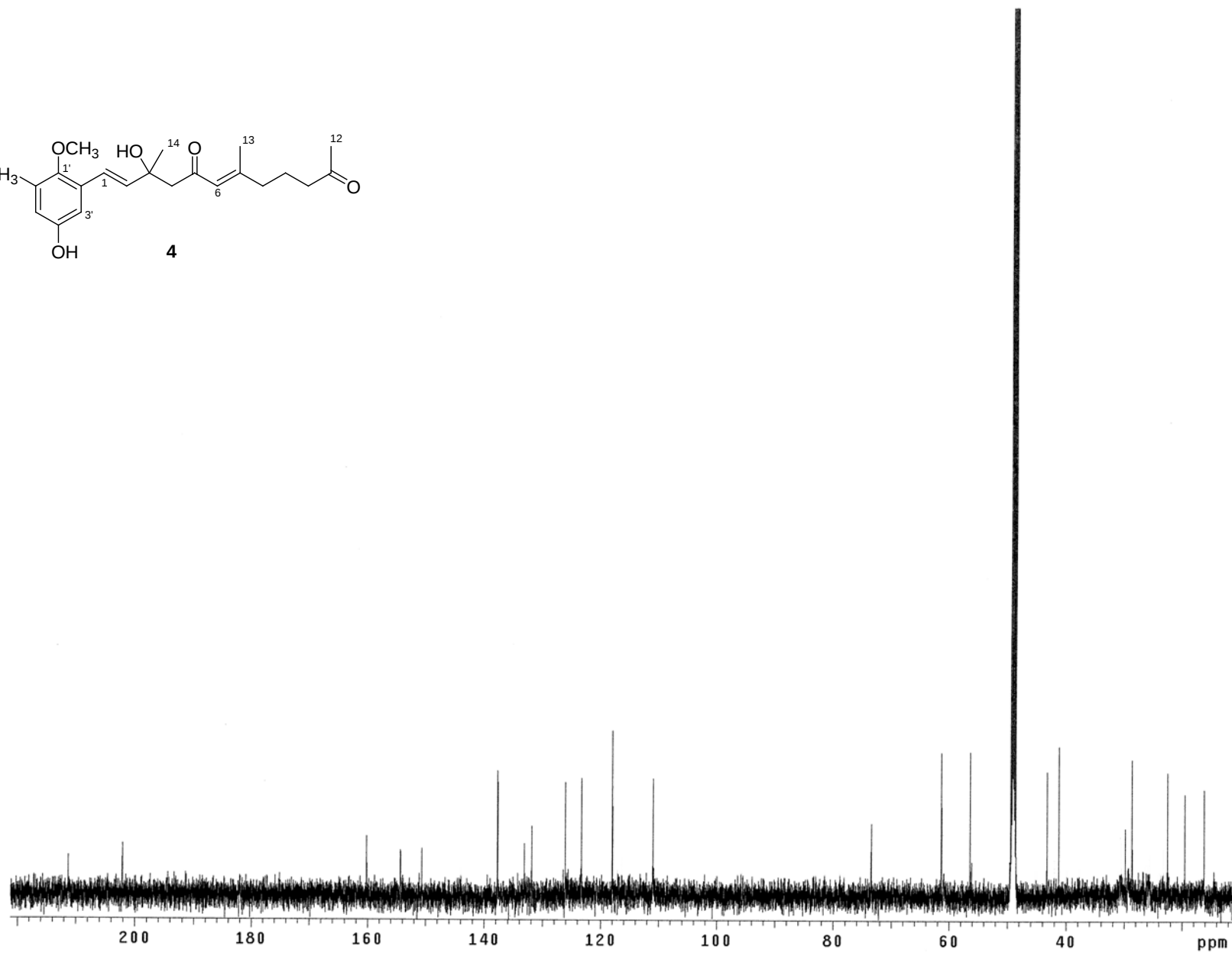
S6.- ^{13}C NMR spectrum of cystodione C (**3**) in CD_3OD



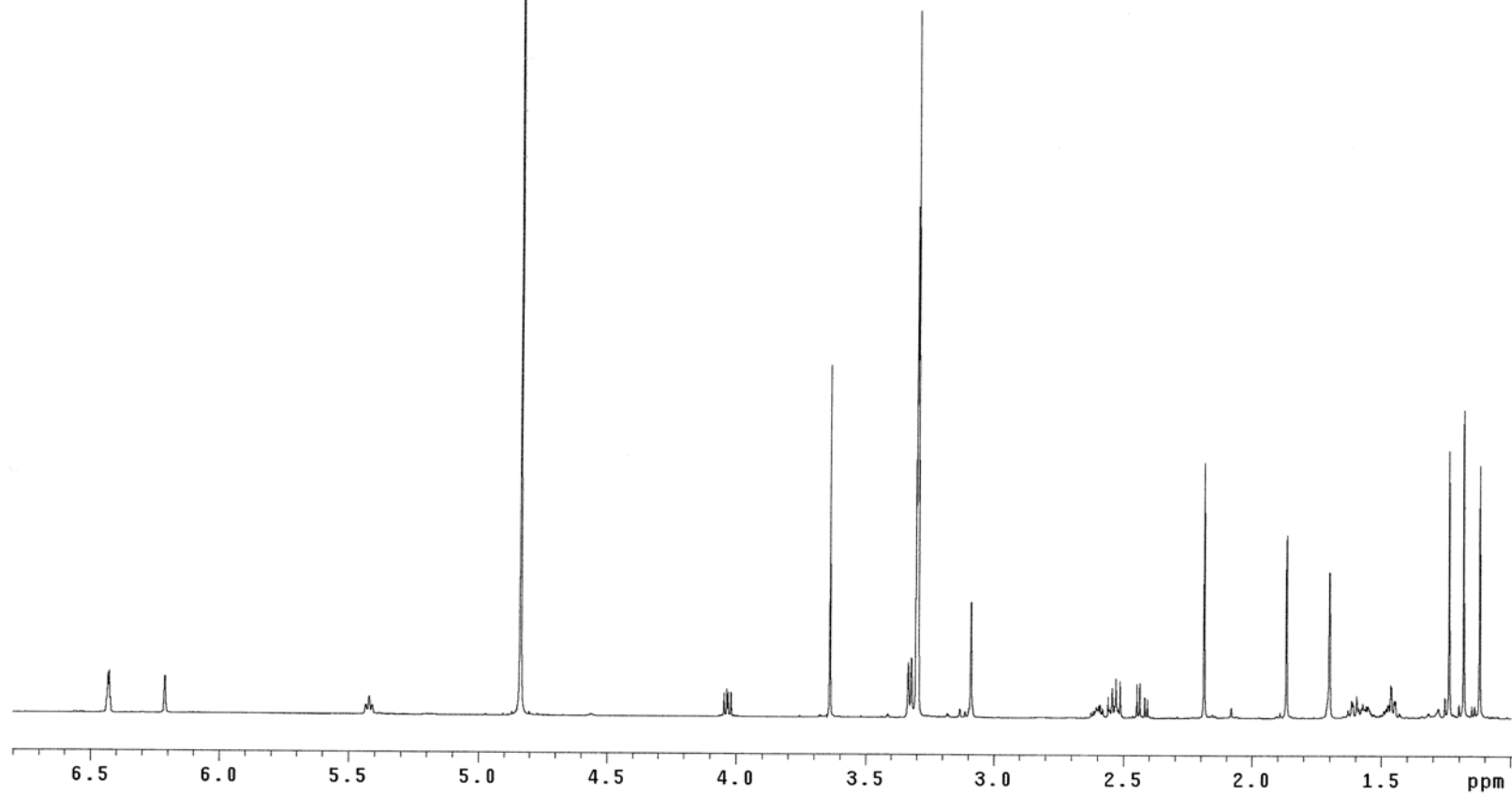
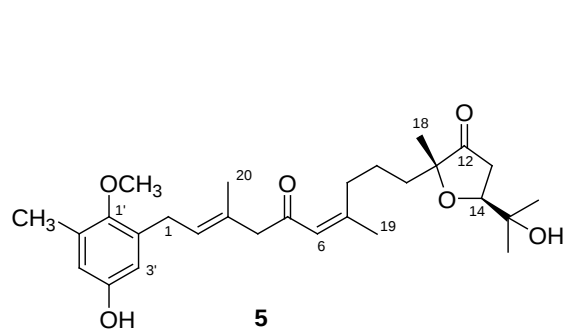
S7.- ¹H NMR spectrum of cystodione D (**4**) in CD₃OD



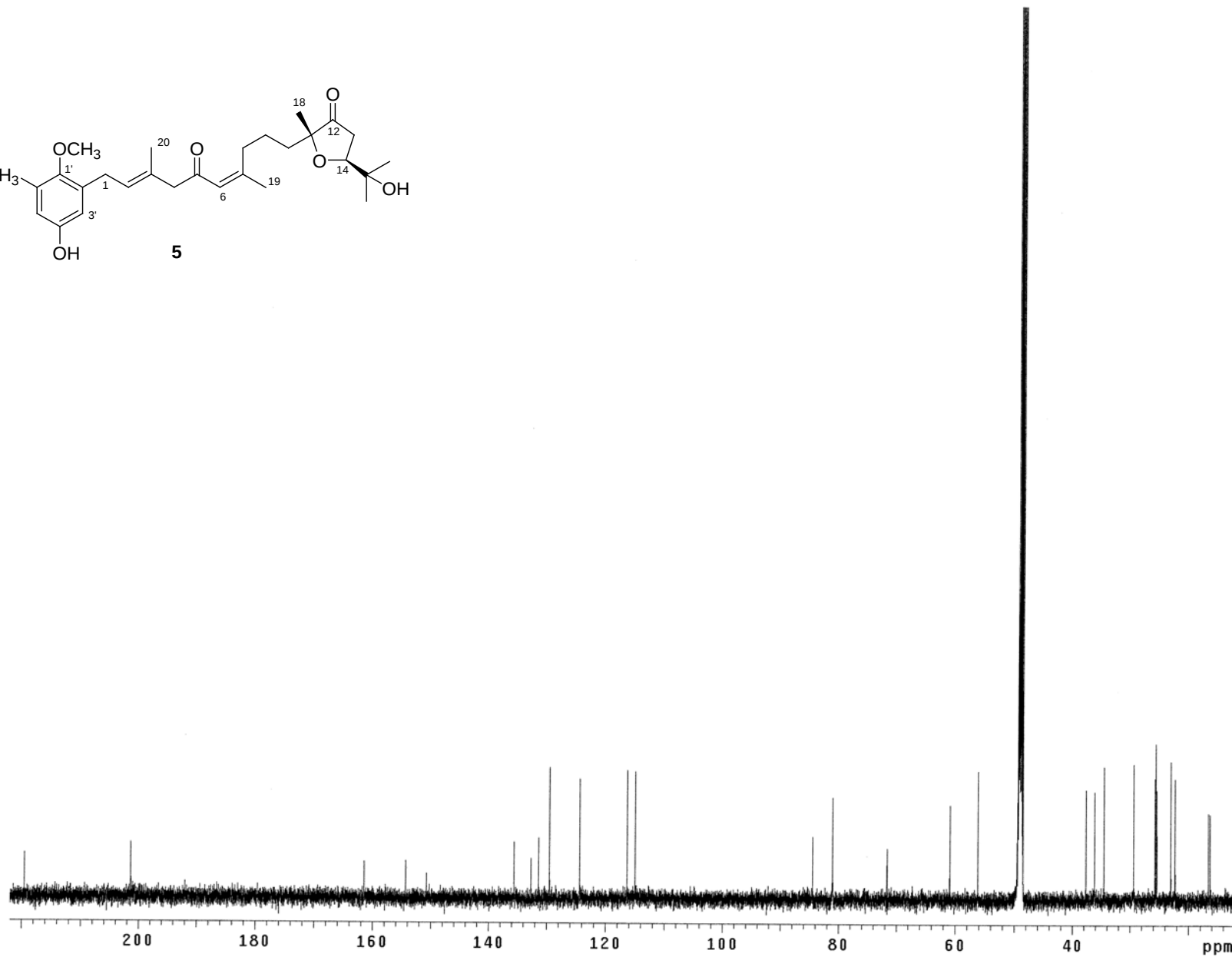
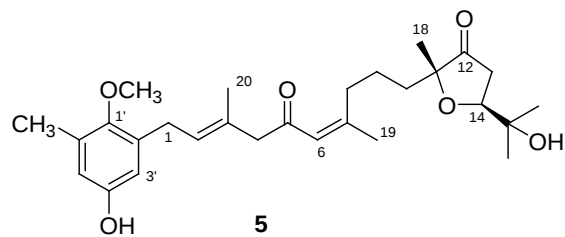
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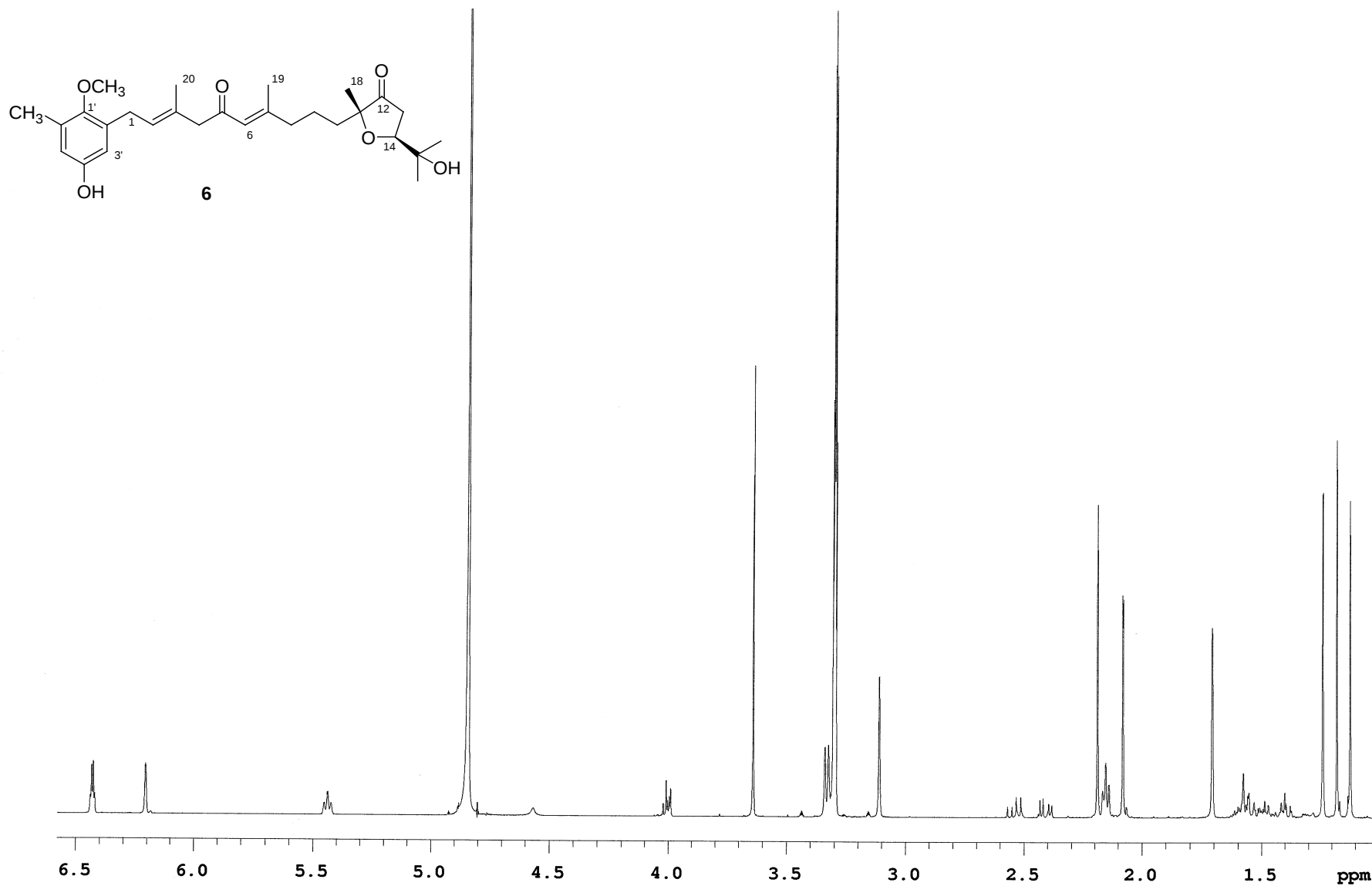
S8.- ^{13}C NMR spectrum of cystodione D (4) in CD_3OD



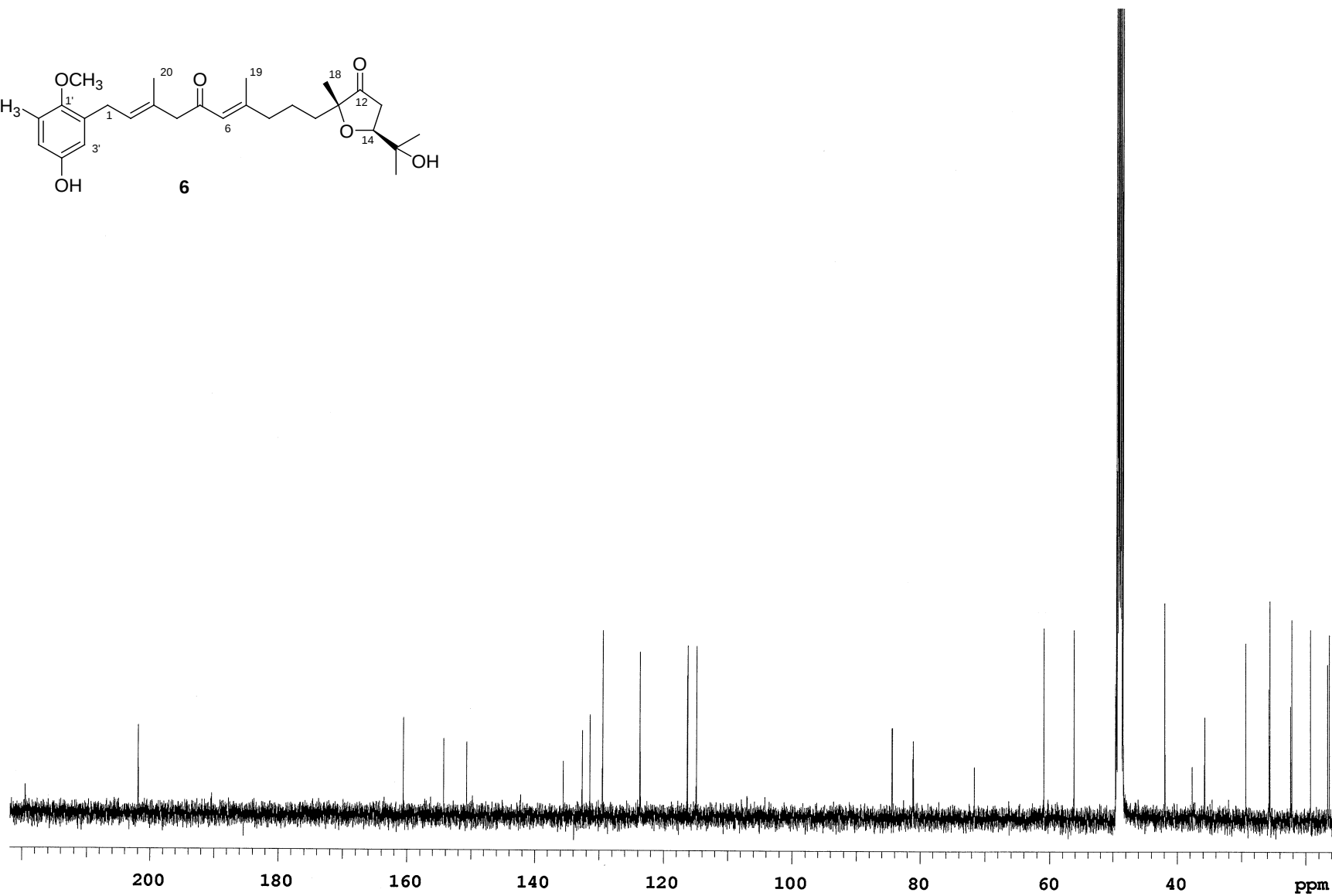
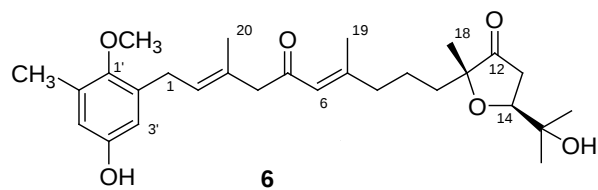
S9.- ^1H NMR spectrum of cystodione E (5) in CD_3OD



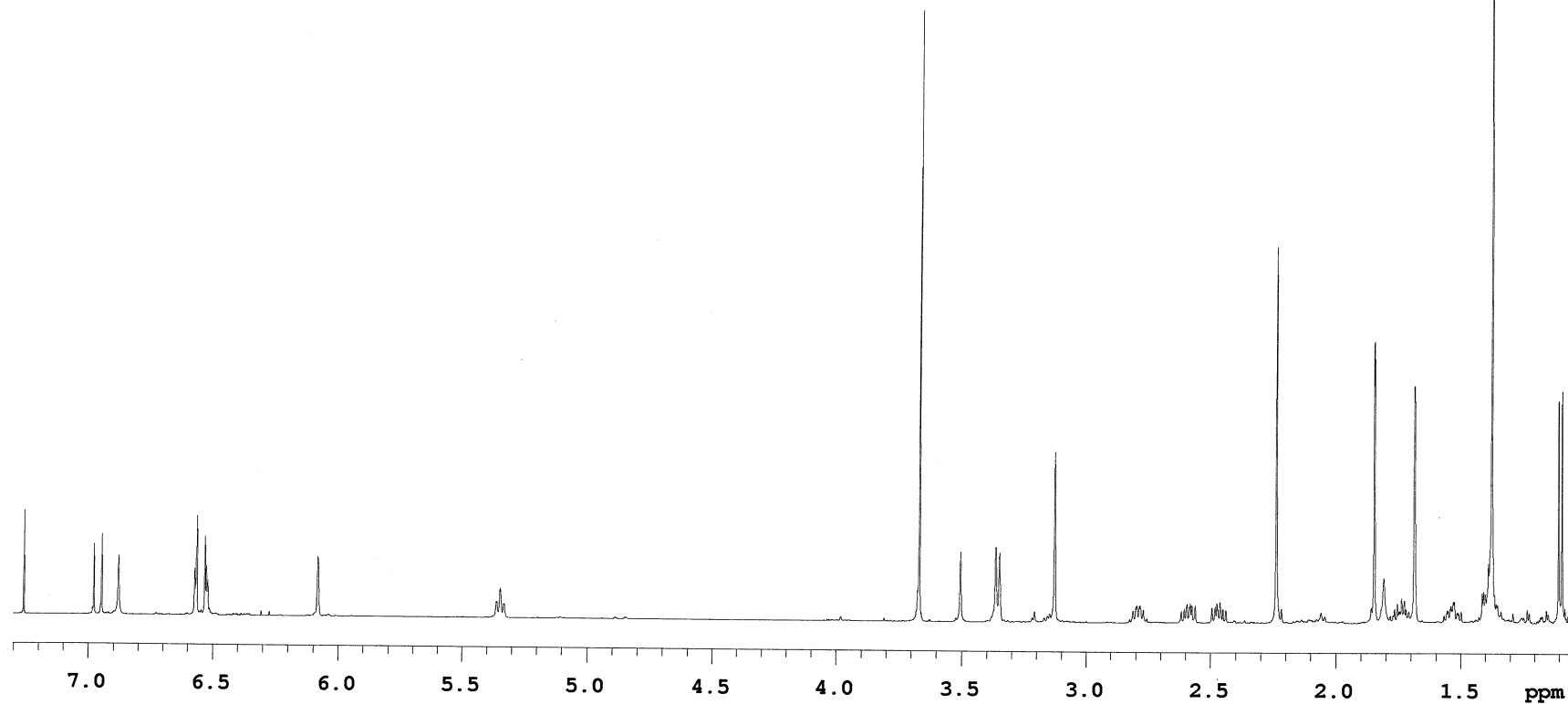
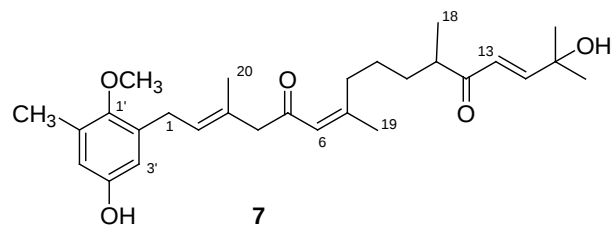
S10.- ^{13}C NMR spectrum of cystodione E (**5**) in CD_3OD



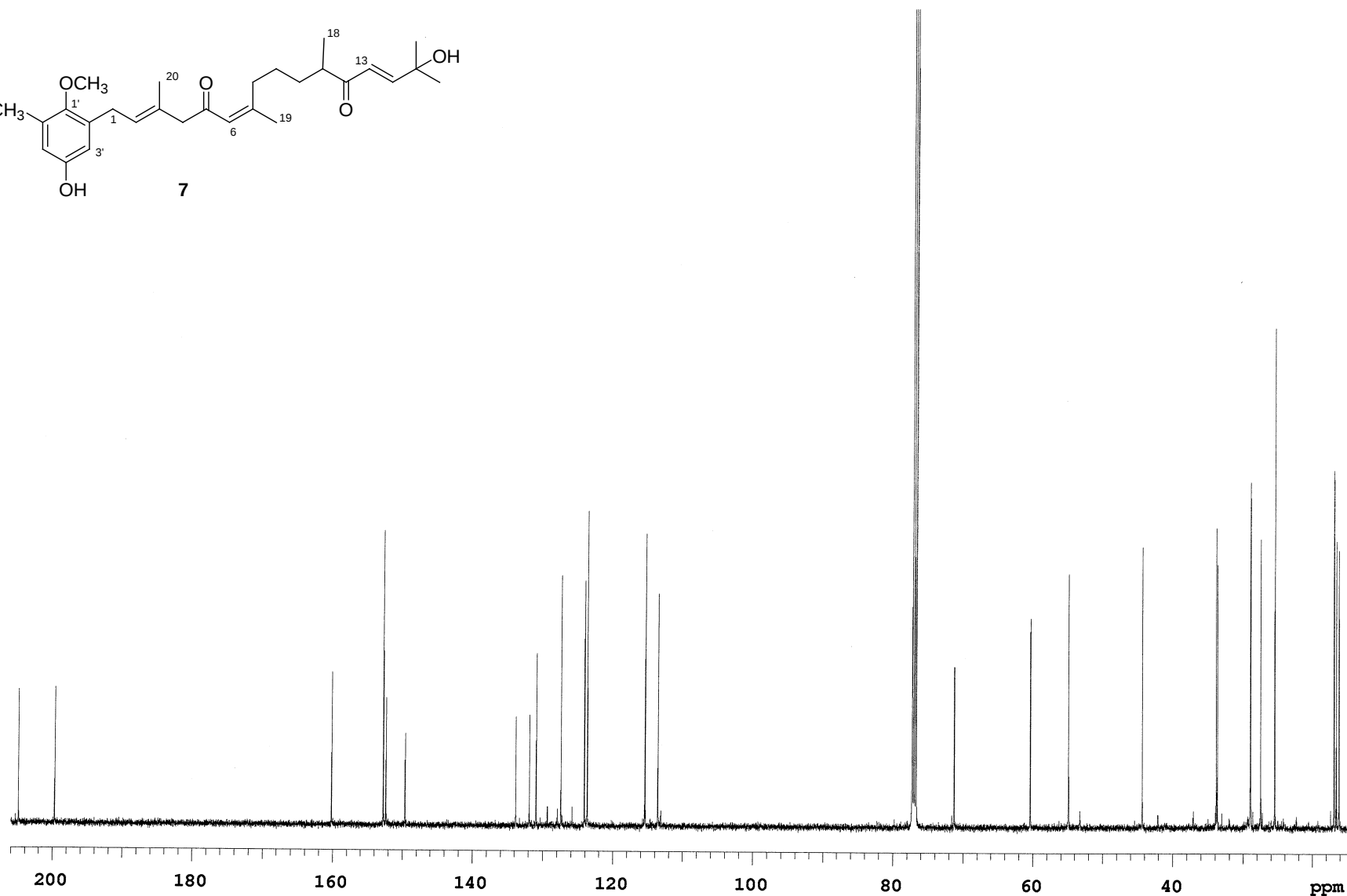
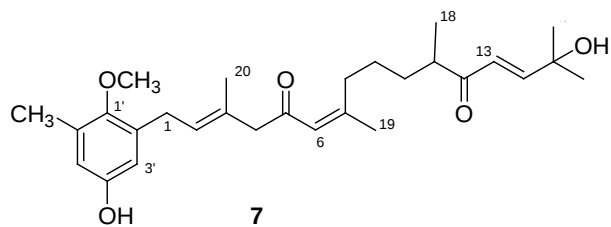
S11.- ^1H NMR spectrum of cystodione F (6) in CD_3OD



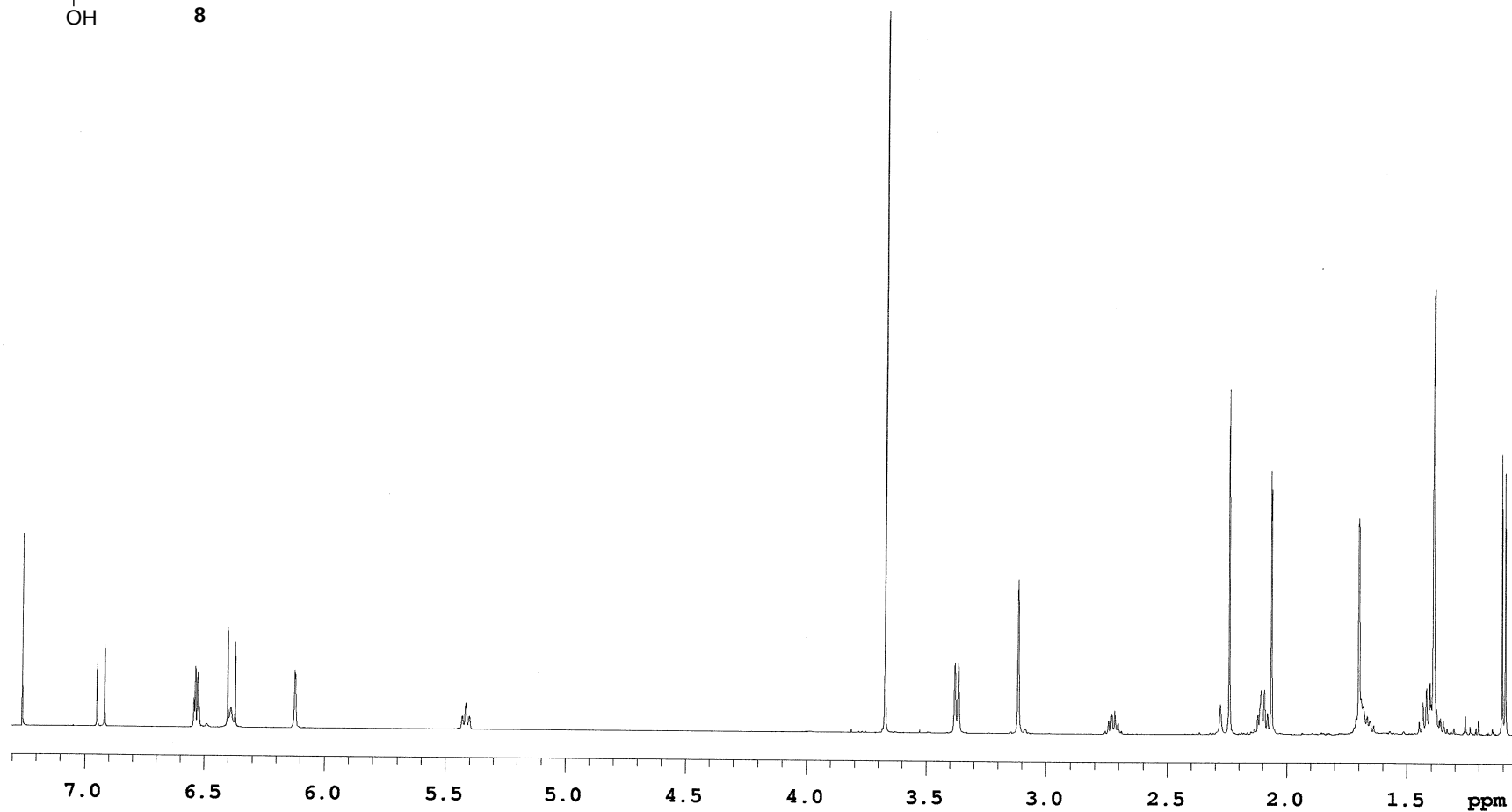
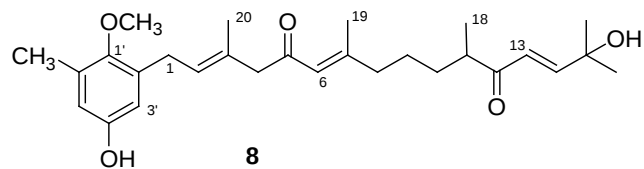
S12.- ¹³C NMR spectrum of cystodione F (**6**) in CD₃OD



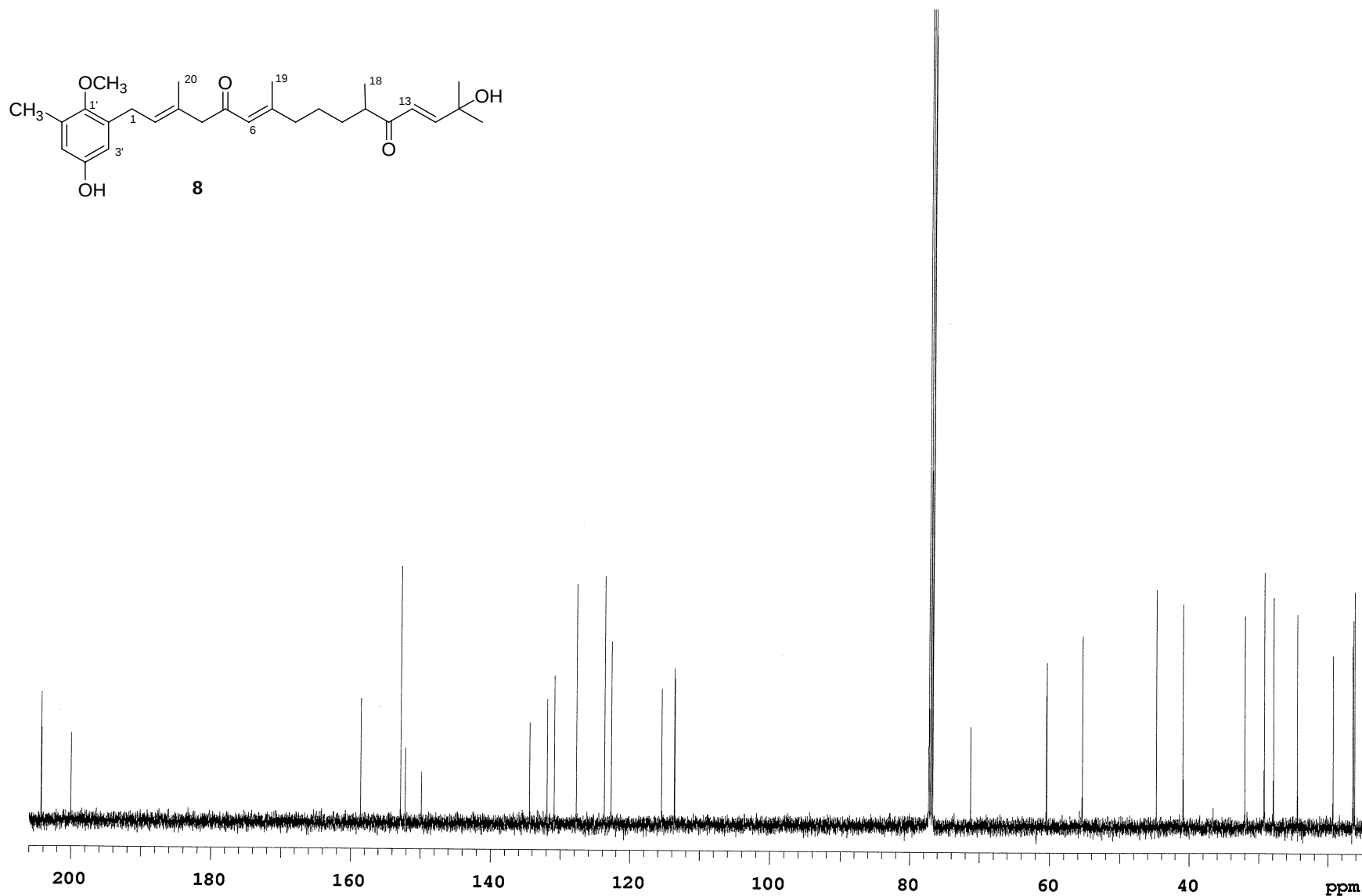
S13.- ^1H NMR spectrum of 6-*cis*-amentadione-1'-methyl ether (**7**) in CDCl_3



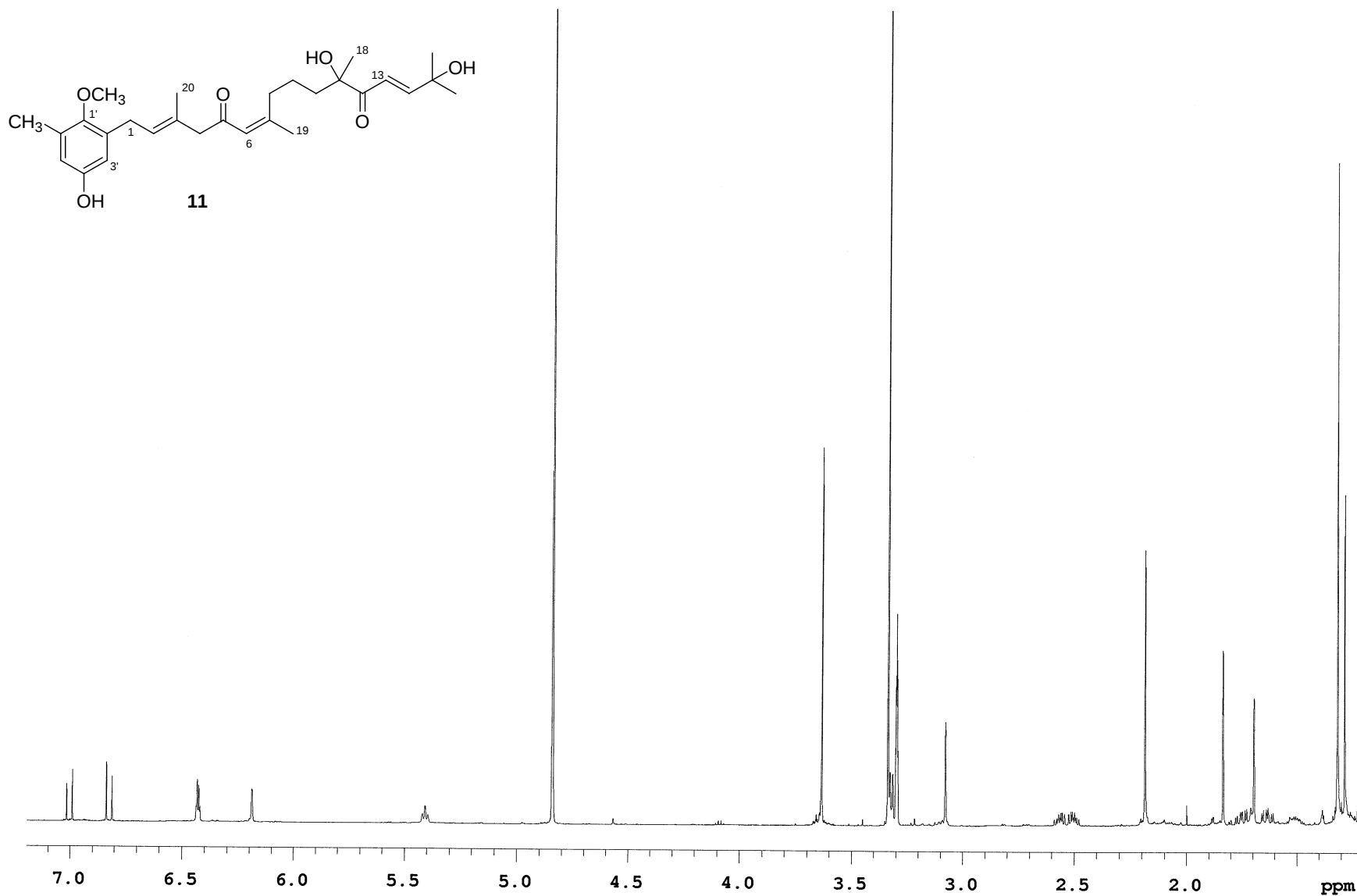
S14.- ^{13}C NMR spectrum of 6-*cis*-amentadione-1'-methyl ether (**7**) in CDCl_3



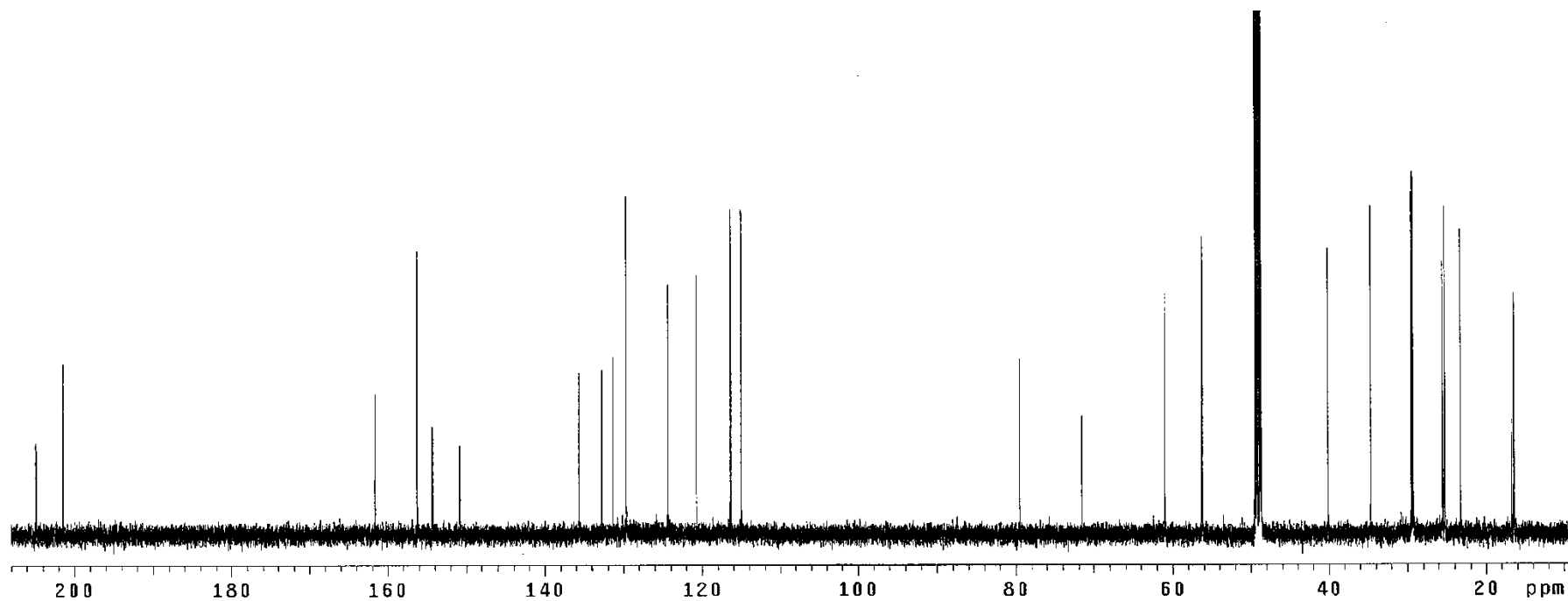
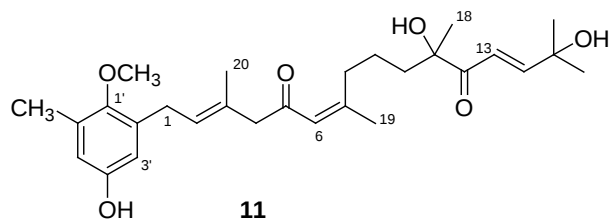
S15.- ^1H NMR spectrum of amentadione-1'-methyl ether (**8**) in CDCl_3



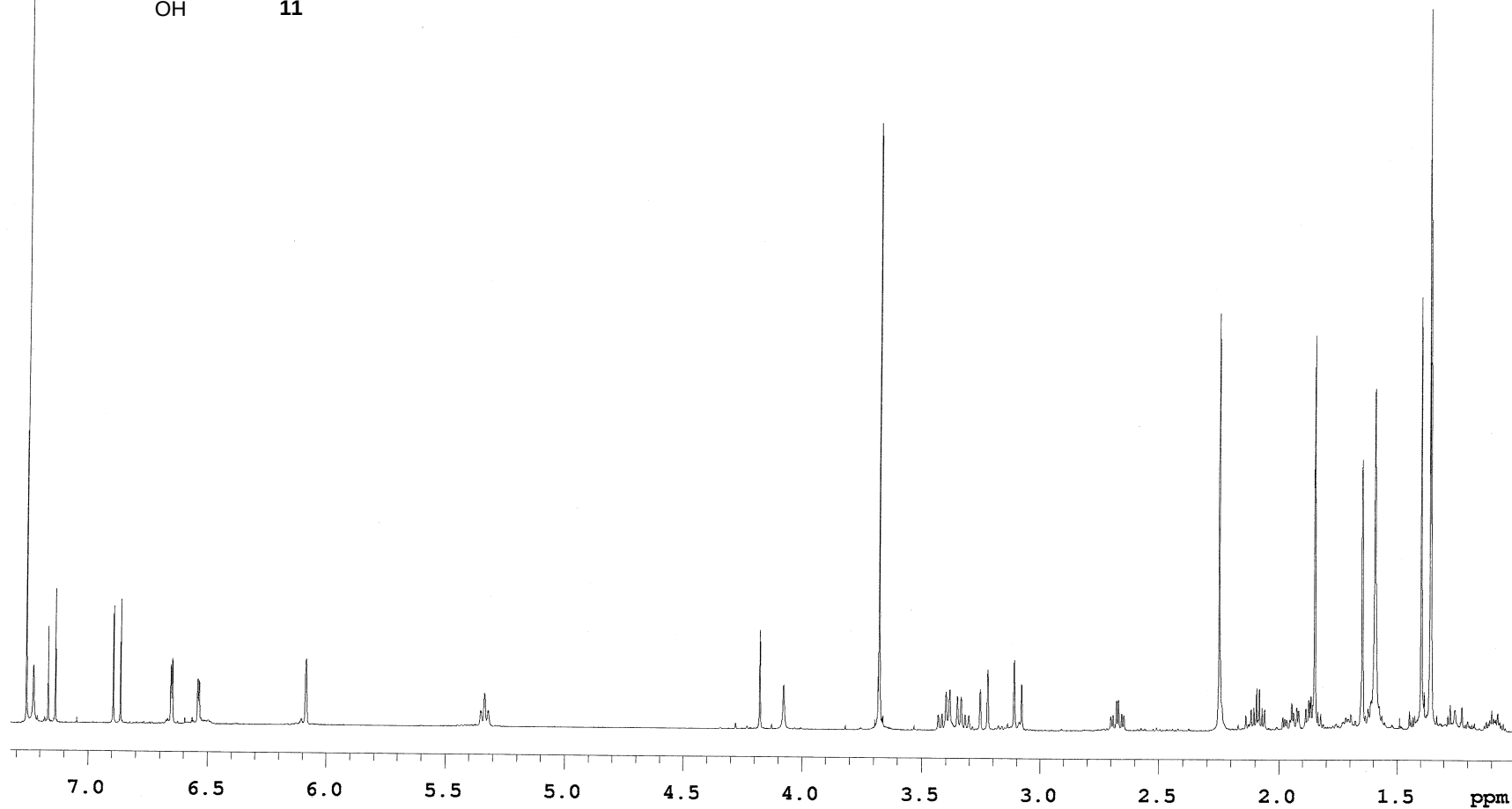
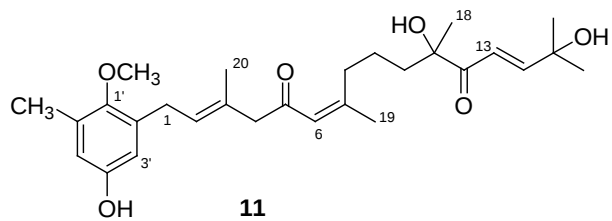
S16.- ^{13}C NMR spectrum of amentadone-1'-methyl ether (**8**) in CDCl₃



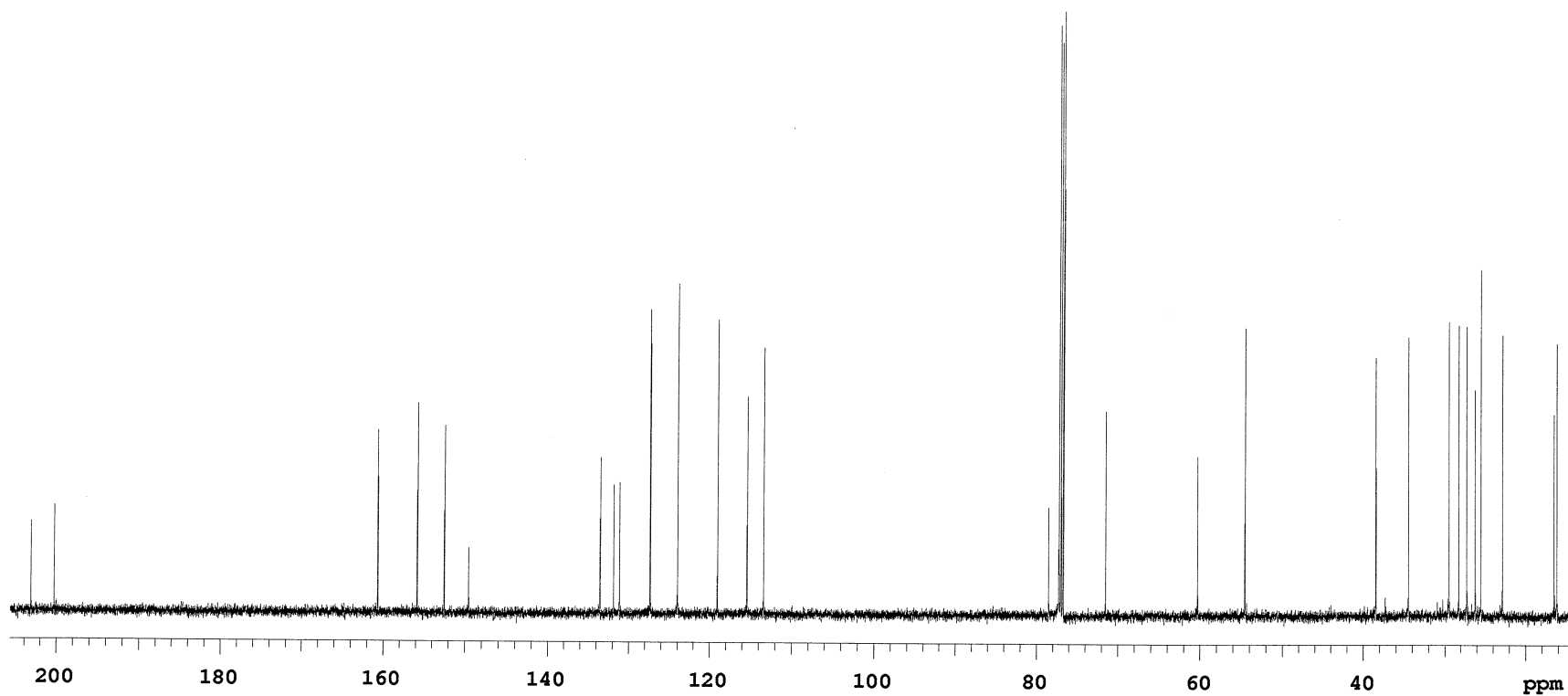
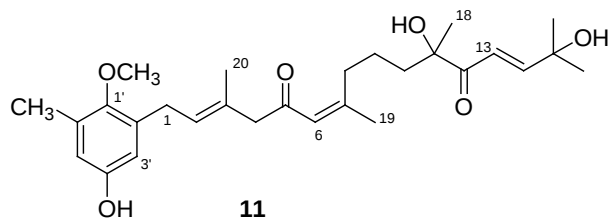
S17.- ^1H NMR spectrum of usneidone Z (**11**) in CD_3OD



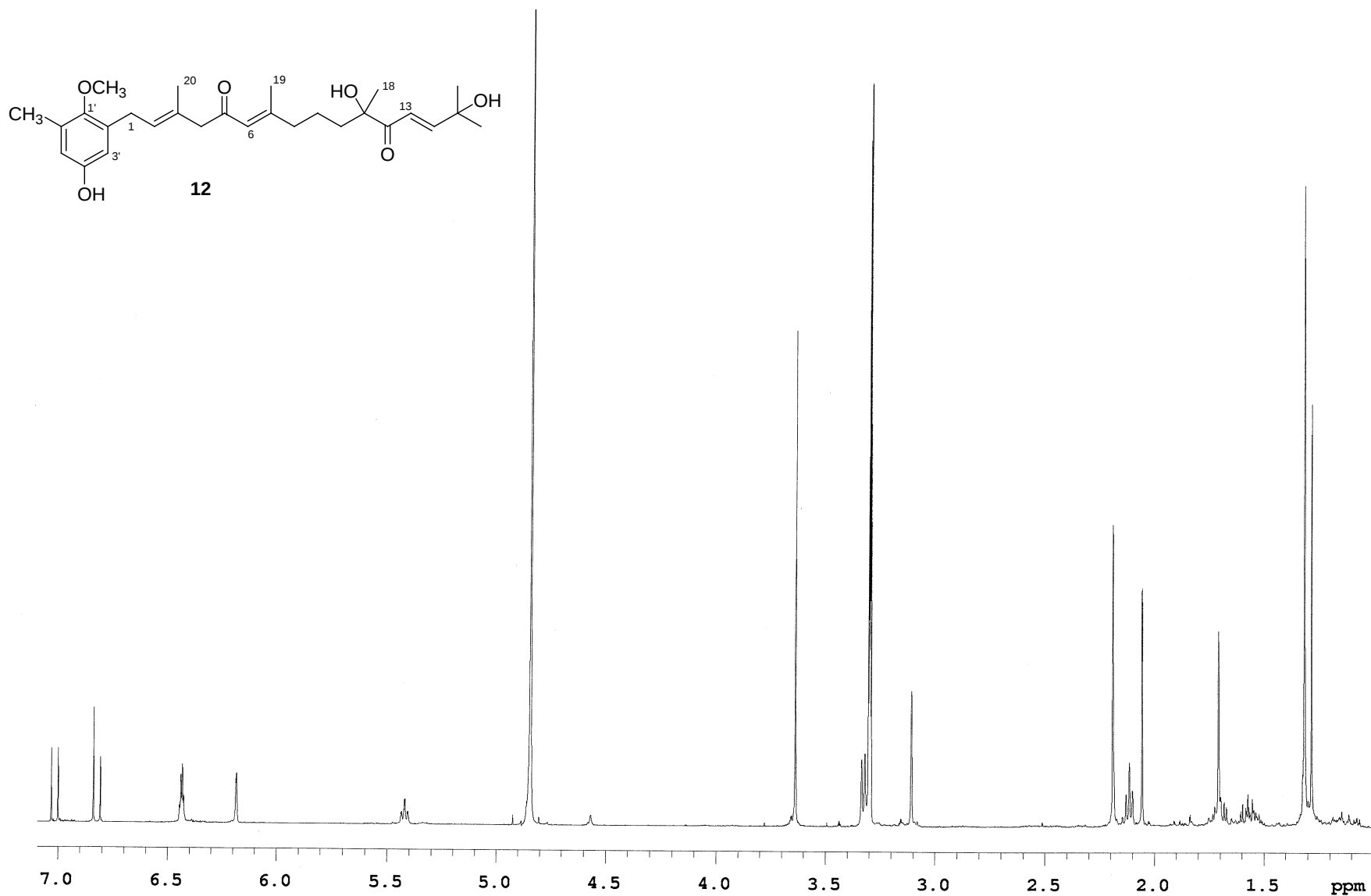
S18.- ^{13}C NMR spectrum of usneoidone Z (**11**) in CD_3OD



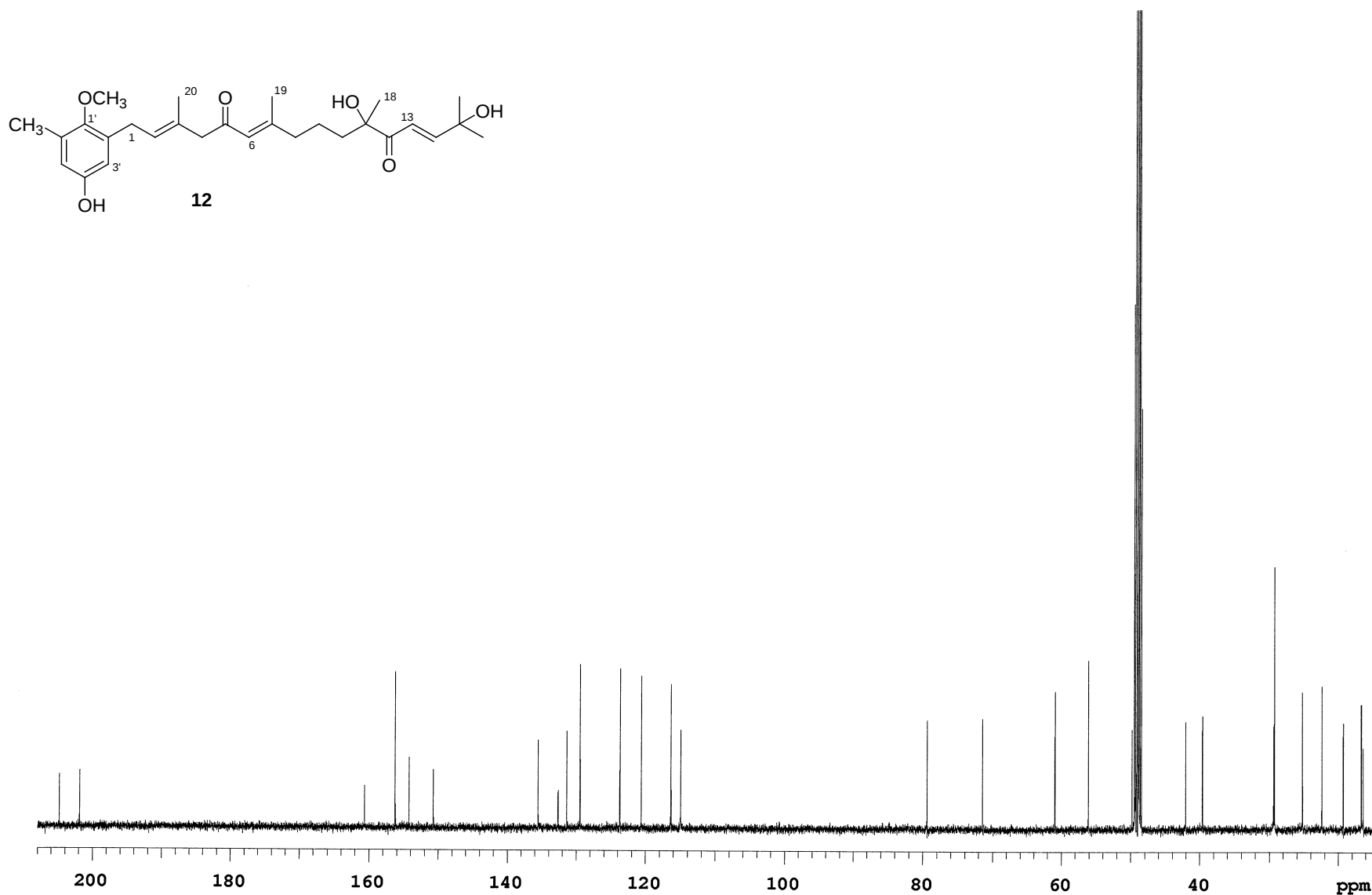
S19.- ¹H NMR spectrum of usneoidone Z (**11**) in CDCl₃



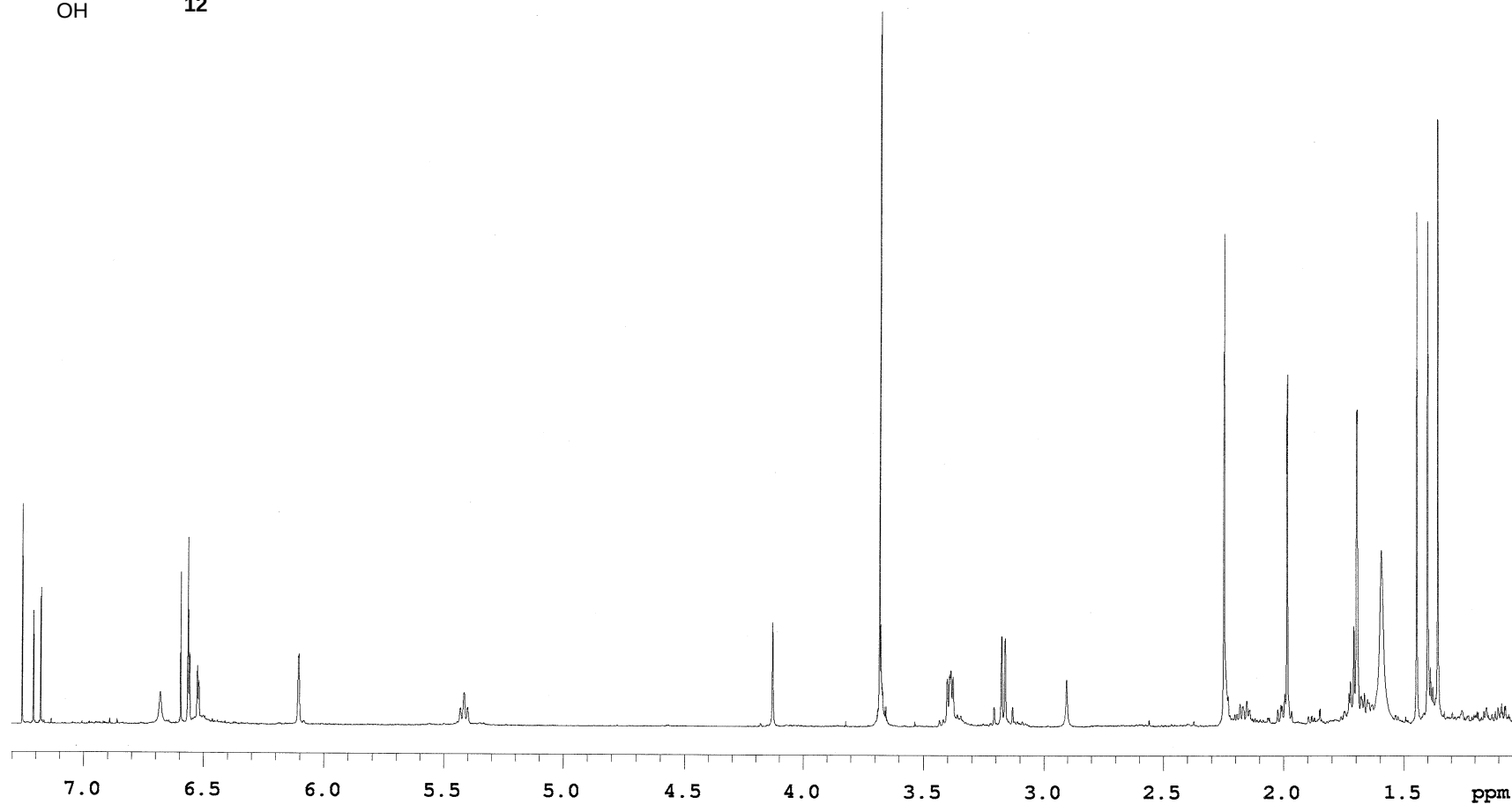
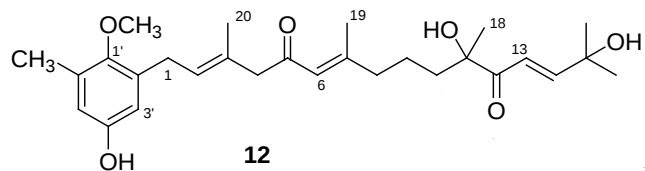
S20.- ^{13}C NMR spectrum of usneoidone Z (**11**) in CDCl_3



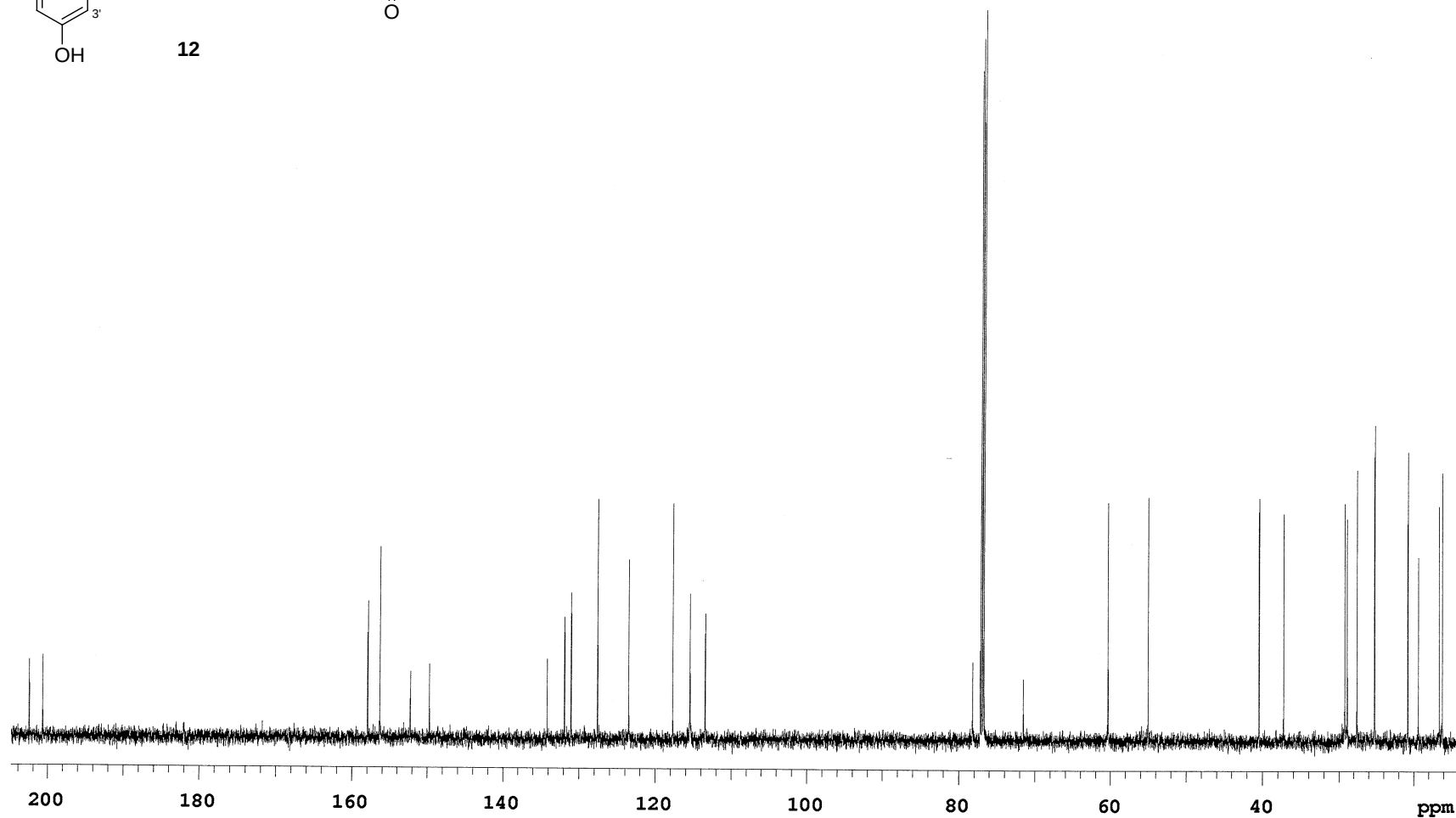
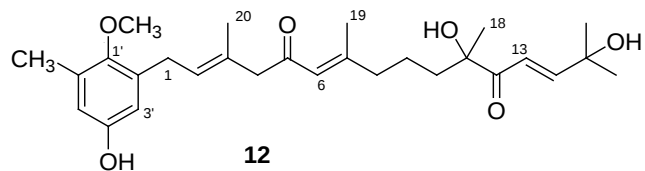
S21.- ^1H NMR spectrum of 11-hydroxyamentadione-1'-methyl ether (**12**) in CD_3OD



S22.- ^{13}C NMR spectrum of 11-hydroxyamentadione-1'-methyl ether (**12**) in CD_3OD



S23.- ^1H NMR spectrum of 11-hydroxyamentadione-1'-methyl ether (**12**) in CDCl_3



S24.- ^{13}C NMR spectrum of 11-hydroxyamentadione-1'-methyl ether (**12**) in CDCl_3

Table T1. HMBC and COSY correlations observed for compounds **1-4**^a

Proton	1		2		3		4	
	HMBC	COSY	HMBC	COSY	HMBC	COSY	HMBC	
1	C-2,C-3,C-1',C-2',C-3'	H-2	C-2,C-3,C-1',C-2',C-3'	H-2	C-3,C-1',C-3'	H-2	C-2,C-3,C-1',C-2',C-3'	H-2
2	C-1,C-3,C-4,C-20,C-2'	H-1	C-1,C-3,C-4,C-20,C-2'	H-1	C-3,C-14,C-2'	H-1	C-1,C-3,C-4,C-14,C-2'	H-1
3								
4	C-2,C-3,C-5,C-6,C-20	a:H-4b b:H-4a	C-2,C-3,C-5,C-6,C-20	a:H-4b b:H-4a	C-2,C-3,C-5,C-14	a:H-4b b:H-4a	C-2,C-3,C-5,C-6,C-14	a:H-4a b:H-4b
5								
6	C-5,C-8,C-19	H-19	C-5,C-8,C-19	H-8,H-19	C-5,C-8,C-13	H-13	C-5,C-8,C-13	H-8,H-13
7								
8	C-6,C-7,C-9,C-10,C-19	a:H-9 b:H-9	C-6,C-7,C-9,C-10,C-19	H-6,H-9	C-9	H-9	C-6,C-7,C-9,C-10,C-13	H-6,H-9
9	C-10	H-8a,H8b,H-10a,H-10b	C-7,C-8,C-10,C-11	H-8,H-10a,H-10b	C-7,C-8,C-10,C-11	H-8,H-10	C-7,C-8,C-10,C-11	H-8,H-10
10	C-9	a:H-9,H-10b,H-11 b:H-9,H-10a,H-11	C-8,C-9,C-11,C-12,C-18	a:H-9,H-10b,H-11 b:H-9,H-10a,H-11	C-8,C-9,C-11	H-9	C-8,C-9,C-11	H-9
11	C-10,C-12	H-10a,H-10b,H-18	C-9,C-10,C-12,C-18	H-10a,H-10b,H-18				
12								
13	C-12,C-15	H-14	C-12,C-14,C-15	H-14	C-11		C-11	
14	C-12,C-15,C-16,C-17	H-13	C-12,C-13,C-15,C-16,C-17	H-13	C-6,C-7,C-8	H-6	C-6,C-7,C-8	H-6
15					C-2,C-3,C-4		C-2,C-3,C-4	
16	C-14,C-15,C-17		C-14,C-15,C-17					
17	C-14,C-15,C-16		C-14,C-15,C-16					
18	C-10,C-11,C-12	H-11	C-10,C-11,C-12	H-11				
19	C-6,C-7,C-8	H-6	C-6,C-7,C-8	H-6				
20	C-2,C-3,C-4		C-2,C-3,C-4					
1'								
2'								
3'	C-1,C-1',C-4',C-5'	H-5'	C-1,C-1',C-4',C-5'	H-5'	C-1,C-1',C-5'	H-5'	C-1,C-1',C-4',C-5'	H-5'
4'								
5'	C-1',C-3',C-4',6'-CH ₃	H-3'	C-1',C-3',C-4',6'-CH ₃	H-3'	C-1',C-3'	H-3'	C-1',C-3',C-4',6'-CH ₃	H-3'
6'								
6'-CH ₃	C-1',C-5',C-6'		C-1',C-5',C-6'		C-1',C-5',C-6'		C-1',C-5',C-6'	
-OCH ₃	C-1'		C-1'		C-1'		C-1'	

a) Spectra recorded in CD₃OD, 600 MHz

Table T2. HMBC and COSY correlations observed for compounds **5**, **6**, **11** and **12**

Proton	5 ^a		6 ^b		11 ^c		12 ^c	
	HMBC	COSY	HMBC	COSY	HMBC	COSY	HMBC	COSY
1	C-2,C-3,C-1',C-2',C-3'	H-2	C-2,C-3,C-1',C-2',C-3'	H-2	C-2,C-3,C-1',C-2',C-3'	H-2	C-2,C-3,C-1',C-2',C-3'	H-2
2	C-1,C-4,C-20	H-1,H-4,H-20	C-1,C-4,C-20	H-1,H-4,H-20	C-1,C-4,C-20	H-1,H-20	C-1,C-4,C-20	H-1,H-20
3								
4	C-2,C-3,C-5,C-6,C-20	H-2,H-20	C-2,C-3,C-5,C-6,C-20	H-2,H-20	C-2,C-3,C-5,C-20	a:H-4b b:H-4a	C-2,C-3,C-5,C-20	a:H-4b b:H-4a
5								
6	C-5,C-8,C-19	H-19	C-5,C-8,C-19	H-8,H-19	C-5,C-8,C-19	H-19	C-5,C-8,C-19	H-19
7								
8	C-6,C-7,C-9,C-10,C-19	a:H-8b,H-9a,H-9b b:H-8a,H-9a,H-9b	C-6,C-7,C-9,C-10,C-19	H-6,H-9a,H-9b	C-6,C-7,C-9,C-10,C-19	a:H-8b,H-9b b:H-8a,H-9a,H-9b	C-6,C-7,C-9,C-10,C-19	a:H-8b,H-9a,H-9b b:H-8a,H-9a,H-9b
9	C-10	a:H-8a,H-8b,H-9b,H-10a b:H-8a,H-8b,H-9a, H-10a,H-10b	C-10	a:H-8,H-9b,H-10a b:H-8,H-9a	a:C-8,C-10	a:H-8b,H-9b,H-10a,H-10b b:H-8a,H-8b,H-9a, H-10a,H-10b	C-8,C-10	a:H-8a,H-8b,H-9b,H-10 b:H-8a,H-8b,H-9a,H-10
10	C-8,C-9,C-11,C-12,C-18	a:H-9a,H-9b,H-10b b:H-9b,H-10a	C-8,C-11,C-12,C-18	a:H-9a,H-10b b:H-10a	a:C-9 b:C-9,C-11,C-12	a:H-9a,H-9b,H-10b b:H-9a,H-9b,H-10a	C-8,C-12	a:H-9a,H-9b b:H-9a,H-9b
11								
12								
13	C-11,C-12,C-14,C-15	a:H-13b,H-14 b:H-13a,H-14	C-12,C-14,C-15	H-14	C-12,C-14,C-15	H-14	C-12,C-14,C-15	H-14
14	C-17	H-13a,H-13b	C-16,C-17	H-13a,H-13b	C-12,C-15	H-13	C-12,C-13,C-15,C-16,C-17	H-13
15								
16	C-14,C-15,C-17		C-14,C-15,C-17		C-14,C-15,C-17		C-14,C-15,C-17	
17	C-14,C-15,C-16		C-14,C-15,C-16		C-14,C-15,C-16		C-14,C-15,C-16	
18	C-10,C-11,C-12		C-10,C-11,C-12		C-10,C-11,C-12		C-10,C-11,C-12	
19	C-6,C-7,C-8	H-6	C-6,C-7,C-8	H-6	C-6,C-7,C-8	H-6	C-6,C-7,C-8	H-6
20	C-2,C-3,C-4	H-2,H-4	C-2,C-3,C-4	H-2,H-4	C-2,C-3,C-4	H-2	C-2,C-3,C-4	H-2
1'								
2'								
3'	C-1,C-1',C-4',C-5'		C-1,C-1',C-4',C-5'		C-1,C-1',C-4',C-5'	H-5'	C-1,C-1',C-5'	H-5'
4'								
5'	C-1',C-3',C-4',6'-CH ₃		C-1',C-3',C-4',6'-CH ₃		C-1',C-3'	H-3'	C-1',C-3',C-4',6'-CH ₃	H-3'
6'								
6'-CH ₃	C-1',C-5',C-6'		C-1',C-5',C-6'		C-1',C-5',C-6'		C-1',C-5',C-6'	
-OCH ₃	C-1'		C-1'		C-1'		C-1'	
11-OH					C-11			
15-OH					C-17			
4'-OH					C-3',C-5'			

a) Recorded in CD₃OD, 600 MHz

b) Recorded in CD₃OD, 500 MHz

c) Recorded in CDCl₃, 500 MHz

Table T3. NMR data reported for usneoidones and NMR data of compounds **11** and **12**

Position	Usneoidone Z ^a		11 ^{b,c}		Usneoidone E ^a		12 ^{c,d}	
	δ_C	δ_H , m (J in Hz)	δ_C	δ_H , m (J in Hz)	δ_C	δ_H , m (J in Hz)	δ_C	δ_H , m (J in Hz)
1	27.62, CH ₂	3.37, d (6.8)	27.3, CH ₂	3.41, dd (16.4, 7.5) 3.33, dd (16.4, 7.5)	28.18, CH ₂	3.39, d (7.3)	27.6, CH ₂	3.41, dd (15.7, 7.3) 3.37, dd (15.7, 6.8)
2	127.62, CH	5.34, t (6.8)	127.4, CH	5.34, <i>br t</i> (7.8)	128.01, CH	5.42, t (7.3)	127.6, CH	5.42, <i>br t</i> (7.3)
3	131.03, C		131.2, C		130.63, C		131.1, C	
4	58.40, CH ₂	3.12, s	54.6, CH ₂	3.24, d (15.9) 3.10, d (15.9)	55.29, CH ₂	3.16, s	55.1, CH ₂	3.19, d (15.7) 3.15, d (15.7)
5	200.07, C		200.3, C		200.41, C		200.8, C	
6	123.96, CH	6.09, s	124.0, CH	6.09, <i>br s</i>	122.90, CH	6.12, s	123.6, CH	6.11, <i>br s</i>
7	160.41, C		160.7, C		158.84, C		158.0, C	
8	34.45, CH ₂		34.5, CH ₂	2.67, ddd (11.2, 11.2, 4.4) 2.09, ddd (11.2, 11.2, 5.9)	40.93, CH ₂	2.0-2.2	40.5, CH ₂	2.18, m 2.00, m
9	22.82, CH ₂		22.9, CH ₂	1.59, m 1.09, m	21.16, CH ₂		20.8, CH ₂	1.64, m 1.09, m
10	38.61, CH ₂		38.5, CH ₂	1.95, ddd (14.3, 11.2, 3.9) 1.86, m	38.10, CH ₂	1.6-1.8	37.3, CH ₂	1.71, m
11	78.59, C		78.6, C		78.25, C		78.3, C	
12	203.27, C		203.2, C		202.93, C		202.6, C	
13	119.33, CH	6.86, d (15.6)	119.1, CH	6.88, d (15.2)	118.41, CH	6.60, d (15.1)	117.8, CH	6.58, d (15.2)
14	155.75, CH	7.16, d (15.6)	155.8, CH	7.15, d (15.2)	156.26, CH	7.20, d (15.1)	156.4, CH	7.20, d (15.2)
15	71.41, C		71.6, C		71.20, C		71.6, C	
16	28.50, CH ₃	1.40, s	29.5 ^e , CH ₃	1.356, s	29.30, CH ₃	1.44, s	29.3 ^f , CH ₃	1.45, s
17	29.52, CH ₃	1.36, s	28.3 ^e , CH ₃	1.40, s	29.30, CH ₃	1.40, s	28.9 ^f , CH ₃	1.40, s
18	26.13, CH ₃	1.36, s	26.3, CH ₃	1.361, s	25.10, CH ₃	1.36, s	25.3, CH ₃	1.36, s
19	25.42, CH ₃	1.85, s	25.5, CH ₃	1.85, d (1.5)	19.27, CH ₃	2.00, s	19.4, CH ₃	1.99, d (1.2)
20	16.60, CH ₃	1.67, s	16.5, CH ₃	1.65, <i>br s</i>	16.55, CH ₃	1.70, s	16.6, CH ₃	1.70, <i>br s</i>
1'	149.96, C		149.6, C		149.83, C		149.8, C	
2'	134.20, C		133.6, C		134.44, C		134.2, C	
3'	113.66, CH	6.63, d (2.9)	113.4, CH	6.65, d (2.9)	114.04, CH	6.57, d (2.3)	113.5, CH	6.56, d (2.9)
4'	152.48, C		152.6, C		152.44, C		152.3, C	
5'	115.57, CH	6.54, d (2.9)	115.4, CH	6.54, d (2.9)	115.72, CH	6.53, d (2.3)	115.5, CH	6.52, d (2.9)
6'	131.94, C		131.9, C		131.74, C		131.9, C	
6'-CH ₃	16.16, CH ₃	2.24, s	16.2, CH ₃	2.25, s	16.21, CH ₃	2.24, s	16.2, CH ₃	2.25, s
-OCH ₃	60.35, CH ₃	3.68, s	60.3, CH ₃	3.68, s	60.41, CH ₃	3.68, s	60.4, CH ₃	3.68, s
11-OH				4.18, s				4.13, s
15-OH				4.08, <i>br s</i>				2.91, <i>br s</i>
4'-OH				7.23, <i>br s</i>				6.68, <i>br s</i>

a) Data from Urones, J. G.; Basabe, P.; Marcos, I. S.; Pineda, J.; Lithgow, A. M.; Moro, R. F.; Brito Palma, F. M. S.; Araújo, M. E. M.; Grávalos, M. D. G. *Phytochemistry* **1992**, 31, 179-182.

b) Recorded in CDCl₃; ¹H at 500 MHz, ¹³C at 125 MHz.

c) Assignments aided by COSY, HSQC, HMBC, and NOESY experiments.

d) Recorded in CDCl₃; ¹H at 500 MHz, ¹³C at 150 MHz.

e,f) Values with the same superscript in the same column can be interchanged.