Supplemental material

Table of contents

1. Plasmid construction

Inactivation of glycosyltransferase genes in the genome of *S. espanaensis*. (i) pKCXY02. The plasmids pKC1132 and pKGLP2 were both digested with ClaI/XbaI. The fragment of pKC1132, containing apramycin resistance-conferring gene and origin of replication and the fragment of pKGLP2 containing *gusA* gene under control of *tipA* promoter were ligated resulting in pKCXY02.

(ii) pLERE-spec-oriT. Spectinomycin resistance-conferring gene together with origin of transfer of vector pIJ778 was amplified using the primers spec-f, 5' –GCGCCAATTGATAG GAACTTCGAAGTTCCC and spec-r, 5' –GCGCCAATTGCTTATTTGCCGACTACCTTG (restriction sites underlined), and cloned via MunI digestion into pLERE.

(iii) pKCΔses44520. Using *S. espanaensis* genomic DNA as template two homologous regions upstream and downstream of *ses44520* were amplified. The upstream region was generated using the primers ses44520-hx-f, 5' –CGCTGCCGGAGGAAGCTTTCGAAGG CGTGAAGC, and ses44520-hx-r, 5' –GACGAGTCTAGACGCGCCCTGCCGGACCTCGC CTAG and the downstream region using the primers ses44520-ex-f, 5' –GCCGACTCTAGA GAGACTGGCGAAGAGCACGCGC and ses44520-ex-r, 5' –GCGAAGGCGGAATTCGG CCTGAGGCCGGGACCTG (restriction sites underlined). The upstream region was cloned into HindIII/XbaI digested pKC1132. The resulting plasmid was XbaI/EcoRI digested and the downstream region was cloned. The spectinomycin resistance-conferring gene flanked by two loxLE and two loxRE sites was excised from pLERE-spec-oriT by XbaI/SpeI digestion and cloned into XbaI site between the homologous regions resulting in the inactivation plasmid pKCΔses44520.

(iv) pKCΔses45900. Using *S. espanaensis* genomic DNA as template two homologous regions upstream and downstream of *ses45900* were amplified. The upstream region was generated using the primers ses45900-hx-f, 5' –CGCGGCAAGCTTCCCCACCTCTCGTGC CGG, and ses45900-hx-r, 5' –GACCAGTCTAGACACGACGAAGAGGAACCTGCTCAC and the downstream region using the primers ses45900-mx-f, 5' –CCACCTTCTAGA GCTGGCGGCGCGGTCGCCCGTCCG and ses45900-mx-r, 5' –GCGCACTATTAAGTAC CAATTGTGAGGTATTATCCC (restriction sites underlined). The upstream region was cloned into HindIII/XbaI digested pKC1132. The resulting plasmid was XbaI/EcoRI digested and the downstream region was cloned. The spectinomycin resistance-conferring gene flanked by two loxLE and two loxRE sites was excised from pLERE-spec-oriT by XbaI/SpeI

digestion and cloned into XbaI site between the homologous regions resulting in the inactivation plasmid pKCΔses45900.

(v) pKCΔses47640. Using *S. espanaensis* genomic DNA as template two homologous regions upstream and downstream of *ses47640* were amplified. The downstream region was generated using the primers ses47640-hx-f, 5' –CACGAATCTAGACCAGGTGGGGGACA TACCGCGTG, and ses47640-hx-r, 5' –GCGCGTCCGGGAAGCTTGGTCAG and the upstream region using the primers ses47640-ex-f, 5' –CCGGACGAATTCTGCGGTTACGT TGTCGTGCCAGGC and ses47640-ex-r, 5' –CGCGGGTCTAGAGAGGAACAGGATG TGTGCGGGC (restriction sites underlined). The downstream region was cloned into HindIII/XbaI digested pKC1132. The resulting plasmid was XbaI/EcoRI digested and the upstream region was cloned. The spectinomycin resistance-conferring gene flanked by two loxLE and two loxRE sites was excised from pLERE-spec-oriT by XbaI/SpeI digestion and cloned into XbaI site between the homologous regions resulting in the inactivation plasmid pKCΔses47640.

(vi) pKCΔses49200. Using *S. espanaensis* genomic DNA as template two homologous regions upstream and downstream of *ses49200* were amplified. The upstream region was generated using the primers ses49200-hx-f, 5' –GCCCGCAAGCTTGACGACCACCATCG GCTCGTTC, and ses49200-hx-r, 5' –CGAATCGACGTCTAGATGGTCGCAACGG and the downstream region using the primers ses49200-mx-f, 5' –CACGACTCTAGACGCCTGCT GCCCGACTACGCGTG and ses49200-mx-r, 5' –CCAACAGATGATACAACATGTCT CAATTGAGACGCTG (restriction sites underlined). The upstream region was cloned into HindIII/XbaI digested pKC1132. The resulting plasmid was XbaI/EcoRI digested and the downstream region was cloned. The spectinomycin resistance-conferring gene flanked by two loxLE and two loxRE sites was excised from pLERE-spec-oriT by XbaI/SpeI digestion and cloned into XbaI site between the homologous regions resulting in the inactivation plasmid pKCΔses49200.

(vii) pKCΔses60310. Using *S. espanaensis* genomic DNA as template two homologous regions upstream and downstream of *ses60310* were amplified. The downstream region was generated using the primers ses60310-ex-f, 5' –GAGGCGGTGCTCTAGAACGGGCTGG, and ses60310-ex-r, 5' –GGTCTCCACGAGGCCGAATTCTCTC and the upstream region using the primers ses60310-px-f, 5' –GACCGTCGACTGCAGCCGGCAGAAC and ses60310-px-r, 5' –CGGATGCCGTGCCTCTAGACCGC (restriction sites underlined). The downstream region was cloned into EcoR/XbaI digested pKCXY02. The resulting plasmid

was XbaI/PstI digested and the upstream region was cloned. The spectinomycin resistance-conferring gene flanked by two loxLE and two loxRE sites was excised from pLERE-spec-oriT by XbaI/SpeI digestion and cloned into XbaI site between the homologous regions resulting in the inactivation plasmid pKCΔses60310.

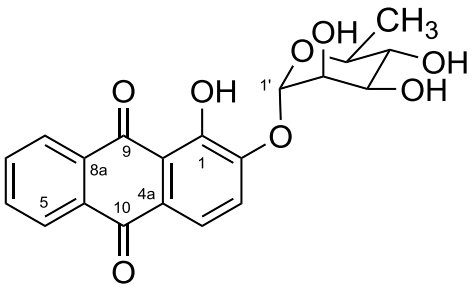
Complementation of *S. espanaensis* Δses60310 with an intact copy of *ses60310*. pSET-ses60310. KpnI/BamHI restriction fragment of pUWL-A-ses60310 containing *ses60310* gene under control of *ermE* promoter was ligated into KpnI/BamHI-digested plasmid pSET-1cerm to produce pSET-ses60310.

Development and application of a heterologous test system. (i) pTOS-Rham. HindIII restriction fragment of pRham containing *oleS, oleE, oleL* and *oleU* under control of *ermE** promoter was cloned into HindIII digested plasmid pTOS resulting in pTOS-Rham. **(ii) pUWL-A-ses60310.** The glycosyltransferase gene *ses60310* of *S. espanaensis* was amplified from genomic DNA using the primers ses60310-f, 5' –GAATGCCGGAATTCATCGGG TGTCG, and ses60310-r, 5' –GCGTCCCGGATCCGTCGAACACCTC (restriction sites underlined), and cloned via EcoRI/BamHI digestion into pUWL-A. **(iii) pUWL-A-ses60350.** The glycosyltransferase gene *ses60350* of *S. espanaensis* was amplified from genomic DNA using the primers ses60350-f, 5' –CGCAGGCACCGA GAATTCGGGCAGC, and ses60350-r, 5' –GTTCGGGCGCTAGCCGGATCCGAAC (restriction sites underlined), and subcloned via EcoRI/BamHI digestion into pUWL-A.

Ses60310 protein synthesis. pET28a-ses60310-N-his-Tev. The glycosyltransferase gene *ses60310* was amplified from plasmid pUWL-A-ses60310 using the primers ses60310-N-his-f, 5' –TATAGCTAGCATGGGTACGATCGAGCCG, and ses60310-N-his-r, 5' –TATAAAG CTTCAGGAGCCGCGGAACAG (restriction sites underlined), and cloned into the NheI/HindIII digested vector pET28a(+). The DNA sequence encoding the thrombin cleavage site at the N-terminal end of the protein were subsequently changed into the DNA sequence encoding a TEV cleavage site via two consecutive mutagenesis PCRs. The sequence of the utilized primers are as follows: tev-half-f, 5' –GCTCGATCGTACCCATGCCCTGAAAATA GCTGCCGCGCGGCACC, tev-half-r, 5' –GGTGCCGCGCGGCAGCTATTTTCAGGGC ATGGGTACGATCGAGC, tev-whole-f, 5' –CCATGCCCTGAAAATA*CAGGTTCTC* CGGCACCAGGCCGCTG, tev-whole-r, 5' –CAGCGGCCTGGTGCCG*GAGAACCTG* TATTTTCAGGGCATGG (base pairs encoding the first half of TEV cleavage site are underlined, base pairs encoding the second half are in italics).

2. Structure elucidation of biotransformation products

Spectroscopic data of AliPro1



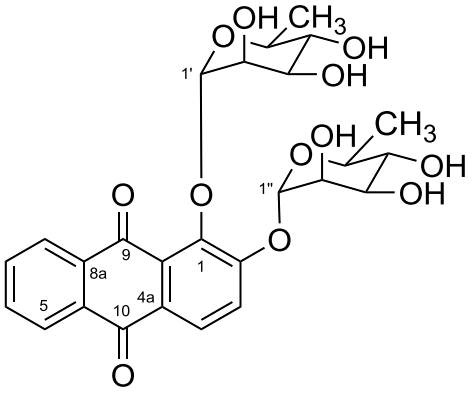
HR-ESI-MS (pos. mode):
measured: m/z = 387.10572 $[M+H]^+$, calculated m/z = 387.10744 $[M+H]^+$

NMR data: 400/100MHz (DMSO-d_6, room temperature)

Pos.	δ_C [ppm]	δ_H (*J* Hz) [ppm]	COSY	$^1H,^{13}C$-HMBC	Sel. NOESY on 1'-H
1	153.4			3-H	
1-OH		12.68 br s			
2	150.3			4-H	
3	121.2	7.58 d (8.3)	4-H		1'-H
4	119.5	7.71 d (8.3)	3-H		
4a	126.3			3-H	
5	126.7	8.19 m	6-H	6-H, 7-H	
6	134.9[a]	7.94 m	5-H		
7	134.2[a]	7.94 m	8-H		
8	126.5	8.25 m	7-H	6-H, 7-H	
8a	133.2[a]			5-H, 8-H	
9	188.0			8-H	
9a	116.5			4-H	
10	181.0				
10a	133.3[a]			8-H	
1'	98.8	5.60 d (6.2)	2'-H		3-H
2'	70.0[b]	3.92 m	1'-H, 2'-OH, 3'-H	1'-H	
2'-OH		5.18 br s	2'-H		
3'	70.3	3.72 dd (9.2, 3.3)	2'-H, 3'-OH, 4'-H	2'-H	
3'-OH		4.86 br s	3'-H		
4'	71.5	3.3[c]	3'-H, 4'-OH	6'-H_3	
4'-OH		4.95 br s	4'-H		
5'	70.0[b]	3.49 dq (9.0, 6.2)	6'-H_3	6'-H_3	
6'	17.8	1.11 d (6.2)	5'-H		

[a,b]signals exchangeable, [c]covered from water signal

Spectroscopic data of AliC1



ESI-MS (pos. mode): m/z = 555.2 $[M+Na]^+$

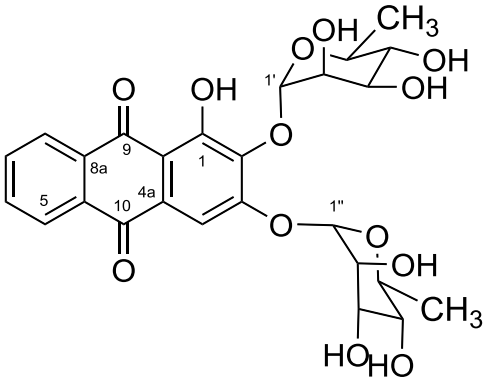
NMR data: 600/150MHz (DMSO-d_6, 35°C)

Pos.	δ_C [ppm]	δ_H (*J* Hz)[a] [ppm]	COSY[b]	$^1H,^{13}C$-HMBC[b]	ROESY[b]
1	146.2			3-H, 1''-H	
2	154.8			3-H, 4-H, 1''-H	
3	120.2	7.69 d (8.6)	4-H	(4-H)	4-H, 1''-H
4	124.2	8.02 d (8.6)	3-H		4-H
4a	127.8			3-H	
5	126.7	8.12 d (8.0)	6-H	7-H	6-H
6	133.9	7.87 m	5-H	5-H	5-H
7	134.7	7.89 m	8-H	6-H	8-H
8	126.7	8.12 d (8.4)	7-H	6-H	7-H
8a	132.2			5-H, 6-H	
9	182.0			5-H	
9a	126.6			4-H	
10	181.6			4-H	
10a	134.3				
1'	104.4	5.23 br s	2'-H	^1J	2'-H
2'	70.3	4.26 br m	1'-H 2'-OH, 3'-H		1'-H, 2'-OH, 3'-H
2'-OH		4.98 br s	2'-H		2'-H
3'	70.6	3.85 br d (9.1)	2'-H, 4'-H		2'-H, 5'-H
4'	71.5	3.32[c]	3'-H	5'-H, 6'-H_3	2'-H, 5'-H
5'	70.8	3.92 dq (9.7, 6.3)	(4'-H), 6'-H_3	6'-H_3	3'-H, 6'-H_3
6'	17.8	1.02 d (6.3)	5'-H	4'-H	4'-H, 5'-H
1''	98.8	5.63 br s	2''-H		3-H, 2''-H
2''	69.9	3.96 m	1''-H, 2''-OH, 3''-H		1''-H, 3''-H
2''-OH		5.26 br s	2''-H		
3''	70.4	3.77 m	2''-H, 4''-H		1''-H, 2''-H, 5''-H
4''	71.6	3.33[c]	3''-H	5''-H, 6''-H_3	
5''	70.1	3.41[c]	6''-H	1''-H, 6''-H_3	3''-H, 6''-H_3
6''	17.8	1.09 d (6.1)	5''-H	4''-H	2''-H, 4''-H, 5''-H

[a]3'-OH, 4'-OH, 3''-OH, 4''-OH are not assignable, [b]weak signals in brackets, [c]covered from water signal

Proof of sugar configuration: ^{1}H-NMR and 1D-TOCSY with excitation of 2'-H and 3''-H after addition of D_2O (600MHz, 35°C, DMSO-d_6/D_2O): δ_H = 8.08 (m, 6-H, 9-H), 7.99 (d, *J* = 9.0 Hz, 4-H) 7.86-7.84 (m, 7-H, 8-H), 7.64 (d, *J* = 9.0 Hz, 3-H), 5.60 (d, *J* = 1.6 Hz, 1''-H), 5.17 (br s, 1'-H), 4.26 (dd, *J* = 3.2, 1.7 Hz, 2'-H), 3.94 (dd, *J* = 3.5, 1.7 Hz, 2''-H), 3.91 (dq, *J* = 9.6, 6.3 Hz, 5'-H), 3.82** (dd, *J* = 9.5, 3.2 Hz, 3'-H), 3.73 (dd, *J* = 9.3, 3.3 Hz, 3''-H), 3.39 (dq, *J* = 9.5, 6.2 Hz, 5''-H), 3.31 (dd, *J* = 9.5, 9.3 Hz, 4''-H), 3.31 (dd, *J* = 9.6, 9.5 Hz, 4'-H), 1.07 (d, *J* = 6.2 Hz, 6''-H_3), 1.02 (d, *J* = 6.3 Hz, 6'-H_3) ppm.
**covered from water signal (coupling pattern and constants deduced from neighbours)

Spectroscopic data of AliPro2



ESI-MS (pos. mode): m/z = 571.3 $[M+Na]^+$
ESI-MS (neg. mode): m/z = 547.1 $[M-Na]^-$

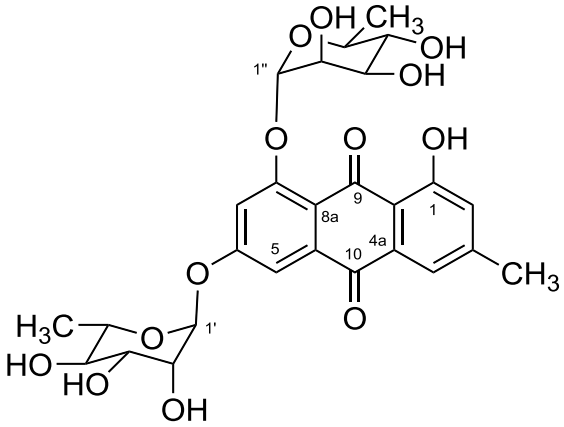
NMR data: 600/150MHz (DMSO-d_6, 35°C)

Pos.	δ_C [ppm]	δ_H (*J* Hz) [ppm]	COSY[a]	^{1}H,^{13}C-HMBC[a]	ROESY[a]
1	156.5 (br)				
1-OH		12.78 bs s			
2	138.2 (br)			4-H	
3	154.8			4-H, 1''-H	
4	106.5	7.57	-		1''-H
4a	128.9			4-H	
5	126.8	8.15 m	6-H	6-H, 7-H	6-H
6	134.7	7.91 m	5-H	8-H	5-H
7	134.4	7.91 m	8-H	5-H, (6-H)	8-H
8	126.4	8.21 m	7-H	6-H, 7-H	7-H
8a	132.9			(5-H), 6-H, 7-H, 8-H	
9	187.1			8-H	
9a	112.2			4-H	
10	181.4			4-H, 5-H	
10a	129.6				
1'	102.1	5.47 s	2'-H	5'-H	2'-H, (3'-H)
2'	70.0	4.03 br m	1'-H, 2'-OH, 3'-H	1'-H	1'-H, 2'-OH, 3'-H
2'-OH		5.01 (br s)	2'-H		2'-H
3'	70.39	3.75 m	2'-H, 3'-OH, 4'-H	1'-H, 4'-OH	2'-H, 3'-OH, 5'-H
3'-OH		4.82 (br s)	3'-H		3'-H
4'	71.5	3.31 m	3'-H, 4'-OH, 5'-H	3'-H, 4'-OH, 3'-OH, 5'-H, 6'-H_3	5'-H, 6'-H_3
4'-OH		4.85 (br s)	4'-H		4'-H
5'	70.42	3.97 m	4'-H, 6'-H_3	1'-H, 4'-OH, 6'-H_3	3'-H, 6'-H_3
6'	17.8	1.09 d (6.2)	5'-H	4'-H, 5'-H, ^{1}J	4'-H, 4'-OH, 5'-H
1''	99.1	5.62 s	2''-H	2'-OH, 5''-H	4-H, 2''-H, 2''-OH
2''	69.8	3.94 br m	1''-H, 2''-OH, 3''-H	2''-OH	1''-H, 2''-OH, 3''-H
2''-OH		5.26 (br s)	2''-H		1''-H, 2''-H
3''	70.3	3.71 m	2''-H, 3''-OH, 4''-H	1''-H, 4''-OH, 5''-H	2''-H, 3''-OH, 4''-OH, 5''-H
3''-OH		4.82 (br s)	3''-H		3''-H
4''	71.5	3.36 m	3''-H, 4''-OH, 5''-H	4''-OH, 5''-H, 6''-H_3	6''-H_3
4''-OH		4.93 (br s)	4''-H		
5''	70.2	3.46 m	4''-H, 6''-H_3	1''-H, 4''-OH	4''-OH, 3''-H, 6''-H_3
6''	17.8	1.13 d (6.2)	5''-H	5''-H, ^1J	4''-H, 5''-H

[a]weak signals in brackets

Proof of sugar configuration: ^{1}H-NMR and 1D-TOCSY with excitation of 1'-H and 1''-H after addition of D_2O (600MHz, 35°C, DMSO-d_6/D_2O): δ_H = 8.13 (d, *J* = 9.0 Hz, 9-H), 8.08 (d, *J* = 9.0 Hz, 6-H), 7.85(dd, *J* = 9.0, 9.0 Hz, 7-H, 8-H), 7.48 (s, 4-H), 5.56 (br s, 1''-H), 5.40 (br s, 1'-H), 4.01 (dd, *J* = 3.1, 1.8 Hz, 2''-H), 3.95 (dq, *J* = 9.4, 6.3 Hz, 5'-H), 3.92 (dd, *J* = 3.4, 1.8 Hz, 2''-H), 3.72 (dd, *J* = 9.5, 3.1 Hz, 3'-H), 3.67 (dd, *J* = 9.5, 3.4 Hz, 3''-H), 3.43 (dq, *J* = 9.2, 6.2 Hz, 5''-H), 3.34 (dd, *J* = 9.5, 9.1 Hz, 4''-H), 3.32 (dd, *J* = 9.5, 9.2Hz, 4'-H), 1.11 (d, *J* = 6.2 Hz, 6''-H_3), 1.09 (d, *J* = 6.2 Hz, 6'-H_3) ppm.

Spectroscopic data of EmoPro3



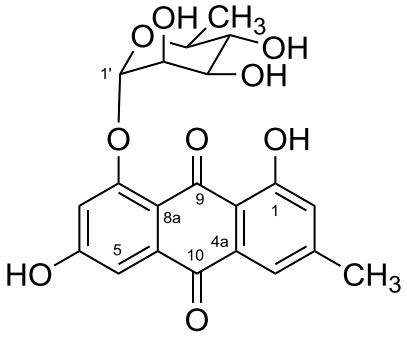
HR-ESI-MS (pos. mode):
measured: m/z = 563.17590 $[M+H]^+$, calculated m/z = 563.17592 $[M+H]^+$

NMR data: 400/100MHz (DMSO-d_6, room temperature)

Pos.	δ_C [ppm]	δ_H (*J* Hz) [ppm]	COSY	^{1}H,^{13}C-HMBC[a]	NOESY
1	161.4			2-H	
1-OH		13.11 s			
2	124.1	7.15 m	3-H_3, 4-H	1-OH, 3-H_3, 4-H	3-H_3
3	147.2			3-H_3	
3-CH_3	21.4	2.39 s	2-H, 4-H	2-H, 4-H	2-H, 4-H
4	119.4	7.44 d (1.3)	2-H, 3-H_3	2-H, 3-H_3	3-H_3
4a	132.0				
5	108.3	7.46 d (2.4)	7-H		1’-H
6	161.7			5-H, 7-H, 1’-H	
7	110.1	7.22 d (2.4)	5-H		1’-H, 1’’-H
8	159.0			7-H, 1’’-H	
8a	115.9			5-H	
9	186.6			(4-H)	
9a	114.4			1-OH, 2-H, 4-H	
10	181.6			4-H, 5-H	
10a	136.6			5-H	
1’	98.7	5.58 d (1.6)	2’-H	2’-OH	5-H, 7-H, 2’-H, 2’-OH
2’	69.8	3.89 m	1’-H, 2’-OH, 3’-H		1’-H, 2’-OH, 3’-H[c]
2’-OH		5.17 d (4.4)	2’-H		
3’	70.2	3.67 ddd (9.2, 5.9, 3.3)	2’-H, 3’-OH, 4’-H	2’-H	2’-H[c], 5’-H[c]
3’-OH		4.80 d (6.1)	3’-H		
4’	71.6	3.34[b]	3’-H, 4’-OH	2’-H	6‘-H_3
4’-OH		4.92 d (5.9)	4’-H		
5’	70.2	3.45 dq (9.3, 6.2)	4’-H, 6’-H_3		3’-H[c], 6’-H_3
6’	17.9	1.13 d (6,2)	5’-H	4’-H, 5’-H	4’-H, 4’-OH, 5’-H
1’’	99.1	5.58 d (1.6)	2’’-H	2’’-OH	7-H, 2’’-H
2’’	70.0	4.00 m	1’’-H, 2’’-OH, 3’’-H	1’’-H	1’’-H, 2’’-OH, 3’’-H[c]
2’’-OH		5.10 d (4.4)	2’’-H		2’’-H
3’’	70.0	3.95 ddd (9.2, 5.9, 3.3)	2’’-H, 3’’-OH, 4’’-H	1’’-H	2’’-H[c], 5’’-H[c]
3’’-OH		4.78 d (6.1)	3’’-H		
4’’	71.6	3.34[b]	3’’-H, 4’’-OH, 5’’-H		6’’-H_3
4’’-OH		4.91d (5.4)	4’’-H		
5’’	70.2	3.52 dq (9.3, 6.2)	4’’-H, 6’’-H_3	6’’-H_3	3’’-H[c], 6’’-H_3
6’’	17.9	1.12 d (6.2)	5’’-H	4’’-H	4’’-H, 4’’-OH, 5’’-H

[a]weak signals in brackets, [b]covered from water, [c]from 1D ROESY

Spectroscopic data of EmoPro1



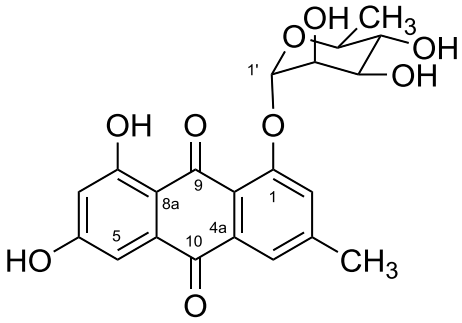
HR-ESI-MS (pos. mode):
measured: m/z = 417.11808 $[M+H]^+$, calculated m/z = 417.11801 $[M+H]^+$

NMR data: 400/100MHz (DMSO-d_6, room temperature)

Pos.	δ_C [ppm]	δ_H (*J* Hz) [ppm]	COSY	^1H,^{13}C-HMBC	NOESY
1	161.9			2-H	
1-OH		14.31 br s			
2	123.7	7.04 dd (1.8, 0.7)	3-H_3, 4-H	3-H_3, 4-H	3-H_3
3	145.0			3-H_3	
3-CH_3	21.3	2.36 s	2-H, 4-H	2-H, 4-H	2-H, 4-H
4	118.2	7.36 dd (1.8, 0.5)	2-H, 3-H_3	2-H, 3-H_3	3-H_3
4a	132.3[a]				
5	113.4	6.89 d (2.3)	7-H		
6	161.9				
7	109.7	6.42 d (2.3)	5-H		1'-H
8	160.6			1'-H	
8a	107.7			5-H, 7-H	
9	183.79				
9a	115.0			2-H, 4-H	
10	183.72			2-H, 5-H	
10a	136.3[a]				
1'	98.4	5.38 d (1.2)	2'-H		7-H, 2'-H
2'	70.2[b]	3.95[c] m	1'-H, 3'-H	1'-H, 4'-H	1'-H
3'	70.1[b]	3.94[c] m	2'-H, 4'-H	1'-H, 4'-H	5'-H
4'	71.9	3.30 dd (9.2, 9.2)	3'-H, 5'-H	2'-H, 3'-H, 6-H_3	6-H_3
5'	69.8	3.57 dq (9.2, 6.2)	4'-H, 6-H_3	1'-H, 4'-H, 6-H_3	3'-H, 6-H_3
6'	17.9	1.12 d (6.2)	5'-H	4'-H	4'-H, 5'-H

[a,b]signals exchangeable, [c]overlapping signals

Spectroscopic data of EmoPro2



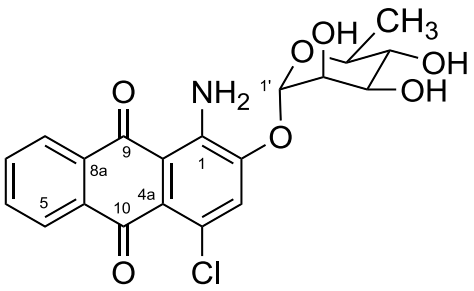
HR-ESI-MS (pos. mode):
measured: m/z = 417.11808 $[M+H]^+$, calculated m/z = 417.11801 $[M+H]^+$

NMR data: 400/100MHz (DMSO-d_6, room temperature)

Pos.	δ_C [ppm]	δ_H (*J* Hz) [ppm]	COSY	$^1H,^{13}C$-HMBC	NOESY
1	156.8			2-H, 1'-H	
2	123.4	7.52 m	3-H_3, 4-H	3-H_3, 4-H	3-H_3, 1'-H
3	146.4			2-H, 3-H_3, 4-H	
3-CH_3	21.6	2.46 s	2-H, 4-H	2-H	2-H, 4-H
4	121.5	7.68 dd (1.6, 0.6)	2-H , 3-H_3	2-H	3-H_3
4a	134.1[a]				
5	107.1	7.06 d (2.4)	7-H	7-H	
6	164.6			7-H	
7	108.2	6.58 d (2.4)	5-H	8-OH	
8	164.6			7-H	
8-OH		13.4			
8a	110.1			8-OH	
9	186.3				
9a	118.8			2-H, 4-H	
10	182.1			4-H, 5-H	
10a	136.7[a]				
1'	98.6	5.64 d (<2.0)	2'-H		2-H, 2'-H
2'	70.0	3.96 m	1'-H, 2'-OH		1'-H, 2'-OH
2'-OH		5.09 d (4.0)	2'-H		
3'	70.12[b]	3.96 m	3'-OH, 4'-H	2'-OH, 3'-OH, 4'-H	2'-OH, 5'-H
3'-OH		4.80 d (5.6)	3'-H		3'-H
4'	71.7	3.30[c]	3'-H, 4'-OH, 5'-H	4'-OH, 6'-H_3	
4'-OH		4.92 d (5.6)	4'-H		6'-H_3
5'	70.15[b]	3.52 dq (9.3, 6.2)	4'-H, 6'-H_3	1'-H6'-H_3	3'-H, 6'-H_3
6'	17.9	1.09 d (6.2)	5'-H		4'-OH, 5'-H

[a,b]signals can be exchanged, [c]covered from water

Spectroscopic data of Ant14pro1



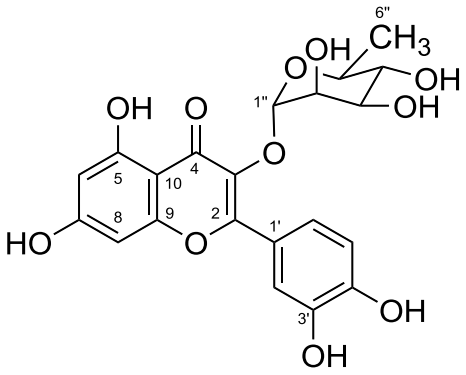
HR-ESI-MS (pos. mode):
measured: m/z = 420.08330 $[M+H]^+$, calculated m/z = 420.08446 $[M+H]^+$

NMR data: 400/100MHz (DMSO-d_6, room temperature)

Pos.	δ_C [ppm]	δ_H (*J* Hz) [ppm]	COSY	^{1}H,^{13}C-HMBC[b]	ROESY[b]
1	143.0			3-H	
2	147.8			3-H, 1'-H	
3	120.0	7.30 s			
4	122.0			3-H	
4a	122.3				
5	126.4	8.11 dd (7.4, 2.3)	6-H	6-H[c], 7-H[c]	6-H
6	133.4	7.85 ddd (7.4, 7.4, 2.5)	5-H, 8-H	5-H[d], 8-H[d]	5-H
7	133.7	7.86 ddd (7.4, 7.3, 2.3)	5-H, 8-H	5-H[b], 8-H[b]	8-H
8	126.0	8.18 dd (7.3, 2.5)	7-H	6-H[c], 7-H[c]	7-H
8a	133.8				
9	183.6			8-H	
9a	112.3				
10	180.9			(3-H), 5-H	
10a	133.7				
1'	99.2	5.65 d (1.7)	2'-H		3-H, 2'-H, 2'-OH
2'	70.0	4.01 m	1'-H, 2'-OH		1'-H, 2'-OH
2'-OH		5.21 d (4.5)	2'-H		1'-H, 2'-H
3'	70.1	3.86 m	3'-OH, 4'-H	1'-H	5'-H
3'-OH		4.70 d (5.9)	3'-H		
4'	71.8	3.3[a]	3'-H, 4'-OH, 5'-H	6'-H_3	
4'-OH		4.96 d (5.5)	4'-H		
5'	70.2	3.41 dq (9.0, 6.0)	4'-H, 6'-H_3	4'-OH, 6'-H_3	3'-H, 6'-H_3
6'	17.9	1.14 d (6.0)	5'-H		5'-H

[a]covered from water, [b]weak signals in brackets, [c]HMBC correlation to C-5 or C-8 possible (not clear resolved), [d]HMBC correlation to C-6, C-7, C-8a or C-10a possible (not clear resolved)

Spectroscopic data of QuercPro1



HR-ESI-MS (pos. mode):
measured: m/z = 449.10665 $[M+H]^+$, calculated m/z = 449.10784 $[M+H]^+$

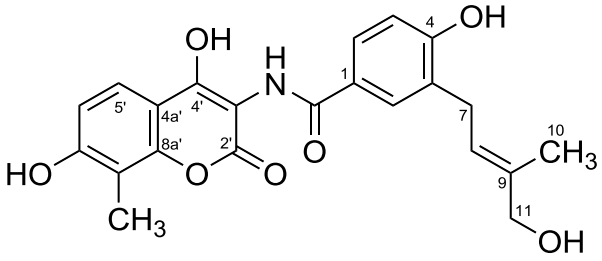
Maxima and minima of the molar circular dichroism:
QuercPro1: 1: 229 nm (−2,08), 2: 252 nm (2,27), 3: 268 nm (0,71), 4: 300 nm (−0,84), 5: 343 nm (−2,37)
3-O-α-L-rhamnosylquercetine (Roth): 1: 229 nm (−2,68), 2: 253 nm (2,15), 3: 268 nm (0,41), 4: 300 nm (−1,00) 5: 346 nm (−2,64).

NMR data: 400/100MHz (DMSO-d_6, room temperature)

Pos.	δ_C [ppm]	δ_H (*J* Hz) [ppm]	COSY	$^1H,^{13}C$-HMBC	ROESY
2	157.0			2'-H, 4'-H	
3	134.1			1''-H	
4	177.6				
5	161.1			6-H	
5-OH		12.64 br s			
6	98.9	6.22 d (2.0)	8-H	8-H	
7	165.3			6-H, 8-H	
8	93.7	6.43 d (2.0)	6-H	6-H	
9	156.4			8-H	
10	103.6			6-H, 8-H	
1'	120.6			5'-H	
2'	115.6[a]	7.33 d(2.1)	6'-H	6'-H	
3'	145.3			2'-H, 4'-H	
4'	148.6			2'-H, 5'-H, 6'-H	
5'	115.5[a]	6.89 d (8.4)	6'-H	6'-H	
6'	121.0	7.25 dd (8.4, 2.1)	2'-H, 5'-H	2'-H	
1''	101.8	5.25 d (1.3)	2''-H		2''-H
2''	70.0	3.99 m	1''-H, 3''-H	4'-H	1'-H
3''	70.4[b]	3.54 dd (9.3, 3.2)	2''-H, 4''-H	1''-H, 2''-H	
4''	71.2	3.15 dd (9.6, 9.3)	3''-H, 5''-H	3''-H, 5''-H, 6''-H_3	6''-H_3
5''	70.5[b]	3.26 dq (9.6, 6.1)	4''-H, 6''-H_3		6''-H_3
6''	17.5	0.82 d (6.1)	5''-H	4''-H	4''-H, 5''-H

[a,b]signals can be exchanged

Spectroscopic data of NovPro1



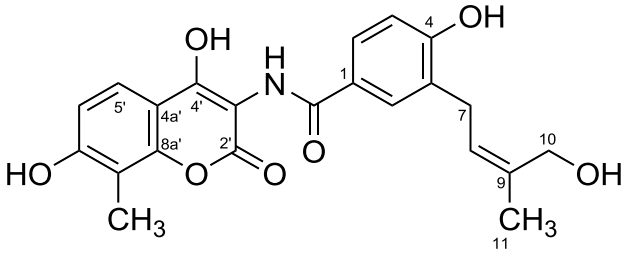
HR-ESI-MS (pos. mode):
measured: m/z = 412.13888 $[M+H]^+$, calculated m/z = 412.13908 $[M+H]^+$

NMR data: 400/100MHz (DMSO-d_6, room temperature)

Pos.	δ_C [ppm]	δ_H (*J* Hz) [ppm]	COSY	$^1H,^{13}C$-HMBC	ROESY
1	124.5			5-H	
2	129.9	7.74 d (1.7)	5-H, 7-H_2	6-H, 7-H_2	7-H_2, 8-H, 3'-NH
3	127.0			2-H, 5-H, 7-H_2	
4	158.2			2-H, 6-H, 7-H_2	
4-OH		10.05 s			5-H
5	114.2	6.85 d (8.3)	6-H		4-OH, 6-H
6	127.4	7.70 dd (8.4, 1.9)	2-H, 5-H	2-H	5-H, 3'-NH
7	27.7	3.30 d (7.3)	2-H, 10-H_3, 11-H_2	2-H, 8-H	2-H, 8-H, 10-H_3
8	121.6[a]	5.52 t (7.3)	7-H_2, 10-H_3, 11-H_2	7-H_2, 10-H_3, 11-H_2	2-H, 7-H_2, 11-H_2
9	135.9			7-H_2, 10-H_3, 11-H_2	
10	13.7	1.67 s	7-H_2, 8-H	7-H_2, 8-H	7-H_2, 11-H_2
11	66.3	3.81 br s	7-H_2, 8-H, 11-OH	8-H, 10-H_3	8-H, 10-H_3
11-OH		4.70 bs s	11-H_2		
12	166.4			2-H	
12-NH		9.04 s			2-H, 6-H
2'	[b]				
3'	99.9				
4'	161.1			5'-H	
4'-OH		[b]			
4a'	[b]				
5'	121.7[a]	7.55 d (8.6)	6'-H		6'-H
6'	111.6	6.85 d (8.5)	5'-H		5'-H, 7-OH
7'	158.7			5'-H, 8'-CH_3	
7'-OH		10.34			
8'	110.2			6'-H, 8-CH_3	
8'-CH_3	8.2	2.16 s			
8a'	151.5			5'-H, 8'-CH_3	

[a]signals can be exchanged, [b]not observed

Spectroscopic data of NovPro3



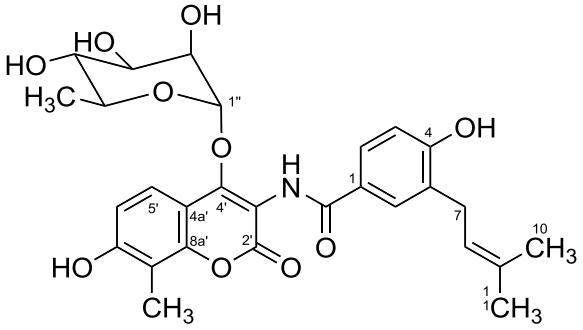
HR-ESI-MS (pos. mode):
measured: m/z = 412.13890 $[M+H]^+$, calculated m/z = 412.13908 $[M+H]^+$

NMR data: 400 MHz (DMSO-d_6, room temperature)

Pos.	δ_H (*J* Hz) [ppm]	COSY[c]	ROESY
2	7.74 m	2-H, 7-H_2	7-H_2, 8-H, 12-NH
4-OH	10.03 s		
5	6.83[a] m	6-H	4-OH, 6-H
6	7.69 dd (8.5, 2.0)	2-H, 5-H	5-H, 12-NH
7	3.3[b]	2-H, 8-H, 11-H_3	2-H, 8-H, 10-H_2
8	5.35 t (7.4)	7-H_2, 10-H_2, 11-H_3	2-H, 7-H_2, 11-H_3
10	4.06 br s	8-H, 10-OH	7-H_2, 11-H_3
10-OH	4.64 br s	10-H	
11	1.73 s	7-H_2, 8-H	8-H, 10-H_2
12-NH	8.96 s		6-H
5’	7.54 d (8.7)	6’-H, (8’-CH_3)	
6’	6.83[a] m	5’-H, (8’-CH_3)	
7’-OH	10.26 s		
8’-CH_3	2.15 s	(5’-H, 6’-H)	

[a]overlapping signals, [b]covered from water, [c]weak signals in brackets

Spectroscopic data of NovPro5



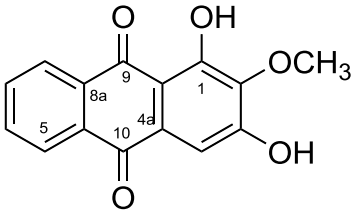
HR-ESI-MS (pos. mode):
measured: m/z = 542.20201 $[M+H]^+$, calculated m/z = 542.20207 $[M+H]^+$

NMR data: 400/100MHz (DMSO-d_6, room temperature)

Pos.	δ_C [ppm]	δ_H (*J* Hz) [ppm]	COSY[a]	$^1H,^{13}C$-HMBC	ROESY
1	125.6			5-H	
2	129.7	7.68 m		7-H_2	7-H_2, 8-H, 12-NH
3	127.1[b]			7-H_2	
4	158.2			7-H_2	
4-OH		10.01 br s			5-H
5	114.2	6.84 d (8.1)	6-H		4-OH, 6-H
6	127.3[b]	7.67 m	5-H		5-H, 12-NH, 1’’-H
7	28.1	3.26 d (6.9)	8-H, 10-H_3, 11-H_3	2-H	2-H, 8-H, 10-H_3
8	122.5	5.30 t (7.0)	7-H_2, 10-H_3, 11-H_3	7-H_2, 10-H_3, 11-H_3	2-H, 7-H_2, 11-H_3
9	131.5			10-H_3, 11-H_3	
10	17.7	1.69 s	7-H_2, 8-H	11-H_3	7-H_2
11	25.6	1.69 s	7-H_2, 8-H	10-H_3	8-H
12	166.1			12-NH	
12-NH		9.33 s			2-H, 6-H, 1’’-H
2’	[c]				
3’	94.1				
4’	161.1				
4a’	108.8			6’-H	
5’	121.3	7.49 d (8.7)	6’-H		6’-H, 1’’-H, 3’’-H, 5’’-H
6’	112.3	6.94 d (8.7)	5’-H		5’-H
7’	159.2			5’-H, 8’-CH_3	
7’-OH		10.58 br s			
8’	110.8			8’-CH_3	
8’-CH_3	8.1	2.18 s			
8a’	150.9			5’-H, 8’-CH_3	
1’’	101.4	5.70 m (<2.0)	(2’’-H)	5’’-H	2-H, 6-H, 12-NH, 2’’-H, 2’’-OH
2’’	70.1	3.86 m	(1’’-H), 2’’-OH, 3’’-H		1’’-H, 2’’-OH, 3’’-H, 3’’-OH
2’’-OH		5.05 d (4.6)	2’’-H		1’’-H, 2’’-H, 4’’-H
3’’	70.3	3.68	2’’-H, 3’’-OH, 4’’-H[d]		5’-H , 2’’-H, 3’’-OH, 4’’-OH
3’’-OH		4.79 d (5.8)	3’’-H		2’’-H, 3’’-H
4’’	71.1	3.26[d]	3’’-H, 4’’-OH, 5’’-H	6’’-H_3	2’’-OH, 4’’-OH, 6’’-H_3
4’’-OH		4.92 d (5.8)	4’’-H		3’’-H, 4’’-H, 6’’-H_3
5’’	71.4	3.56 dq (9.2, 6.0)	4’’-H[d], 6’’-H_3		5’-H, 6’’-H_3
6’’	17.7	1.05 (d, 6.0)	5’’-H		4’’-H, 4’’-OH, 5’’-H

[a]weak signals in brachets, [b]signals can be exchanged, [c]not observed, [d]covered from water

Spectroscopic data of AliPro4

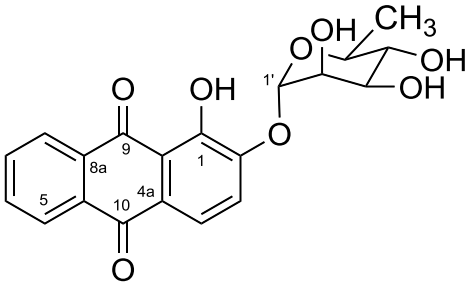


ESI-MS (neg. mode): m/z = 269.1 $[M-H]^-$

NMR data: 600/150MHz (DMSO-d_6, 35°C)

Pos.	δ_C [ppm]	δ_H (*J* Hz) [ppm]	COSY	$^1H,^{13}C$-HMBC
1	157.0			
1-OH		13.23 s (br)		
2	140.1			2-OCH_3, 4-H
2-OCH_3	58.9	3.76 s		
3	157.0			
4	114.5	6.88 s		
4a	129.3			
10	182.9			4-H, 5-H
10a	132.8			6-H, 8-H
5	126.2	8.06 dd (7.7, 1.2)	6-H	7-H
6	133.9	7.76 dd (7.7, 7.5)	5-H, 7-H	5-H
7	132.8	7.83 dd (7.7, 7.5)	6-H, 8-H	6-H, 8-H
8	125.6	8.13 dd (7.7, 1.2)	7-H	6-H
8a	134.5			5-H, 7-H
9	181.6			8-H
9a	105.7			4-H

Spectroscopic data of AliProN



ESI-MS (neg. mode) m/z = 269 $[M-H]^-$

NMR data: 600/150MHz (DMSO-d_6, 35°C)

Pos.	δ_C [ppm]	δ_H (*J* Hz) [ppm]	COSY	$^1H,^{13}C$-HMBC	ROESY[a]
1	156.6				
2	152.5			3-H, 4-H	
3	119.8	7.37 d (7.9)	4-H	4-H	1'-H
4	125.4	7.52 d (7.9)	3-H		
4a	126.6			3-H	
5	126.4	8.13 dd (7.2, 1.6)	6-H, 7-H	6-H, 7-H	6-H
6	133.9	7.86 ddd (7.3, 7.2, 1.6)	5-H, 7-H, 8-H	5-H, 8-H, ^1J	5-H
7	133.9	7.86 ddd (7.3, 7.3, 1.6)	5-H, 6-H, 8-H	5-H, 8-H, ^1J	8-H
8	126.5	8.21 dd (7.3, 1.6)	6-H, 7-H	6-H, 7-H	7-H
8a	134.1			5-H, 7-H, 8-H	
9	185.9			8-H	
9a	116.8			4-H	
10	181.3			4-H, 5-H	
10a	133.3			6-H	
1'	96.0	5.81 d (2.8)	-	2'-H_e, 5'-H	3-H, 2'-H_a, 2'-H_e,
2'	37.6	H_a: 1.69 m	2'-H_e, 3'-H	3'-H, ^1J	1'-H, 2'-H_e, 4'-H
		H_e: 2.20 dd (13.3, 6.3)	2'-H_a, 3'-H		1'-H, 2'-H_a,3'-H
3'	67.3	3.85 m	2'-H_a, 2'-H_e, 4'-H	1'-H, 2'-H_a, 4'-H, 5'-H	2'-H_e, 4'-H, 5'-H
4'	77.0	2.92 dd (9.2, 9.0)	3'-H, 5'-H	2'-H_a, 3'-H, 5'-H, 6'-H_3	2'-H_a, 3'-H, 5'-H, 6'-H_3
5'	69.2	3.53 dd (9.2, 6.4)	5'-H, 6'-H_3	1'-H, 4'-H, 6'-H_3	3'-H, (4'-H), 6'-H_3
6'	18.0	1.10 d (6.4)	5'-H	4'-H, 5'-H	5'-H, 4'-H

[a]weak signals in brackets