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Electronic Supporting Information

Synthesis of Furostanol Glycosides: Discovery of a Potent a-Glucosidase Inhibitor

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The ¹³C NMR spectrum of **11** (CDCl₃, 150 MHz)







The ¹³C NMR spectrum of **10** (CDCl₃, 150 MHz)







The ¹³C NMR spectrum of **19** (CDCl₃, 150 MHz)







The ¹³C NMR spectrum of **20** (CDCl₃, 150 MHz)







The ¹³C NMR spectrum of 22 (CDCl₃, 150 MHz)



The ¹³C NMR spectrum of **17** (CDCl₃, 150 MHz)







The ¹³C NMR spectrum of 9 (CDCl₃, 150 MHz)







The ¹³C NMR spectrum of **23** (CDCl₃, 150 MHz)



The ¹³C NMR spectrum of 24 (CDCl₃, 150 MHz)

The ¹³C NMR spectrum of **25** (CDCl₃, 150 MHz)

The ¹³C NMR spectrum of 8 (CDCl₃, 150 MHz)

The ¹³C NMR spectrum of 26 (CDCl₃, 150 MHz)

The ¹³C NMR spectrum of **27** (CDCl₃, 150 MHz)

The ¹H NMR spectrum of **28** (CDCl₃, 600 MHz)

The ¹³C NMR spectrum of **28** (CDCl₃, 150 MHz)

The ¹³C NMR spectrum of **29** (CDCl₃, 150 MHz)

170 160 150 140 130 120 110 100 90 80 70 f1 (ppm)

220

210 200

190 180

-10

0

30

20 10

60 50 40

The ¹³C NMR spectrum of **30** (CDCl₃, 150 MHz)

The ¹³C NMR spectrum of **31** (CDCl₃, 150 MHz)

The ¹³C NMR spectrum of **32** (CDCl₃, 150 MHz)

The ¹³C NMR spectrum of **33** (CDCl₃, 150 MHz)

The ¹³C NMR spectrum of **1** (pyridine-*d*₅, 125 MHz)

¹³C NMR data for funloside B (1).

Aglycon No.	Reported	Synthesized
C-1	37.8	38.2
C-2	32.6	33.0
C-3	71.3	71.7
C-4	43.5	43.9
C-5	142.0	142.4
C-6	121.1	121.5
C-7	32.4	32.8
C-8	31.8	32.2
C-9	50.5	50.9
C-10	37.1	37.4
C-11	21.2	21.6
C-12	40.1	40.4
C-13	40.8	41.1
C-14	56.7	57.1
C-15	32.5	32.8
C-16	81.1	81.5
C-17	63.9	64.3
C-18	16.5	16.9
C-19	19.6	20.0
C-20	40.7	41.1
C-21	16.5	16.9
C-22	110.7	111.1
C-23	37.2	37.6
C-24	28.4	28.8
C-25	34.3	34.7
C-26	75.2	75.6
C-27	17.5	17.9
(26- <i>0</i>)-β-D-Glc		
1′	105.0	105.3
2'	75.3	75.7
3'	78.6	78.9
4'	71.7	72.1
5'	78.5	78.9
6'	62.9	63.2

The ¹³C NMR spectrum of **2** (pyridine- d_5 , 125 MHz)

¹³C NMR data for lilioglycoside (2).

Aglycon No.	Reported	Synthesized
C-1	37.5	38.0
C-2	30.1	30.8
C-3	78.2	78.7
C-4	39.4	39.9
C-5	141.0	141.4
C-6	121.8	122.3
C-7	32.4	32.8
C-8	31.7	32.2
C-9	50.4	50.8
C-10	37.3	37.7
C-11	21.2	21.7
C-12	40.0	40.5
C-13	40.9	41.3
C-14	56.7	57.1
C-15	32.5	32.8
C-16	81.2	81.6
C-17	63.9	64.3
C-18	16.6	17.0
C-19	19.5	19.9
C-20	40.8	41.2
C-21	16.6	16.9
C-22	110.8	111.2
C-23	37.1	37.6
C-24	28.4	28.9
C-25	34.4	34.8
C-26	75.3	75.7
C-27	17.5	18.0
(26- <i>0</i>)-β-D-Glc		
1'	105.0	105.4
2'	75.4	75.9
3'	78.7	79.1
4'	71.8	72.2
5'	78.6	79.0
6'	62.9	63.3
(3- <i>0</i>)-β-D-Glc		
1″	102.7	103.1
2″	75.4	75.9
3″	78.7	79.1
4″	71.8	72.2
5″	78.6	79.0
6″	62.9	63.3

2 2 2 2 2 2 2 2 2 2 2 2 2 2		2008839999999999999999999999999999999999		
	Aglycon No.	Reported	Synthesized	- [
	C-1	37.4	37.9	-
The ¹ H NMR	C-2	29.9	30.6	spectrum
	С-3	78.5	78.9	speenan
(pyridine- d_5 ,	Cr4	39.1	39.4	500 M
H00400H	xxxxx CL5 0 mH	141.0	141.2	-
		第985年17年数 1995年2月2日 1995年2月2日 1995年2月21日 1995年2月11日 1995年2	8 2 14 22 8 2 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	19:19 19:19
The ¹³ C MR	C-8	31.6	32.1	spectrun
ю	C-9	50.3	50.7	1
(pyridine- d_5 ,	C -10	36.9	37.6	125 M
	C -11	21.1	21.5	
	C -12	39.8	от 41.2	
	¢-13	он 40.7	но Дана 41.1	
°C NMR	С-14 он С	58.5	он 57.0	data for
	€-15 но Дост	32.2	32.9	
protobioside I	С-16 но	в 80.7	81.5	(3).
	С-17 С-18 м.	M MARINA A	641.B	"/W.
	¢-19	19.2	19.8	
	€-20 <u></u>	™ ⁻ <u>- </u> <u>-</u> <u>-</u> <u>-</u> <u>-</u> <u>-</u> <u>-</u> <u>-</u> <u>-</u> <u>-</u>		2.31 2.37 4.50 4.50
9.0 8.5 8.0	7.1 7.0 C-2 .1 6.0 5	.5 5.0 16.0 4.0 3.5	3.0 2.516.80 1.5	1.0 0.5
	C -22	^{f1} (ppm) 110.7	111.0	-
	C -23	36.8	37.5	
	C- 24	28.1	28.8	-
	C- 25	34.0	34.7	
<u>_</u>	L ₫+26	75111111	1 1 7516 1111	<u> </u>
	C-27	17.2	17.9	-
	(26- <i>0</i>)-β-D-Glc			
170 160 150 14	40 130 1 120 110	100 90 1040.7 70 6 f1 (ppm)	o 50 10 9 .4 30	20 10
	2'	75.1	75.7	
	3'	78.5	78.7	
	4'	71.9	72.1	
	5'	78.1	78.2	
	6'	63.0	63.2	
	(3- <i>0</i>)-β-D-Glc	100 -		
	1″	100.5	100.8	
	2″	79.5	80.1	
	3″	78.1	78.3	
	4″	72.1	72.2	
	5"	77.9	78.2	
	6"	62.9	63.1	
	(Glc²)-α-L-Rha			
	1′″	101.8	102.5	
	2′″	72.4	73.0	
	3′″	72.8	73.2	
	4′″	74.2	74.6	
	5′″	69.3	69.9	
	6'"	18.5	191	

The ¹H NMR spectrum of **4** (pyridine- d_5 , 500 MHz)

The ¹³C NMR spectrum of **4** (pyridine-*d*₅, 125 MHz)

¹³C NMR data for protodioscin (4).

Aglycon No.	Reported	Synthesized
C-1	37.5	37.9
C-2	30.2	30.6
C-3	78.5	78.9
C-4	39.0	39.4
C-5	140.8	141.2
C-6	121.8	122.2
C-7	32.2	32.7
C-8	31.7	32.1
C-9	50.4	50.7
C-10	37.1	37.6
C-11	21.0	21.5
C-12	39.9	41.2
C-13	40.8	41.1
C-14	56.6	57.0
C-15	32.3	32.9
C-16	81.1	81.5
C-17	63.8	64.2
C-18	16.3	16.9
C-19	19.4	19.8
C-20	40.7	40.3
C-21	16.4	16.9
C-22	110.7	111.0
C-23	30.0	30.6
C-24	28.3	28.8
C-25	34.4	34.7
C-26	75.0	75.6
C-27	17.5	17.9
(26- <i>0</i>)-β-D-Glc		
1'	105.1	105.3
2'	75.2	75.7
3'	78.4	78.9
4'	71.7	72.1
5'	78.3	78.4
6'	62.9	63.2
(3- <i>0</i>)-β-D-Glc		
1″	100.3	100.7
2″	78.1	78.2
3″	76.9	77.3
4″	77.9	78.2
5″	77.8	78.2
6″	61.3	61.7
(Glc²)-α-L-Rha		
1′‴	102.0	102.4
2′″	72.5	72.9
3′″	72.7	73.1
4′″	74.1	74.5
5′″	69.5	69.9
6′″	18.6	19.0
(Glc ⁴)-α-L-Rha		
1‴″	102.9	103.3
2""	72.5	72.9
3""	72.8	73.1
4""	73.9	74.3
5""	70.4	70.8
6""	18.5	18.9

¹³C NMR data for pallidifloside I (5).

Aglycon No.	Reported	Synthesized
C-1	37.2	37.9
C-2	29.9	30.6
C-3	77.8	78.6
C-4	38.7	39.4
C-5	140.4	141.2
C-6	121.6	122.2
C-7	32.1	32.9
C-8	31.4	32.1
C-9	50.0	50.7
C-10	36.9	37.6
C-11	20.8	21.5
C-12	39.7	40.3
C-12	40.4	40.5
C-15	56.2	50.7
C-14	20.5	30.7
C-15	32.2 91.1	32.9 91.0
C-10	61.1	61.9
C-1/	63.6	64.3
C-18	16.2	16.9
C-19	19.1	21.5
C-20	40.5	41.2
C-21	16.2	16.9
C-22	110.4	111.0
C-23	37.0	37.6
C-24	28.1	28.8
C-25	34.0	34.7
C-26	75.0	75.7
C-27	17.2	17.9
(26- <i>0</i>)-β-D-Glc		
1'	104.7	105.4
2'	74.9	75.6
3'	78.3	78.9
4'	71.4	72.1
5'	78.3	78.9
6'	62.5	63.2
(3-0)-B-D-Glc		
1"	99.7	100.5
2"	77.2	77.9
3"	77.0	ר דר
<u> </u>	80.8	81.5
	76.0	76.6
5	61.2	62.1
(Cla2) or L Bha	01.5	02.1
(GIC ⁻)-α-L-KΠa	101.7	102.4
2///	101./	102.4
2	12.2	72.9
3'''	/2.5	73.2
4′′′	73.9	74.5
5'"	69.3	69.9
6'''	18.5	19.1
(Glc ⁴)-β-D-Xyl-		
1""	105.5	106.2
2""	74.7	75.4
3""	78.1	78.8
4""	70.5	71.2
5""	67.1	67.8

The ¹³C NMR spectrum of **6** (pyridine-*d*₅, 125 MHz)

Aglycon No.	Reported (in CD ₃ OD)	Synthesized (in C ₅ D ₅ N)*	Methyl coreajaponins A (in C ₅ D ₅ N)**
C-1	37.1	37.7	37.4
C-2	29.3	30.6	30.1
C-3	77.9	79.0	78.5
C-4	39.4	39.5	39.2
C-5	140.4	141.2	140.8
C-6	121.2	122.3	121.5
C-7	31.7	32.8	32.2
C-8	31.3	32.1	31.6
C-9	50.2	50.8	50.3
C-10	36.6	37.6	37.1
C-11	20.5	21.6	21.1
C-12	39.4	40.4	39.7
C-13	40.4	41.2	40.7
C-14	56.3	57.1	56.5
C-15	31.3	32.2	32.0
C-16	81.0	81.9	81.3
C-17	63.6	64.3	64.1
C-18	15.3	18.0	17.1
C-19	18.4	19.9	19.3
C-20	39.7	41.3	41.2
C-21	14.6	16.9	16.2
C-22	112.5	111.1	112.6
C-23	29.9	30.7	30.6
C-24	27.5	28.9	28.1
C-25	33.5	34.8	34.2
C-26	74.5	75.7	75.1
C-27	15.8	19.2	18.6
(26- <i>0</i>)-β-D-Glc			
1'	103.1	105.4	104.9
2'	74.7	75.7	75.1
3'	76.7	78.7	78.3
4'	70.3	72.2	71.7
5'	76.4	79.0	78.6
6'	61.4	63.3	62.5
(3- <i>0</i>)-β-D-Glc			
1″	98.9	100.5	100.1
2″	77.0	78.0	77.8
3″	77.1	77.8	77.3
4″	79.5	81.9	81.4
5″	76.1	76.7	76.3
6″	60.4	62.1	61.6
(Glc²)-α-L-Rha			
1′″	100.5	102.5	102.5
2′″	70.7	73.0	72.5
3′″	71.1	73.3	72.8
4′″	72.9	74.6	74.2
5′″	68.5	70.0	69.4
6'''	16.5	19.2	18.9
(Glc ⁴)-β-L-Arap			
1‴″	104.0	106.4	105.9
2""	70.9	73.0	72.6
3""	73.7	75.0	74.6
4""	68.3	70.0	69.6
5""	66.3	68.3	67.8

¹³C NMR data for Coreajaponins A (6).

* ¹³C NMR data for synthesized **6** (in C_5D_5N) are different from the reported coreajaponins A (in CD₃OD), which are ascribed to solvent effect. However, the acquired ¹³C NMR data are in agreement with those for Coreajaponins B (Methyl coreajaponins A) except that for C-22. ** ¹³C NMR data for Coreajaponins B.

The ¹H NMR spectrum of 7 (pyridine- d_5 , 500 MHz)

The ${}^{13}C$ NMR spectrum of 7 (pyridine- d_5 , 125 MHz)

Aglycon No.	Reported	Synthesized	
C-1	37.5	37.9	
C-2	30.2	30.6	
C-3	78.2	78.5	
C-4	39.0	39.4	
C-5	140.8	141.1	
C-6	121.9	122.2	
C-7	32.4	32.7	
C-8	31.7	32.1	
C-9	50.4	50.7	
C-10	37.2	37.5	
C-11	21.2	21.5	
C-12	40.0	40.3	
C-13	40.7	41.1	
C-14	56.6	56.9	
C-15	32.5	32.9	
C-16	81.1	81.5	
C-17	63.9	64.2	
C-18	16.5	16.8	
C-19	19.4	19.8	
C-20	40.8	41.1	
C-21	16.5	16.8	
C-22	110.7	111.0	
C-23	37.2	37.5	
C-24	28.4	28.8	
C-25	34.3	34.7	
C-26	75.3	75.7	
C-27	17.5	17.9	
(26- <i>0</i>)-β-D-Glc			
1'	105.0	105.3	
2'	75.2	75.6	
3'	78.6	79.0	
4'	71.7	72.1	
5'	78.5	78.9	
6'	62.9	63.2	
(3- <i>0</i>)-β- _D -Glc			
1"	100.2	100.6	
2″	77.4	77.8	
3″	77.7	78.1	
4″	77.1	77.4	
5″	76.7	77.1	
6"	61.4	61.7	
(Glc ²)-α-L-Rha	0111	01.7	
1′″	101.9	102.3	
2'"	72.5	72.8	
3'"	72.5	73.2	
4'''	74.2	74.5	
	69.5	60.0	
5 6'''	18 7	10.1	
(Glc ⁴)-a-L-Araf	10./	17.1	
1""	100.7	110.0	
2""	109.7	110.0	
2""	82.7 78.0	83.1	
5	/8.0	/8.3	
4	80./	87.1	

¹³C NMR data for Parisaponin I (7).