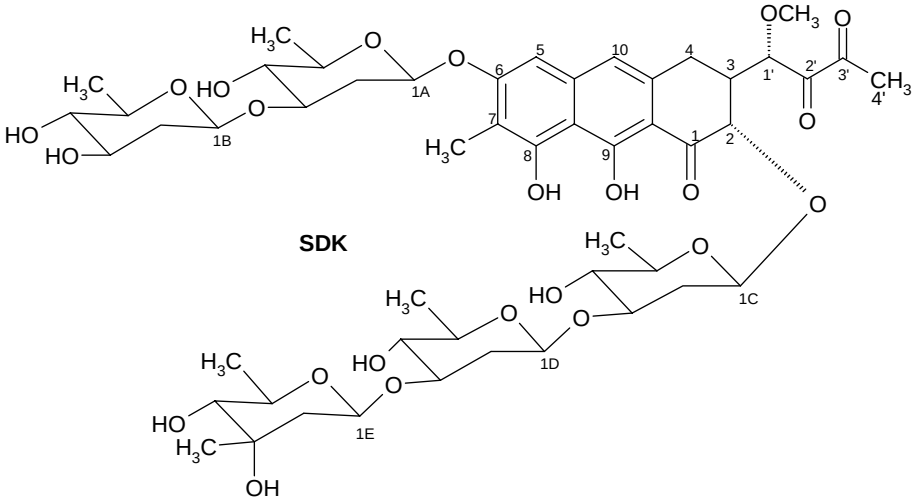
Supplemental Document S2

Physicochemical Data of Mithramycin SDK (SDK)



Mithramycin SDK

Molecular formula = 1052 ($C_{51}H_{72}O_{23}$), Positive mode ESI-MS: m/z 1075.4 (M+Na, HR: calc. for $C_{51}H_{72}O_{23}Na$: m/z 1075.4464, found: 1075.4492) Negative mode ESI-MS: m/z 1051.4 (M-H), IR (KBr): ν = 3433 (OH), 2983 (CH), 2935 (CH), 2886 (CH), 1712 (C=O), 1703 (C=O), 1600 (C=O), 1521(C=C), 1371, 1164, 1068 cm^{-1}. UV/Vis (Methanol): $\lambda_{max}(\epsilon)$ = 431 (9200), 317 (6400), 282 (55300) nm.

^{1}H-NMR (400 MHz, pyridine-d_5, TMS) and ^{13}C-NMR (100.6 MHz, pyridine-d_5, TMS) data of Mithramycin SDK.*

Position	δ ^{1}H (ppm)	Multiplicity *J* (Hz)	δ ^{13}C (ppm)	Important ^{3}J HMBC
Aglycon				
1	-	-	204.3	-
2	4.87	d (12)	78.0	1C, 4, 9a
3	3.09	dddd (12, 12, 3, 1)	43.6	1, 4a, 2’
4_{ax} 4_{eq}	3.27 2.85	dd (16, 12) dd (16, 3)	28.4	2, 10, 9a, 1’ 2, 9a, 1’
4a	-	-	136.6	-
5	7.09	S	100.9	7, 8a, 10
6	-	-	160.3	-
7	-	-	111.5	-
7-CH_3	2.44	S	9.4	6, 8
8	-	-	157.4	-
8a	-	-	109.6	-
9	-	-	166.8	-
9a	-	-	109.6	-
10	6.70	br. S	117.4	5, 8a, 9a, 4
10a	-	-	139.5	-
1’	5.49	d (1)	83.5	2, 4, -OCH_3,
1’-OCH_3	3.72	S	59.7	1’

2’	-	-	198.6	-
3’	-	-	199.5	-
4’	2.42	S	26.4	2’
Sugar A (□-D-olivose)				
1A	5.62	dd (10, 2)	98.4	6
$2A_{ax}$ $2A_{eq}$	2.16 2.51	ddd (12, 12, 10) m (overlap)	37.4	
3A	4.54	ddd (12, 9, 5)	81.3	1B
4A	3.43	dd (9, 9)	75.4	
5A	3.55	m (overlap)	72.6	
6A	1.56	d (6)	18.0	
Sugar B (□-D-olivose)				
1B	5.56	dd (10, 2)	100.2	3A
$2B_{ax}$ $2B_{eq}$	2.04 2.46	ddd (12, 12, 10) m (overlap)	40.0	
3B	4.44	m (overlap)	71.4	
4B	3.33	dd (9, 9)	77.6	
5B	3.41	dq (9, 6)	72.6	
6B	1.45	d (6)	17.7	
Sugar C (□-D-olivose)				
1C	5.39	dd (10, 2)	100.8	2
$2C_{ax}$ $2C_{eq}$	1.80 2.95	ddd (12, 12, 10) ddd (12, 5, 2)	37.9	
3C	4.09	m (overlap)	81.8	1D
4C	3.47	dd (9, 9)	75.7	
5C	3.65	dq (9, 6)	72.6	
6C	1.38	d (6)	17.9	
Sugar D (□-D-oliose)				
1D	4.74	dd (10, 2)	100.3	3C
$2D_{ax}$ $2D_{eq}$	1.79 2.43	ddd (12, 12, 10) ddd (12, 5, 2)	32.5	
3D	3.98	ddd (12, 5, 3)	77.3	1E
4D	3.53	br. S	68.9	
5D	3.63	m (overlap)	71.0	
6D	1.39	d (6)	16.5	
Sugar E (□-D-macarose)				
1E	5.34	dd (9.5, 2)	97.9	3D
$2E_{ax}$ $2E_{eq}$	2.34 2.46	dd (13, 9.5) dd (13, 2)	44.3	
3E	-	-	70.7	
$3E\text{-}CH_3$	1.93	S	27.0	2E, 4E
4E	3.09	d (9)	76.8	
5E	4.65	m (overlap)	71.0	
6E	1.57	d (6)	17.7	

* Assignments were initially based on comparison with MTM and SK, but were also independently confirmed by 2D NMR experiments, including H,H-COSY, TOCSY and HMBC; br. = broad; overlap = overlapped by other signals or solvent signals