Supporting information

Steroid glycosides hyrcanoside and deglucohyrcanoside: On isolation, structural identification and anticancer activity

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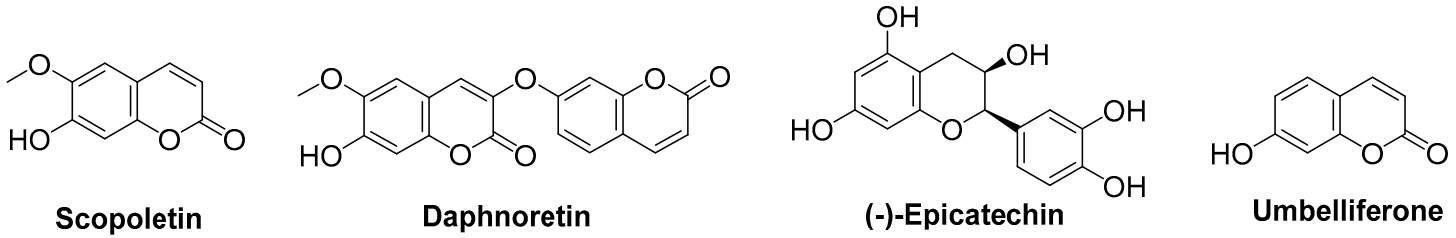


Figure S1. Other known components of *C. varia* [1]

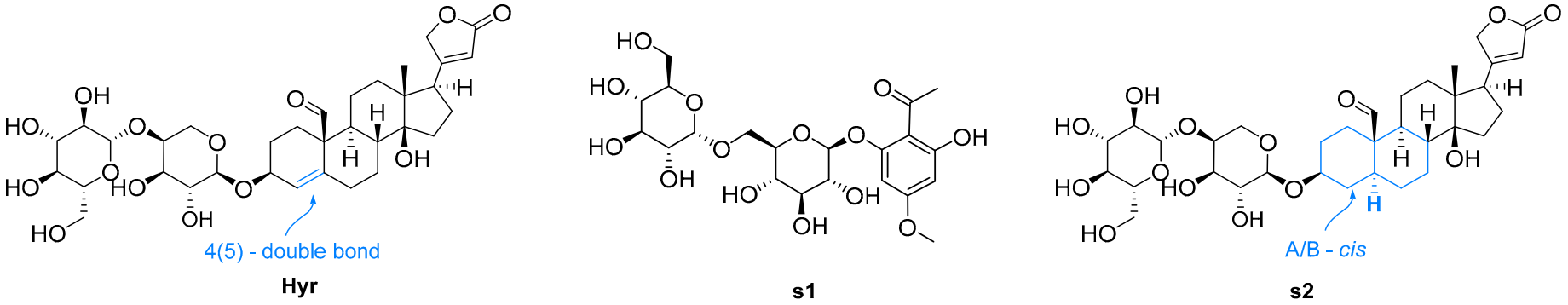


Figure S2. Structures related to different nomenclature (s1 [2, 3]; s2 [4-6])

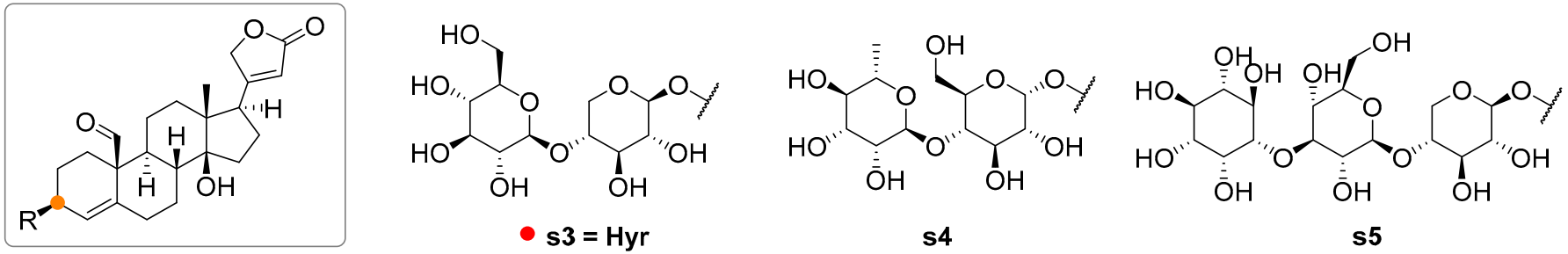


Figure S3. Structures of so-called „securigenin glycosides“ [7]

Table S1. ^{1}H and ^{13}C NMR characteristics of **Hyr** (securigenin **s3**), **deHyr**, and related securigenins **s4** and **s5** (Figure S3)

	Hyr in CD_3OD	**s3 [7] (Hyr) in CD_3OD**	**s4 [7] in CD_3OD**	**s5 [7] in CD_3OD**	**deHyr in CD_3OD**	**deHyr in DMSO-d_6**	**deHyr [8] in DMSO-d_6**	**Hyr in DMSO-d_6**	**Hyr [8] in DMSO-d_6**
C1	29.695	29.7	29.6	29.6	29.707	27.981	27.92	27.713	27.61
H1a	1.366 m covered	1.30 m	1.35 m	1.32 m	1.356 m	1.253 m		1.258 m	
H1b	2.433 m covered	2.38 m	2.44 m	2.40 m	2.432 m	2.318 m		2.323 m	
C2	28.695	28.7	28.7	28.4	28.695	27.432	27.50	27.163	27.46
H2a	2.023 m	1.99 m	2.04 m	2.01 m	2.022 m	1.875 m		1.882 m	
H2b	1.423 m	1.34 m	1.39 m	1.37 m	1.428 m	1.199 m		1.194 m	
C3	75.845	75.8	75.8	76.0	75.835	73.079	73.16	72.875	73.32
H3	4.198 ddt $^{3}J_{H3,H2b}$ = 9.4 $^{3}J_{H3,H2a}$ = 5.8 $^{3,5}J_{H3,H6b+H4}$ = 2.1	4.16 t 7.4	4.21 t 7.4	3.21 dd 8.9 8.0	4.192 dddd $^{3}J_{H3,H2b}$ = 9.5 $^{3}J_{H3,H2a}$ = 5.7 $^{3}J_{H3,H4}$ = 2.4 $^{5}J_{H3,H6b}$ = 1.7	4.076 dddd $^{3}J_{H3,H2b}$ = 9.5 $^{3}J_{H3,H2a}$ = 5.8 $^{3}J_{H3,H4}$ = 2.4 $^{5}J_{H3,H6b}$ = 1.6		4.090 ddt $^{3}J_{H3,H2b}$ = 9.6 $^{3}J_{H3,H2a}$ = 5.8 $^{4,5}J_{H3,H4+H6b}$ = 2.0	
C4	127.740 $^{1}J_{C4,H4}$ ~ 156	127.7	127.7	127.3	127.775 $^{1}J_{C4,H4}$ ~ 157	126.573	126.62	126.258	126.59
H4	5.819 dt $^{4}J_{H4,H6b}$ ~ 2.1 $^{3,4}J_{H4,H2a+H3}$ ~ 1.3	5.78 s	5.83 s	5.70 s	5.818 ~q $^{3,4}J_{H4,H2a+H3+H6b}$ ~1.7	5.699 ~q $^{3,4}J_{H4,H2a+H3+H6b}$ ~1.6		5.699 br q $^{3,4}J_{H4,H2a+H3+H6b}$ ~1.5	
C5	140.042	140.0	140.0	140.1	140.013	137.936	137.98	137.772	138.10
C6	34.153	34.1	34.1	34.1	34.154	32.546	28.05	32.303	27.92
H6a	2.317 ddd $^{2}J_{H6a,H6b}$ = 14.2 $^{3}J_{H6a,H7a}$ = 4.3 $^{3}J_{H6a,H7b}$ = 2.9	2.28 m	2.34 m	2.30 m	2.317 ~ddd $^{2}J_{H6a,H6b}$ = 14.1 $^{3}J_{H6a,H7a}$ = 4.3 $^{3}J_{H6a,H7b}$ = 2.9	2.226 ~ddd $^{2}J_{H6a,H6b}$ = 14.1 $^{3}J_{H6a,H7a}$ = 4.3 $^{3}J_{H6a,H7b}$ = 2.8		2.226 ~ddd $^{2}J_{H6a,H6b}$ ~ 14.1 $^{3}J_{H6a,H7a}$ ~ 4.3 $^{3}J_{H6a,H7b}$ ~ 2.9	
H6b	2.392 tdt $^{2,3}J_{H6b,H6a+H7a}$ ~ 13.6 $^{3}J_{H6b,H7b}$ = 4.6 $^{4,5}J_{H6b,H4+H3}$ ~ 2.1	2.33 m	2.39 m	2.35 m	2.391 tdt covered $^{2,3}J_{H6b,H6a+H7a}$ ~ 13.7 $^{3}J_{H6b,H7b}$ = 4.6 $^{4,5}J_{H6b,H4+H3}$ ~ 2.1	2.303 br t covered $^{2,3}J_{H6b,H6a+H7a}$ ~ 13.7		2.307 tdt covered $^{2,3}J_{H6b,H6a+H7a}$ ~ 13.2 $^{3}J_{H6b,H7b}$ = 4.5 $^{4,5}J_{H6b,H4+H3}$ ~ 2.0	
C7	29.366	29.3	29.3	29.3	29.370	27.754	26.36	27.511	26.39
H7a	1.139 dtd $^{2}J_{H7a,H6b}$ = 13.5 $^{2,3}J_{H7a,H7b+H8}$ ~ 12.4 $^{3}J_{H7a,H6a}$ = 4.3	1.10 m	1.15 m	1.13 m	1.140 dtd $^{2}J_{H7a,H6b}$ = 13.4 $^{2,3}J_{H7a,H7b+H8}$ ~ 12.4 $^{3}J_{H7a,H6a}$ = 4.3	0.987 dtd $^{2}J_{H7a,H6b}$ = 13.4 $^{2,3}J_{H7a,H7b+H8}$ ~ 12.2 $^{3}J_{H7a,H6a}$ = 4.3		0.987 dtd $^{2}J_{H7a,H6b}$ = 13.5 $^{2,3}J_{H7a,H7b+H8}$ ~ 12.6	

								$^{3}J_{H7a,H6a}$ = 4.3	
H7b	2.201 ddt $^{2}J_{H7b,H7a}$ = 12.6 $^{3}J_{H7b,H6b}$ = 4.6 $^{3}J_{H7b,H6a+H8}$ = 2.9	2.15 m	2.21 m	2.19 m	2.201 ddt $^{2}J_{H7b,H7a}$ = 12.6 $^{3}J_{H7b,H6b}$ = 4.6 $^{3}J_{H7b,H6a+H8}$ = 2.9	2.150 ddt $^{2}J_{H7b,H7a}$ = 12.6 $^{3}J_{H7b,H6b}$ = 4.7 $^{3}J_{H7b,H6a+H8}$ = 2.9		2.152 ddt $^{2}J_{H7b,H7a}$ = 12.5 $^{3}J_{H7b,H6b}$ = 4.3 $^{3}J_{H7b,H6a+H8}$ = 2.9	
C8	43.985	43.9	43.9	43.9	43.996	42.293	31.52	42.049	31.59
H8	1.889 td $^{3}J_{H8,H7a+H9}$ = 12.0 $^{3}J_{H8,H7b}$ = 3.1	1.84 m	1.89 m	1.86 m	1.887 td $^{3}J_{H8,H7a+H9}$ = 12.1 $^{3}J_{H8,H7b}$ = 2.9	1.682 td $^{3}J_{H8,H7a+H9}$ ~ 11.8 $^{3}J_{H8,H7b}$ = 2.9		1.683 td $^{3}J_{H8,H7a+H9}$ ~ 11.7 $^{3}J_{H8,H7b}$ = 3.0	
C9	50.806	50.8	50.8	50.7	50.814	48.808	49.86	48.563	49.89
H9	1.326 ~tm covered $^{3}J_{H9,H8+H11b}$ ~ 11.8	1.27 m	1.32 m	1.29 m	1.325 ~tm covered $^{3}J_{H9,H8+H11b}$ ~ 11.6	1.249 m covered		1.245 m covered	
C10	54.848	54.8	54.8	54.8	54.854	53.208	53.25	52.970	53.25
C11	22.759	22.7	22.7	22.7	22.761	21.226	21.32	20.980	21.29
H11a	1.695 m	1.65 m	1.70 m	1.68 m	1.705 m	1.582 m		1.583 m	
H11b	~ 1.45 m covered	1.39 m	1.43 m	1.41 m	~ 1.45 m	1.277 m		1.276 m covered	
C12	40.561	40.5	40.5	40.5	40.566	38.578	32.64	38.339	31.68
H12a	~ 1.44 m covered	1.36 m	1.41 m	1.38 m	~ 1.44 m	1.302 m		1.299 m covered	
H12b	1.539 ~dd $^{3}J_{H12b,H12a}$ ~ 9.9 $^{3}J_{H12b,H11a}$ ~ 3.2	1.49 m	1.54 m	1.52 m	1.539 ~dd $^{3}J_{H12b,H12a}$ ~ 9.5 $^{3}J_{H12b,H11a}$ ~ 3.0	1.423 ~dd $^{3}J_{H12b,H12a}$ ~ 9.8 $^{3}J_{H12b,H11a}$ ~ 2.7		1.426 m ~dd $^{3}J_{H12b,H12a}$ ~ 9.7 $^{3}J_{H12b,H11a}$ ~ 2.6	
C13	50.798	50.8	50.8	50.7	50.806	49.117	49.17	48.874	49.18
C14	85.676	85.6	85.6	85.7	85.685	83.198	83.28	82.953	83.29
OH	-				-	4.274 br s		4.274 br covered	
C15	32.701	32.7	32.7	32.7	32.703	31.453	28.05	31.208	28.05
H15a	1.627 ddd $^{2}J_{H15a,H15b}$ = 13.4 $^{3}J_{H15a,H16b}$ = 9.0 $^{3}J_{H15a,H16a}$ = 1.7	1.58 m	1.64 m	1.61 m	1.628 ddd $^{2}J_{H15a,H15b}$ = 13.4 $^{3}J_{H15a,H16b}$ = 9.1 $^{3}J_{H15a,H16a}$ = 1.8	1.507 ddd $^{2}J_{H15a,H15b}$ = 13.0 $^{3}J_{H15a,H16b}$ = 8.8 $^{3}J_{H15a,H16a}$ = 1.8		1.507 ddd $^{2}J_{H15a,H15b}$ = 12.8 $^{3}J_{H15a,H16b}$ = 8.8 $^{3}J_{H15a,H16a}$ = 1.8	
H15b	2.032 dt $^{2}J_{H15b,H15a}$ = 13.4 $^{3}J_{H15b,H16a+H16b}$ = 9.9	1.99 m	2.04 m	2.01 m	2.032 dt $^{2}J_{H15b,H15a}$ = 13.4 $^{3}J_{H15b,H16a+H16b}$ = 9.9	1.887 dt $^{2}J_{H15b,H15a}$ = 13.0 $^{3}J_{H15b,H16a+H16b}$ = 9.7		1.886 covered $^{2}J_{H15b,H15a}$ = 13.3 $^{3}J_{H15b,H16a+H16b}$ = 9.7	
C16	27.911	27.9	27.9	27.9	27.915	26.268	27.81	26.030	27.92

H16a	2.150 dtd $^{2}J_{H16a,H16b}$ = 13.3 $^{3}J_{H16a,H15b+H17}$ = 9.8 $^{3}J_{H16a,H15a}$ = 1.7	2.09 m	2.15 m	2.13 m	2.150 dtd $^{2}J_{H16a,H16b}$ = 13.4 $^{3}J_{H16a,H15b+H17}$ = 9.9 $^{3}J_{H16a,H15a}$ = 1.8	1.998 dtd $^{2}J_{H16a,H16b}$ = 13.2 $^{3}J_{H16a,H15b+H17}$ = 9.7 $^{3}J_{H16a,H15a}$ = 1.7		1.998 dtd $^{2}J_{H16a,H16b}$ = 13.0 $^{3}J_{H16a,H15b+H17}$ = 9.7 $^{3}J_{H16a,H15a}$ = 1.7	
H16b	1.870 dtd $^{2}J_{H16b,H16a}$ = 13.3 $^{3}J_{H16b,H15b+H15a}$ = 9.3 $^{3}J_{H16b,H17}$ = 5.5	1.84 m	1.89 m	1.86 m	1.870 dtd $^{2}J_{H16b,H16a}$ = 13.4 $^{3}J_{H16b,H15b+H15a}$ = 9.0 $^{3}J_{H16b,H17}$ = 5.5	1.779 dtd $^{2}J_{H16b,H16a}$ = 13.2 $^{3}J_{H16b,H15b+H15a}$ = 9.2 $^{3}J_{H16b,H17}$ = 5.3		1.775 dtd $^{2}J_{H16b,H16a}$ = 13.1 $^{3}J_{H16b,H15b+H15a}$ = 9.3 $^{3}J_{H16b,H17}$ = 5.3	
C17	51.748	51.7	51.7	51.6	51.756	49.785	48.90	49.537	48.91
H17	2.825 dd weak COSY to H22 $^{3}J_{H17,H16a}$ = 9.6 $^{3}J_{H17,H16b}$ = 5.5	2.78 dd 9.5 5.6	2.84 dd 9.5 5.6	2.81 dd 9.5 5.6	2.826 dd weak COSY to H22 and H21a $^{3}J_{H17,H16a}$ = 9.6 $^{3}J_{H17,H16b}$ = 5.5	2.726 dd weak COSY to H22 and H21a $^{3}J_{H17,H16a}$ = 9.5 $^{3}J_{H17,H16b}$ = 5.3		2.726 dd $^{3}J_{H17,H16a}$ = 9.5 $^{3}J_{H17,H16b}$ = 5.4	
C18	16.203	16.2	16.2	16.2	16.203	15.487	15.54	15.424	15.55
H18	0.892 s weak COSY to H17 and H12a	0.85 s	0.90 s	0.85 s	0.892 s	0.764 s		0.764 s	
C19	205.381	205.4	205.5	205.5	205.392	204.815	204.79	204.568	204.82
H19	9.817 s weak COSY to H9 $^{1}J_{H19,C19}$ = 173.5 $^{2}J_{H19,C10}$ = 20.5	9.78 s	9.83 s	9.83 s	9.816 d $^{4}J_{H19,H9}$ = 0.8 $^{1}J_{H19,C19}$ = 173.6 $^{2}J_{H19,C10}$ = 20.5	9.798 s weak COSY to H9 $^{1}J_{H19,C19}$ = 174.4 $^{2}J_{H19,C10}$ = 20.7		9.800 s weak COSY to H9 $^{1}J_{H19,C19}$ = 174.5 $^{2}J_{H19,C10}$ = 20.7	
C20	178.172	178.2	178.2	178.2	178.180	176.118	176.17	175.877	176.17
C21	75.319	75.3	75.3	75.3	75.324	73.122	73.23	72.881	73.16
H21a	5.020 ddd $^{2}J_{H21a,H21b}$ = 18.4 $^{4}J_{H21a,H22}$ = 1.9 $^{4}J_{H21a,H17}$ = 0.7	4.98 dd 18.4 1.6	5.04 dd 18.4 1.6	5.02 dd 18.4 1.6	5.024 ddd $^{2}J_{H21a,H21b}$ = 18.4 $^{4}J_{H21a,H22}$ = 1.8 $^{4}J_{H21a,H17}$ = 0.7	4.944 ddd [a] $^{2}J_{H21a,H21b}$ = 18.4 $^{4}J_{H21a,H22}$ = 1.9 $^{4}J_{H21a,H17}$ = 0.7		4.942 ddd $^{2}J_{H21a,H21b}$ = 18.4 $^{4}J_{H21a,H22}$ = 1.8 $^{4}J_{H21a,H17}$ = 0.7	
H21b	4.912 dd $^{2}J_{H21b,H21a}$ = 18.4 Hz $^{4}J_{H21b,H22}$ = 1.8 Hz	4.87 dd 18.4 1.6	4.93 dd 18.4 1.6	4.91 dd 18.4 1.6	4.912 dd $^{2}J_{H21b,H21a}$ = 18.4 Hz $^{4}J_{H21b,H22}$ = 1.8 Hz	4.882 dd [a] $^{2}J_{H21b,H21a}$ = 18.4 $^{4}J_{H21b,H22}$ = 1.8		4.844 dd $^{2}J_{H21b,H21a}$ = 18.4 $^{4}J_{H21b,H22}$ = 1.8	
C22	117.936 $^{1}J_{C22,H22}$ = 179.7	117.9	117.9	117.9	117.937 $^{1}J_{C22,H22}$ = 179.6	116.343	116.41	116.097	116.48
H22	5.902 td	5.87 s	5.93 s	5.90 s	5.902 td	5.912 td		5.912 td	

	$^4J_{H22,H21a+H21b}$ = 1.8 $^4J_{H22,H17}$ = 0.7				$^4J_{H22,H21a+H21b}$ = 1.8 $^4J_{H22,H17}$ = 0.7	$^4J_{H22,H21a+H21b}$ = 1.8 $^4J_{H22,H17}$ = 0.7		$^4J_{H22,H21a+H21b}$ = 1.8 $^4J_{H22,H17}$ = 0.7	
C23	177.207	177.2	177.2	177.3	177.217	173.824	173.85	173.584	173.87
C1'	104.211 $^1J_{C1',H1'}$ ~ 157	104.1	104.1	100.8	104.433 $^1J_{C1',H1'}$ = 155.8	102.797		102.259	
H1'	4.374 d $^3J_{H1',H2'}$ = 7.6	4.34 d 7.9	4.40 d 7.9	4.88 d 1.5	4.349 d $^3J_{H1',H2'}$ = 7.6	4.221 d $^3J_{H1',H2'}$ = 7.7		4.273 d $^3J_{H1',H2'}$ = 7.6	
C2'	74.804	74.7	74.7	72.4	74.948	73.264		72.875	
H2'	3.179 dd $^3J_{H2',H3'}$ = 9.2 $^3J_{H2',H1'}$ = 7.6	3.14 m	3.19 m	3.82 dd 3.1 1.6	3.123 dd $^3J_{H2',H3'}$ = 9.1 $^3J_{H2',H1'}$ = 7.6	2.885 ddd $^3J_{H2',H3'}$ = 8.8 $^3J_{H2',H1'}$ = 7.7 $^3J_{H2',OH}$ = 4.5		2.952 br td $^3J_{H2',H1'+H3'}$ = 8.3 $^3J_{H2',OH}$ = 3.6	
OH	-	-	-	-	-	4.968 br covered		5.111 br d $^3J_{OH,H2'}$ = 5.1	
C3'	76.137	76.0	76.0	74.0	77.905	76.674		74.489	
H3'	3.461 t $^3J_{H3',H2'+H4'}$ = 9.0	3.43 t 9.0	3.49 t 9.0	4.14 m	3.298 dd $^3J_{H3',H2'}$ = 9.1 $^3J_{H3',H4'}$ = 8.8	3.075 td $^3J_{H3',H2'}$ = 8.8 $^3J_{H3',OH}$ = 3.7		3.249 br td $^3J_{H3',H2'+H4'}$ = 8.9 $^3J_{H3',OH}$ = 2.5	
OH	-	-	-	-	-	4.906 br covered		4.935 br covered	
C4'	78.609	78.5	78.5	83.4	71.200	69.559		76.274	
H4'	3.665 ddd $^3J_{H4',H5b'}$ = 10.2 $^3J_{H4',H3'}$ = 8.8 $^3J_{H4',H5a'}$ = 5.3	3.63 m	3.70 m	3.63 t 9.4	3.466 ddd $^3J_{H4',H5b'}$ = 10.3 $^3J_{H4',H3'}$ = 8.8 $^3J_{H4',H5a'}$ = 5.3	3.247 ddd $^3J_{H4',H5b'}$ = 10.3 $^3J_{H4',H3'}$ = 8.8 $^3J_{H4',H5a'}$ = 5.3 $^3J_{H4',OH}$ = 4.8		3.500 ddd $^3J_{H4',H5b'}$ = 10.1 $^3J_{H4',H3'}$ = 8.8 $^3J_{H4',H5a'}$ = 5.3	
OH	-	-	-	-	-	4.914 br covered		-	
C5'	64.557	64.5	64.5	71.4	66.926	65.628		63.008	
H5a'	3.297 dd $^2J_{H5b',H5a'}$ = 11.8 $^3J_{H5b',H4'}$ = 10.1	3.96 dd 11.7 5.3	4.02 dd 11.9 2.0	3.31 m	3.189 dd $^2J_{H5b',H5a'}$ = 11.4 $^3J_{H5b',H4'}$ = 10.3	3.020 dd $^2J_{H5b',H5a'}$ = 11.2 $^3J_{H5b',H4'}$ = 10.3		3.148 dd $^2J_{H5b',H5a'}$ = 11.2 $^3J_{H5b',H4'}$ = 10.1	
H5b'	4.000 dd $^2J_{H5a',H5b'}$ = 11.7 $^3J_{H5a',H4'}$ = 5.4	3.26 m	3.31 m	-	3.824 dd $^2J_{H5a',H5b'}$ = 11.4 $^3J_{H5a',H4'}$ = 5.3	3.648 dd $^2J_{H5a',H5b'}$ = 11.2 $^3J_{H5a',H4'}$ = 5.3		3.849 dd $^2J_{H5a',H5b'}$ = 11.5 $^3J_{H5a',H4'}$ = 5.3	
C1''	103.468 $^1J_{C1',H1'}$ ~ 159	103.4	103.4	105.6				101.395	

H1''	4.355 d $^{3}J_{H1'',H2''}$ = 7.8	4.32 d 8.0	4.38 d 8.0	4.59 br s	4.251 d $^{3}J_{H1'',H2''}$ = 7.9
C2''	74.659	74.6	74.6	77.9	72.455
H2''	3.200 dd $^{3}J_{H2'',H3''}$ = 9.2 $^{3}J_{H2'',H1''}$ = 7.8	3.16 m	3.21 m	3.31 m	3.000 br td $^{3}J_{H2'',H1''+H3''}$ ~ 8.0 $^{3}J_{H2'',OH}$ ~ 2.4
OH	-	-	-	-	4.949 br covered
C3''	77.851	77.7	77.7	78.0	76.129
H3''	3.350 t $^{3}J_{H3'',H2''+H4''}$ = 8.8	3.34 m	3.39 m	3.40 m	3.138 br t $^{3}J_{H3'',H2''+H4''}$ ~ 8.5
OH	-	-	-	-	4.950 br covered
C4''	71.530	71.4	71.4	72.4	69.893
H4''	3.271 dd $^{3}J_{H4'',H5''}$ = 9.7 $^{3}J_{H4'',H3''}$ = 8.4	3.24 m	3.29 m	3.86 m	3.023 br covered
OH	-	-	-	-	4.928 br covered
C5''	78.110	78.0	78.0	68.7	76.771
H5''	3.310 ~ddd covered $^{3}J_{H5'',H6a''}$ = ~ 9.7 $^{3}J_{H5'',H6b''}$ = ~ 5.7 $^{3}J_{H5'',H4''}$ = ~ 2.1	3.28 m	3.33 m	3.70 m	3.145 ddd covered $^{3}J_{H5'',H4''}$ ~ 9.8 $^{3}J_{H5'',H6b''}$ ~ 6.4 $^{3}J_{H5'',H6a''}$ ~ 2.2
C6''	62.624	62.6	62.6	-	60.887
H6a''	3.869 dd $^{2}J_{H6a'',H6b''}$ = 11.9 $^{3}J_{H6a'',H5''}$ ~ 2.2	3.83 dd 11.9 2.0	3.89 dd 11.9 2.0	-	3.681 br dt $^{2}J_{H6a'',H6b''}$ ~ 11.5 $^{3}J_{H6a'',H5''+OH}$ ~ 2.4
H6b''	3.644 dd $^{2}J_{H6b'',H6a''}$ = 11.9 $^{3}J_{H6b'',H5''}$ = 5.9	3.60 m	3.66 m	-	3.403 br ddd $^{2}J_{H6b'',H6a''}$ ~ 11.5 $^{3}J_{H6b'',H5''}$ ~ 6.3 $^{3}J_{H6b'',OH}$ ~ 2.3
OH	-	-	-	-	4.529 br t $^{3}J_{OH,H6a''+H6b''}$ ~ 2.4

[a] The signals H21a and H21b have almost identical NOE, therefore, they were assigned based on the similarity of the chemical shifts and multiplicity.

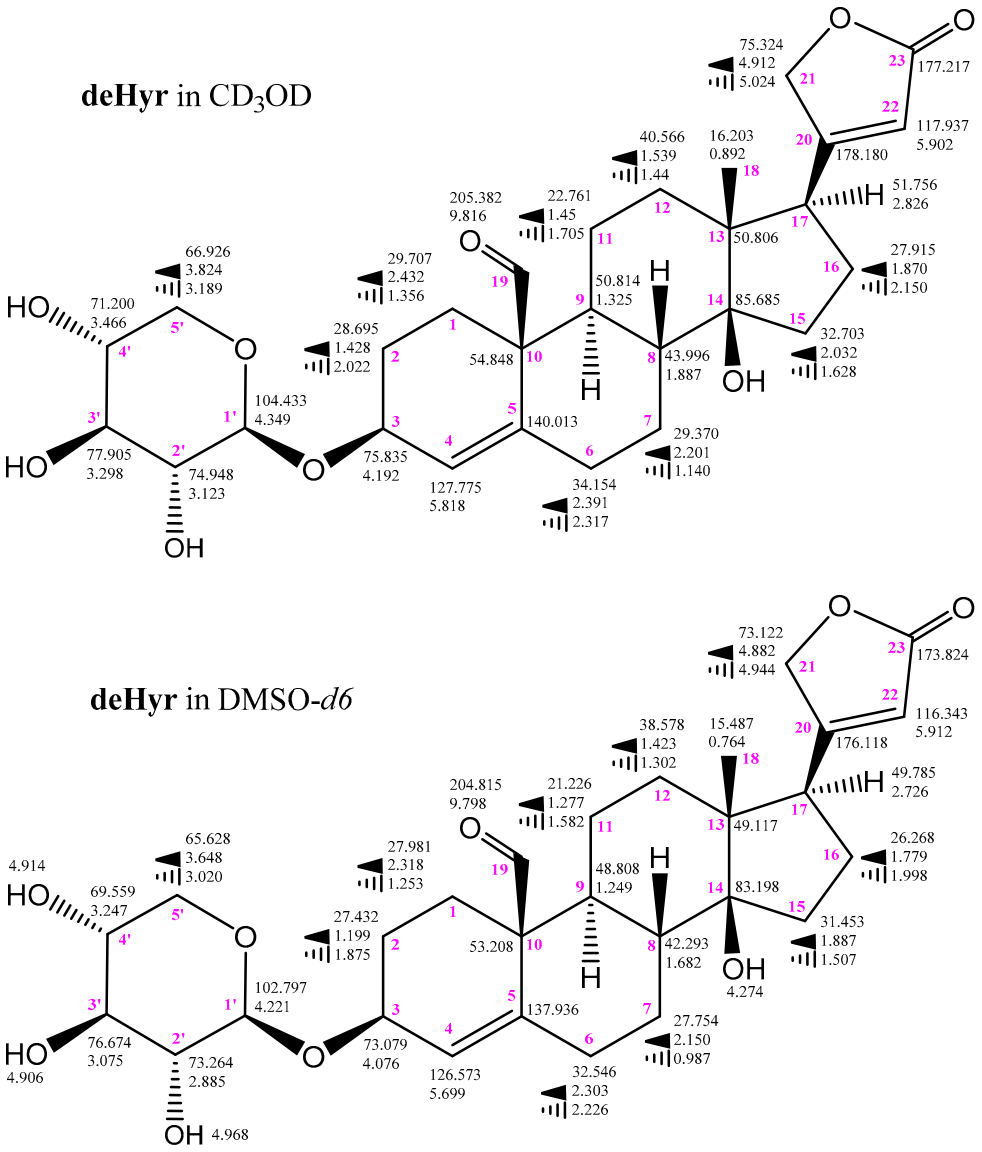


Figure S4. The ^{1}H and ^{13}C chemical shifts of **deHyr** in CD_3OD and DMSO-*d6*

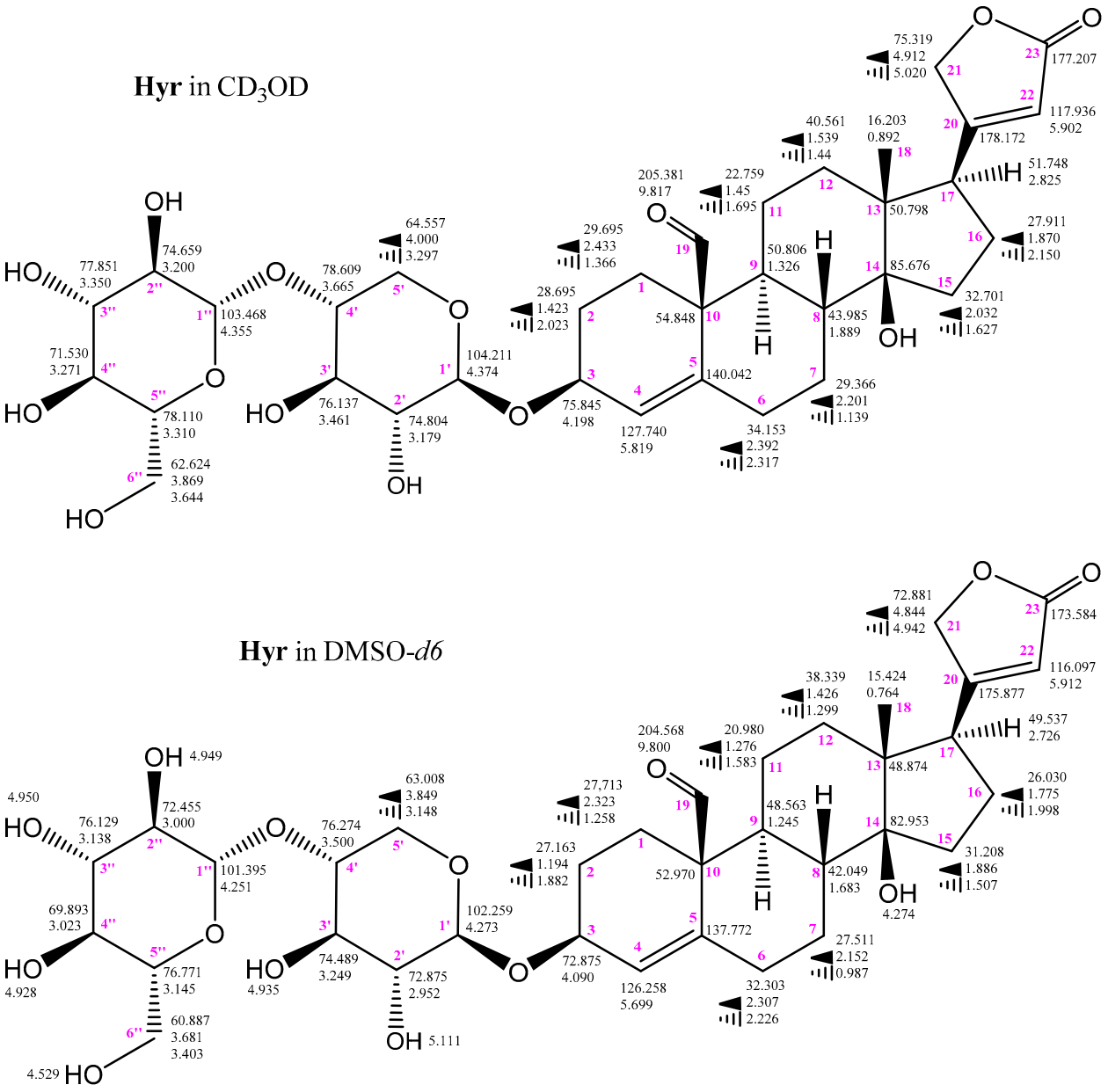


Figure S5. The ^{1}H and ^{13}C chemical shifts of **Hyr** in CD_3OD and DMSO-*d6*

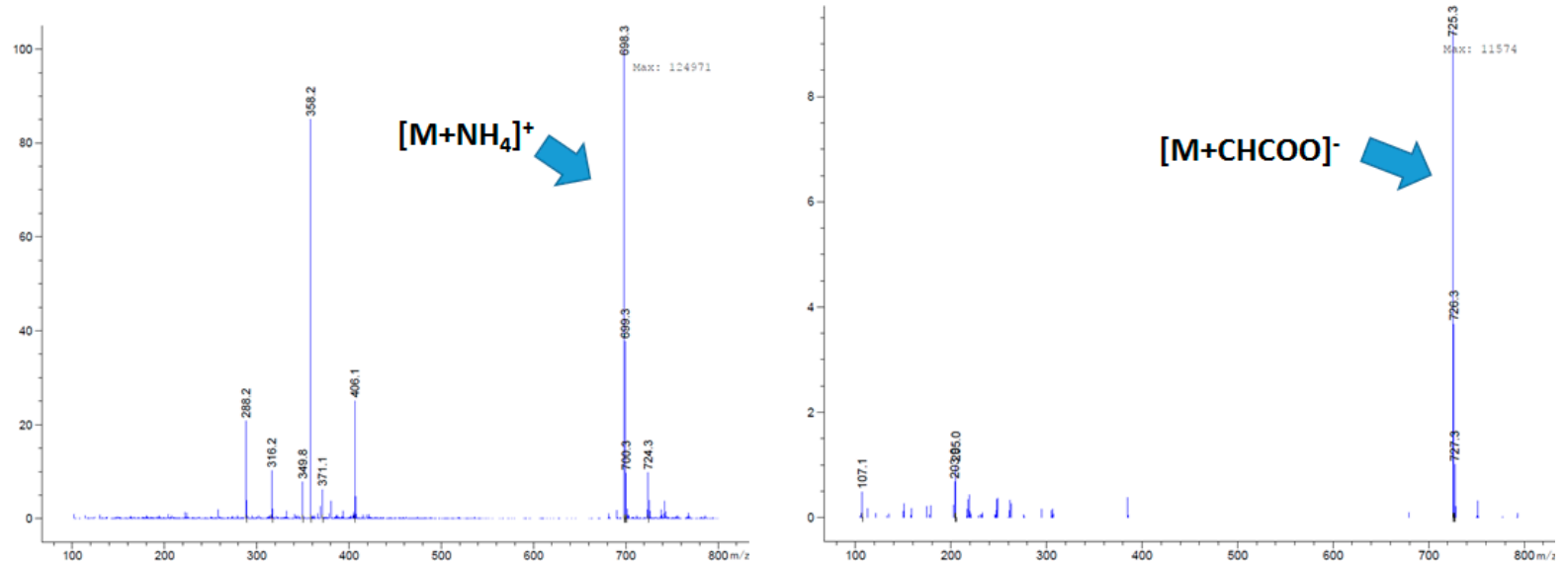


Figure S6. MS spectrum of **Hyr**

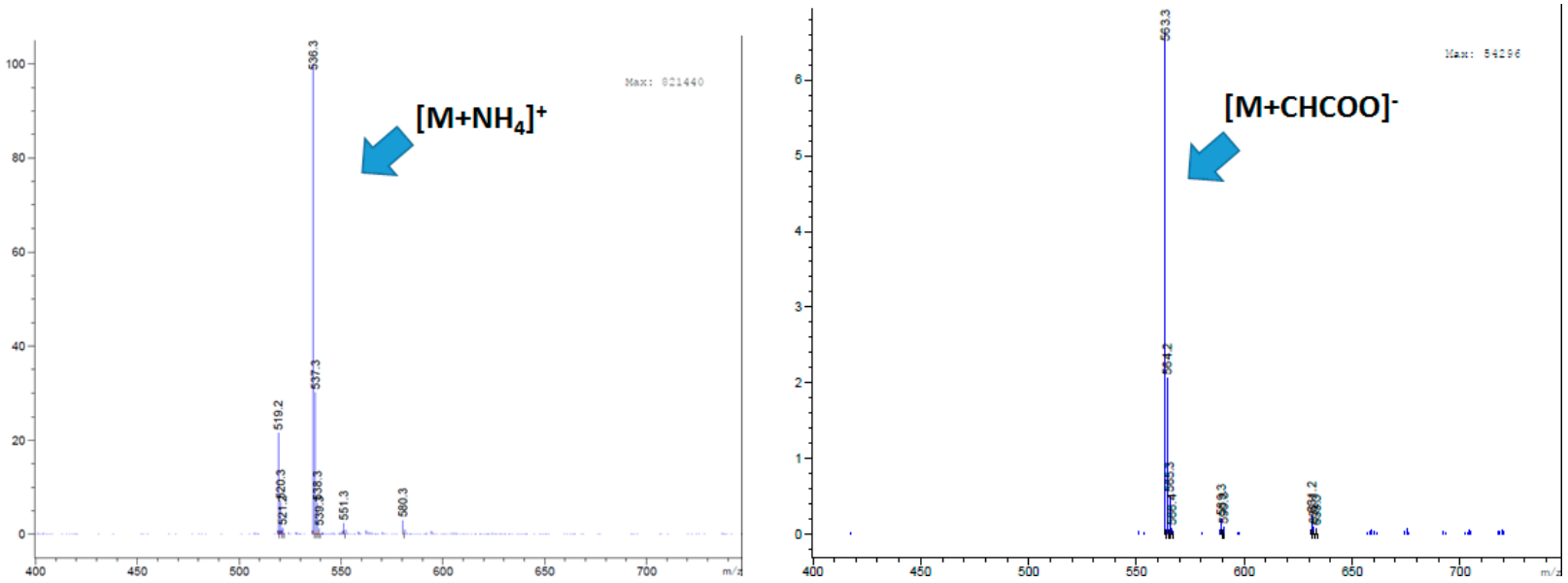
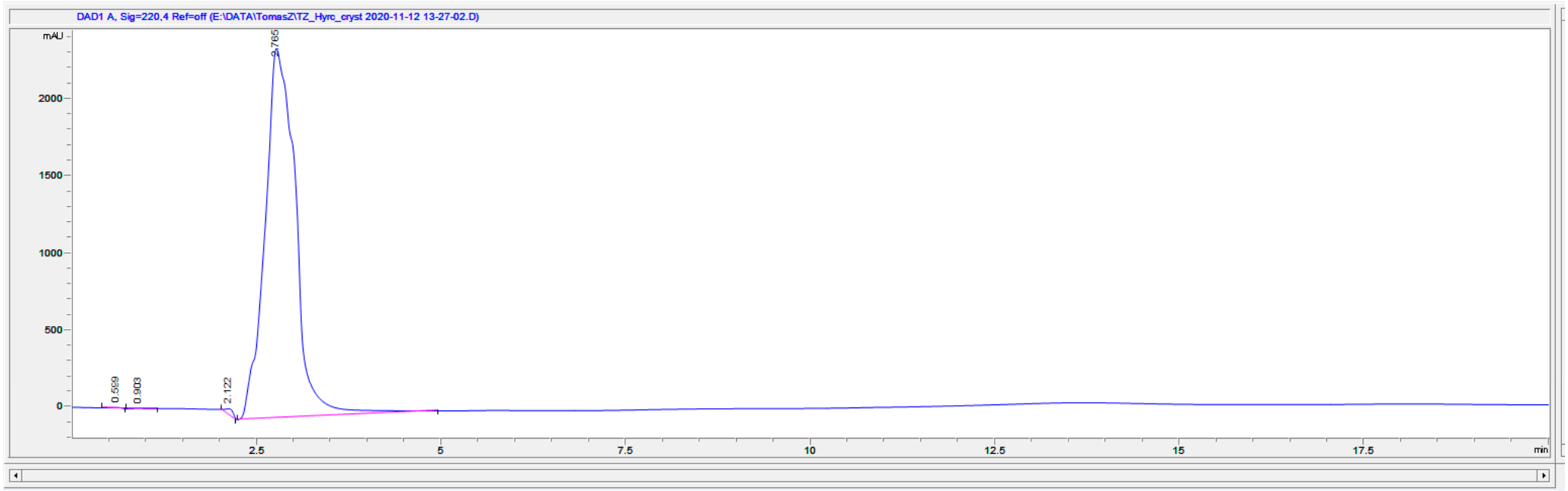


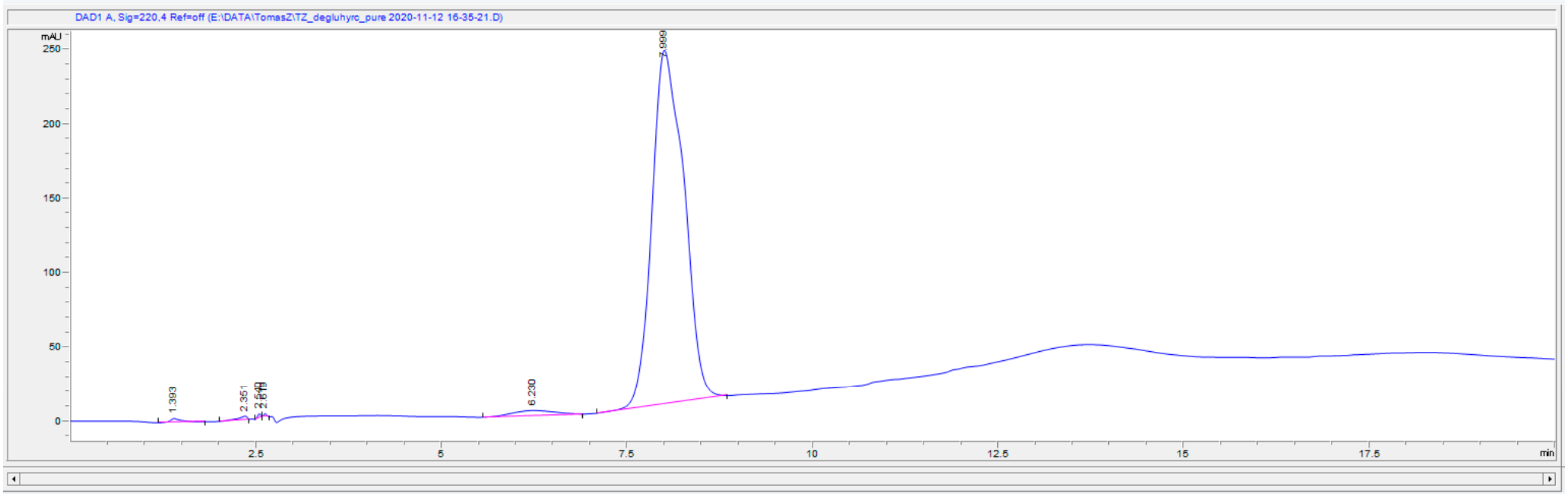
Figure S7. MS spectrum of **deHyr**



File Information	
LC-File	TZ_Hyrc_cryst 2020-11-12 13-27-02.D
File Path	E:\DATA\TomasZ
Date	12-Nov-20, 13:27:59
Sample	TZ_Hyrc_cryst
Sample Info	
Barcode	
Operator	TOmas Zimmerman
Method	Screen-H2O-to-MeOH-UV-Kamil.M
Reference	
Analysis Time	20.007 min
Sampling Rate	0.0067 min (0.402 sec), 3002 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	0.599	BB	53.6	5.3	0.1661	0.077	1.204
2	0.903	BB	26.3	1.7	0.2294	0.038	0.927
3	2.122	BB	255.2	34.5	0.1144	0.367	0.701
4	2.765	BB	69276	2394.8	0.3735	99.519	0.607

Figure S8. HPLC chromatogram of **Hyr**



File Information

LC-File	TZ_degluhyrc_pure 2020-11-12 16-35-21.D
File Path	E:\DATA\TomasZ
Date	12-Nov-20, 16:36:09
Sample	TZ_degluhyrc_pure
Sample Info	
Barcode	
Operator	TOmas Zimmerman
Method	Screen-H2O-to-MeOH-UV-Kamil.M
Reference	
Analysis Time	20.007 min
Sampling Rate	0.0067 min (0.402 sec), 3002 datapoints

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	1.393	BB	29	2.7	0.1495	0.395	0.494
2	2.351	BB	21	2.3	0.1266	0.286	3.959
3	2.54	BB	7	2.5	0.0474	0.096	1.451
4	2.619	BB	5.1	1.8	0.0468	0.069	0.746
5	6.23	BB	134.3	3.4	0.5328	1.831	0.954
6	7.999	BB	7139.8	238.2	0.4237	97.322	0.645

Figure S9. HPLC chromatogram of **deHyr**

References

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Note: *the stereo positions of hydrogen atoms were not estimated in the original article, they are suggested based on similarity of the chemical shifts to our determined values; the signals C3' and H3' are probably accidentally interchanged with the signals C5'' and H5'', resp., in the original article at least for* **Suc 1** (**Hyr**) *and* **Suc**.

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Note: *the signals C4 and H22 are probably interchanged in the original article*