

Electronic Supplementary Information

Towards the synthesis of glycosylated dihydrochalcone natural products using glycosyltransferase-catalysed cascade reactions

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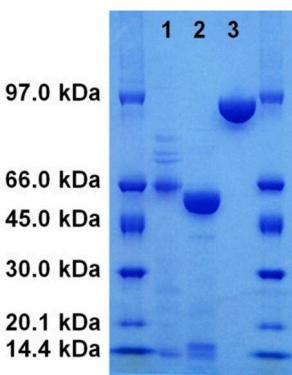


Fig. S1 SDS-PAGE of enzymes from *E. coli* overexpression cultures purified by *Strep*-tag affinity chromatography; lane 1: *PcOGT* (55.4 kDa), lane 2: *OsCGT I121D* (51.3 kDa), lane 3: *GmSuSy* (94.1 kDa)

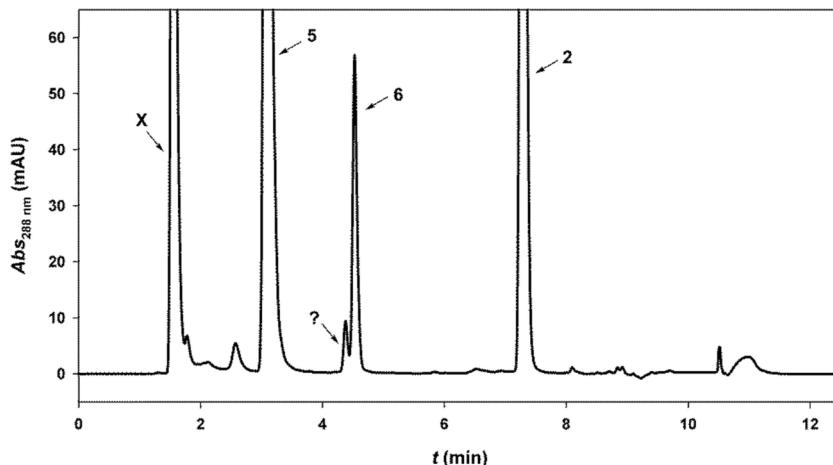


Fig. S2 Reversed-phase C-18 HPLC-analysis of a mixture of glucosylations of **2** by *PcOGT* and *OsCGT I121D* clearly shows that the minor product of the *PcOGT* reaction (?) is distinct from confusoside (6), formed by the *OsCGT* variant.

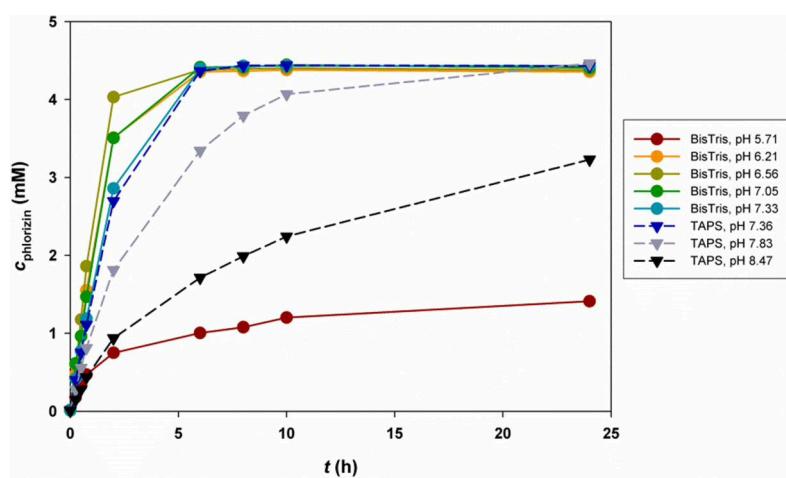


Fig. S3 Time courses of **3** formation through glucosylation of 5 mM **1** by coupled *PcOGT-GmSuSy* reaction (0.5 mM **9**, 100 mM **8**) using BisTris and TAPS reaction buffers at various pH.

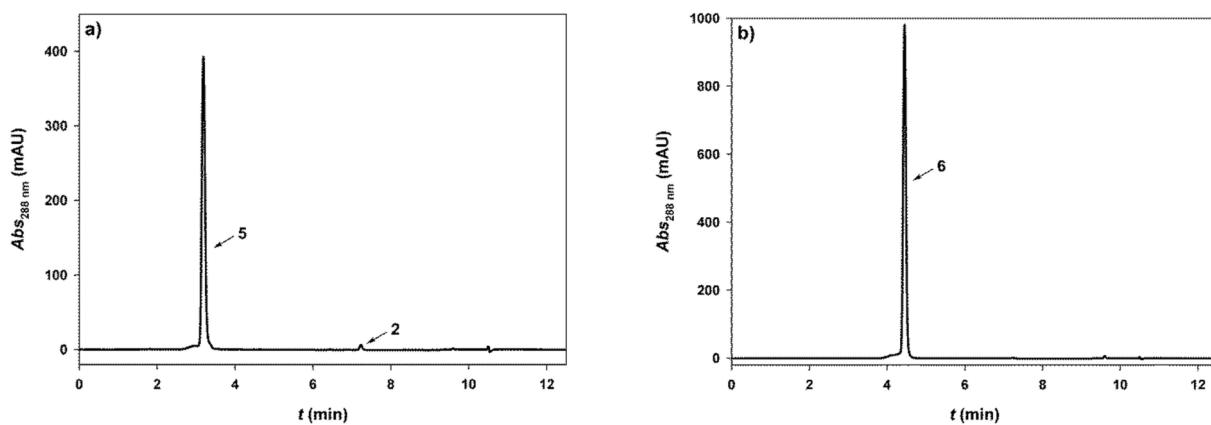


Fig. S4 Reversed-phase C-18 HPLC-analysis of (a) davydioside (**5**) and (b) confusoside (**6**) after purification by preparative HPLC confirms them to be of high purity (>98% based on HPLC peak area).

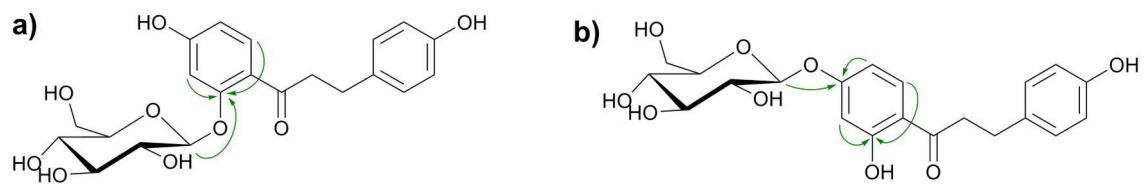
Table S1 ^1H and ^{13}C -NMR spectral data of davydigenin (**2**), davydioside (**5**) and confusoside (**6**)

nr	davydigenin (2) ($\text{R}_1, \text{R}_2 = \text{H}$) ^a		davydioside (5) ($\text{R}_1 = \text{glucose}, \text{R}_2 = \text{H}$) ^b		confusoside (6) ($\text{R}_1 = \text{H}, \text{R}_2 = \text{glucose}$) ^b	
	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}
1	133.0		133.8		133.4	
2 / 6	129.2	7.07 (2H, d, $J = 8.5$ Hz)	130.3	7.03 (2H, d, $J = 8.4$ Hz)	130.4	7.05 (2H, d, $J = 8.4$ Hz)
3 / 5	115.0	6.68 (2H, d, $J = 8.5$ Hz)	116.1	6.67 (2H, d, $J = 8.2$ Hz)	116.2	6.69 (2H, d, $J = 8.4$ Hz)
4	155.5	9.17 (1H, s)	156.4		156.7	
C=O	203.9		202.9		206.2	
α	39.4	3.22 (2H, t, $J = 7.6$ Hz)	46.2	~3.3 ^c	41.2	3.23 (2H, t, $J = 7.3$ Hz)
β	29.1	2.83 (2H, t, $J = 7.4$ Hz)	31.0	2.86 (2H, t, $J = 7.5$ Hz)	30.9	2.92 (2H, t, $J = 7.3$ Hz)
1'	112.5		121.9		116.0	
2'	164.7	10.62 (1H, s)	160.3		165.8	
3'	102.4	6.26 (1H, d, $J = 2.2$ Hz)	103.9	6.70 (1H, d, $J = 2.0$ Hz)	105.1	6.58 (1H, d, $J = 2.2$ Hz)
4'	164.3	12.65 (1H, s)	164.4		165.1	
5'	108.1	6.37 (1H, dd, $J = 8.74, 2.3$ Hz)	110.8	6.50 (1H, dd, $J = 8.5, 1.9$ Hz)	109.4	6.62 (1H, dd, $J = 8.9, 2.3$ Hz)
6'	131.0	7.81 (1H, d, $J = 8.8$ Hz)	133.2	7.58 (1H, d, $J = 8.6$ Hz)	133.1	7.81 (1H, d, $J = 8.9$ Hz)
1"			102.6	4.99 (1H, d, $J = 7.1$ Hz)	101.3	5.00 (1H, d, $J = 7.2$ Hz)
2"			74.9		74.7	
3"			78.3	3.33-3.48-(4H, unresolved)	77.9	3.45-3.50 (3H, unresolved)
4"			71.2		71.2	
5"			78.4		78.3	3.41 (1H, m)
6"			62.6	3.91 (1H, dd, $J = 12.4, 2.0$ Hz) 3.72 (1H, dd, $J = 12.1, 5.7$ Hz)	62.4	3.89 (1H, dd, $J = 12.1, 2.1$ Hz) 3.70 (1H, dd, $J = 12.3, 5.5$ Hz)

^a ^1H : 300.36 MHz, ^{13}C : 75.53 MHz; (DMSO- d_6 , δ in ppm)

^b ^1H : 499.89 MHz, ^{13}C : 125.70 MHz; (CD_3OD , δ in ppm)

^c overlap with MeOH signal



Scheme S1 Key HMBC couplings to identify (a) davydioside (**5**) and (b) confusoside (**6**), respectively

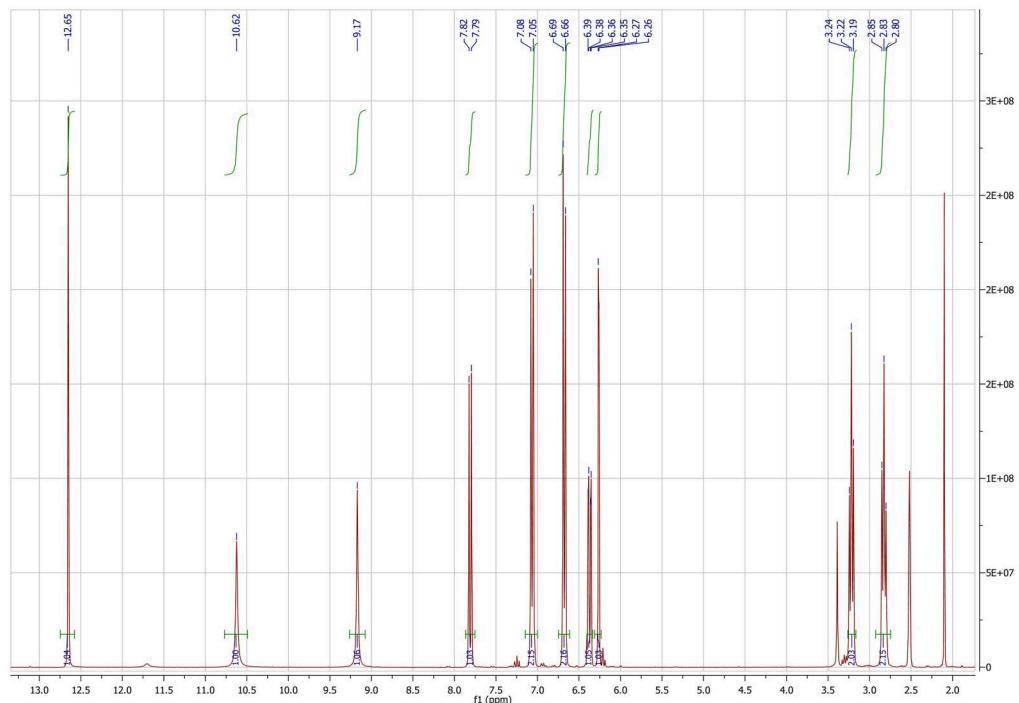


Fig. S5 ^1H -NMR of davydigenin (**2**)

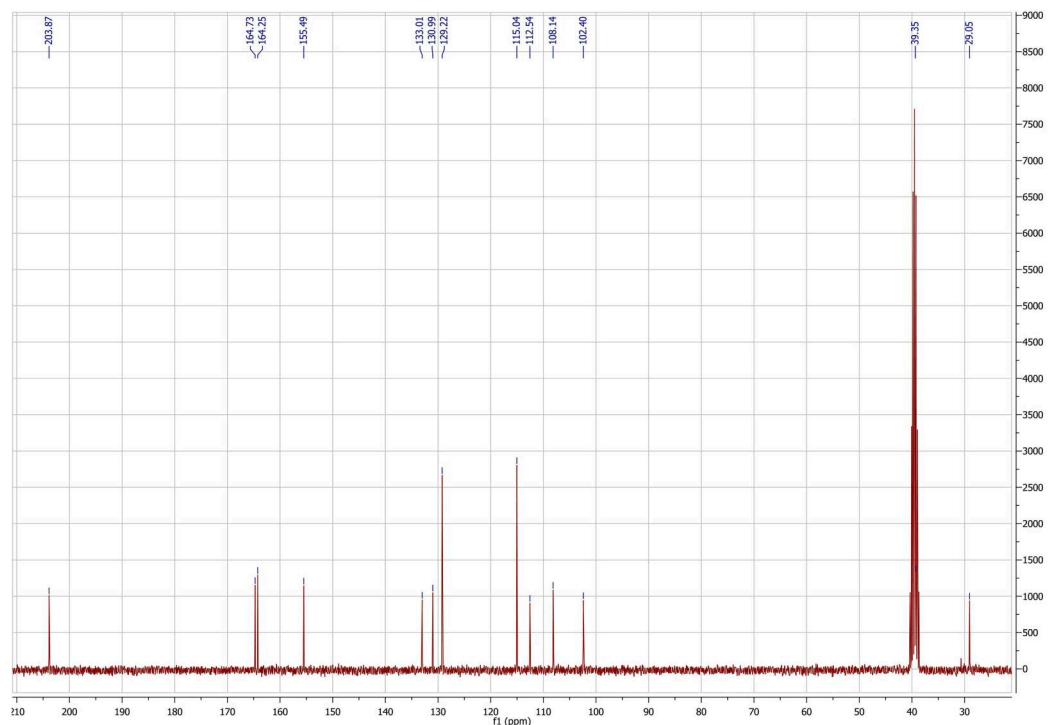


Fig. S6 ^{13}C -NMR of davydigenin (**2**)

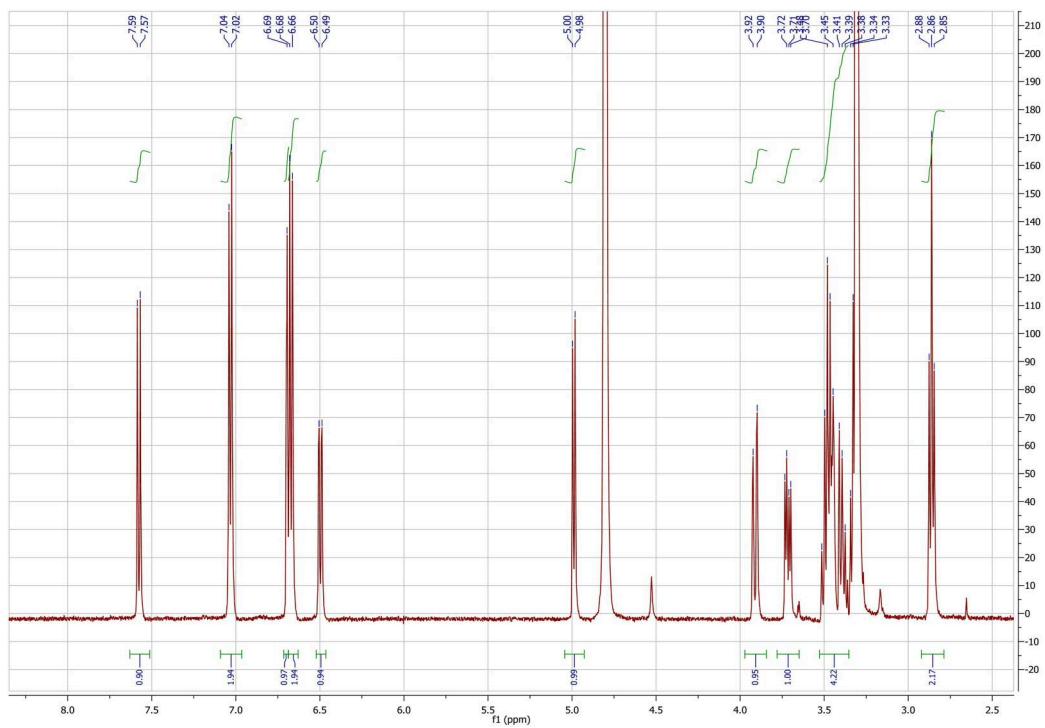


Fig. S7 ^1H -NMR of HPLC purified davidioideside (**5**)

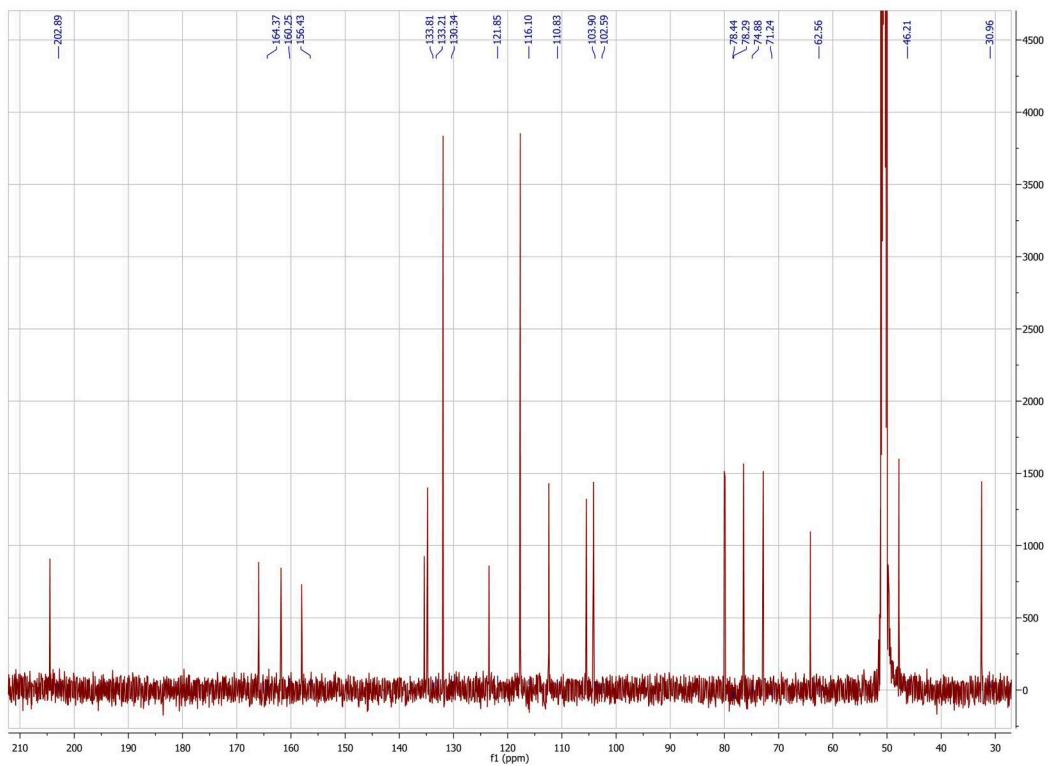


Fig. S8 ^{13}C -NMR of HPLC purified davidiносide (5)

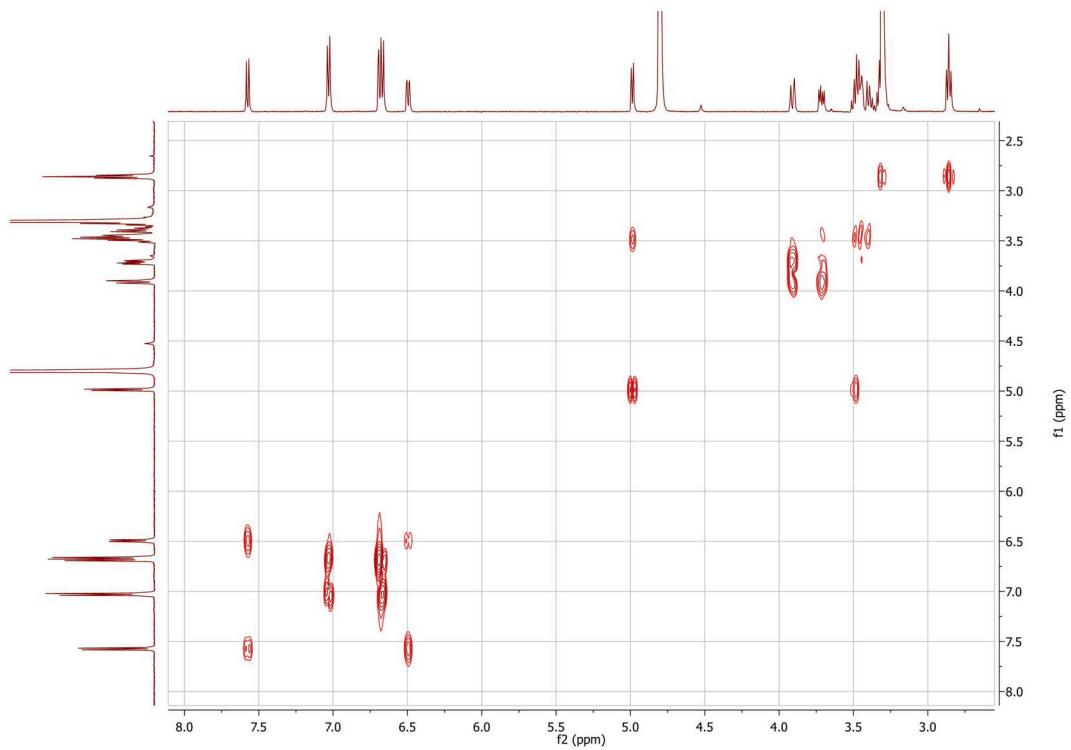


Fig. S9 2D COSY-NMR of HPLC purified davidiносide (5)

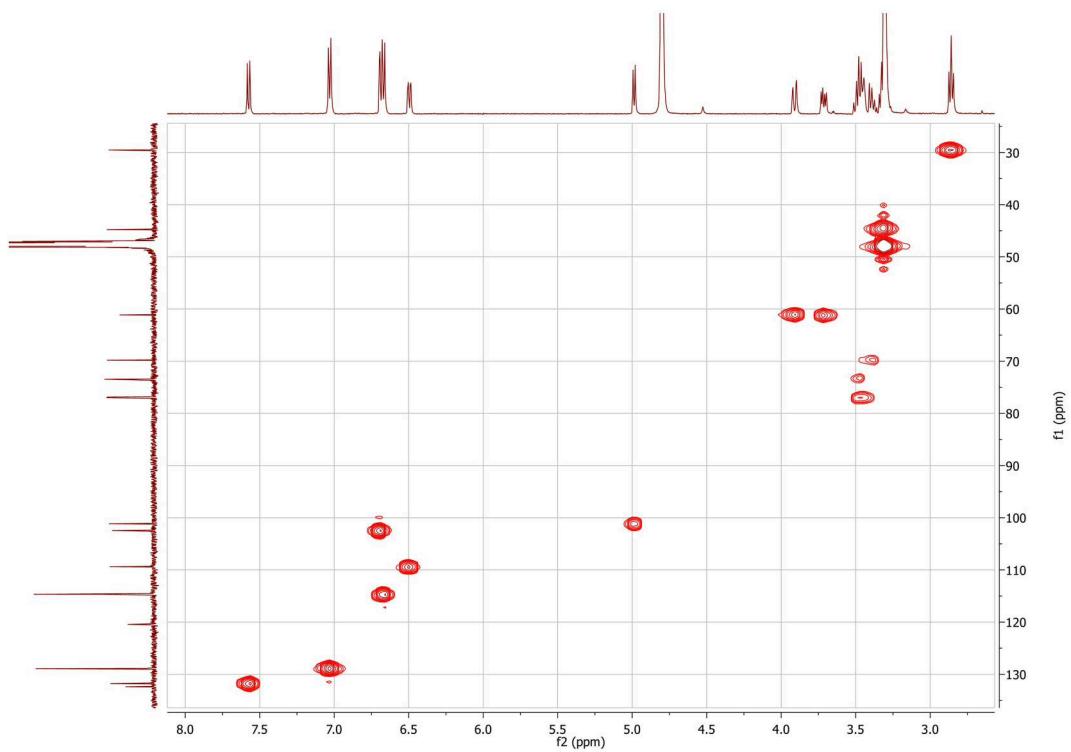


Fig. S10 2D HMQC-NMR of HPLC purified davidioideside (**5**)

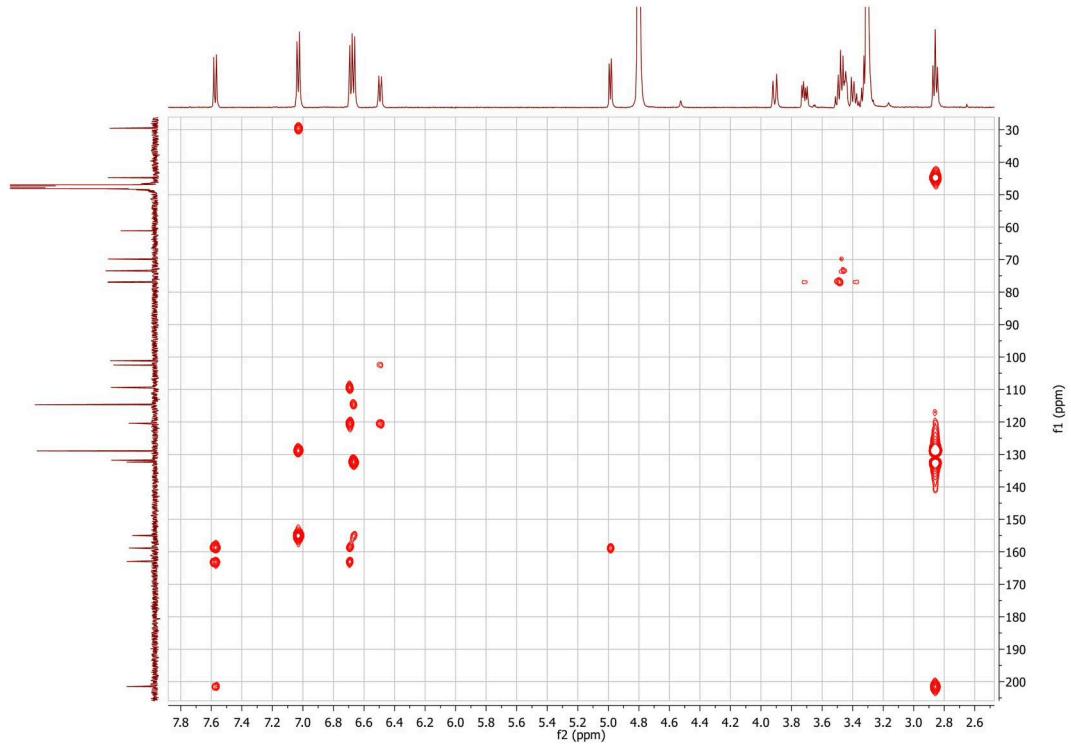


Fig. S11 2D HMBC-NMR of HPLC purified davidioideside (**5**)

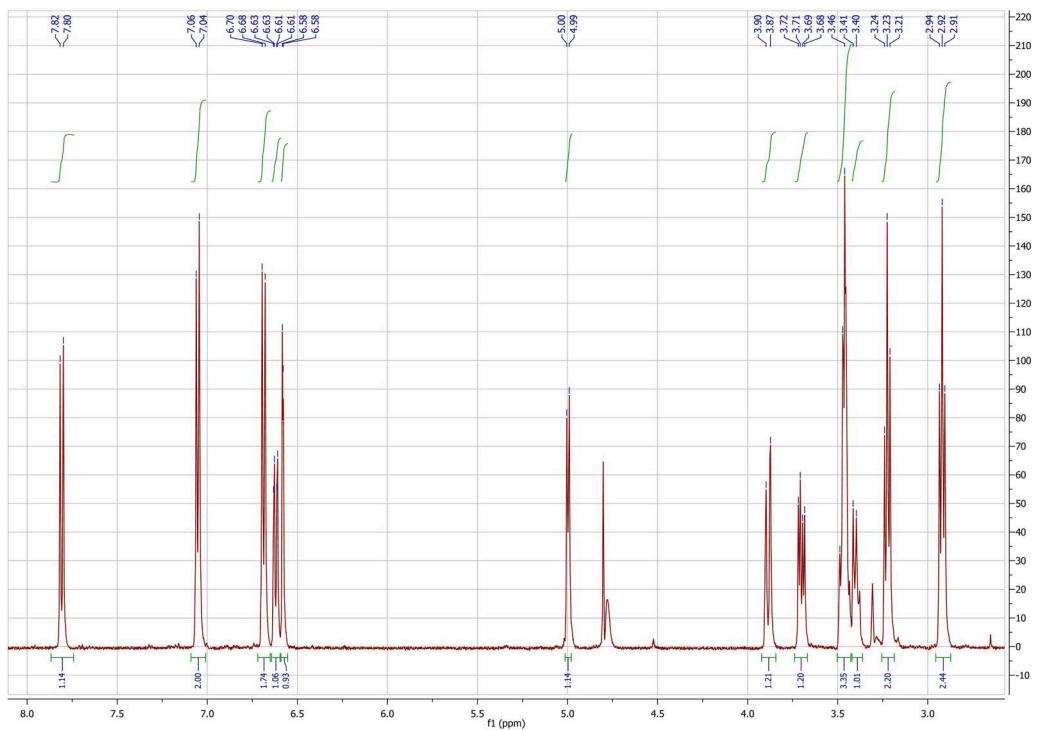


Fig. S12 ¹H-NMR of HPLC purified confusoside (**6**)

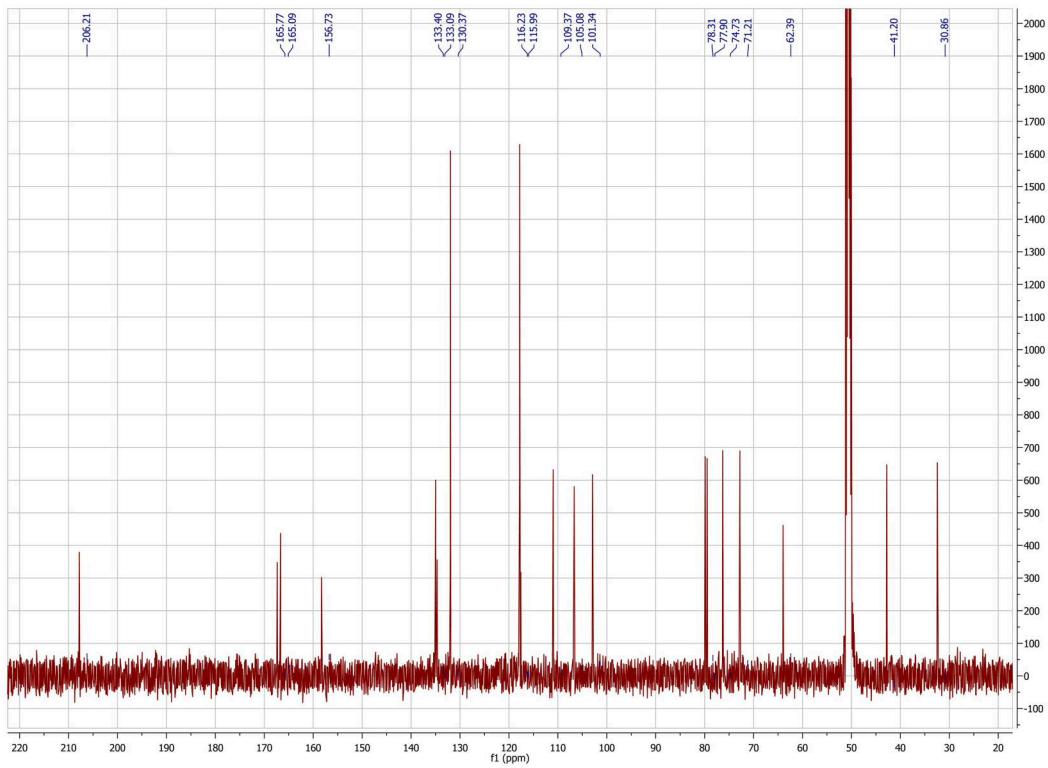


Fig. S13 ¹³C-NMR of HPLC purified confusoside (**6**)

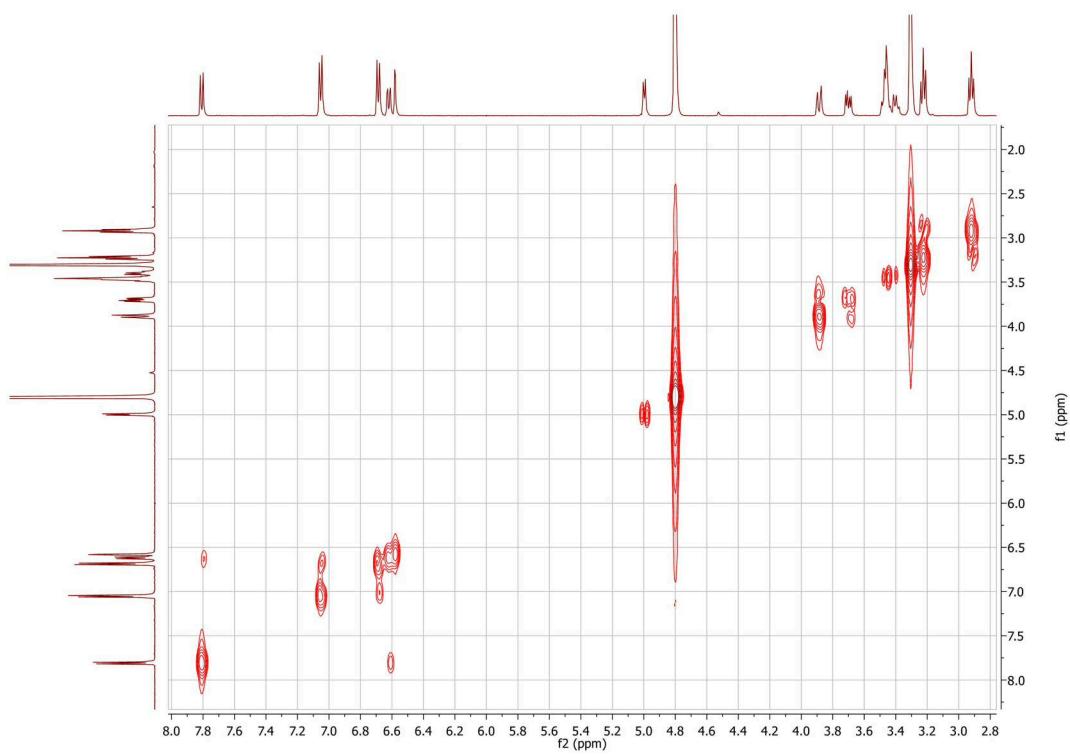


Fig. S14 2D COSY-NMR of HPLC purified confusoside (**6**)

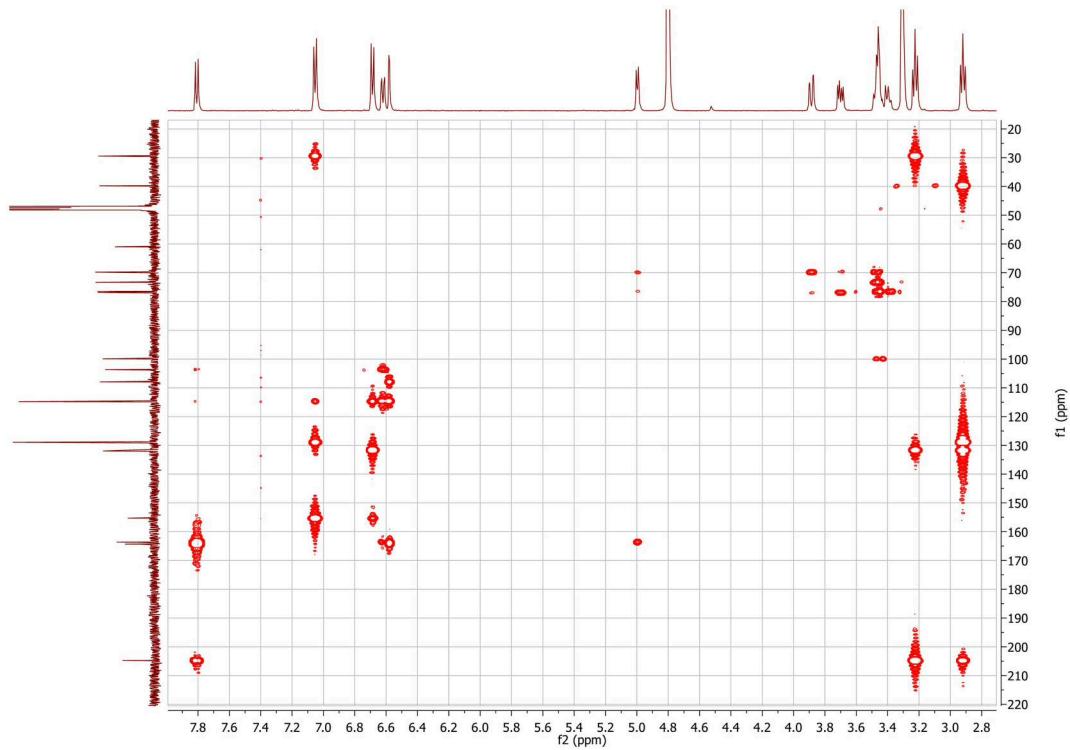


Fig. S15 2D HMBC-NMR of HPLC purified confusoside (**6**)