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Diacylated Triterpenoid Saponin from *Silene szechuensis*

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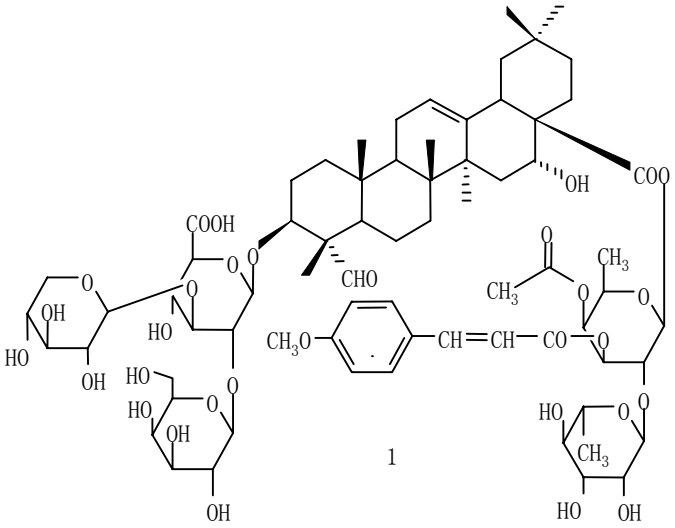
Abstract: A new triterpenoid saponin, named silenoside, with sugar chains esterified by two different acyl groups was isolated from *Silene szechuensis*. Its structure was elucidated by chemical and spectral methods.

Keywords: Silenoside, acylated triterpenoids saponin, *Silene szechuensis.*

The root of *Silene szechuensis* is a Chinese traditional medicine which can be used to treat gastralgia[1]. From ethanolic extract of the plant a new diacylated triterpenoid saponin, silenoside **1**, was isolated. The structure of the saponin was elucidated after derivatives **2**~**10** were obtained. Selective cleavage of the bisdesmoside with glycyrrhizin hydrolase[2] afforded a trisaccharide **2** and a diacylated monodesmoside **3**.



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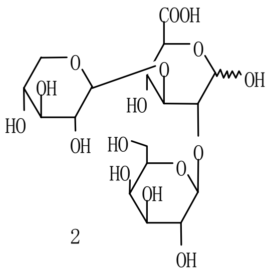
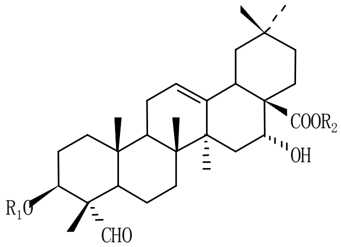
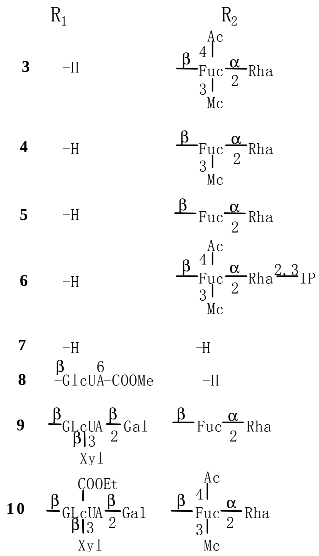

Ac=acetyl, MC=methoxy cinnamoyl, IP=isopropylidene, Fuc=fucose, Rha=rhamnose, GlCUA=glucuronic acid, Gal=galactose, Xyl=xylose

Table 1. ^{13}C NMR Chemical Shifts (aglycone m78 oiety)

C	1	2[a]	3	4	5	6	7	8	10
1	38.3		38.8	38.8	38.9	38.8	38.6	38.2	38.2
2	25.1		27.1	27.2	27.2	27.2	27.1	25.2	25.1
3	78.6		71.7	71.7	71.8	71.7	71.7	82.1	78.3
4	55.4		56.4	55.4	56.5	56.4	56.3	55.5	54.9
5	48.7		47.9	48.0	48.1	48.0	47.9	47.9	48.5
6	20.6		21.2	21.3	21.3	21.2	21.1	20.5	20.5
7	32.9		33.0	33.0	33.0	33.1	32.9	32.8	32.9
8	40.5		40.5	40.6	40.6	40.6	40.3	40.1	40.2
9	47.1		47.2	47.3	47.3	47.2	47.2	47.9	46.8
10	36.4		36.3	36.3	36.3	36.3	36.2	36.2	36.1
11	23.9		23.9	24.0	24.0	24.0	23.8	23.8	23.6
12	122.4		122.4	122.3	122.2	122.6	122.1	122.1	122.0
13	144.6		144.5	144.7	144.9	144.4	145.2	145.4	144.3
14	42.3		42.3	42.4	42.4	42.4	42.2	42.2	42.3
15	36.1		36.0	36.0	36.2	36.0	36.1	36.1	36.8
16	74.0		74.0	74.0	74.1	74.0	74.7	74.7	73.7
17	49.6		49.6	49.6	49.6	49.6	48.9	48.9	49.3
18	41.7		41.4	41.7	41.8	41.7	41.5	41.5	42.0
19	47.6		47.6	47.6	47.8	47.4	47.3	47.3	46.8
20	30.9		30.8	30.8	30.9	30.9	31.0	31.0	30.6
21	36.4		36.3	36.3	36.3	36.3	36.2	36.2	36.1
22	32.9		33.0	33.0	33.0	33.1	32.8	32.8	32.7
23	209.9		207.4	207.4	207.4	207.3	207.2	206.8	209.7
24	11.5		9.8	9.8	9.8	9.7	9.7	10.4	10.9
25	16.0		16.0	16.0	16.1	16.1	15.8	15.9	15.7
26	17.5		17.5	17.5	17.5	17.6	17.5	17.4	17.2
27	27.1		27.1	27.1	27.2	27.2	27.2	27.2	26.8
28	175.9		175.9	175.9	176.2	175.9	179.9	180.0	176.1
29	33.3		33.2	33.2	33.4	33.2	33.3	33.4	33.0
30	24.7		24.6	24.6	24.7	24.7	24.1	24.8	24.4

Table 1. ^{13}C NMR Chemical Shifts (sugar moiety)

C	1	2[a]	3	4	5	6	7	8	10
GlcUA-1	103.9	94.7						105.2	103.7
2	84.6	81.9						75.0	80.4
3	86.3	82.9						77.8	85.6
4	72.6	73.3						73.0	73.7
5	75.0	74.3						77.2	75.2
6	b	179.4						170.6	169.2
COOMe /COOEt								52.1	65.6
									15.3
Gal-1	104.3	105.8							104.0
2	73.8	73.9							74.7
3	75.3	75.7							76.3
4	71.5	71.6							71.7
5	76.8	77.9							78.2
6	61.9	63.8							61.2
Xyl-1	105.9	106.7							104.7
2	75.6	76.3							76.5
3	77.4	78.8							78.3
4	72.5	72.2							73.4
5	67.9	67.9							67.1
Fuc-1	94.5		94.5	95.0	95.1	94.1			94.1
2	75.0		74.9	74.1	76.9	74.4			75.0
3	70.9		70.9	74.9	73.5	71.9			70.6
4	71.3		71.2	71.0	73.3	71.2			70.9
5	70.5		70.4	72.4	72.3	70.5			70.8
6	16.3		16.3	16.7	17.1	16.3			16.0
Rha-1	103.3		102.3	102.0	101.4	98.1			102.0
2	72.0		71.9	72.3	72.5	76.8			72.0
3	72.4		72.3	72.5	72.6	79.7			73.4
4	73.9		73.6	73.8	73.8	68.2			74.7
5	70.3		70.3	70.2	69.9	75.3			69.9
6	18.9		18.8	19.0	18.8	18.4			18.6
Me_2C						109.3			
						26.5			
						28.3			

Table 1. ^{13}C NMR Chemical Shifts (acyl moiety)

C	1	2[a]	3	4	5	6	7	8	10
MC-1	166.4		166.4	166.7		166.3			166.1
	167.3		167.3	167.7		167.3			167.0
2	116.1		116.0	117.0		116.0			115.7
	115.3		105.3	116.2		115.2			145.9
3	145.3		145.2	144.1		144.4			115.1
	146.3		146.1	145.3		145.4			145.9
4	127.8		127.7	127.7		127.7			127.4
	127.5		127.4	127.5		127.4			127.1
5, 9	130.7		133.3	133.3		133.3			130.4
	133.3		130.7	130.5		130.7			133.1
6, 8	115.0		114.1	114.0		114.2			114.9
	114.2		114.9	114.8		114.9			133.9
7	161.4		161.3	161.1		161.4			161.5
	162.3		162.2	162.0		162.3			161.9
10	55.3		55.4	55.3		55.4			55.2
	55.6		55.5	55.5		55.5			55.3
Ac	20.8		20.7			20.9			20.5
	170.3		170.2			170.1			170.0

a: recorded in D_2O. b: not observed.

And the structure elucidation was remarkably simplified. The acquisition of a monoacylated prosapogenin **4** from mild alkaline saponification of **3** was also crucial for the study. FAB-MS and 2D NMR techniques including ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY, COLOC were used to determine the linking pattern of sugars. Acylation shifts[3] were used to determine the position of the acyl groups. ^{13}C NMR data (Py-d_5, 400 MHz) were shown in **Table 1**.

Acknowledgment

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