Supporting Information

Aristolic Acid Derivatives from the Bark of *Antidesma ghaesembilla*

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Dedicated to Professor Dr. Max Wichtl in recognition of his outstanding contribution to phytotherapy research.

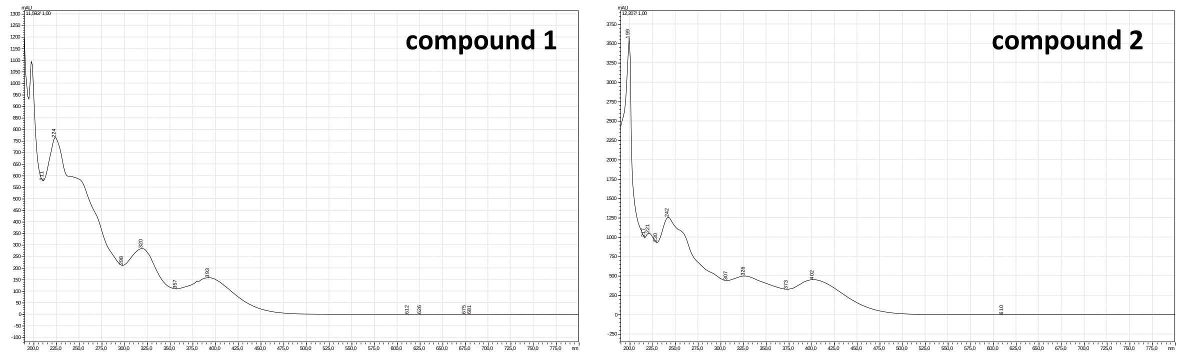

Fig. 1S LC-online UV spectra of **1** (left) and **2** (right).

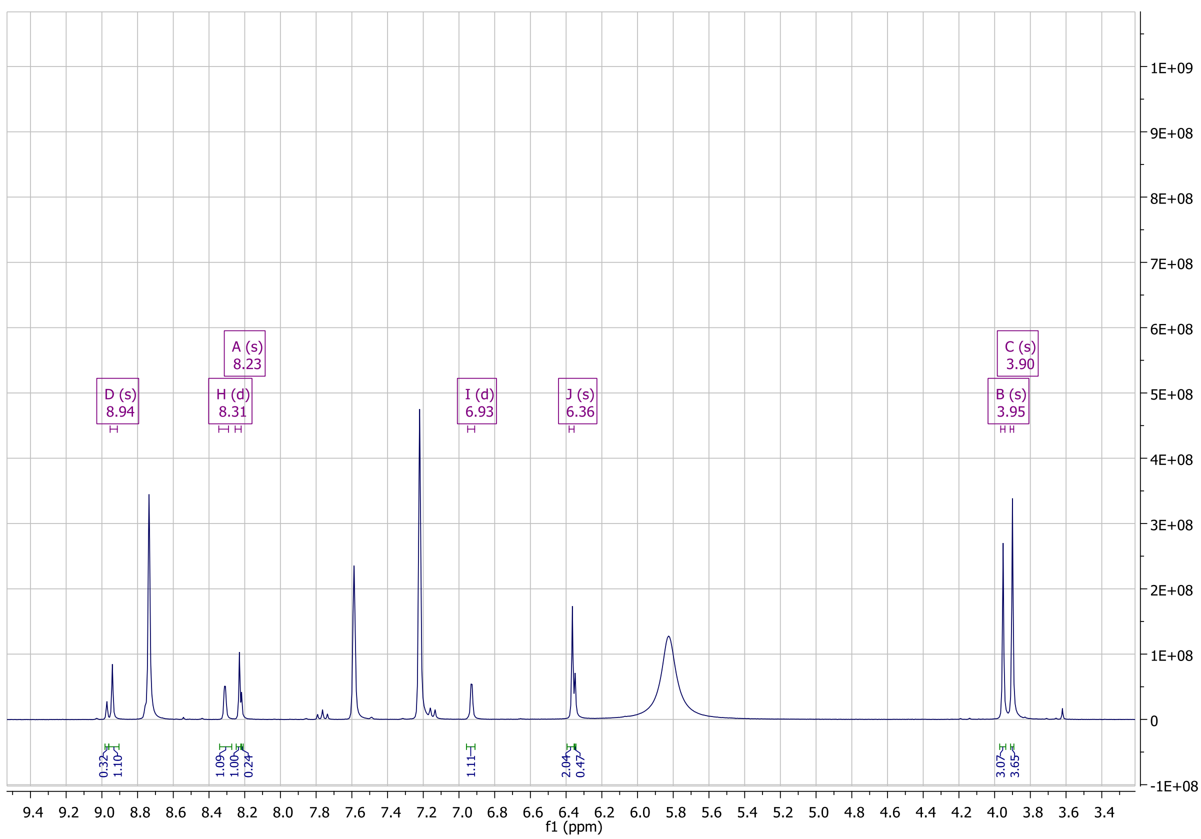

Fig. 2S ^{1}H NMR (600.19 MHz, pyridine-d_5) spectrum of **1**.

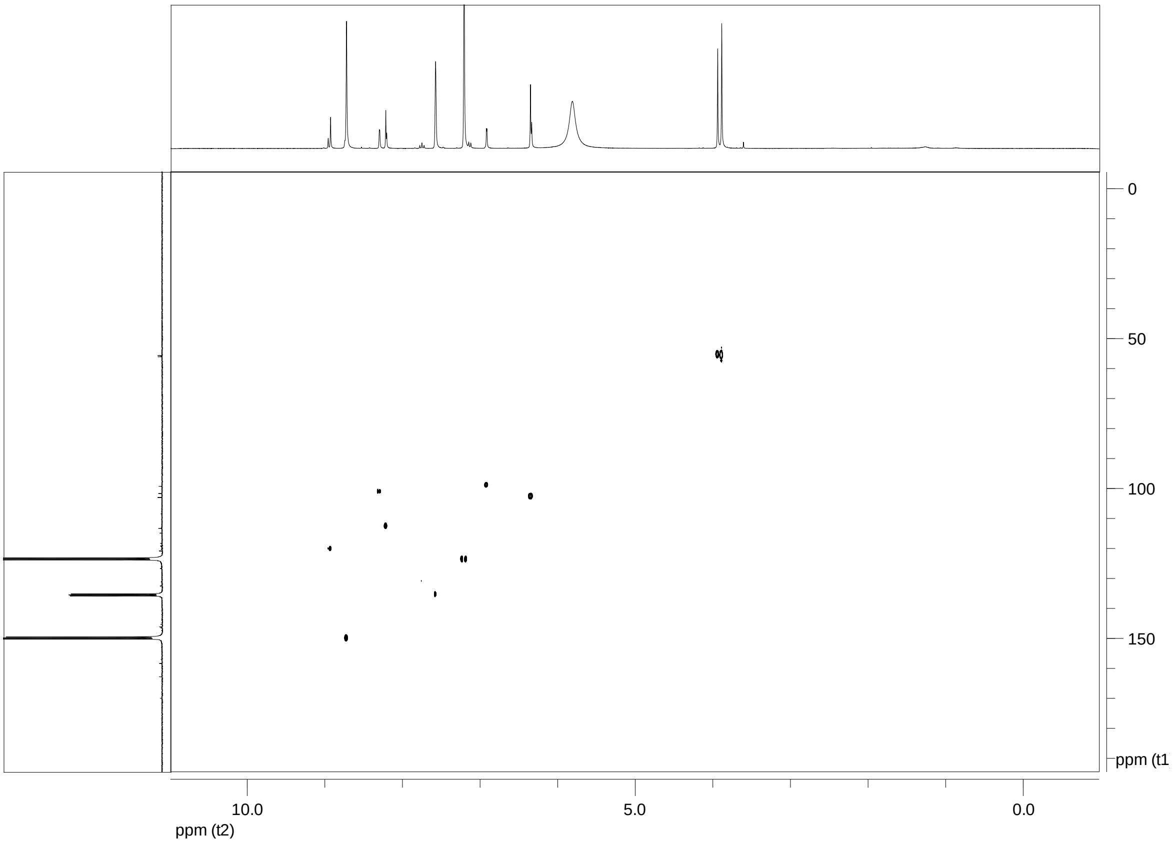

Fig. 3S HSQC NMR (600.19 MHz, pyridine-d_5) spectrum of **1**.

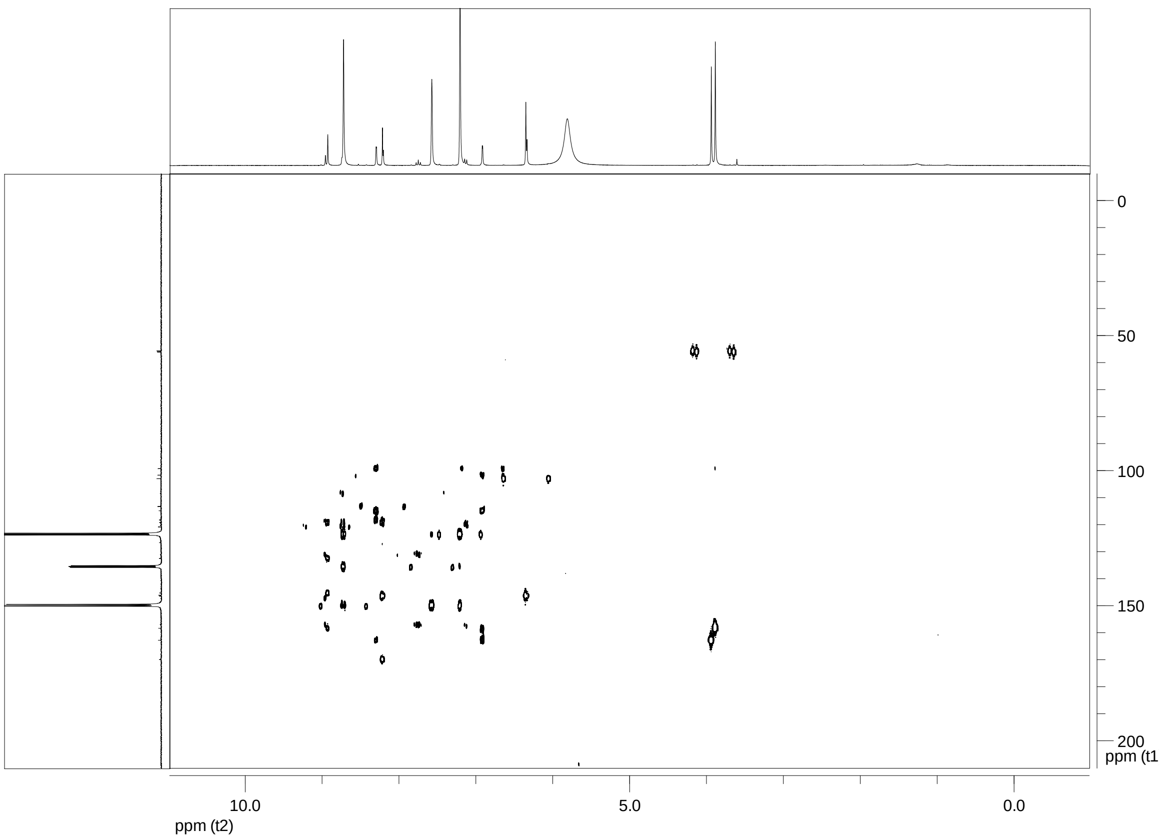

Fig. 4S HMBC NMR (600.19 MHz, pyridine-d_5) spectrum of **1**.

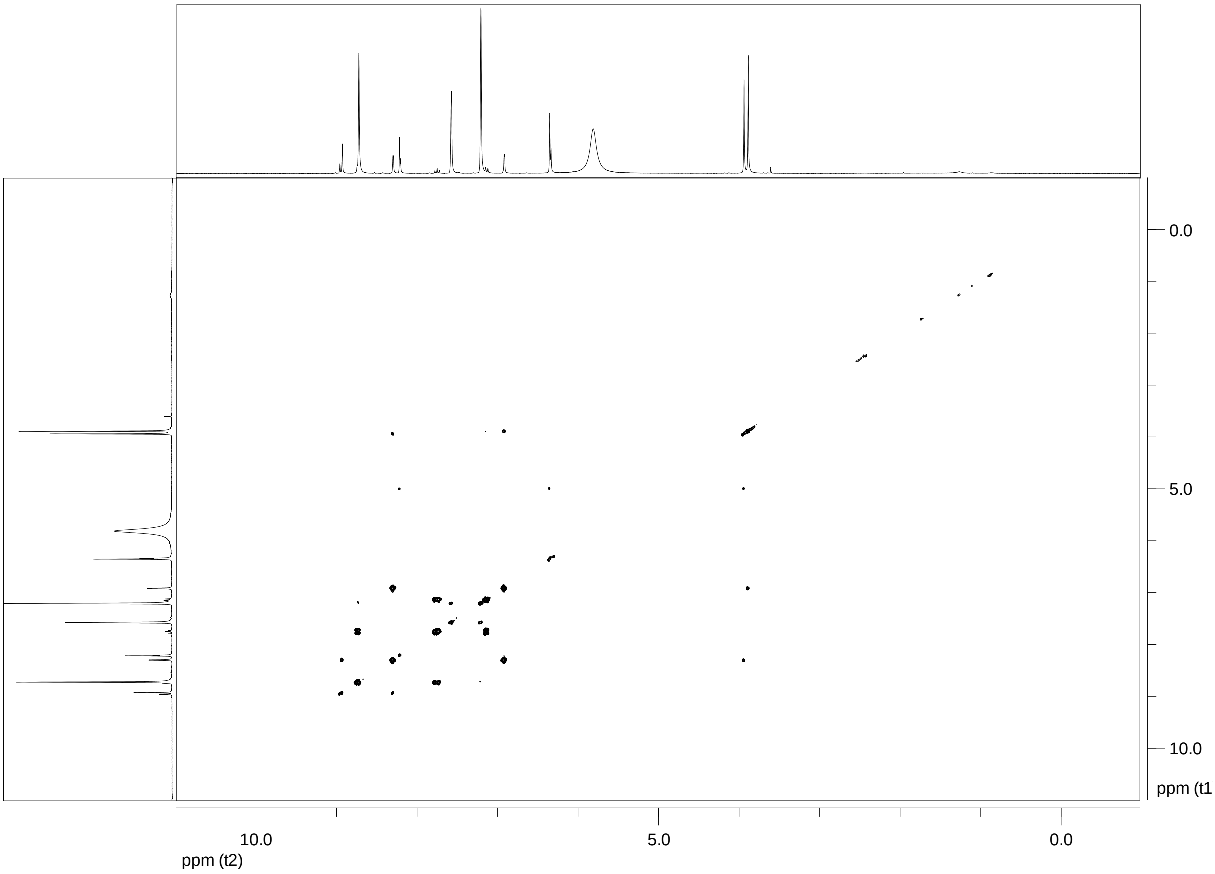

Fig. 5S COSY NMR (600.19 MHz, pyridine-d_5) spectrum of **1**.

Table 1S ^{1}H (600.19 MHz) and ^{13}C (150.91 MHz) NMR data of **1** in pyridine-d_5. Numbering is as shown in **Fig. 1**.

Position	δ_H [ppm], multiplicity (*J* in Hz)	δ_C [ppm]	^1H-^1H COSY correlations	HMBC correlations
1	-	126.8	-	-
2	8.21 *s*, 1H	113.3	-	C-1, C-3, C-4a, C-12
3	-	146.4	-	-
4	-	146.3	-	-
4a	-	118.3	-	-
4b	-	114.9	-	-
5	-	158.4	-	-
6	6.91 *d* (1.9), 1H	99.3	H-8, H-13	C-4b, C-5, C-7, C-8
7	-	162.8	-	-
8	8.29 *d* (1.6), 1H	101.7	H-6, H-9, H-14	C-4a, C-4b, C-6, C-7
8a	-	132.5	-	-
9	8.92 *s*, 1H	120.8	H-8	C-5, C-8a, C-10, C-10a
10	-	145.3	-	-
10a	-	119.2	-	-
11	6.35 *s*, 2H	103.0	-	C-3, C-4
12	-	170.0	-	-
-OCH_3 at C-5	3.88 *s*, 3H	56.1	H-6	C-5

-OCH_3 at C-7	3.94 *s*, 3H	55.7	H-8	C-7

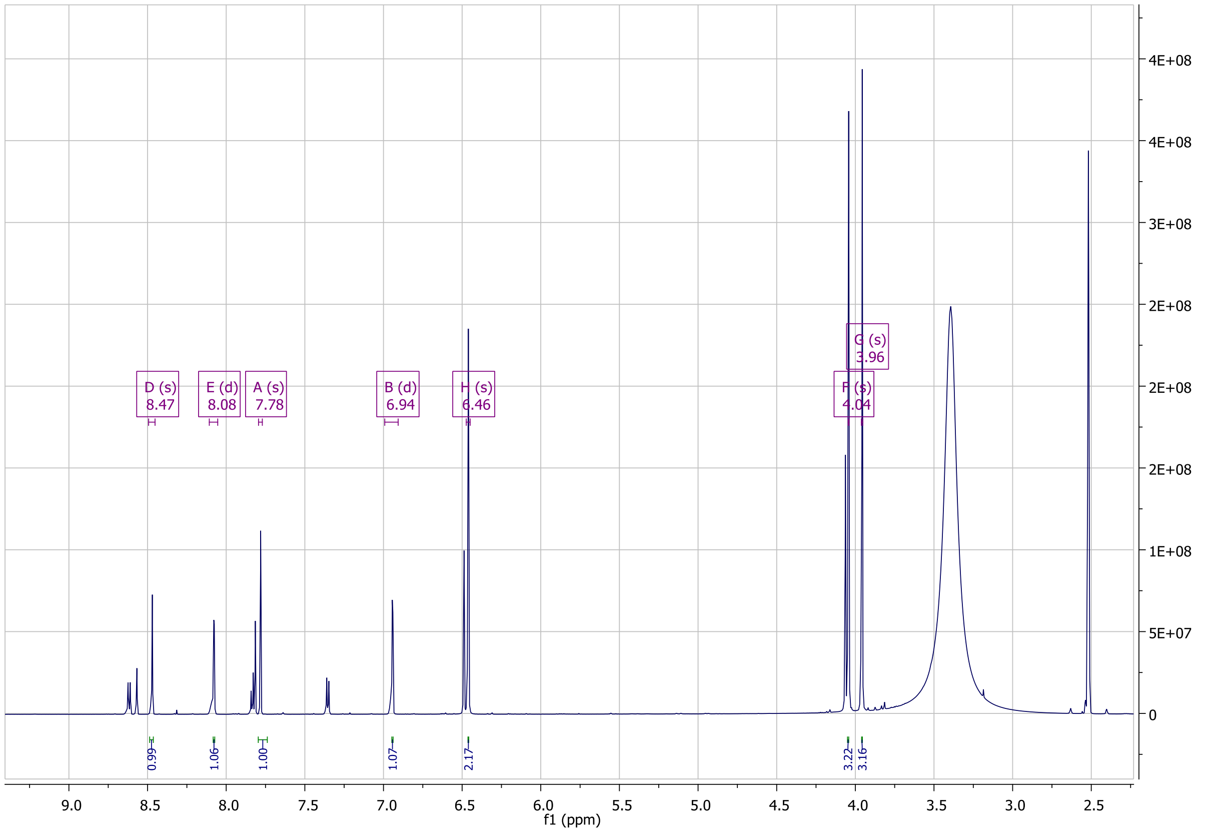

Fig. 6S ^{1}H NMR (600.19 MHz, DMSO-d_6) spectrum of **1**.

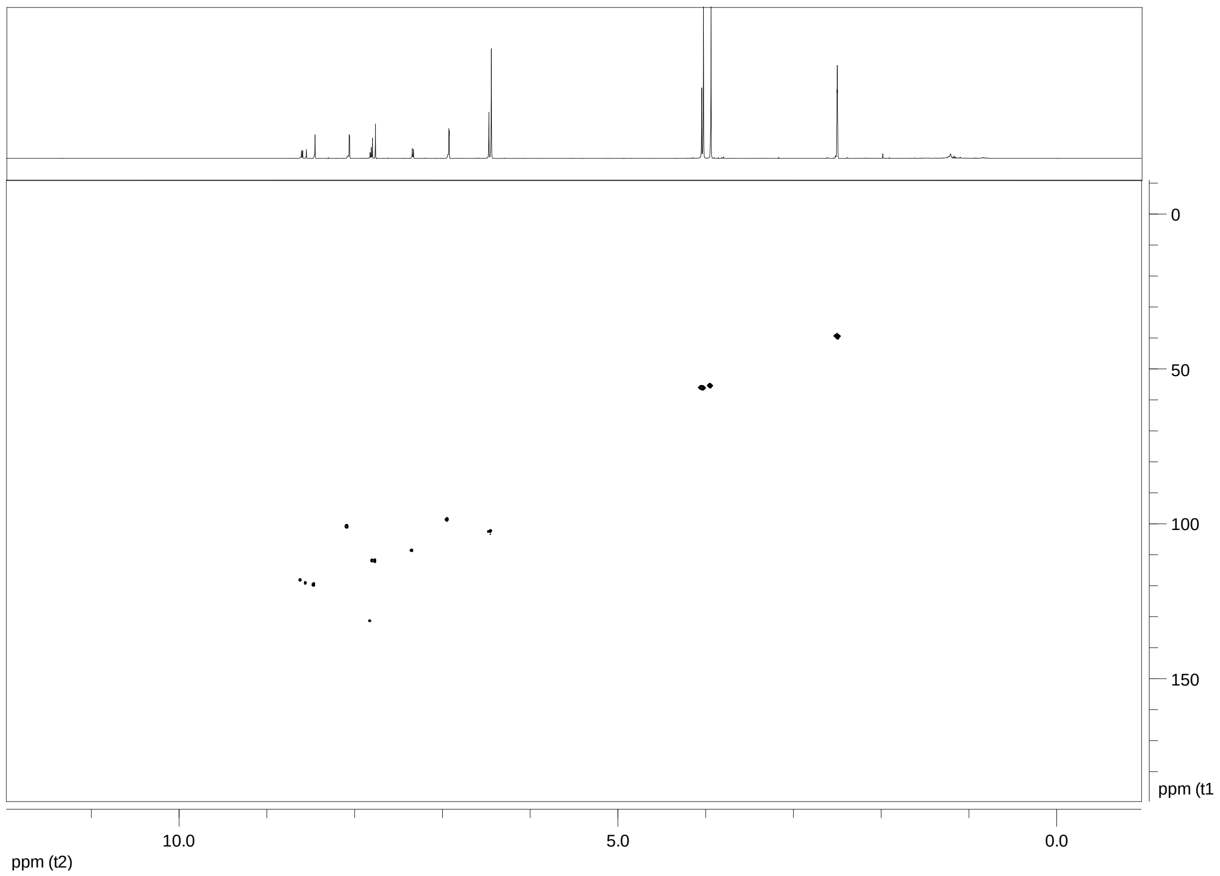

Fig. 7S HSQC NMR (600.19 MHz, DMSO-d_6) spectrum of **1**.

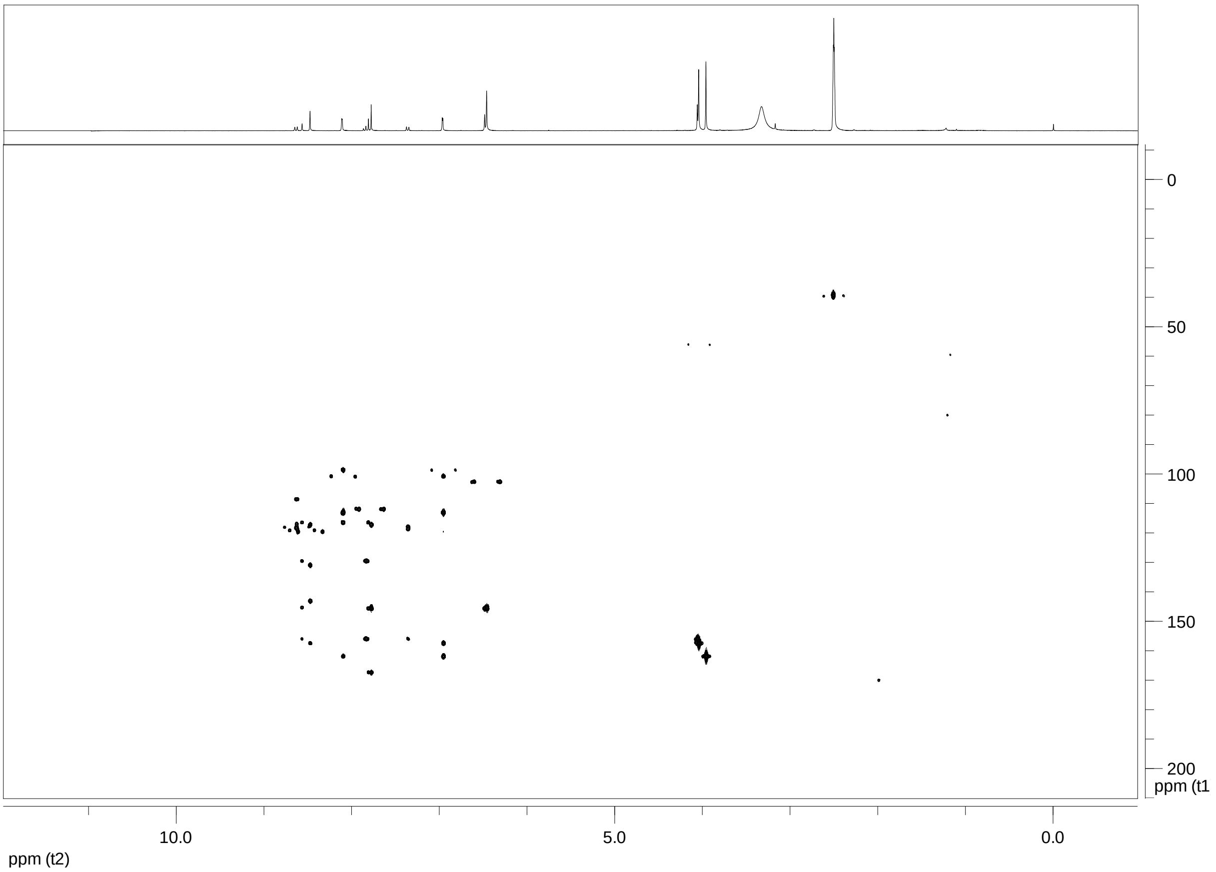

Fig. 8S HMBC NMR (600.19 MHz, DMSO-d_6) spectrum of **1**.

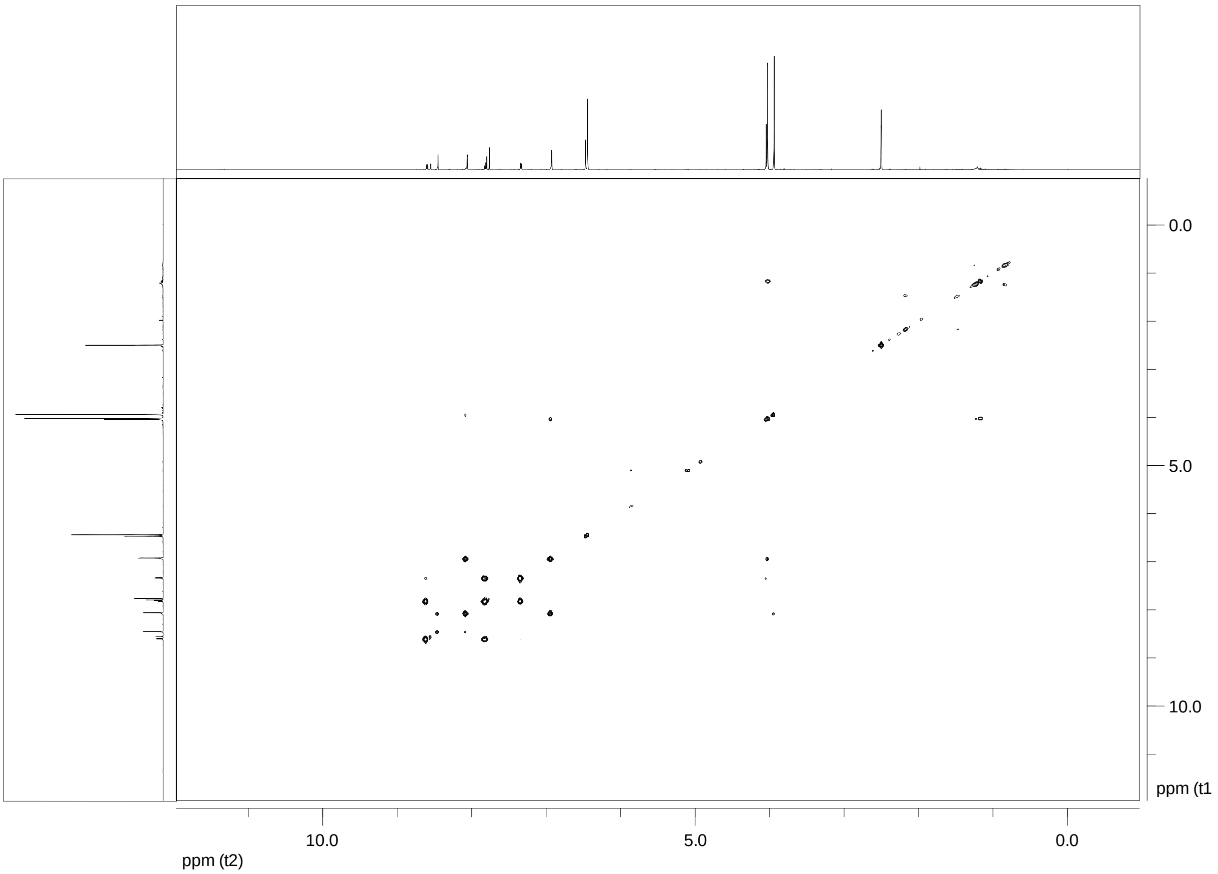

Fig. 9S COSY NMR (600.19 MHz, DMSO-d_6) spectrum of **1**.

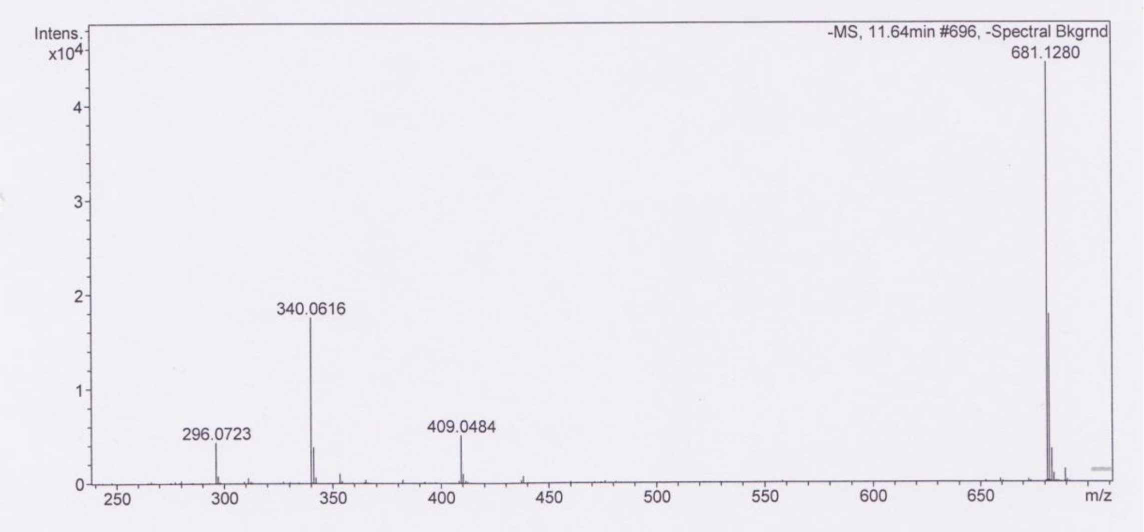

Fig. 10S LC-HR-MS spectrum of **1** (ESI, negative mode).

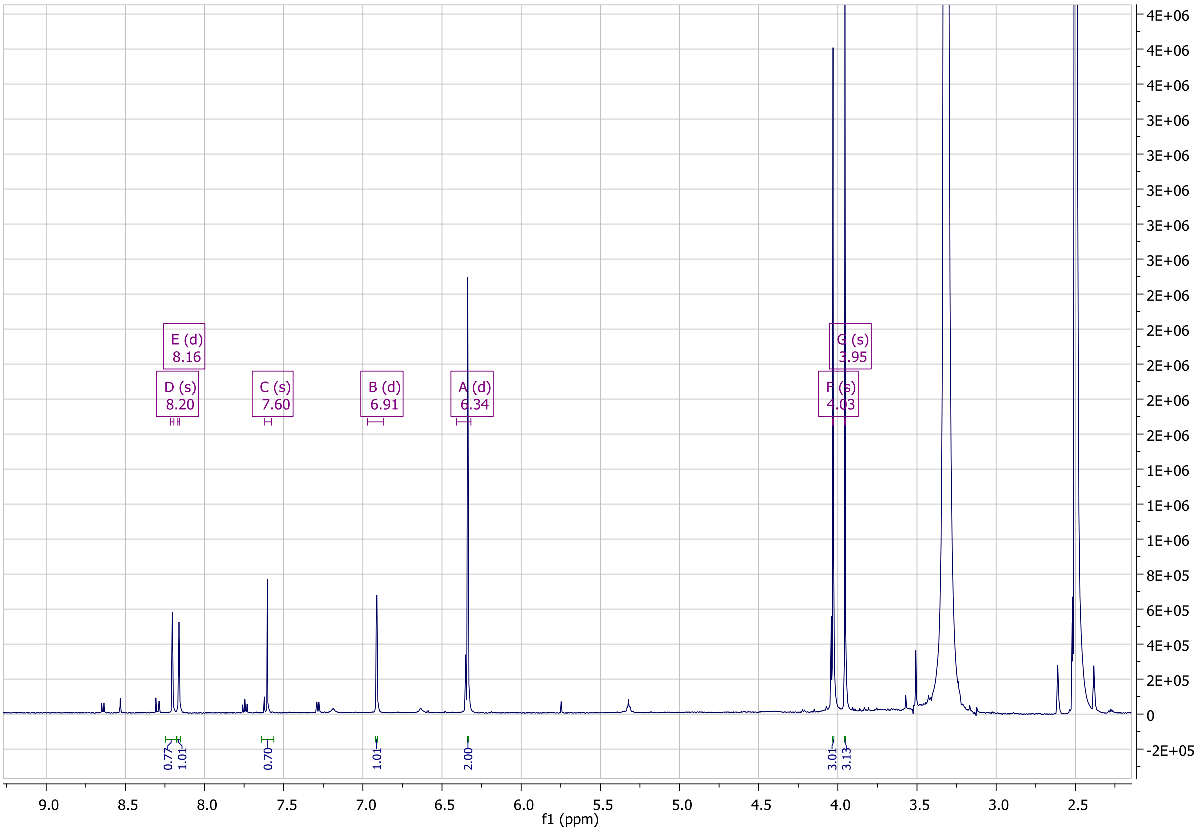

Fig. 11S ^{1}H NMR (600.19 MHz, DMSO-d_6) spectrum of **2**.

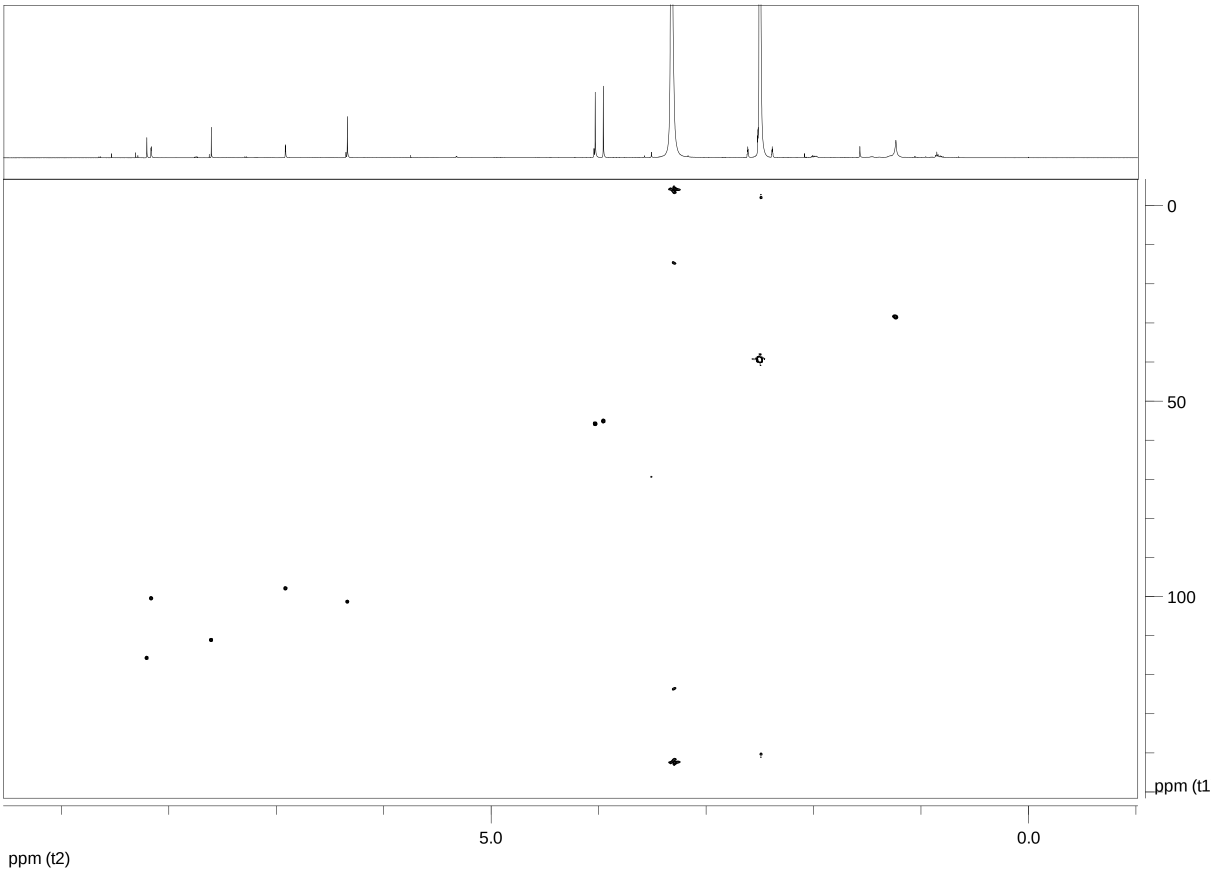

Fig. 12S HSQC NMR (600.19 MHz, DMSO-d_6) spectrum of **2**.

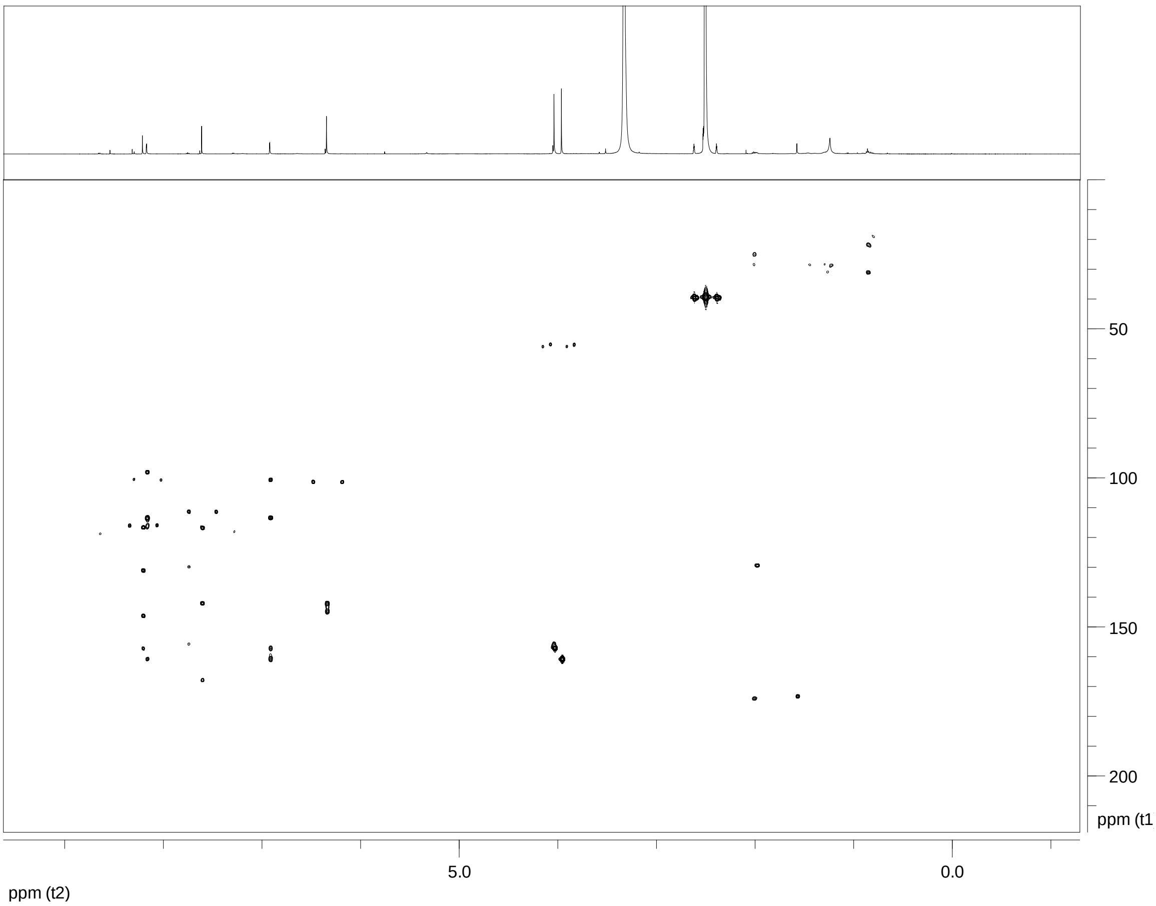

Fig. 13S HMBC NMR (600.19 MHz, DMSO-d_6) spectrum of **2**.

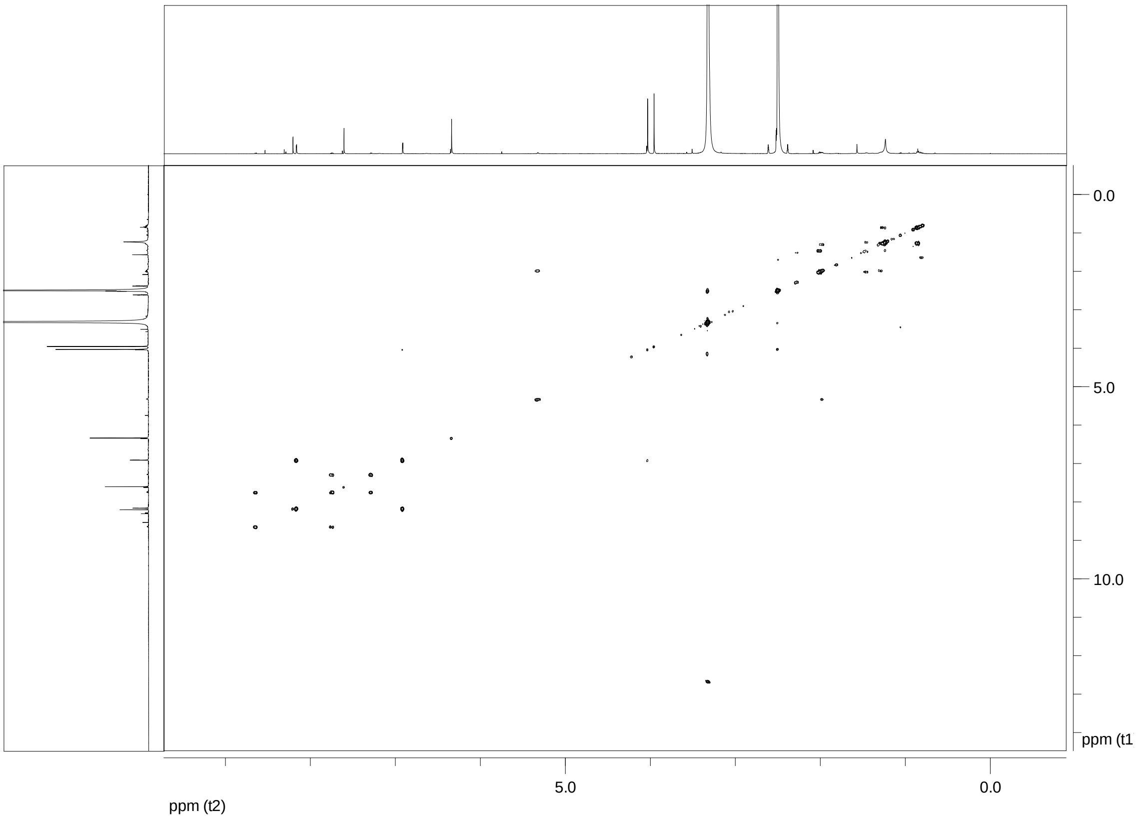

Fig. 14S COSY NMR (600.19 MHz, DMSO-d_6) spectrum of **2**.

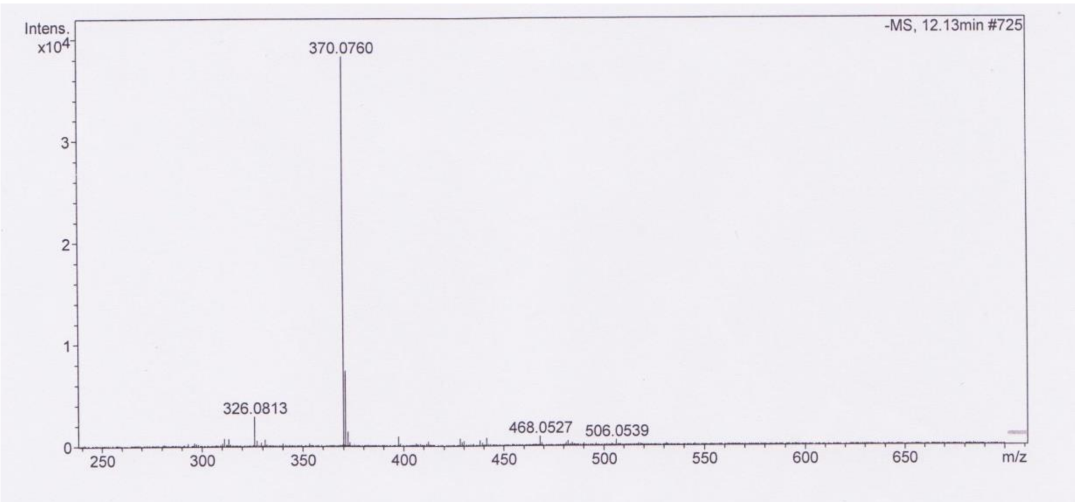

Fig. 15S LC-HR-MS spectrum of **2** (ESI, negative mode).

Fig. 16S LC-online UV spectra of aristolic acid II-8-*O*-*β*-D-glucoside (**10**).

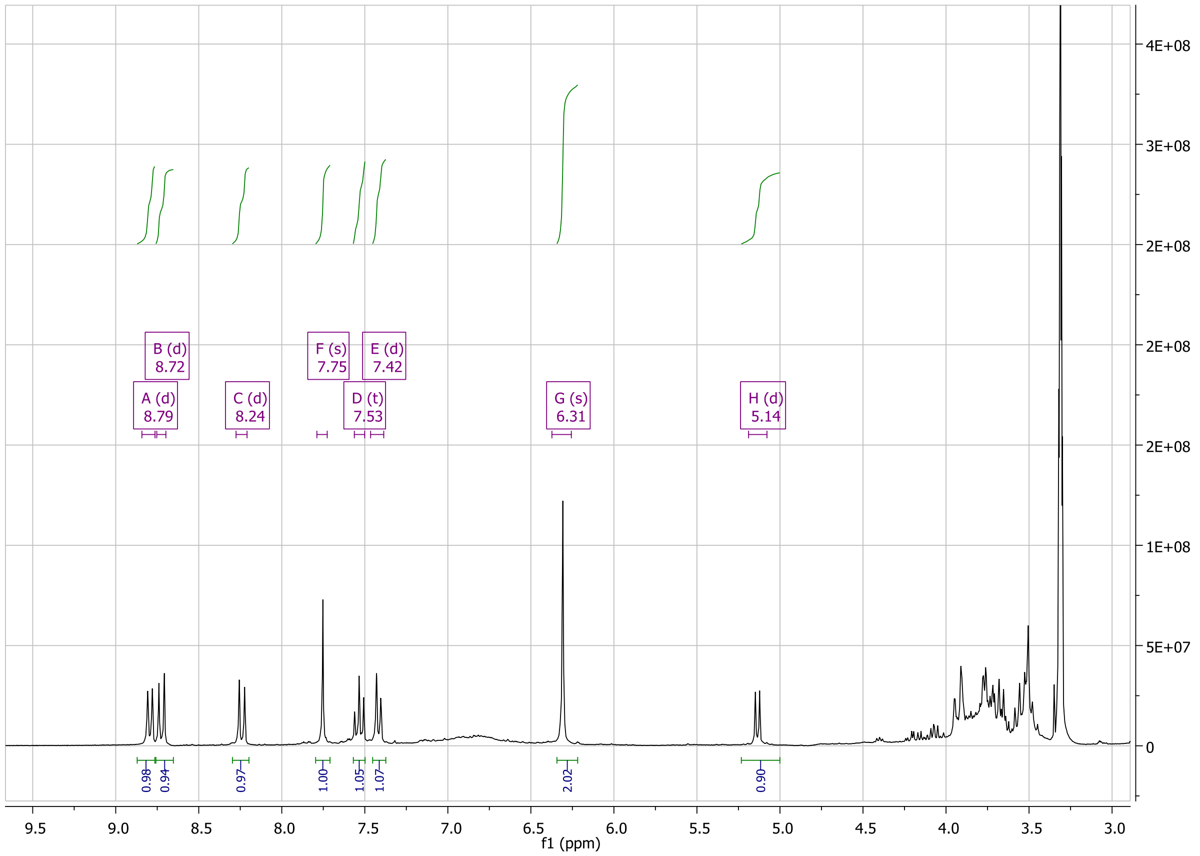

Fig. 17S ^{1}H NMR (600.19 MHz, MeOH-d_4) spectrum of **10**.

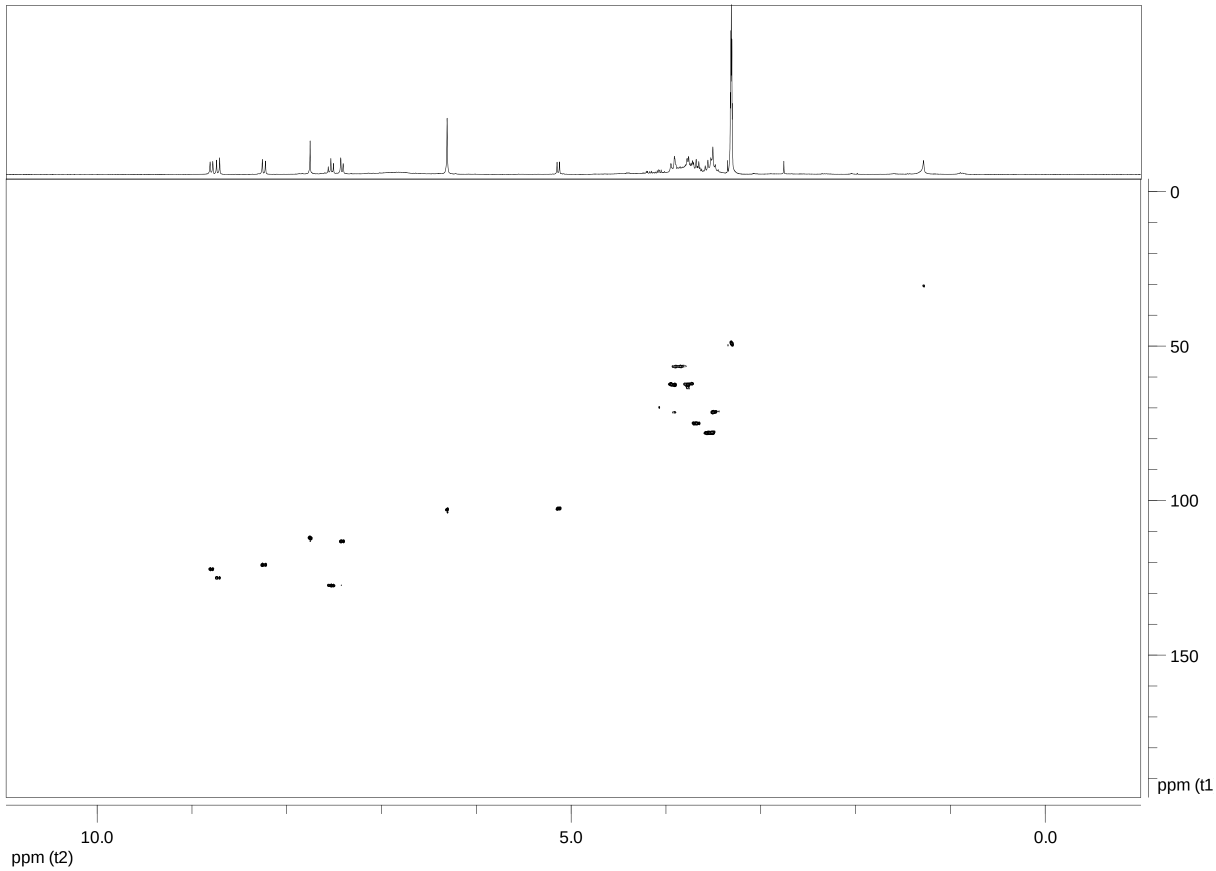

Fig. 18S HSQC NMR (600.19 MHz, MeOH-d_4) spectrum of **10**.

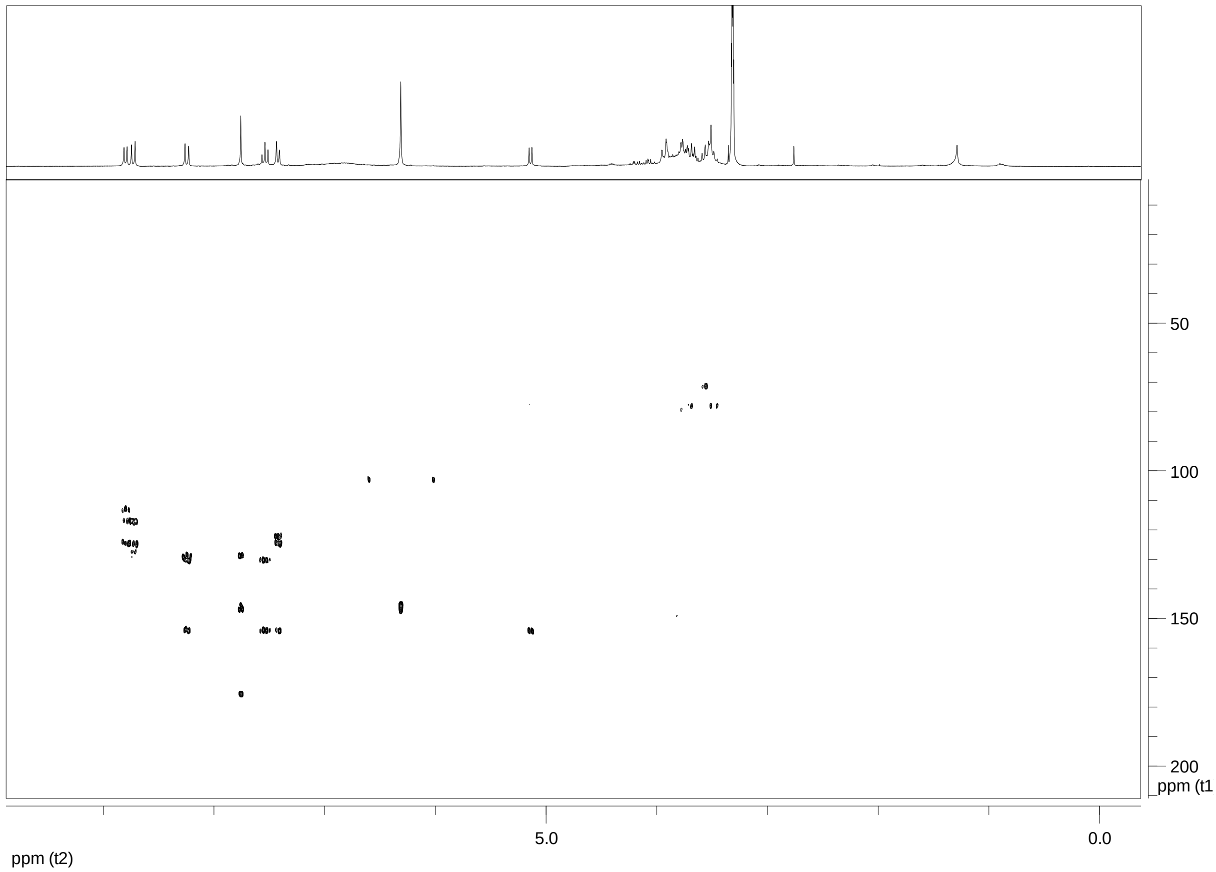

Fig. 19S HMBC NMR (600.19 MHz, MeOH-d_4) spectrum of **10**.

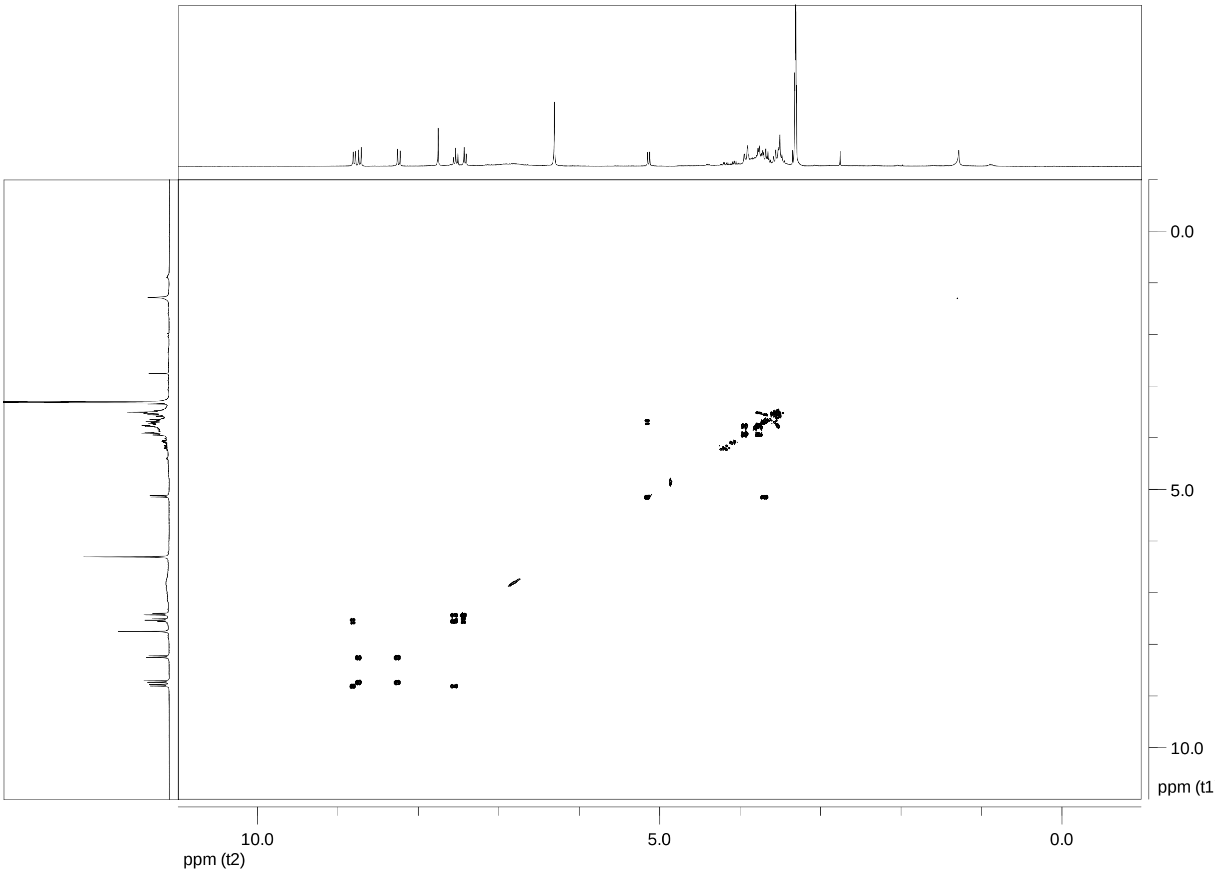

Fig. 20S COSY NMR (600.19 MHz, MeOH-d_4) spectrum of **10**.

Table 2S ^{13}C (150.91 MHz) NMR data of isolated steroids.

Position	**Sitostenon** δ_C **[ppm] (MeOH-d_4)**	**Daucosterol** δ_C **[ppm] (DMSO-d_6)**
1	36.5	36.5
2	34.4	29.1
3	201.6	76.7
4	123.7	38.1
5	175.3	140.5
6	34.2	120.8
7	33.1	31.1
8	36.6	31.0
9	55.2	49.4
10	39.8	36.0
11	21.7	20.4
12	40.8	39.1
13	43.1	41.7
14	57.0	55.9
15	24.9	23.6
16	28.9	27.3
17	57.2	55.1
18	12.1	11.0
19	17.4	19.3
20	37.2	35.2
21	18.9	18.3
22	34.7	33.0

23	27.0	25.1
24	47.0	44.7
25	30.1	28.5
26	19.2	19.3
27	20.0	19.5
28	23.9	22.2
29	12.0	14.2
1’	-	100.5
2’	-	73.2
3’	-	76.3
4’	-	69.6
5’	-	76.3
6’	-	60.6

Table 3S ^{1}H NMR (600.19 MHz) data of isolated steroids (*J* in Hz). o.s. = overlapping signal.

Position	**Sitostenon** **δ_H [ppm] mult. (*J* in Hz)** **(MeOH-d_4)**	**Daucosterol** **δ_H [ppm] mult. (*J* in Hz)** **(DMSO-d_6)**
1	2.08 *m* 1.70 *m*	0.99 *m* 1.78 *m*
2	2.47 *m* 2.28 *m*	1.80 *m* 1.47 *m*
3	-	3.47 *m*
4	5.70 *s*	2.38 *m* 2.12 *m*
5	-	-
6	2.47 *m* 2.28 *m*	5.36 *t* (2.6)
7	1.87 *m* 1.03 *m*	1.91 *m* 1.49 *m*
8	1.66 *m*	1.39 *m*
9	0.96 *m*	0.89 *m*
10	-	-
11	1.55 *m* 1.50 *m*	1.47 *m* 1.39 *m*
12	2.07 *m* 1.20 *m*	1.96 *m* 1.14 *m*
13	-	-
14	1.05 *m*	0.99 *m*
15	1.64 *m* 1.17 *m*	1.54 *m* 1.06 *m*
16	1.89 *m* 1.30 *m*	1.79 *m* 1.24 *m*
17	1.15 *m*	1.09 *m*
18	0.76 *s*	0.65 *s*
19	1.23 *s*	0.95 *s*
20	1.39 *m*	1.34 *m*
21	0.95 *d* (5.5)	0.90 *d* (6.6)
22	1.39 m 1.05 m	1.31 *m* 1.00 *m*
23	1.21 *m* 1.21 *m*	1.17 *m* 1.13 *m*
24	0.95 *m*	0.91 *m*
25	1.68 m	1.63 *m*
26	0.84 *d* (6.8)	0.80 d (6.8)
27	0.86 *d* (6.7)	0.83 d (o.s)
28	1.32 *m* 1.26 *m*	1.28 *m* 1.23 *m*

29	0.87 *d* (3.0)	0.81 (o.s).
1’	-	4.22 *d* (7.8)
2’	-	2.89 *m*
3’	-	3.11 *dt* (4.6, 8.8)
4’	-	3.00 *m*
5’	-	3.07 *m*
6’	-	3.60 *ddd* (1.8, 5.6, 11.6) 3.40 *td* (5.9, 5.9, 11.7)

Table 4S ^{1}H (600.19 MHz) and ^{13}C (150.91 MHz) NMR data of chavibetol in $CDCl_3$.

Position	**δ_H [ppm] mult. (*J* in Hz)**	**δ_C [ppm]**
1	-	145.6
2	-	144.6
3	6.77 (o.s).	110.7
4	6.66 *dd* (1.9, 8.2)	119.7
5	-	133.4
6	6.78 *d* (5.7)	114.9
7	3.29 d (6.7); 2H	39.5
8	5.94 *tdd* (6.7, 6.7, 10.0, 16.9)	137.5
9	H_a 5.08 *m*; H_b 5.04 *m*	115.6
OC**H₃**	3.85 *s*	56.1
OH	5.57 *br s*	-

Table 5S ^{1}H (600.19 MHz) and ^{13}C (150.91 MHz) NMR data of **asperphenamate** in $CDCl_3$; o.s. = overlapping signal.

Position	**Int. H**	**Multiplicity (*J* in Hz)**	**δ_H [ppm]**	**δ_C [ppm]**	**COSY contact**	**HMBC contact**
1				133.9		
2/6/2’/6’	o.s.	o.s.	7.22	129.9	7.29	127.0, 129.9, 135.4
3/5/3’/5’	o.s.	*t* (7.3, 7.3)	7.29	128.7	7.22, 7.24	127.0, 128.7, 133.9, 135.4
4/4’	o.s.	o.s.	7.24	127.0	7.29	129.6
7	1.07	*dd* (8.4, 13.7)	2.89	37.0	2.99, 4.62	49.9, 129.6, 137.8
7	1.05	*dd* (6.5, 7.1)	2.99	37.0	2.89, 4.62	49.9, 129.6, 137.8
8	1.04	*M*	4.62	49.9	2.89, 2.99, 4.04, 6.63	133.9, 170.8
NH8	*br d*	*d* (8.3)	6.63		4.62	49.9
9	1.04	*dd* (4.3, 11.4)	4.04	65.1	4.53, 4.62	49.9, 172.2
9	1.05	*dd* (3.1, 11.4)	4.53	65.1	4.04, 4.62	49.9, 172.2
1’				135.4		
7’	1.06	*dd* (7.0, 13.9)	3.21	37.3	3.29, 4.92	54.1, 129.2, 135.4, 172.2
7’	1.06	*dd* (6.5, 13.9)	3.29	37.3	3.21, 4.92	54.1, 129.2, 135.4, 172.2
8’	1.00	*q* (6.7, 6.7, 6.7)	4.92	54.1	3.21, 3.29, 6.58	37.3, 132.8, 168.4
NH8’	*br d*	*d* (6.4)	6.58		4.92	54.1
9’				172.2		
1’’				132.8		
2’’/6’’	1.97	*d* (7.5)	7.70	126.7	7.30	130.9
3’’/5’’	o.s.	*t* (7.3, 7.3)	7.30	128.3	o.s.	o.s.
4’’	0.98	*t* (7.4, 7.4)	7.43	130.9	7.30	128.3, 132.8
7’’				168.4		
1’’’				132.4		132.4

2'''/6'''	1.94	*d* (7.5)	7.65	126.7	7.39	131.6, 170.8
3'''/5'''	1.95	*t* (7.7, 7.7)	7.39	128.2	7.50, 7.65	128.2, 132.4
4'''	0.94	*t* (7.4, 7.4)	7.50	131.6	7.39	128.2
7'''				170.8		

Table 6S ^{13}C (150.91 MHz) NMR data of isolated protocatechuic acid and vanillic acid 4-*O*-*β*-D-glucoside.

Position	**Protocatechuic acid** δ_C **[ppm] DMSO-d_6**	**Vanillic acid-4-*β*-D-glucoside** δ_C **[ppm] MeOH-d_4**
1	128.0	130.0
2	116.6	114.3
3	144.4	149.9
4	147.2	150.4
5	114.0	116.2
6	120.5	123.9
7	169.9	172.5
8	-	56.4
1'	-	102.0
2'	-	77.5
3'	-	71.1
4'	-	74.4
5'	-	77.9
6'	-	62.1

Table 7S ^{1}H NMR (600.19 MHz) of isolated protocatechuic acid and vanillic acid 4-*O*-*β*-D-glucoside.

Position	**Protocatechuic acid** δ_H **[ppm] mult. (*J* in Hz) DMSO-d_6**	**Vanillic acid 4-*O*-*β*-D-glucoside** δ_H **[ppm] mult. (*J* in Hz) MeOH-d_4**
2	7.30 *d* (1.69)	7.63 *d* (1.85)
5	6.61 *d* (8.10)	7.16 *d* (8.45)
6	7.18 *dd* (1.82, 8.10)	7.60 *dd* (1.90, 8.42)
8	-	3.91 *s*
1'	-	5.00 *d* (7.5)
2'	-	3.50 *m*
3'	-	3.43 *m*
4'	-	3.52 *m*
5'	-	3.44 *dd* (2.17, 5.21)
6'	-	3.88 *dd* (2.14, 12.32) 3.70 *dd* (5.24, 12.12)

Table 8S ^{1}H (600.19 MHz) and ^{13}C (150.91 MHz) NMR data of 1-*O*-*β*-D-glucopyranosyl-3-*O*-methyl-phloroglucinol in DMSO-d_6.

Position	δ_H **[ppm] mult. (*J* in Hz)**	δ_C **[ppm]**
1	-	159.0

2	5.99 *t* (2.02, 2.02)	92.9
3	-	160.5
4	6.06 *m*	92.9
5	-	158.9
6	6.07 *m*	96.0
7	3.65 *s*	54.5
1’	4.73 *d* (7.78)	100.1
2’	3.17 *dd* (7.19, 10.10)	72.8
3’	3.25 *m*	76.4
4’	3.14 *d* (9.51)	69.2
5’	3.24	76.4
6’	3.68 *dd* (1.74, 11.80) 3.47 *dd* (5.70, 11.79)	60.2

Fig. 21S Chromatograms of the HPLC analysis of AGD (5 mg/mL MeOH), AGM (5 mg/mL MeOH), compound **1**, and compound **2** at 225 nm. Analytical conditions: HP 1100 system (Agilent) equipped with an autosampler, DAD, and column thermostat; stationary phase: Phenomenex Gemini (3 µm, 150 × 4.60 mm) with a SecurityGuard Cartridge Fusion-RP (4 × 3.0 mm ID); mobile phase: solvent A: water with 0.02% TFA; solvent B: acetonitrile; temp.: 30°C; injection volume: 5.0 µL; flow: 0.400 mL/min; conditions during run: start: 5% B; 30 min: 98% B; 35 min: stop; post-time: 10 min.