Supporting Information

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Antioxidant Activities of Hydrolysable Tannins and Flavonoids Glycosides Isolated from *Eugenia uniflora* L.

Gilmara A. C. Fortes[1], Ariadne G. Carvalho[1], Ruver R. F. Ramalho[1], Antônio J. R. da Silva[2], Pedro H. Ferri[1] and Suzana C. Santos[1*]

[1]Instituto de Química, Universidade Federal de Goiás, 74001-970, Goiânia, GO, Brazil

[2]Núcleo de Pesquisas de Produtos Naturais, Centro de Ciências da Saúde, Universidade Federal do Rio de Janeiro, 21941-590, Rio de Janeiro, RJ, Brazil

Table of Contents **Page**

S1. General experimental information 3

S2. ^{1}H-NMR (500 MHz, acetone-d_6) Spectrum of Compound **1** 3

S3. Expansion of the COSY NMR experiment of Compound **1** 4

S4. ESI-TOF mass Spectrum of Compound **1** 4

S5. ^{1}H-NMR (500 MHz, acetone-d_6) Spectrum of Compound **2** 5

S6. ESI-TOF mass Spectrum of Compound **2** 5

S7. ^{1}H-NMR (500 MHz, acetone-d_6) Spectrum of Compound **3** 6

S8. Expansion of the COSY NMR experiment of Compound **3** 7

S9. Expansion of the HSQC NMR experiment of Compound **3** 7

S10. Expansion of the HMBC NMR experiment of Compound **3** 8

S11. ESI-TOF mass Spectrum of Compound **3** 8

S12. ^{1}H-NMR (500 MHz, acetone-d_6) Spectrum of Compound **4** 9

S13. Expansion of the COSY NMR experiment of Compound **4** 10

S14. Expansion of the HSQC NMR experiment of Compound **4** 10

S15. ESI-TOF mass Spectrum of Compound **4** 11

S16. ^{1}H-NMR (500 MHz, acetone-d_6 + D_2O, - 20 ^{o}C) Spectrum of Compound **5** 11

S17. Expansion of the COSY NMR experiment of Compound **5** 13

S18. Expansion of the HSQC NMR experiment of Compound **5** 13

S19. Expansion of the HMBC NMR experiment of Compound **5** 14

S20. ESI-TOF mass Spectrum of Compound **5** 14

S21. ^{1}H-NMR (500 MHz, acetone-d_6 + D_2O) Spectrum of Compound **6** 15

S22. Expansion of the COSY NMR experiment of Compound **6** 15

S23. Expansion of the HSQC NMR experiment of Compound **6** 16

S24. Expansion of the HMBC NMR experiment of Compound **6** 17

S25. ESI-TOF mass Spectrum of Compound **6** 17

S26. ^{1}H-NMR (500 MHz, acetone-d_6 + D_2O) Spectrum of Compound **7** 18

S27. Expansion of the ^{1}H-NMR Spectrum of Compound **7** 18

S28. Expansion of the COSY NMR experiment of Compound **7** 20

S29. Expansion of the HSQC NMR experiment of Compound **7** 20

S30. Expansion of the HMBC NMR experiment of Compound **7** 21

S31. ESI-TOF mass Spectrum of Compound **7** 21

S32. ^{1}H-NMR (500 MHz, methanol-d_4) Spectrum of Compound **8** 22

S33. Expansion of the HSQC NMR experiment of Compound **8** 22

S34. ^{1}H-NMR (500 MHz, methanol-d_4) Spectrum of Compound **9** 23

S35. Expansion of the HSQC NMR experiment of Compound **9** 23

S36. ^{1}H-NMR (500 MHz, methanol-d_4) Spectrum of Compound **10** 24

S37. Expansion of the HSQC NMR experiment of Compound **10** 24

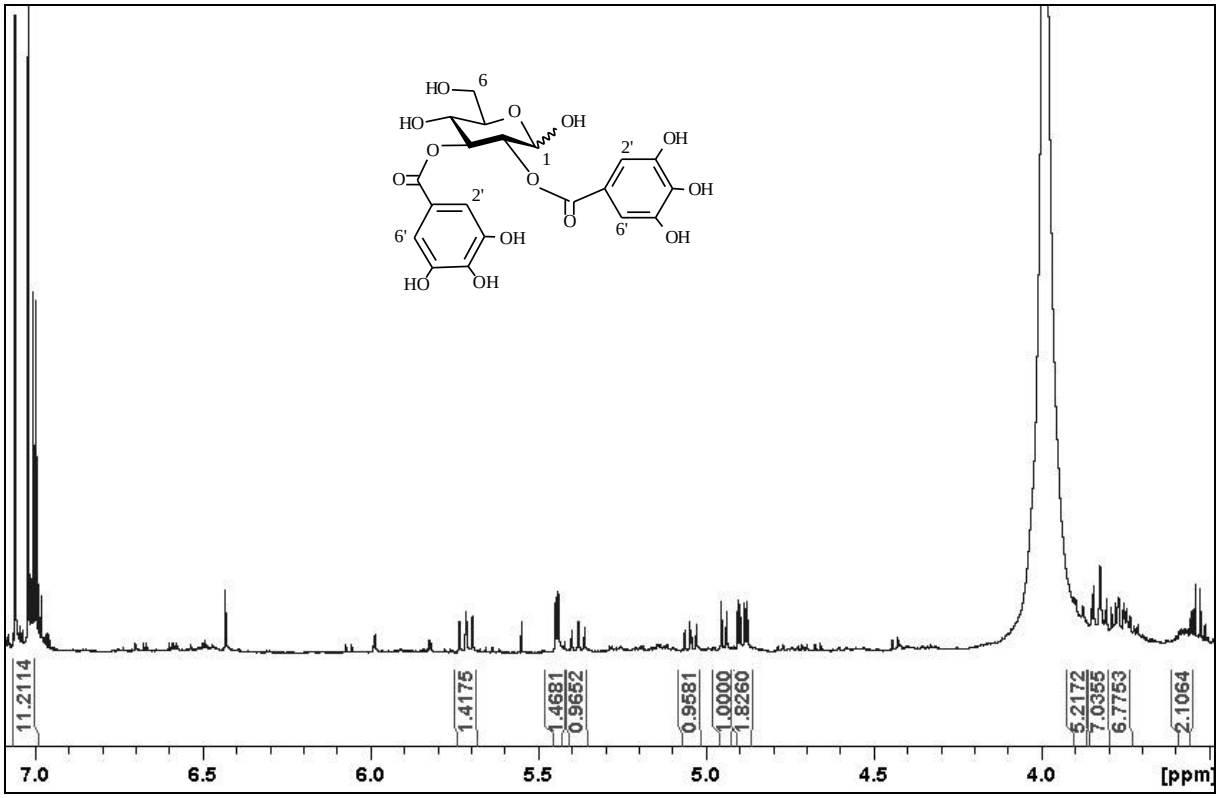
S38. ^{1}H-NMR (500 MHz, methanol-d_4) Spectrum of Compound **11** 25

S39. Expansion of the HSQC NMR experiment of Compound **11** 26

S40. ESI-TOF mass Spectrum of Compound **11** 26

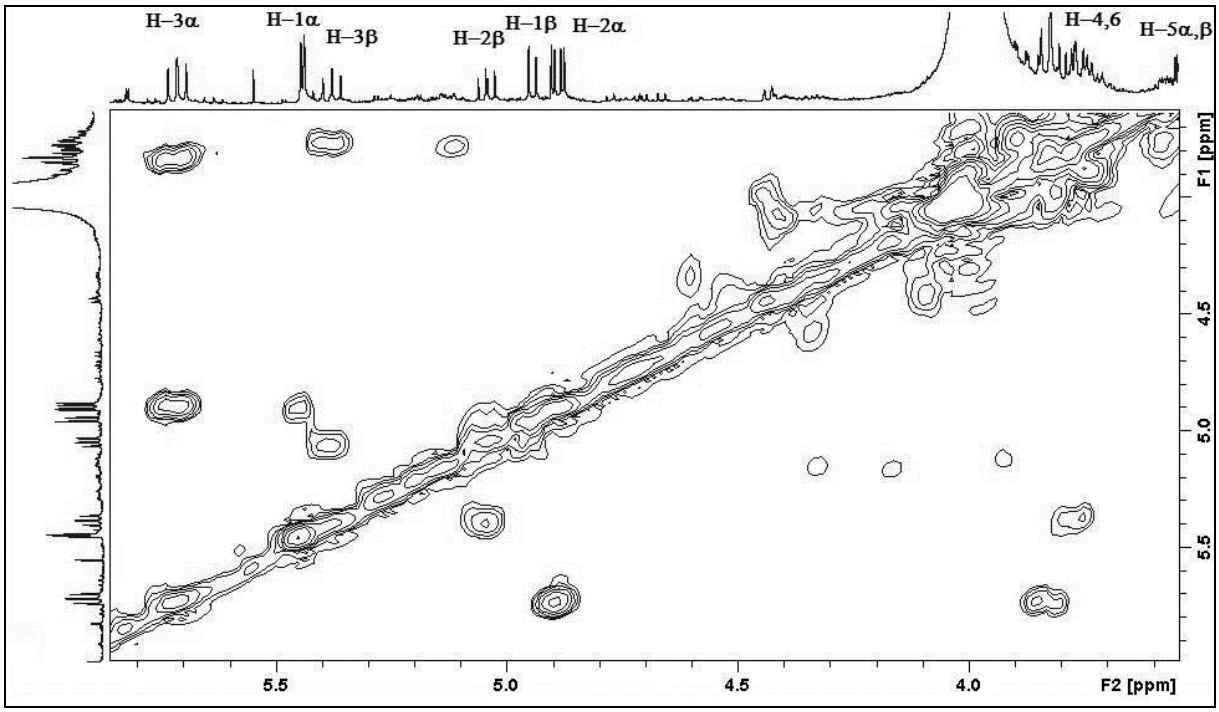
S1. General experimental information

Column chromatography was run using Diaion HP-20 (Supelco) or Sephadex LH-20 (Sigma-Aldrich). Analytical TLC was carried out with Silica gel 60 F_{254} (Merck) plates, using formic acid-ethyl formiate-toluene (1:7:1) as the mobile phase. TLC spots were visualized by spraying plates with a 1% ethanolic solution of ferric chloride in HCl (0.1%) and UV light. All NMR experiments were recorded on a Bruker Avance III 500 spectrometer operating at 500.13 MHz for ^{1}H and 125 MHz for ^{13}C, using TMS as internal reference. ESI-TOF MS spectra were recorded on a Bruker microTOF instrument.

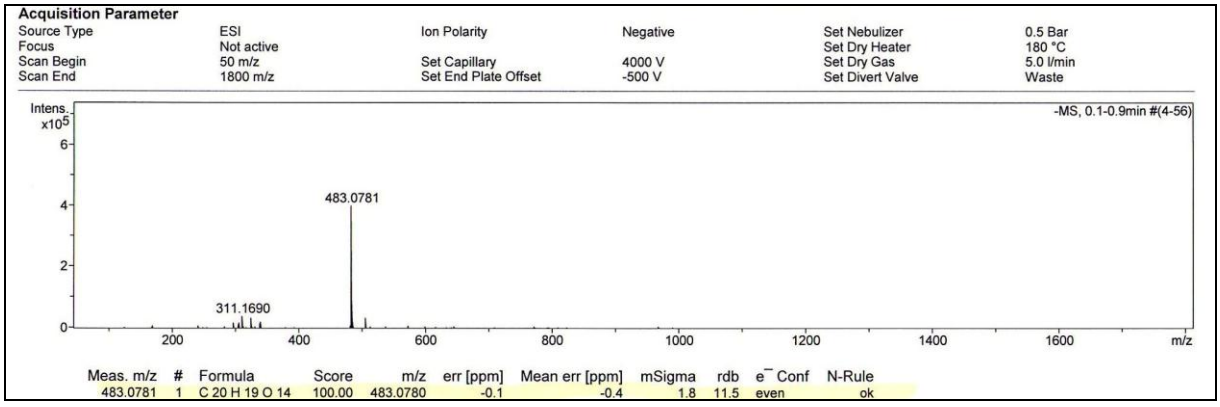


S2: ^{1}H-NMR (500 MHz, acetone-d_6) Spectrum of Compound **1**

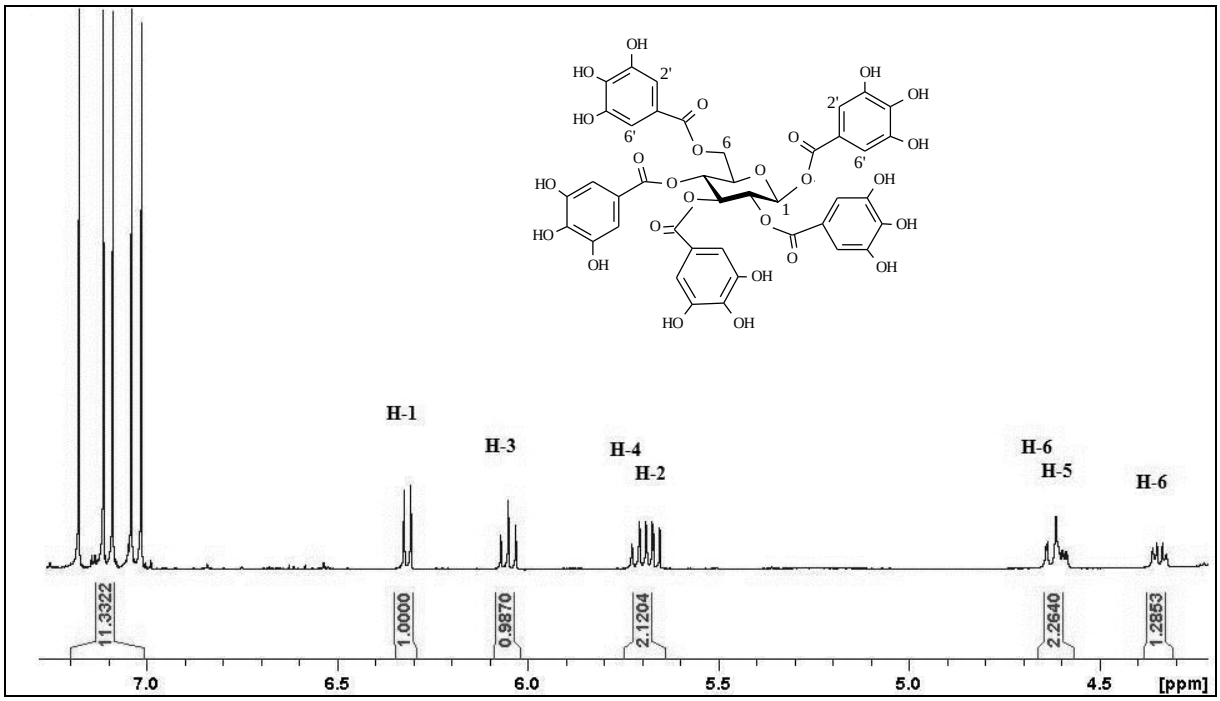
Compound 1 (2,3-di-*O*-galloyl-D-glucose): this compound is a mixture of α-anomer and β-anomer. White amorphous powder, ESI-TOF MS: *m/z* 483.0781 $[M-H]^-$ (calc. for $C_{20}H_{19}O_{14}$, 483.0780). ^{1}H-NMR (acetone-d_6, 500 MHz), δ: 3.58 (2H, m, H-5α/β), 3.72-3.79 (2H, m, H-6α/β), 3.78 (1H, t, *J* = 9.8 Hz, H-4β), 3.83 (1H, dd, *J* = 9.5, 10 Hz, H-4α), 3.83 (1H, dd, *J* = 2.7, 12 Hz, H-6α), 3.89 (1H, dd, *J* = 2.4, 12 Hz, H-6β), 4.90 (1H, dd, *J* = 3.8, 10 Hz, H-2α), 4.95 (1H, d, *J* = 8.1 Hz, H-1β), 5.05 (1H, dd, *J* = 8.1, 9.8 Hz, H-2β), 5.38 (1H, t, *J* = 9.8 Hz, H-3β), 5.45 (1H, d, *J* = 3.8 Hz, H-1α), 5.72 (1H, dd, *J* = 9.5, 10 Hz, H-3α), 6.99 (2H, s, H-2'/6'β), 7.00 (2H, s, H-2'/6'β), 7.02 (2H, s, H-2'/6'α), 7.06 (2H, s, H-2'/6'α).



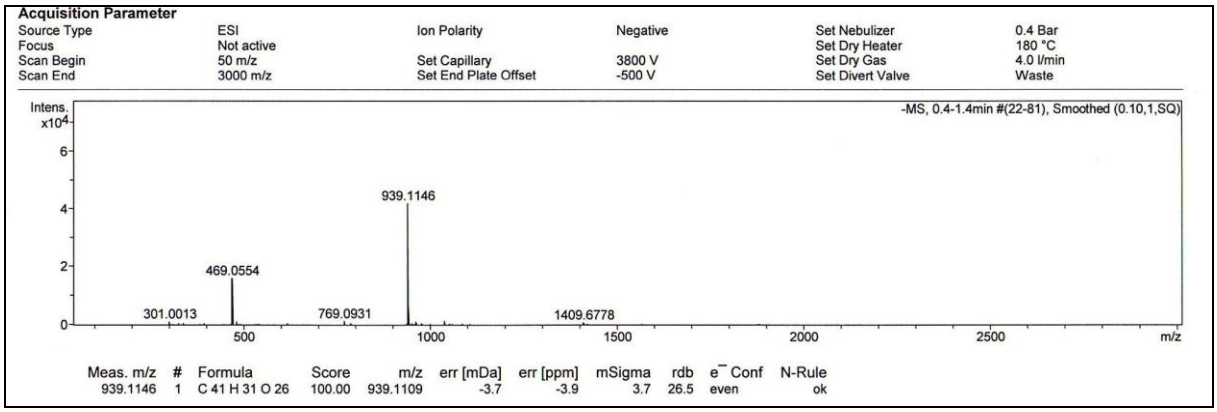
S3. Expansion of the COSY NMR experiment of Compound **1**



S4. ESI-TOF mass Spectrum of Compound **1**

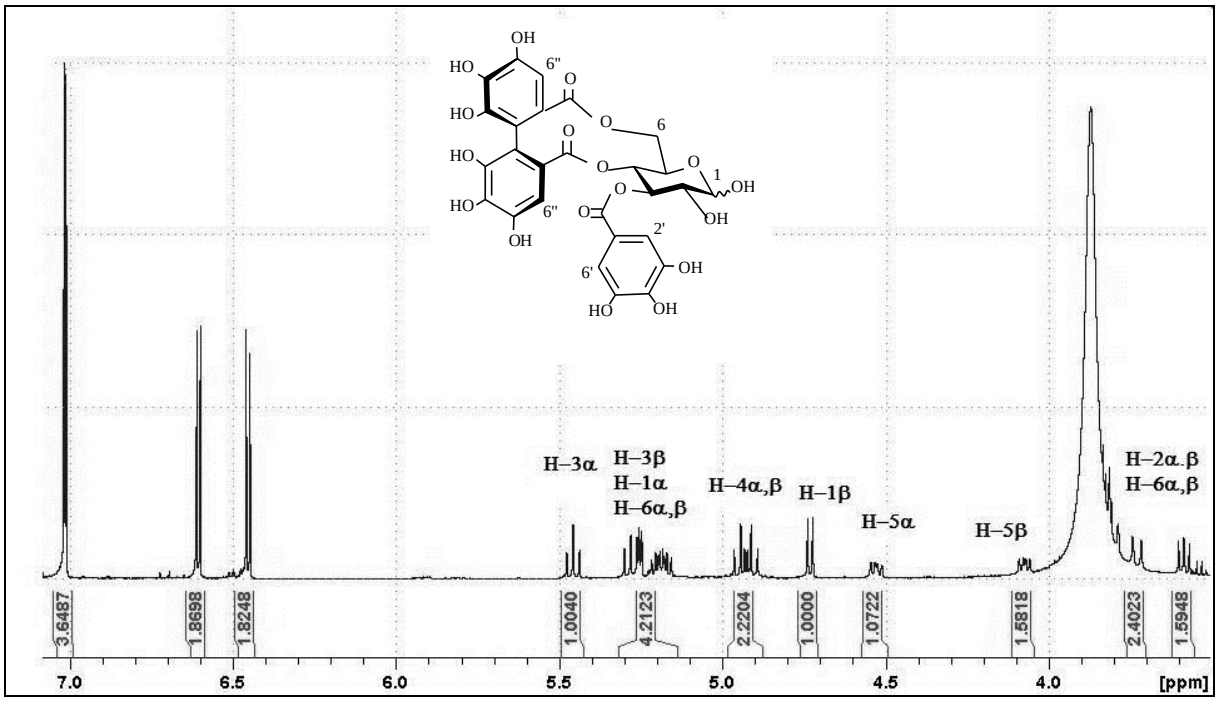


S5. ^{1}H-NMR (500 MHz, acetone-d_6) Spectrum of Compound **2**



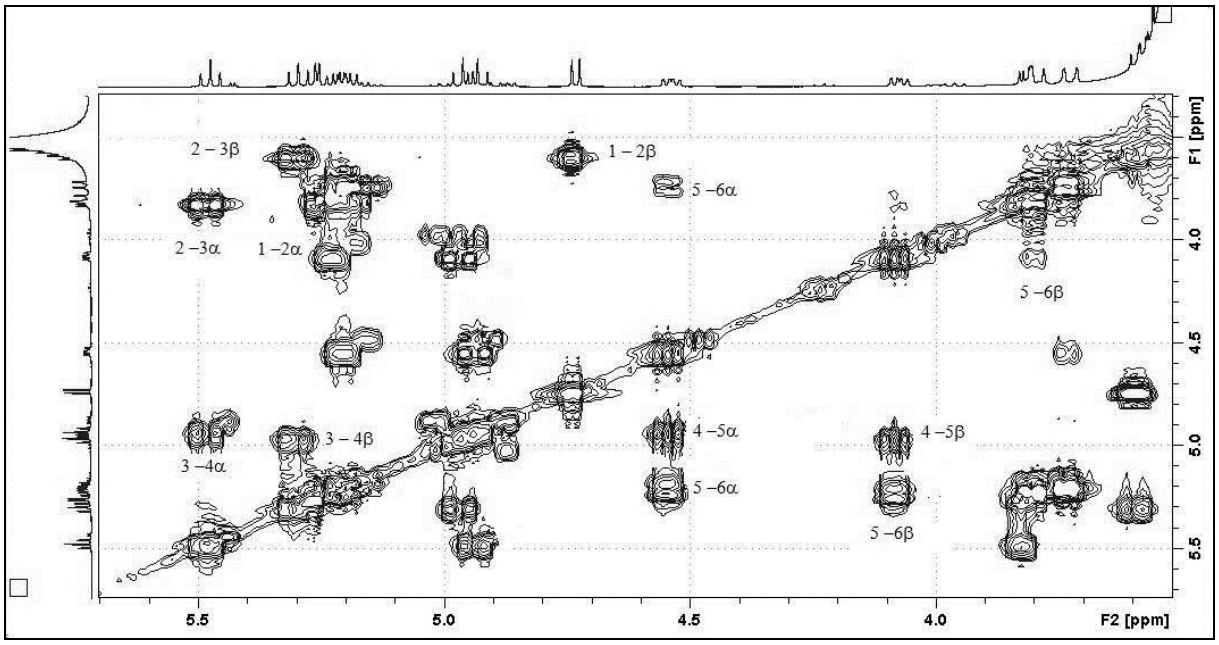
S6. ESI-TOF mass Spectrum of Compound **2**

Compound 2 (1,2,3,4,6-penta-*O*-galloyl-*β*-D-glucose), white amorphous powder, ESI-TOF MS: *m/z* 939.1146 $[M-H]^-$ (calc. for $C_{41}H_{31}O_{26}$, 939.1109). ^{1}H-NMR (acetone-d_6, 500 MHz), δ: 4.30 (1H, dd, *J* = 5, 13 Hz, H-6), 4.58 (1H, dd, *J* = 2, 13 Hz, H-6), 4.55 (1H, m, H-5), 5.62 (1H, dd, *J* = 8, 10 Hz, H-2), 5.68 (1H, t, *J* = 10, H-4), 6.01 (1H, t, *J* = 10, H-3), 6.32 (1H, d, *J* = 8, H-1), 7.02 (2H, s, H-2'/6'), 7.04 (2H, s, H-2'/6'), 7.09 (2H, s, H-2'/6'), 7.11 (2H, s, H-2'/6'), 7.18 (2H, s, H-2'/6'). ^{13}C-NMR (acetone-d_6, 125 MHz), δ: 62.9 (C-6), 69.5 (C-4), 71.9 (C-2), 73.5 (C-3), 74.1 (C-5), 93.4 (C-1), 110 (10C, C-2'/6').

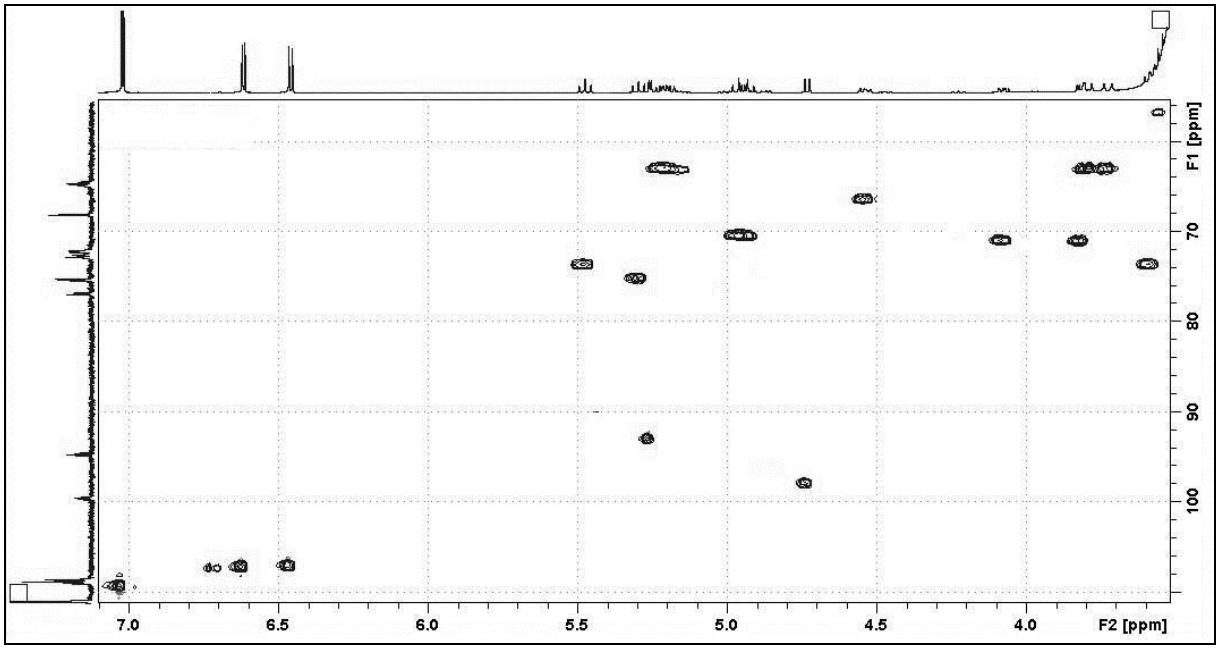


S7. ^{1}H-NMR (500 MHz, acetone-d_6) Spectrum of Compound **3**

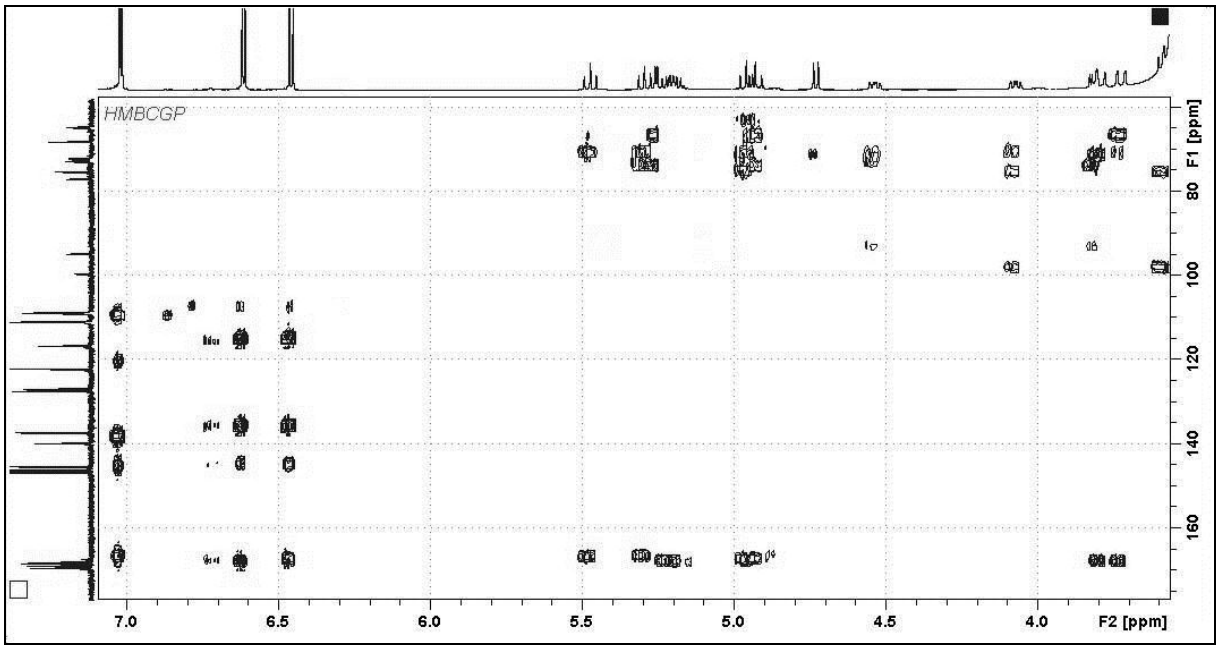
Compound 3 (gemin D), this compound is a mixture of α-anomer and β-anomer. Light brown amorphous powder, ESI-TOF MS: *m/z* 633.0719 $[M-H]^-$ (calc. for $C_{27}H_{21}O_{18}$, 633.0733). ^{1}H-NMR (acetone-d_6, 500 MHz), δ: 3.73 (1H, d, *J* = 13 Hz, H-6α), 3.79 (1H, d, *J* = 13 Hz, H-6β), 3.57 (1H, m, H-2β), 3.81 (1H, dd, *J* = 4, 10 Hz, H-2α), 4.07 (1H, dd, *J* = 6, 10, H-5β), 4.54 (1H, dd, *J* = 6, 10, H-5α), 4.73 (1H, d, *J* = 8, H-1β), 4.93 (1H, t, *J* = 10, H-4α), 4.96 (1H, t, *J* = 9.5, H-4β), 5.20 (1H, dd, *J* = 6, 13 Hz, H-6α), 5.22 (1H, dd, *J* = 6, 13 Hz, H-6β), 5.26 (1H, d, *J* = 4, H-1α), 5.30 (1H, t, *J* = 10 Hz, H-3β), 5.48 (1H, , t, *J* = 10 Hz, H-3α), 6.45 and 6.62 (2H, s, HHDP-6''/6''β), 6.46 and 6.61 (2H, s, HHDP-6''/6''α), 7.01 (2H, s, G-2'/6'β), 7.02 (2H, s, G-2'/6'α). ^{13}C-NMR (acetone-d_6, 125 MHz), δ: 63.5 (2C, C-6α/β), 66.9 (C-5α), 71.0 (C-4α/β), 71.5 (C-5β), 71.6 (C-2α), 74.0 (C-2β), 74.2 (C-3α), 75.7 (C-3β), 93.5 (C-1α), 98.5 (C-1β), 107.6 and 107.7 (4C, HHDP-6''/6''α/β), 109.8 (4C, G-2'/6'α/β).



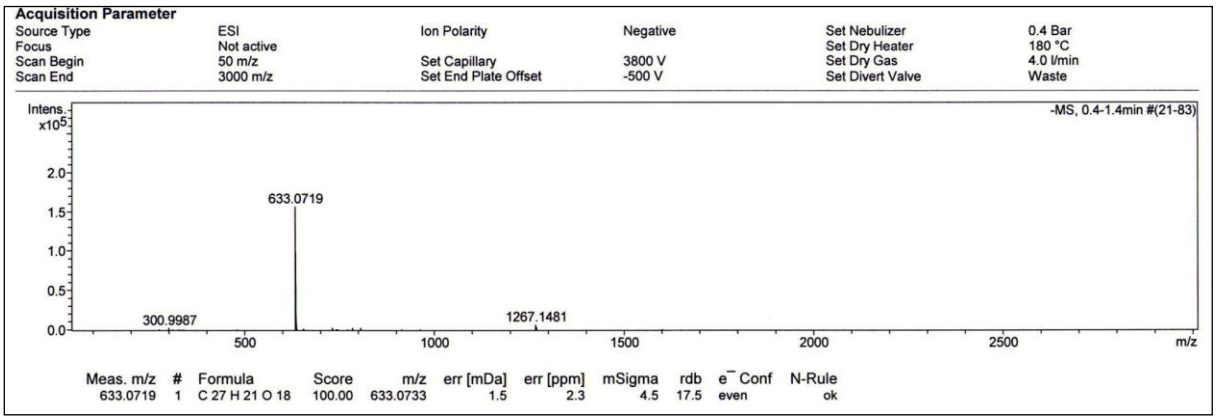
S8. Expansion of the COSY NMR experiment of Compound **3**



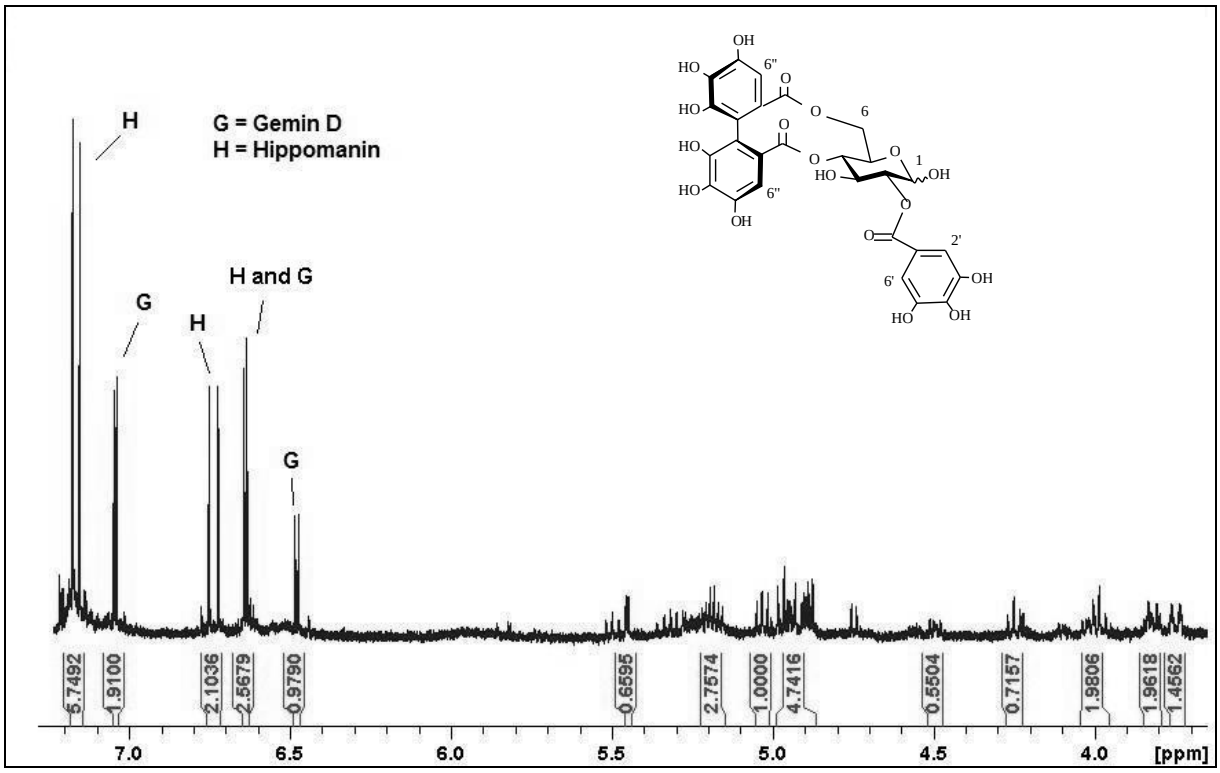
S9. Expansion of the HSQC NMR experiment of Compound **3**



S10. Expansion of the HMBC NMR experiment of Compound **3**

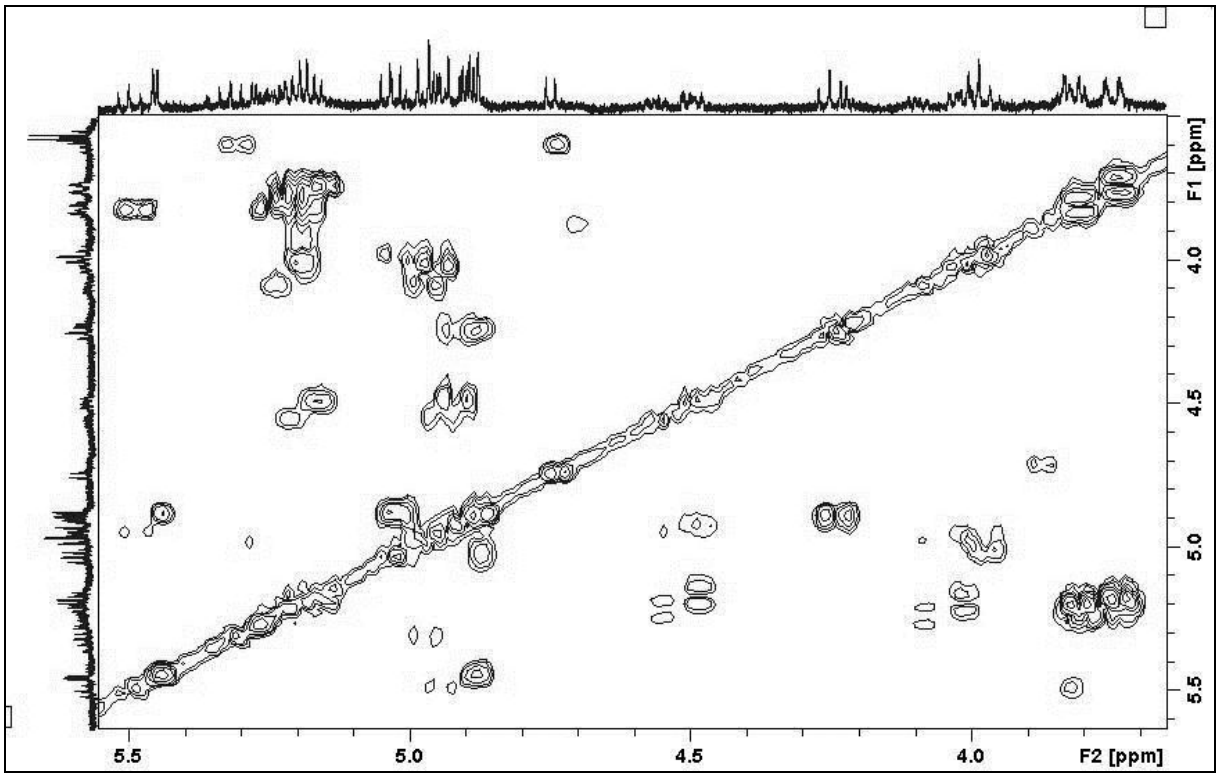


S11. ESI-TOF mass Spectrum of Compound **3**

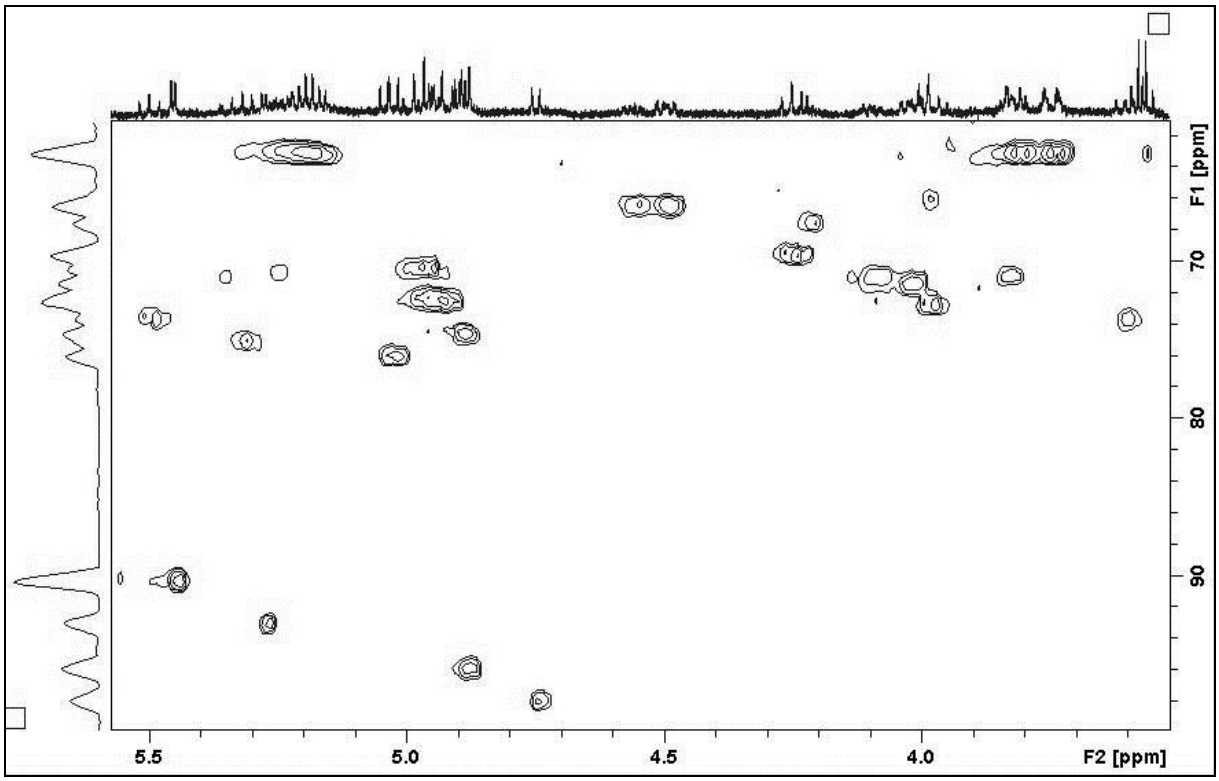


S12. ^{1}H-NMR (500 MHz, acetone-d_6) Spectrum of Compound **4**

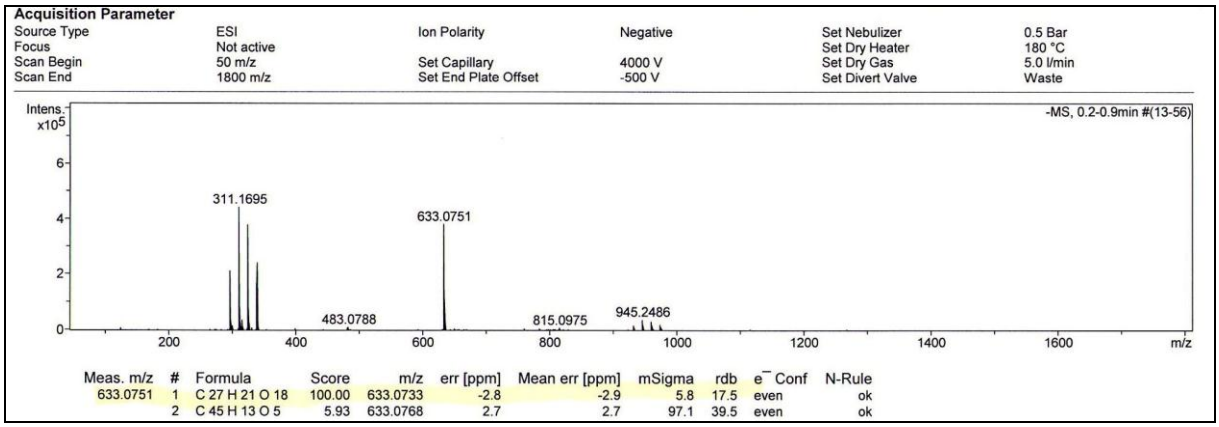
Compound 4 (hippomanin A), this compound is a mixture of α-anomer and β-anomer. Light brown amorphous powder, ESI-TOF MS: *m/z* 633.0751 $[M-H]^-$ (calc. for $C_{27}H_{21}O_{18}$, 633.0733). ^{1}H-NMR (acetone-d_6, 500 MHz), δ: 3.73 (1H, dd, *J* = 1.7, 13 Hz, H-6α), 3.80 (1H, dd, *J* = 1.6, 13 Hz, H-6β), 3.97 (1H, t, *J* = 9.5 Hz, H-3β), 4.01 (1H, m, H-5β), 4.23 (1H, , t, *J* = 10 Hz, H-3α), 4.48 (1H, m, H-5α), 4.87 (1H, dd, *J* = 3.6, 10 Hz, H-2α), 4.88 (1H, d, *J* = 8, H-1β), 4.93 (1H, t, *J* = 10, H-4α), 4.94 (1H, t, *J* = 9.5, H-4β), 5.02 (1H, dd, *J* = 8, 9.5 Hz, H-2β), 5.17 (1H, dd, *J* = 6, 13 Hz, H-6α), 5.22 (1H, dd, *J* = 6, 13 Hz, H-6β), 5.45 (1H, d, *J* = 3.6, H-1α), 6.63 and 6.72 (2H, s, HHDP-6''/6''β), 6.64 and 6.75 (2H, s, HHDP-6''/6''α), 7.15 (2H, s, G-2'/6'β), 7.18 (2H, s, G-2'/6'α). ^{13}C-NMR (acetone-d_6, 125 MHz), δ: 63.1 (2C, C-6α/β), 66.9 (C-5α), 72.2 (C-4α), 72.5 (C-4β), 72.6 (C-3α), 72.6 (C-5β), 73.1 (C-3β), 74.6 (C-2α), 76.1 (C-2β), 90.5 (C-1α), 96.3 (C-1β), 107.5 and 107.6 (4C, HHDP-6''/6''α/β), 109.7 (4C, G-2'/6'α/β).



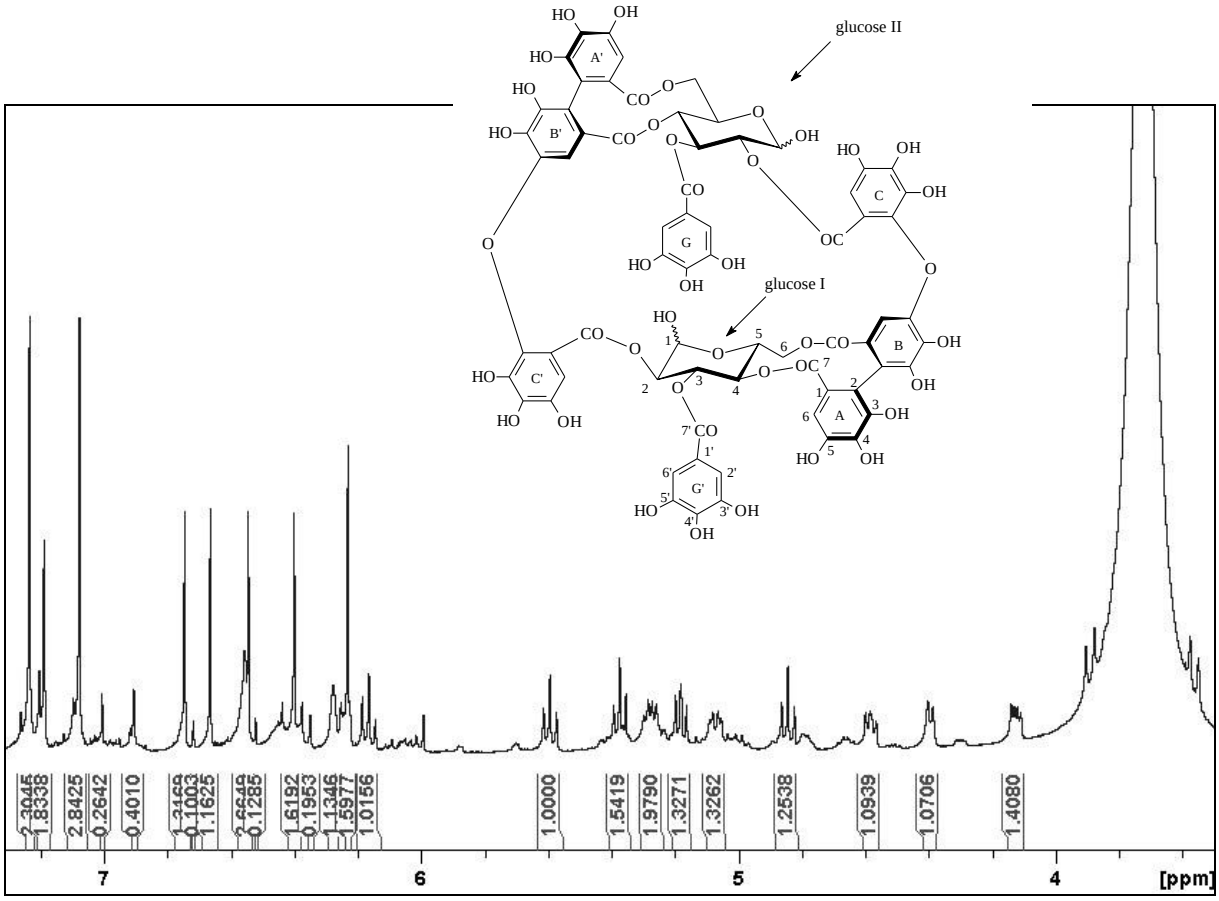
S13. Expansion of the COSY NMR experiment of Compound **4**



S14. Expansion of the HSQC NMR experiment of Compound **4**



S15. ESI-TOF mass Spectrum of Compound **4**



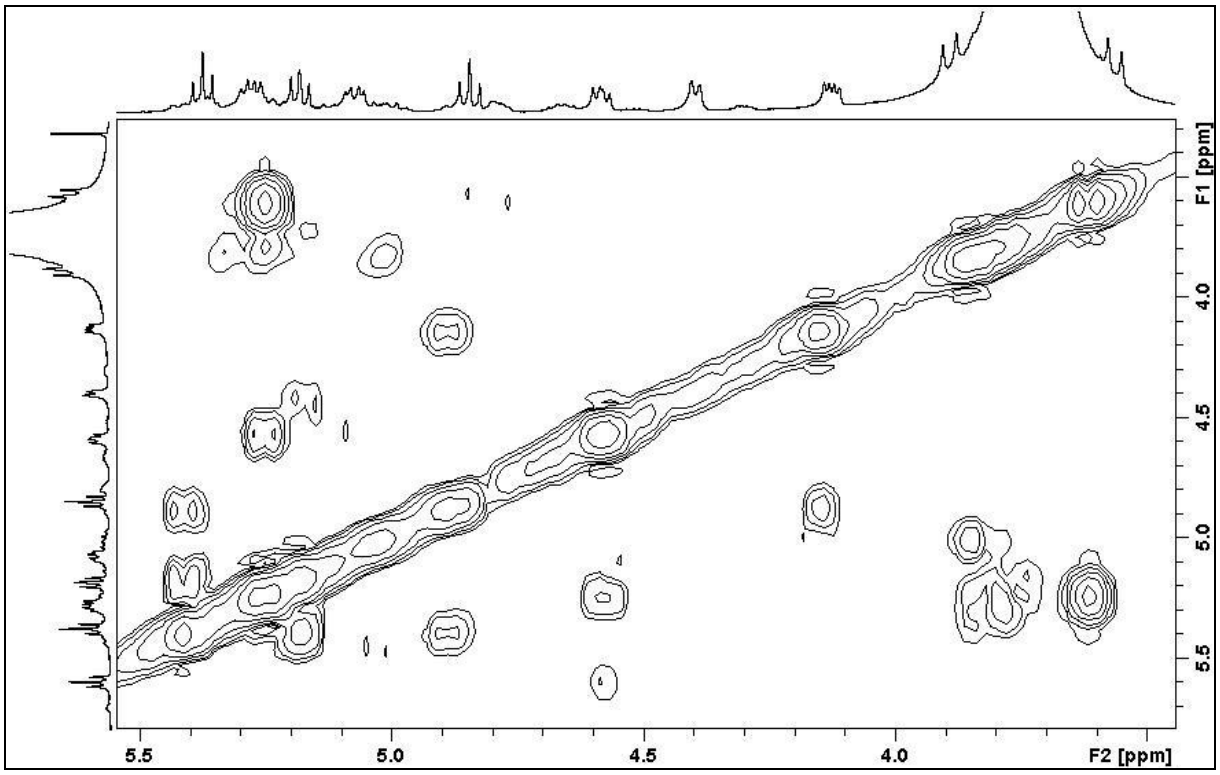
S16. ^{1}H-NMR (500 MHz, acetone-d_6 + D_2O, - 20 ^{o}C) Spectrum of Compound **5**

Compound 5 (oenothein B), white amorphous powder, ESI-TOF MS: *m/z* 1567.1438 $[M-H]^-$ (calc. for $C_{68}H_{47}O_{44}$, 1567.1446).

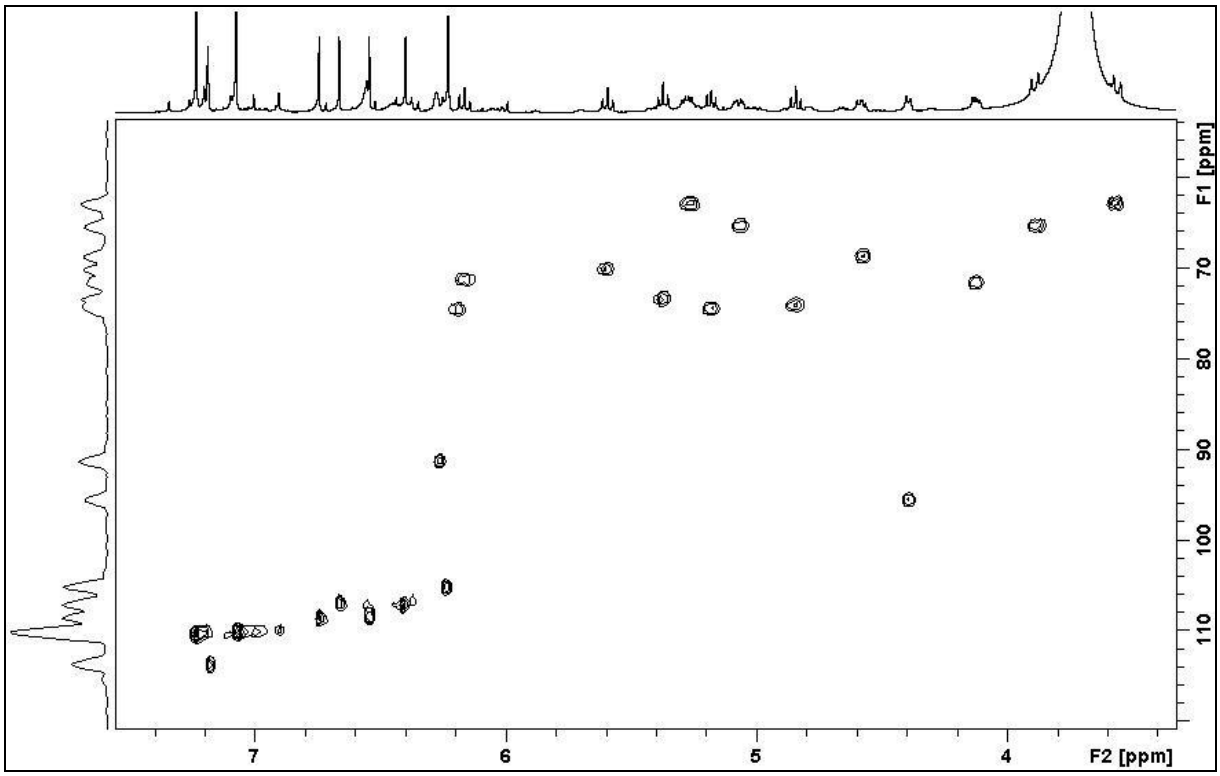
^{1}H and ^{13}C-NMR data for oenothein B (acetone-d_6 + D_2O, - 20 ^{o}C)

Position	δ_H (m, *J*/Hz)	δ_C	Position	δ_H (m, *J*/Hz)	δ_C
Glucose I[a]			Glucose II[b]		
1	6.28 (br[c])	91.2	1	4.40 (d, *J* 8)	95.5
2	6.18 (d, *J* 10)	74.4	2	5.18 (t, *J* 9)	74.4
3	6.16 (t, *J* 10)	71.2	3	5.38 (t, *J* 10)	73.4
4	5.59 (t, *J* 10)	70.1	4	4.84 (t, *J* 10)	73.9
5	4.58 (dd, *J* 7, 10)	68.6	5	4.13 (dd, *J* 5, 10)	71.6
6	5.27 (dd, *J* 7, 13)	62.8	6	5.07 (dd, *J* 5, 13)	65.2
	3.56 (d, *J* 13)			3.89 (d, *J* 13)	
Valoneoyl (ring A)			Valoneoyl (ring A')		
1'		[d]	1'		[d]
2'		114.5	2'		116.3
3'		[d]	3'		[d]
4'		136.2	4'		136.4
5'		144.8	5'		145.3
6'	6.40 (s)	107.1	6'	6.67 (s)	106.8
7'		168.1	7'		169.4
Valoneoyl (ring B)			Valoneoyl (ring B')		
1'		[d]	1'		[d]
2'		117.2	2'		120.9
3'		[d]	3'		[d]
4'		135.2	4'		140.1
5'		147.2	5'		147.0
6'	6.23 (s)	105.1	6'	7.19 (s)	113.6
7'		167.3	7'		167.4
Valoneoyl (ring C)			Valoneoyl (ring C')		
1'		[d]	1'		[d]
2'		143.3	2'		142.6
3'		[d]	3'		[d]
4'		134.0	4'		138.4
5'		139.1	5'		138.4
6'	6.75 (s)	108.6	6'	6.55 (s)	108.3
7'		167.1	7'		168.4
Galloyl (ring G)			Galloyl (ring G')		
1"		120.7	1"		121.4
2"	7.23 (s)	110.3	2"	7.08 (s)	110.1
3"		145.5	3"		145.5
4"		138.6	4"		138.6
5"		145.5	5"		145.5
6"	7.23 (s)	110.3	6"	7.08 (s)	110.1
7"		166.0	7"		167.8

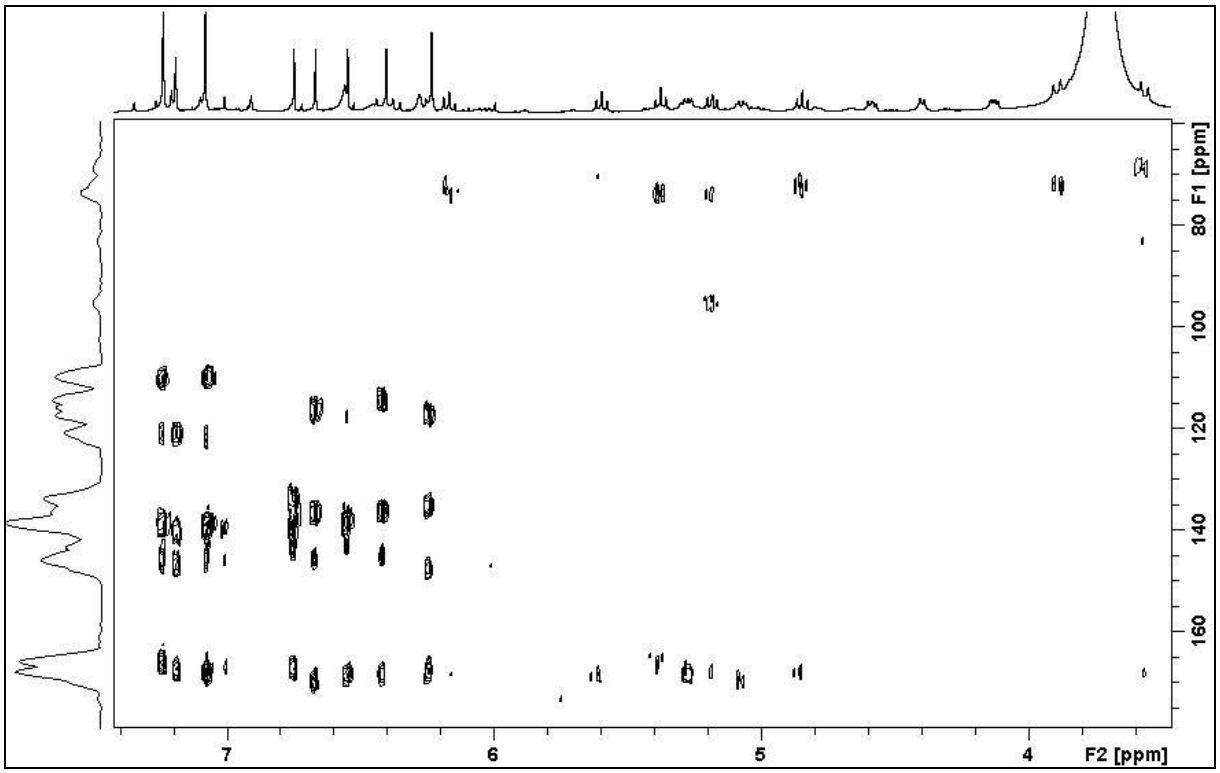
a) *α*-Anomer is predominant. *b*) *β*-Anomer is predominant. *c*) Broadened signal. *d*) Unidentified carbon signals.



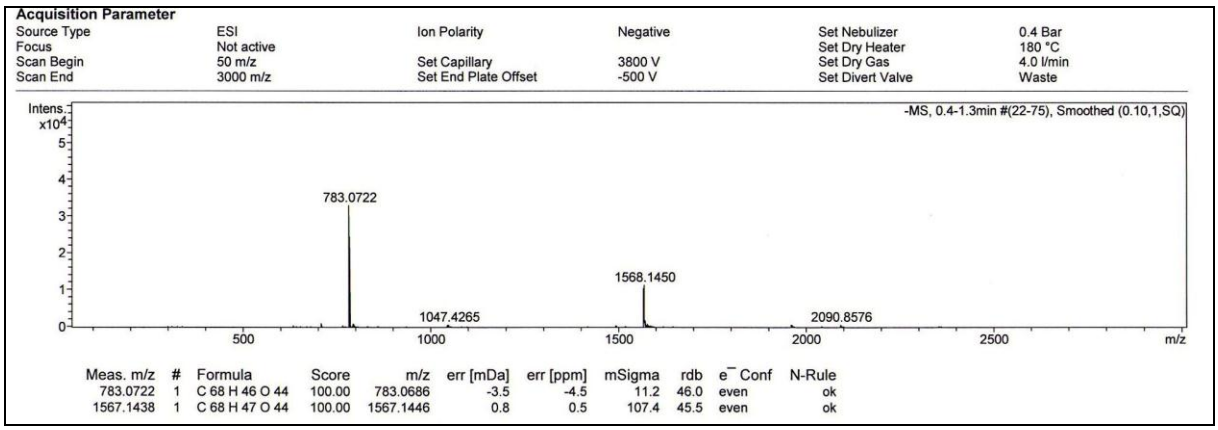
S17. Expansion of the COSY NMR (- 20 ^{o}C) experiment of Compound **5**



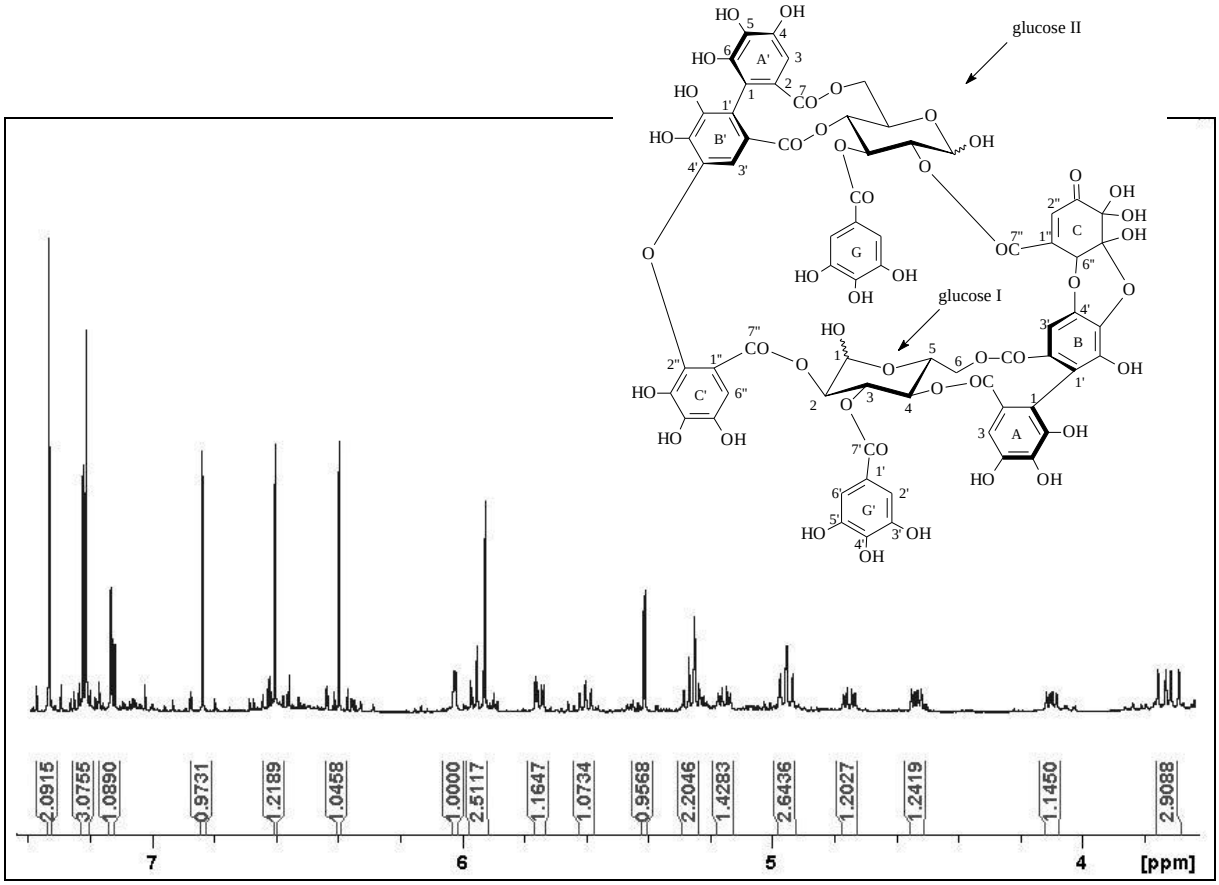
S18. Expansion of the HSQC NMR (- 20 ^{o}C) experiment of Compound **5**



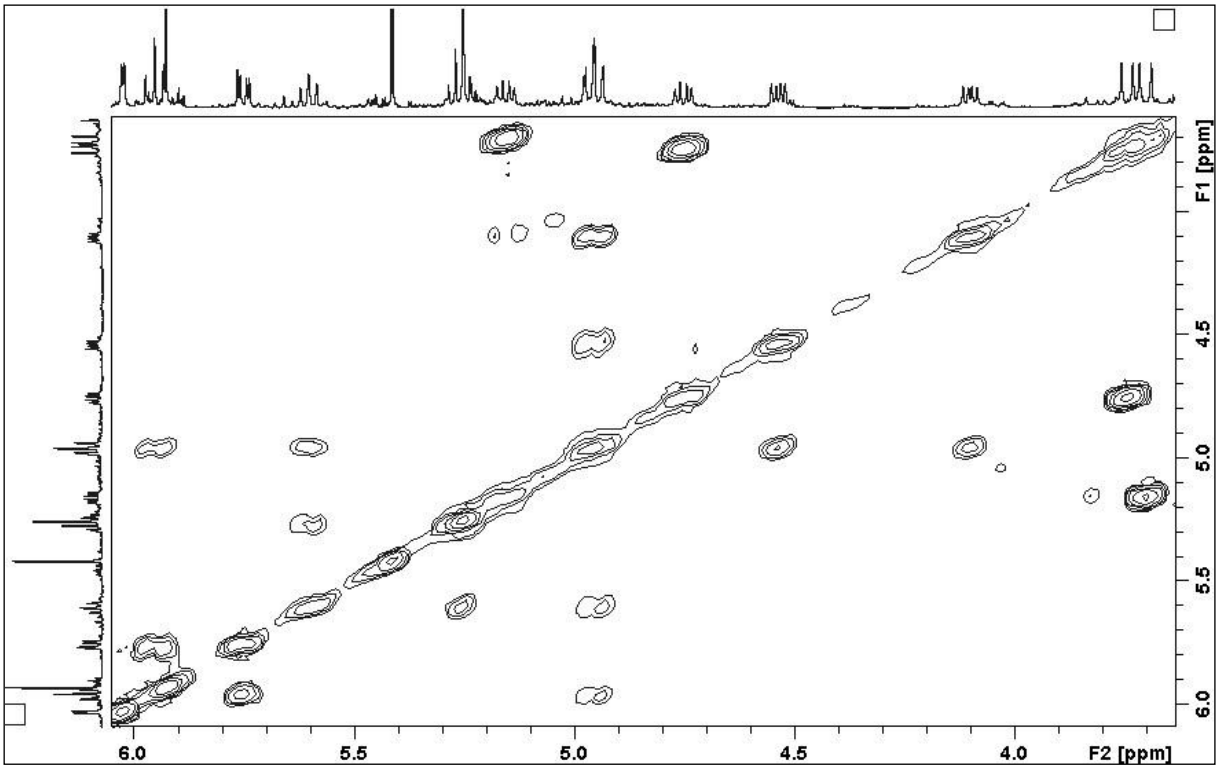
S19. Expansion of the HMBC NMR (- 20 ^{o}C) experiment of Compound **5**



S20. ESI-TOF mass Spectrum of Compound **5**



S21. ^{1}H-NMR (500 MHz, acetone-d_6 + D_2O) Spectrum of Compound **6**



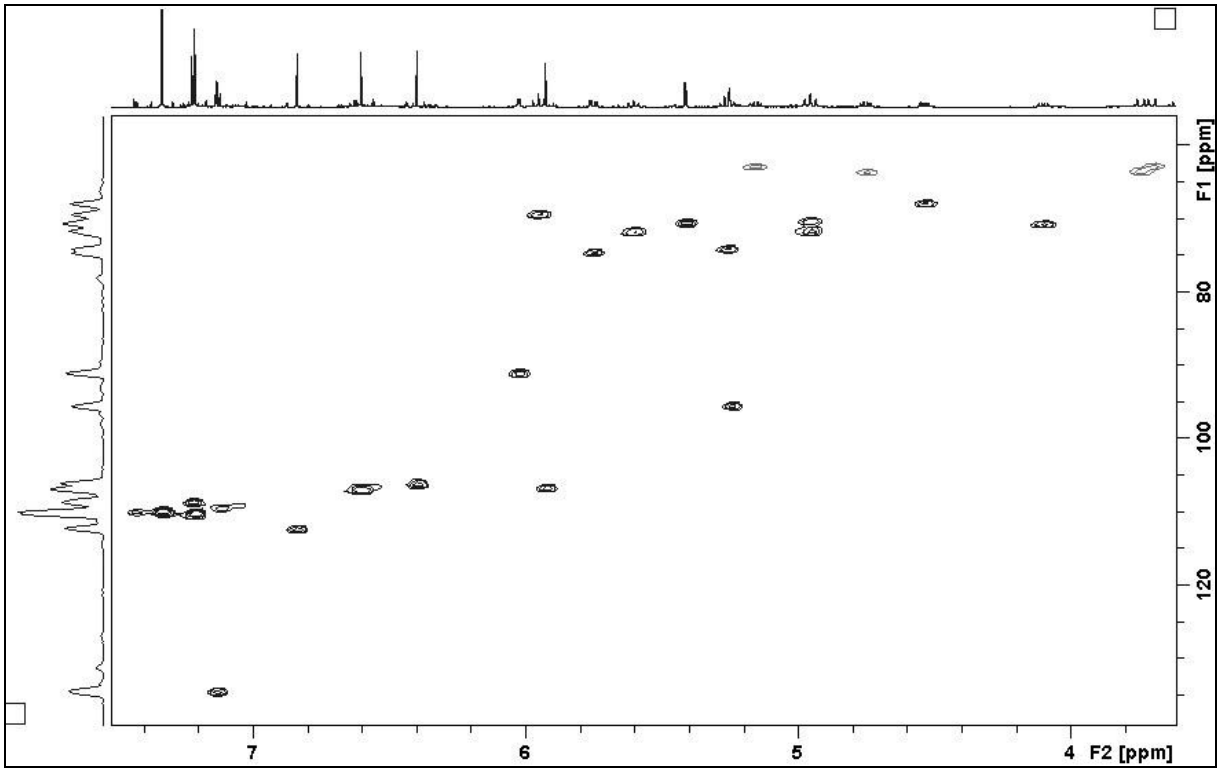
S22. Expansion of the COSY NMR experiment of Compound **6**

Compound 6 (eugeniflorin D_2), white amorphous powder, ESI-TOF MS: *m/z* 1583.1390 $[M-H]^-$ (calc. for $C_{68}H_{47}O_{45}$, 1583.1395).

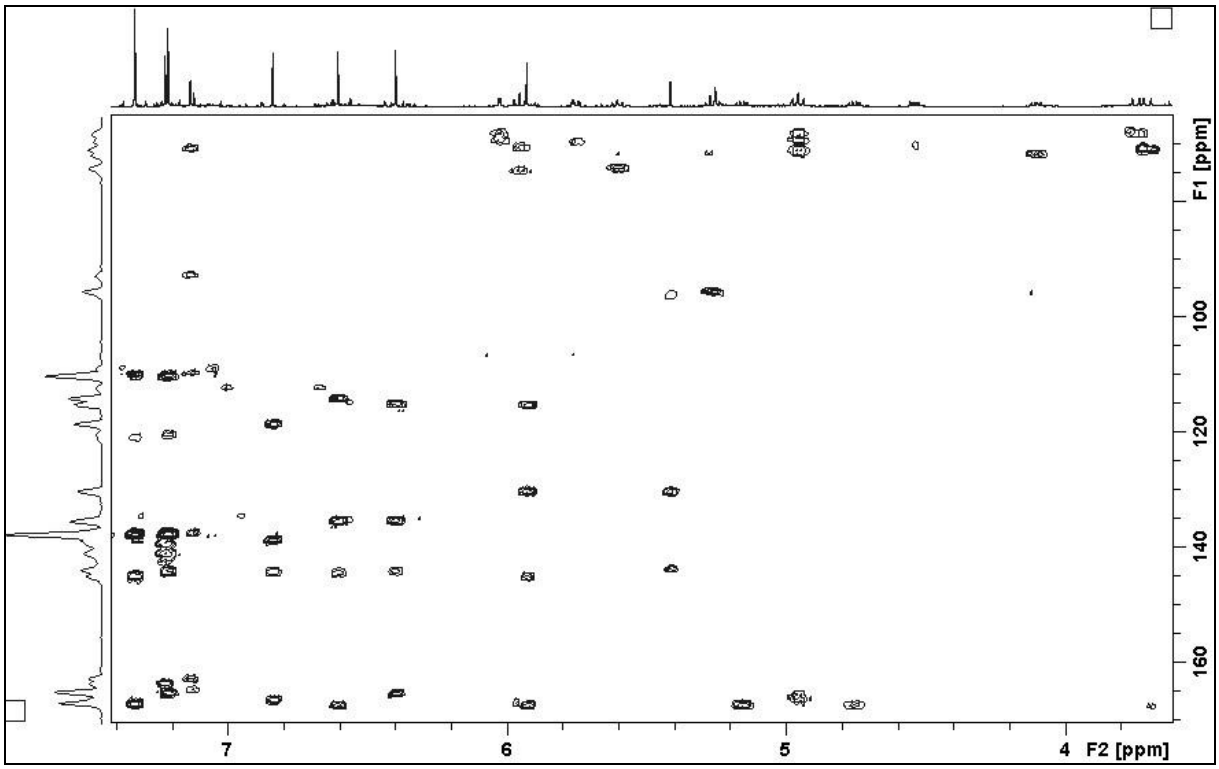
^1H and ^{13}C-NMR data for eugeniflorin D_2 (acetone-d_6 + D_2O).

Position	δ_H (m, *J*/Hz)	δ_C	Position	δ_H (m, *J*/Hz)	δ_C
Glucose I[a)]			Glucose II[b)]		
1	6.02 (d, *J* 3.2)	91.0	1’	5.26 (d, *J* 8)	95.5
2	5.75 (dd, *J* 3.2, 10)	74.5	2’	5.27 (t, *J* 9)	74.0
3	5.95 (t, *J* 10)	69.4	3’	5.61 (t, *J* 9)	71.6
4	4.96 (t, *J* 10)	71.6	4’	4.95 (t, *J* 9)	70.3
5	4.54 (dd, *J* 5.6, 10)	67.8	5’	4.10 (dd, *J* 6.2, 10)	70.7
6	4.75 (dd, *J* 5.6, 13)	63.5	6’	5.16 (dd, *J* 6.2, 13)	62.8
	3.75 (d, *J* 13)			3.71 (d, *J* 13)	
Dehydrovaloneoyl (ring A)			Valoneoyl (ring A’)		
3	6.84 (s)	112.3	3	5.92 (s)	106.6
Dehydrovaloneoyl (ring B)			Valoneoyl (ring B’)		
3’	6.60 (s)	106.8	3’	6.40 (s)	106.1
Dehydrovaloneoyl (ring C)			Valoneoyl (ring C’)		
2’’	7.13 (d, *J* 2.1)	134.5	6’’	7.23 (s)	108.6
6’’	5.41 (d, *J* 2.1)	70.7			
Galloyl (ring G)			Galloyl (ring G’)		
2 and 6	7.22 (s)	110.2	2’ and 6’	7.33 (s)	110.0

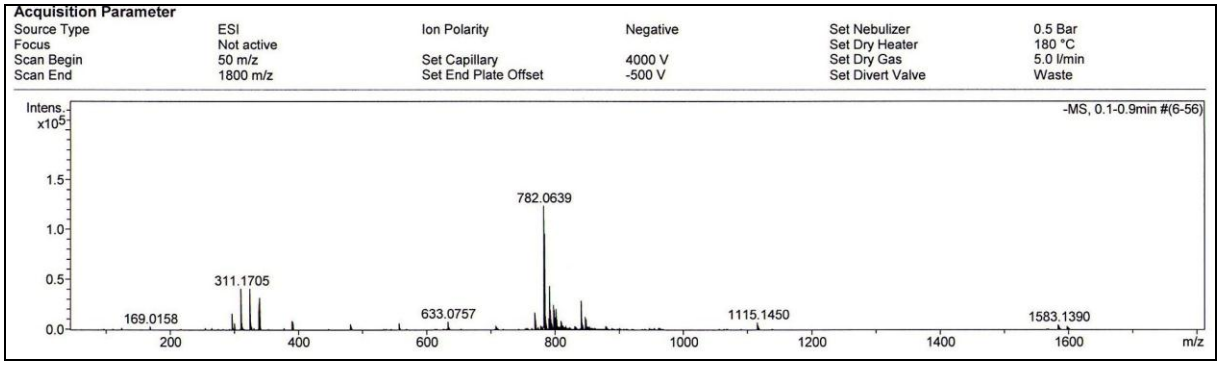
a) *α*-Anomer is predominant. *b*) *β*-Anomer is predominant.



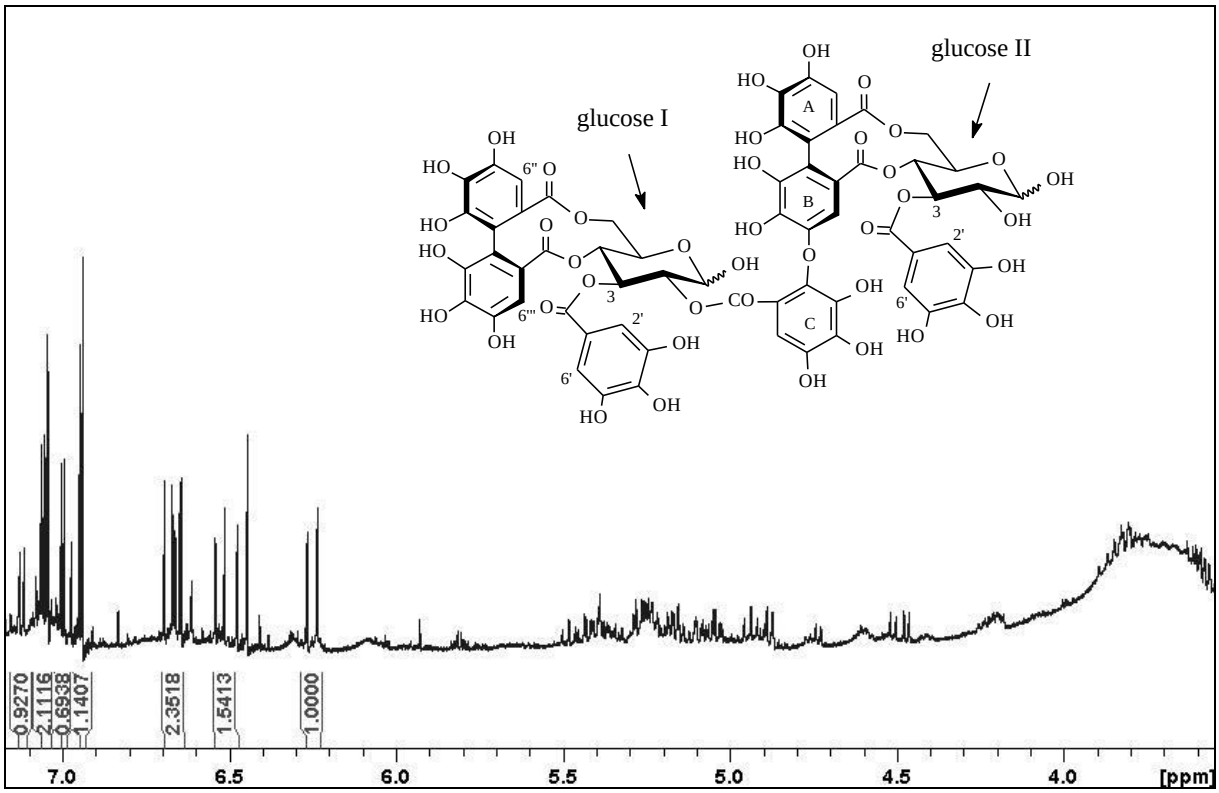
S23. Expansion of the HSQC NMR experiment of Compound **6**



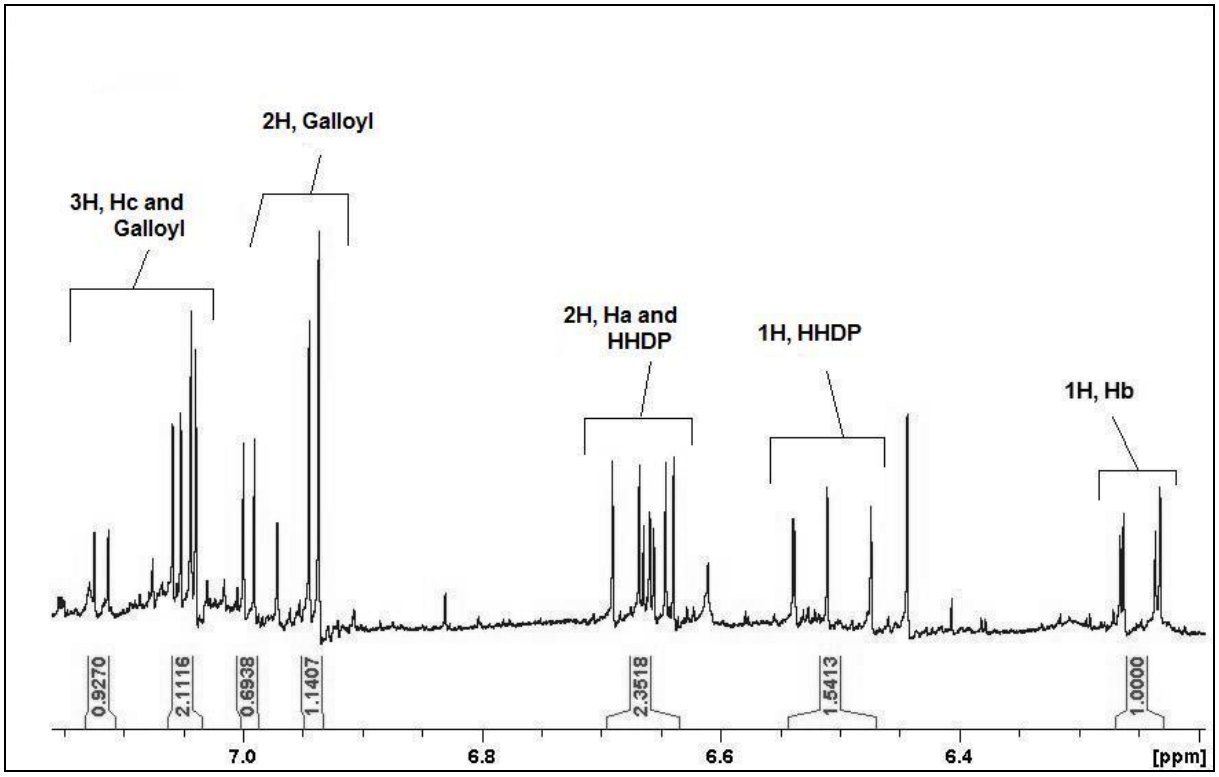
S24. Expansion of the HMBC NMR experiment of Compound **6**



S25. ESI-TOF mass Spectrum of Compound **6**



S26. ^{1}H-NMR (500 MHz, acetone-d_6 + D_2O) Spectrum of Compound **7**



S27. Expansion of the ^{1}H-NMR Spectrum of Compound **7**

Compound 7 (camptothin A), this compound is an equilibrium mixture of four anomers: *α/α*, *α/β*, *β/α* and *β/β*. White amorphous powder, ESI-TOF MS: *m/z* 1417.1458 $[M-H]^-$ (calc. for $C_{61}H_{45}O_{40}$, 1417.1483).

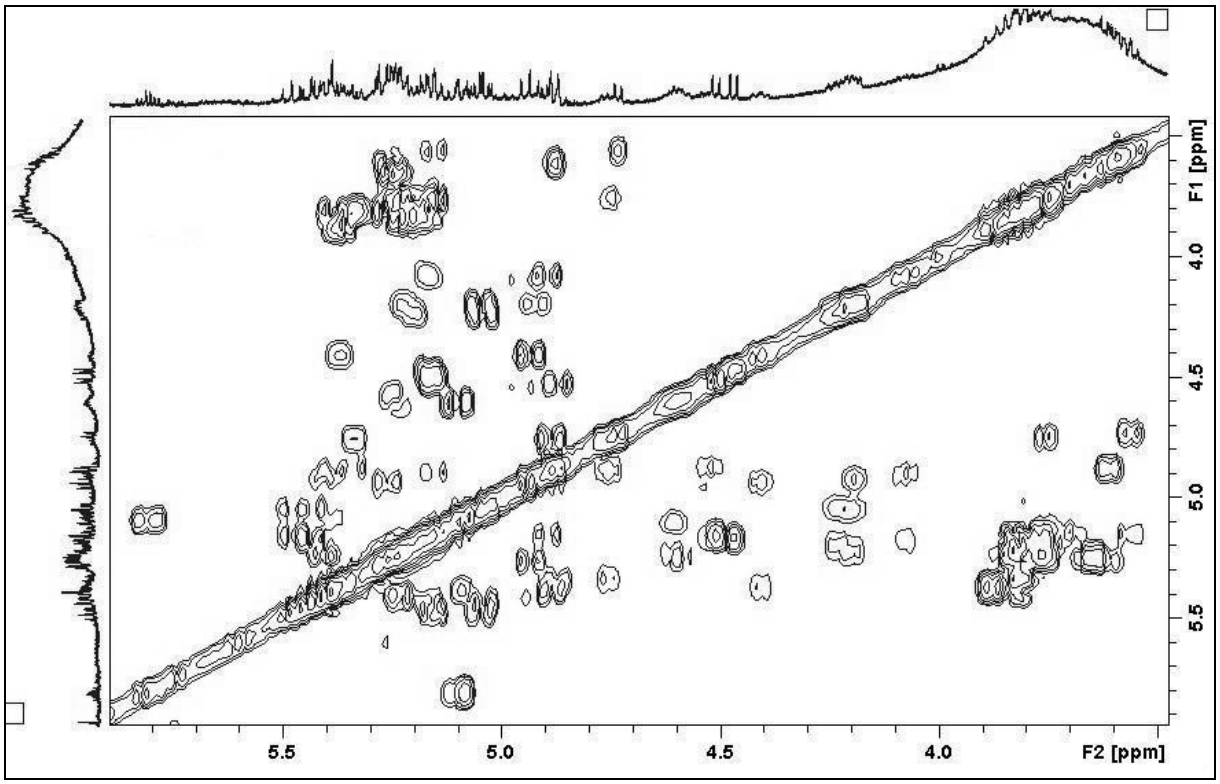
^1H and ^{13}C-NMR data for camptotin A (acetone-d_6 + D_2O).

	δ_C	δ_H (m, *J*/Hz)			δ_C	δ_H (m, *J*/Hz)	
Position		*α*	*β*	Position		*α*	*β*
Glucose I				Glucose II			
1	91.0	5.38 (br[a)])		1	93.8	5.25 (br)	
	90.6	5.39 (br)			93.9	5.28 (d, *J* 3.5)	
	96.0		4.47 (d, *J* 8)		98.5		4.73 (d, *J* 8)
	96.0		4.51 (d, *J* 8)		98.6		4.88 (d, *J* 8)
2	70.8	5.00 (dd, *J* 3.5, 10)		2	70.8	3.82 (m)	
	72.9	5.09 (dd, *J* 3.5, 10)			71.6	3.80 (m)	
	74.4		5.15 (dd, *J* 8, 10)		74.5		3.56 (dd, *J* 8, 10)
	74.4		5.16 (dd, *J* 8, 10)		74.5		3.61 (dd, *J* 8, 10)
3	71.5	5.81 (t, *J* 10)		3	74.0	5.48 (t, *J* 10)	
	71.5	5.80 (t, *J* 10)			74.0	5.44 (t, *J* 10)	
	73.7		5.41 (t, *J* 10)				
4	71.3	5.05 (t, *J* 10)	5.04 (t, *J* 10)	4	71.2	5.04 (t, *J* 10)	
					71.7	4.89 (t, *J* 10)	4.93 (t, *J* 10)
5	65.6	4.53 (m)		5	66.2	4.60 (m)	
	67.2	4.59 (m)			67.2	4.75 (m)	
	71.7		4.25 (m)		70.6		4.08 (m)
	71.7		4.20 (m)		70.8		4.41 (dd, *J* 6, 10)
6	63.7	5.18 (m)		6	63.3	5.20 (m)	
	64.0	5.23 (m)			63.4	5.23 (m)	
6	63.7	3.82 (m)		6	63.2	3.77 (m)	
	63.9	3.89 (m)			63.6	3.66 (m)	

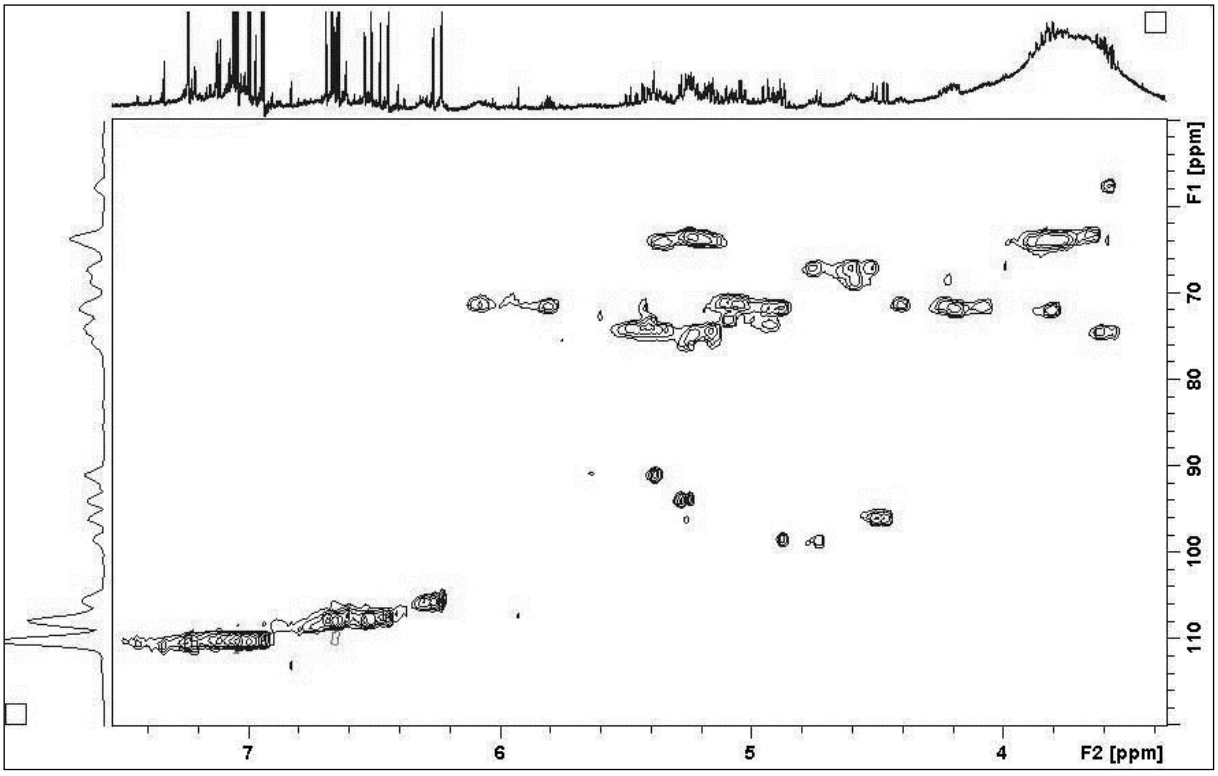
Aromatic carbons and hydrogens[b)]

Position	δ_C	δ_H
Galloyl (2' and 6')	110.2	6.93, 6.94, 6.99, 7.00, 7.04, 7.04, 7.05, 7.06
Valoneoyl (ring A) and HHDP (6'')	107.6	6.64, 6.64, 6.65, 6.66, 6.66, 6.66, 6.68, 6.69
HHDP (6''')	107.6	6.47, 6.51, 6.54, 6.54
Valoneoyl (ring B)	105.7	6.23, 6.24, 6.26, 6.26
Valoneoyl (ring C)	110.2	7.11, 7.12

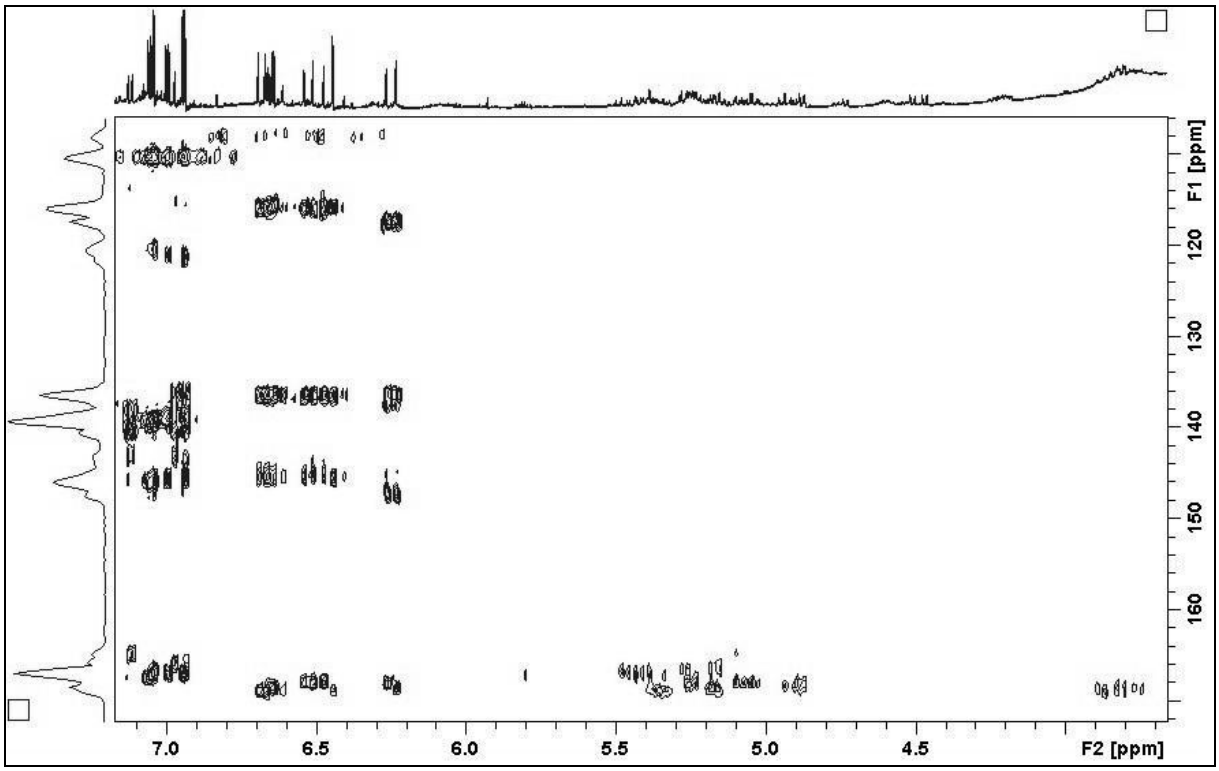
a) Broadened signal, *b)* all singlets.



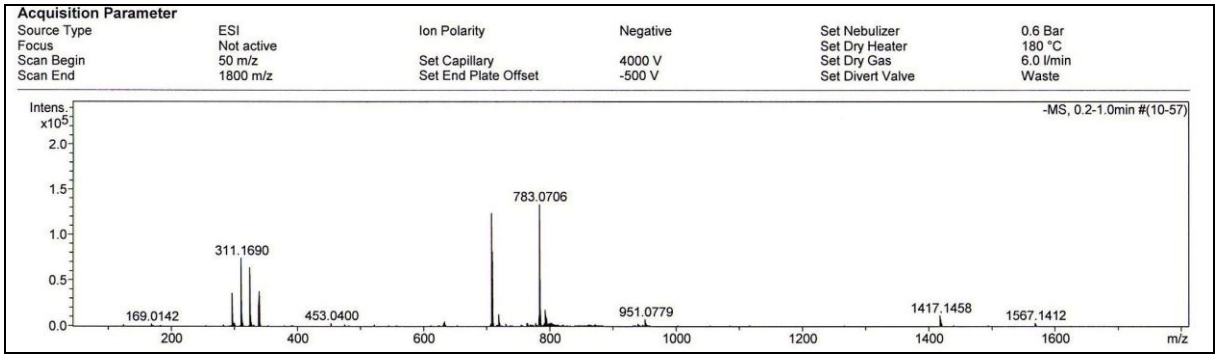
S28. Expansion of the COSY NMR experiment of Compound **7**



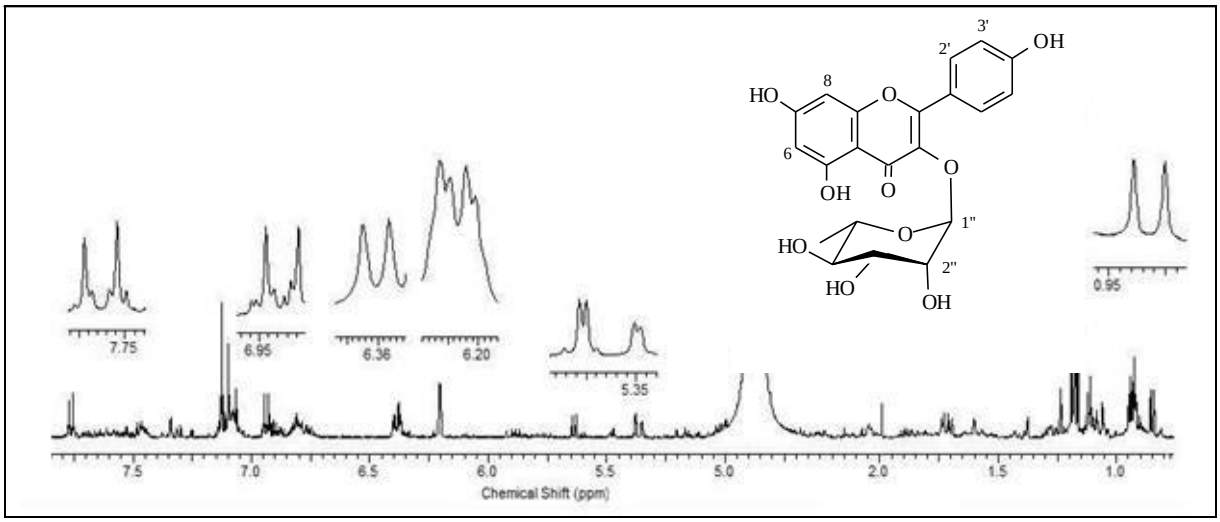
S29. Expansion of the HSQC NMR experiment of Compound **7**



S30. Expansion of the HMBC NMR experiment of Compound **7**

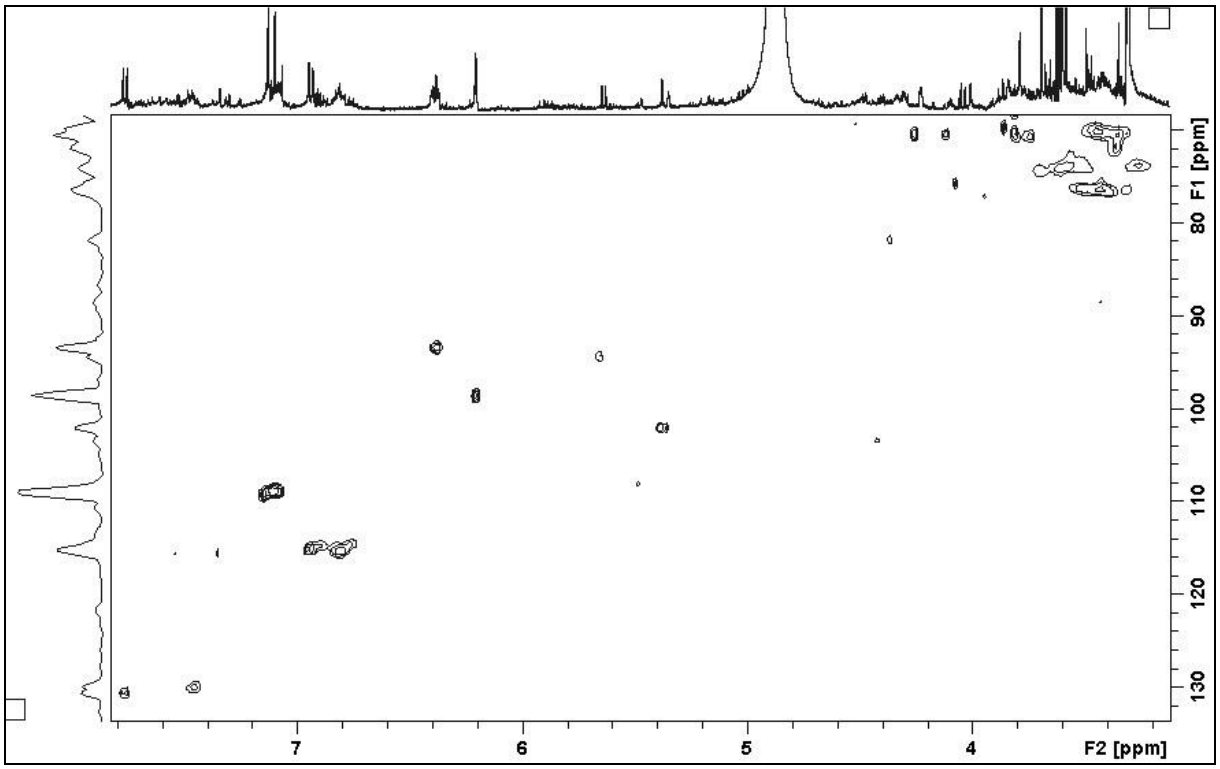


S31. ESI-TOF mass Spectrum of Compound **7**

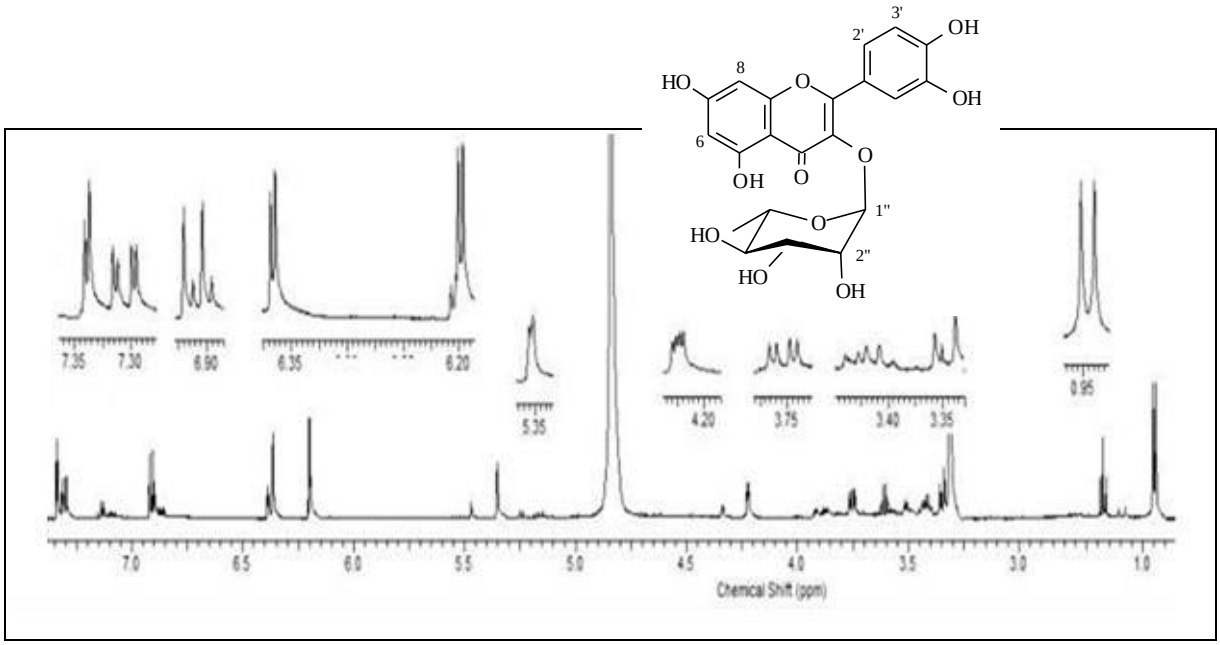


S32. [1]H-NMR (500 MHz, methanol-d_4) Spectrum of Compound **8**

Compound 8 (afzelin)**,** light yellow amorphous powder, [1]H-NMR (methanol-d_4, 500 MHz), δ: 6.20 (1H, d, *J* = 2, H-6), 6.36 (1H, d, *J* = 2, H-8), 7.75 (2H, d, *J* = 8.8, H-2’/6’), 6.93 (2H, d, *J* = 8.8, H-3’/5’), 5.38 (1H, d, *J* = 1.6, H-1’’), 4.25 (1H, dd, *J* = 1.6, 3.3 Hz, H-2’’), 3.76 (1H, dd, *J* = 3.3, 9 Hz, H-3’’), 3.37 (1H, m, H-4’’), 3.36 (1H, m, H-5’’), 0.94 (3H, d, *J* = 6.9, CH_3). [13]C-NMR (methanol-d_4, 125 MHz), δ: 98.4 (C-6), 93.4 (C-8), 130.4 (C-2'/6'), 115.0 (C-3’/5’), 101.9 (C-1’’), 70.4 (C-2’’), 70.8 (C-3’’), 72.1 (C-4’’), 70.2 (C-5’’), 15.8 (CH_3).

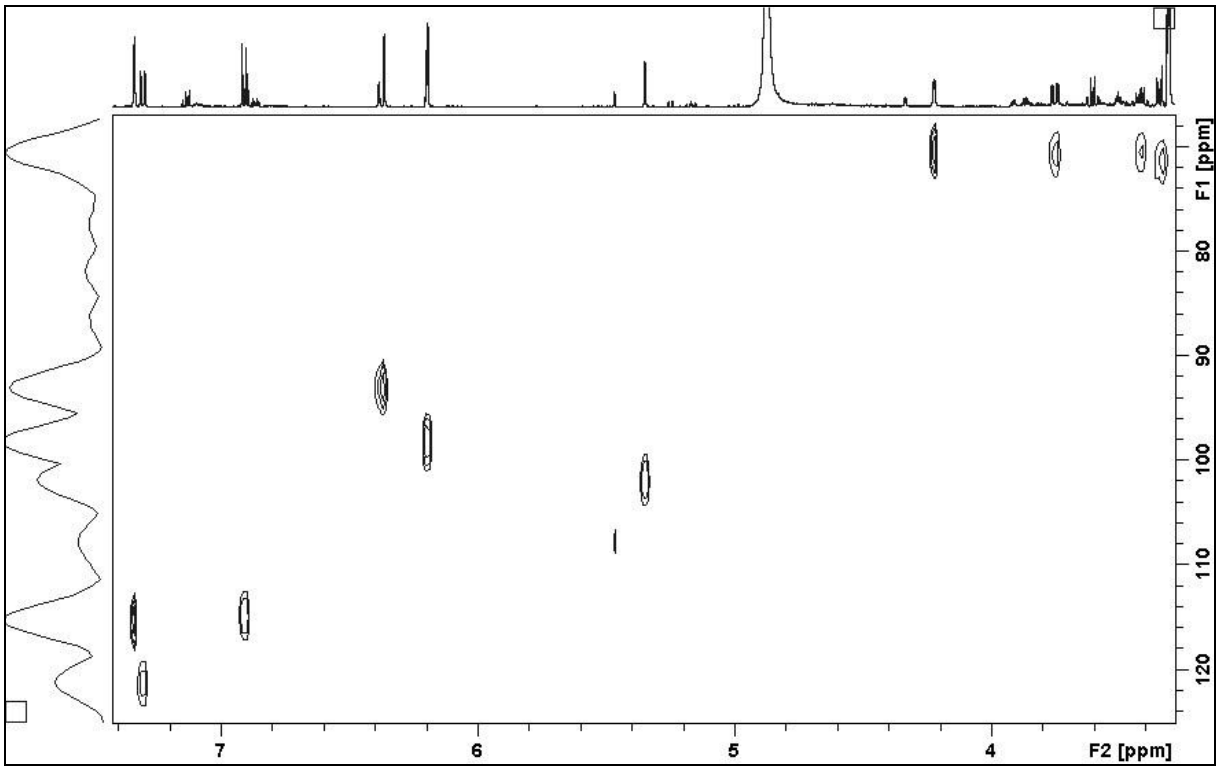


S33. Expansion of the HSQC NMR experiment of Compound **8**

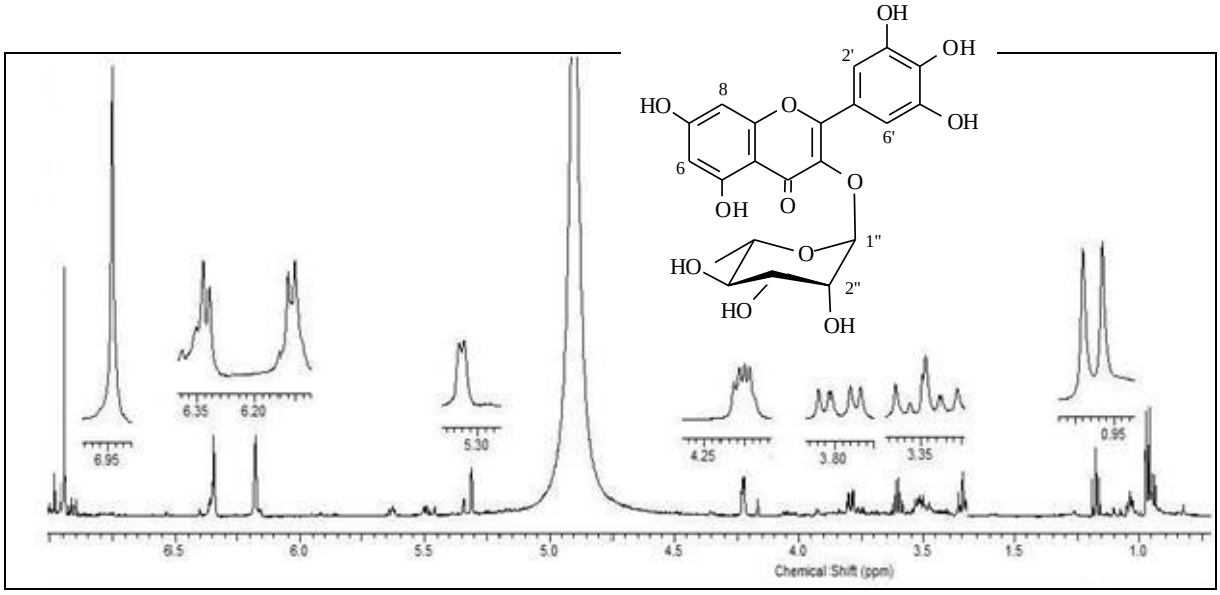


S34. [1]H-NMR (500 MHz, methanol-d_4) Spectrum of Compound **9**

Compound 9 (quercitrin), light yellow amorphous powder, [1]H-NMR (methanol-d_4, 500 MHz), δ: 6.20 (1H, d, *J* = 2, H-6), 6.37 (1H, d, *J* = 2, H-8), 7.34 (1H, d, *J* = 2.1, H-2'), 6.91 (1H, d, *J* = 8.3, H-5'), 7.30 (1H, dd, *J* = 2.1, 8.3 Hz, H-6'), 5.35 (1H, d, *J* = 1.7, H-1''), 4.22 (1H, dd, *J* = 1.7, 3.5 Hz, H-2''), 3.75 (1H, dd, *J* = 3.5, 9.6 Hz, H-3''), 3.34 (1H, t, *J* = 9.6, H-4''), 3.42 (1H, m, H-5''), 0.95 (3H, d, *J* = 6.1, CH_3). [13]C-NMR (methanol-d_4, 125 MHz), δ: 98.2 (C-6), 93.0 (C-8), 115.3 (C-2'), 115.2 (C-5'), 121.4 (C-6'), 101.8 (C-1''), 70.3 (C-2''), 70.7 (C-3''), 71.5 (C-4''), 70.5 (C-5''), 16.3 (CH_3).

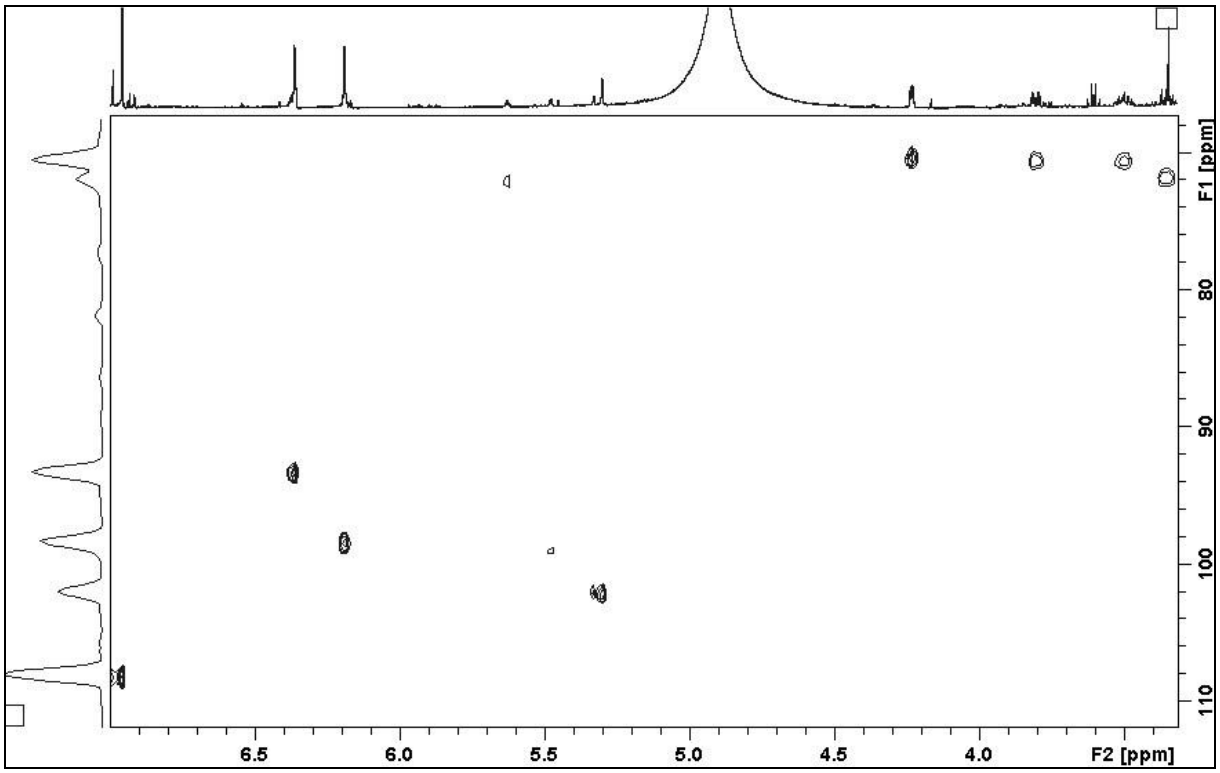


S35. Expansion of the HSQC NMR experiment of Compound **9**

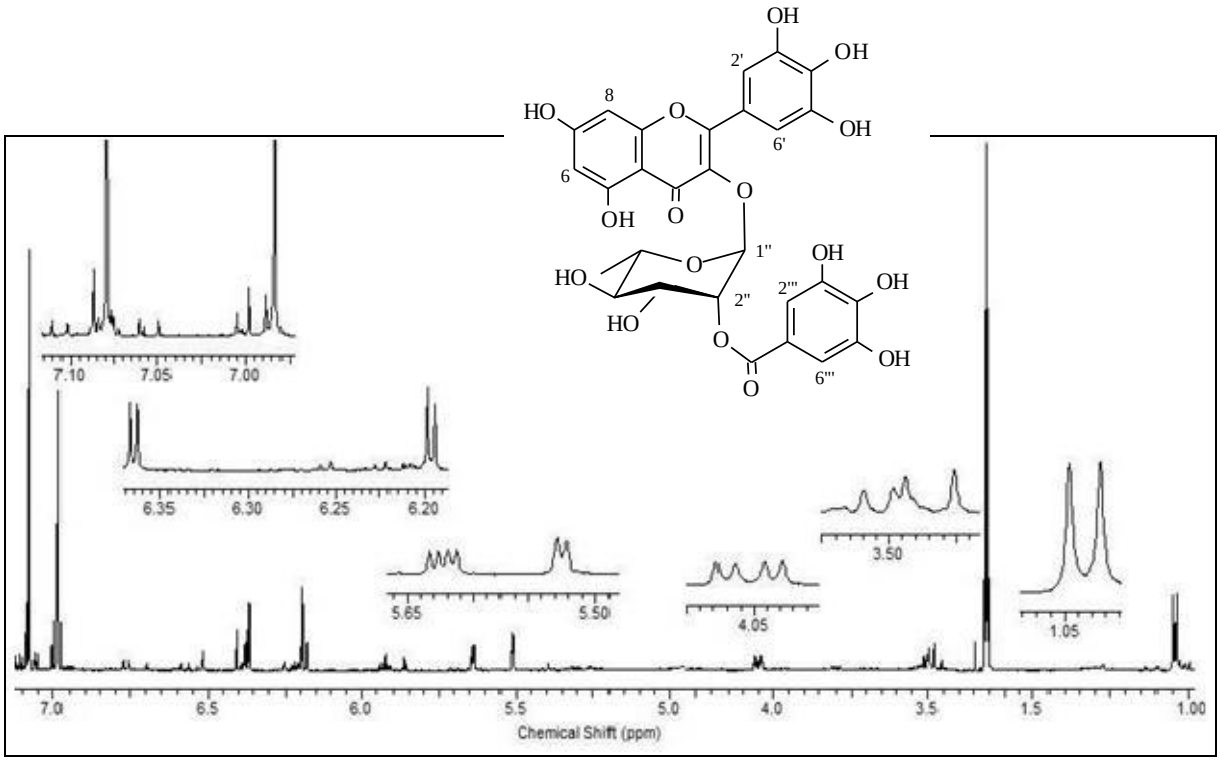


S36. [1]H-NMR (500 MHz, methanol-d_4) Spectrum of Compound **10**

Compound 10 (myricitrin), light yellow amorphous powder, [1]H-NMR (methanol-d_4, 500 MHz), δ: 6.19 (1H, d, *J* = 2.2, H-6), 6.36 (1H, d, *J* = 2.2, H-8), 6.95 (2H, s, H-2’/6’), 5.30 (1H, d, *J* = 1.6, H-1’’), 4.24 (1H, dd, *J* = 1.6, 3.4 Hz, H-2’’), 3.81 (1H, dd, *J* = 3.4, 9.3 Hz, H-3’’), 3.35 (1H, t, *J* = 9.7, H-4’’), 3.50 (1H, m, H-5’’), 0.96 (3H, d, *J* = 6.3, CH_3). [13]C-NMR (methanol-d_4, 125 MHz), δ: 98.3 (C-6), 93.2 (C-8), 108.1 (C-2'/6'), 101.9 (C-1’’), 70.4 (C-2’’), 70.6 (C-3’’), 71.7 (C-4’’), 70.6 (C-5’’), 16.2 (CH_3).

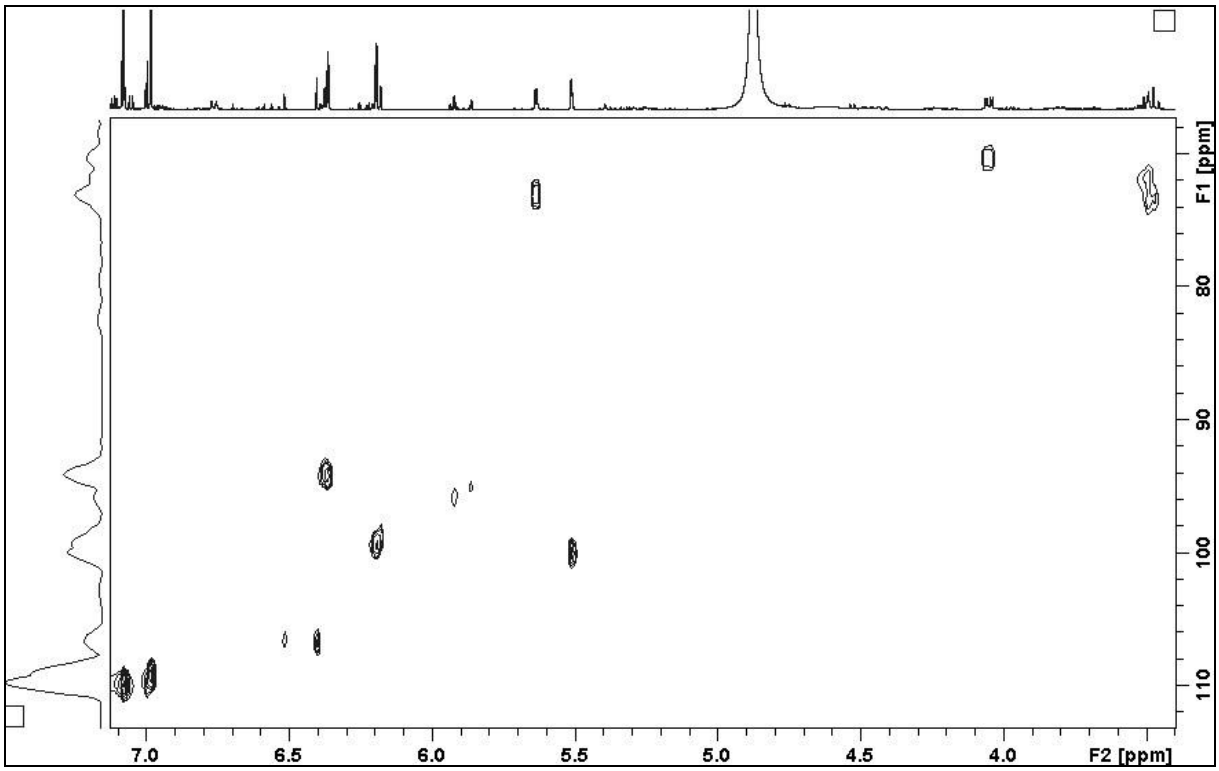


S37. Expansion of the HSQC NMR experiment of Compound **10**

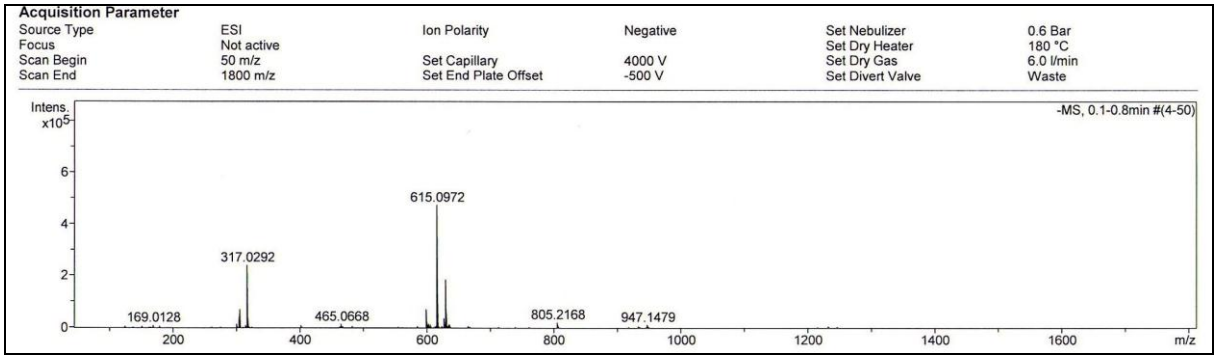


S38. ^{1}H-NMR (500 MHz, methanol-d_4) Spectrum of Compound **11**

Compound 11 (desmanthin-1), light yellow amorphous powder, ESI-TOF MS: *m/z* 615.0972 [M-H]$^-$ (calc. for $C_{28}H_{23}O_{16}$, 615.0992). ^{1}H-NMR (methanol-d_4, 500 MHz), δ: 6.20 (1H, d, *J* = 2.1, H-6), 6.36 (1H, d, *J* = 2.1, H-8), 7.08 (2H, s, H-2'/6'), 5.51 (1H, d, *J* = 1.7, H-1''), 5.64 (1H, dd, *J* = 1.7, 3.5 Hz, H-2''), 4.05 (1H, dd, *J* = 3.5, 8.9 Hz, H-3''), 3.48 (1H, t, *J* = 8.9, H-4''), 3.50 (1H, m, H-5''), 1.05 (3H, d, *J* = 5.7, CH_3), 6.98 (2H, s, H-2'''/6'''). ^{13}C-NMR (methanol-d_4, 125 MHz), δ: 99.3 (C-6), 94.0 (C-8), 109.9 (C-2'/6'), 100.0 (C-1''), 73.1 (C-2''), 70.3 (C-3''), 73.2 (C-4''), 71.7 (C-5''), 16.7 (CH_3), 109.1 (C-2'''/6''').



S39. Expansion of the HSQC NMR experiment of Compound **11**



S40. ESI-TOF mass Spectrum of Compound **11**