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Two New Iridoid Glucosides from *Clerodendrum serratum*

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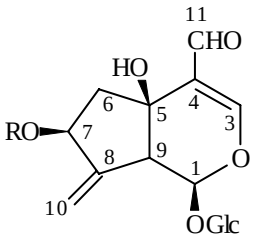
Abstract: Two new iridoid glucosides, named 7β -coumaroyloxyugandoside (**1**) and 7β -cinnamoyloxyugandoside (**2**) were isolated from the leaves of *Clerodendrum serratum*, and their structures were elucidated by spectral means.

Keywords: *Clerodendrum serratum*, Verbenaceae, iridoid glucoside, 7β-coumaroyloxyugandoside (**1**), 7 β -cinnamoyloxyugandoside (**2**).

Clerodendrum serratum called as "San Dui Jie" in Chinese, is a small shrub with fragrant flowers found widely in the forests of the south of China. It has been used as a folk medicine in Yunnan for treatment of many diseases such as hepatitis and malaria. In order to find the bioactive components, studies on the chemical constituents of the leaves of *Clerodendrum serratum*, collected at Long Ling of Yunnan province, were carried out. We have reported two new glycosides previously[1]. Now, further investigation of glycosides of this plant resulted in two new iridoid glucosides 7 β-coumaroyloxyugandoside (**1**) and 7 β -cinnamoyloxyugandoside (**2**).

Figure 1 Structure of compounds **1** and **2**



1. R= *p*-coumaroyl

2. R = cinnamoyl

7 β -coumaroyloxyugandoside (**1**)**:** crystalline prisms mp. 168-170°C. The FAB-MS data (*m/z* 527 $[M+Li]^+$; 543 $[M+Na]^+$), ^{1}HNMR, ^{13}CNMR and DEPT data established its formula to be $C_{25}H_{28}O_{12}$. Its IR spectrum indicated the presence of a enol ether system (1621cm^{-1}), an aldehyde function (1681cm^{-1}) and an ester group (1731cm^{-1}). The UV spectrum revealed the presence of an α, β unsat. ester [314 nm,242 nm (MeOH)]. Its FAB-MS data *m/z* 358 $[M\text{-glu}]^+$, EIMS data *m/z* 193 [M-glu-(*p*-coumaroyl-)-H_2O], ^{1}HNMR and ^{13}CNMR spectra confirmed the presence of one glucose and *p*-coumaroyloxy-moiety. All protons and carbons signals (see **Table 1**) of compound **1**

can be assigned by the analysis of its 1D and 2D NMR spectra (H-H COSY, HMBC, HMQC and NOE), and by further comparison with those of ugandoside[2], 7 β -coumaroyltecomoside and tecmoside[3] and strictoloside[4]. According to the results of HMBC spectrum, the *p*-coumaroyloxy- was attached to C-7, not to the sugar part , because C-10 was related to H-7, -C=O to H-7 and C-4 related to H-6. The HMQC NMR of **1** showed that the carbon at δ72.66 was related to the hydrogen at δ5.16. If the coumaroyloxy was attached to sugar part, the chemical shift of H-7 would be upfield (<δ4.9)[2-4]. The stereochemistry of C-7 was determined as β orientation , mainly by NOESY (H-7 relate to H-6 α).

7 β -cinnamoyloxyugandoside (**2**)**:** powderline prisms mp: 132-134°C. Its formula was established as $C_{25}H_{28}O_{11}$ by FAB-MS data (*m/z* 511 $[M+Li]^+$ and 527 $[M+Na]^+$), ^{1}HNMR, ^{13}CNMR and DEPT. The UV spectrum of compound **2** was closely to that of **1**. The difference of its IR spectrum was an additional peak at 857cm^{-1} for mono-substituted and no the peak at 832 cm^{-1} and 980cm^{-1}. The NMR spectra of **2** were very similar to those of **1** (see **Table 1**), except that the former had signals of a cinnamoyl moiety instead of the coumaroyl group.

Table 1. ^{1}HNMR, ^{13}CNMR chemical shift of 1 and 2 (DMSO-*d6*, 400MHz)

C	1*	2	H	1*	2
1	95.04	95.08	1	5.93 *d* (1.1)	5.94 *d* (1.2)
3	163.29	163.34	3	7.54 *s*	7.55 *s*
4	122.19	122.24	6α	1.87 *dd* (12.4, 9.6)	1.89 *dd* (11.4, 9.3)
5	68.01	68.07	6β	3.03 *d* (9.2)	3.05 *d* (9.2)
6	40.66	40.73	7α	5.16 *m*	5.21 *m*
7	72.66	72.91	9	2.95-2.99	2.96-3.01
8	145.62	145.52	10	5.32 *s*	5.34 *s*
9	51.61	51.65	11	9.26 *s*	9.27 *s*
10	113.54	113.61	1'	4.43 *d* (8.0)	4.43 *d* (8.0)
11	190.66	190.70	2', 4'	2.95-2.99	2.96-3.01
1'	98.69	98.94	3', 5'	3.14-3.19	3.13-3.18
2'	71.78	72.20	6'	3.66, 3.71 *br d*	3.63, 3.71 *br d*
3'	77.43	77.48	2", 6"	6.76 *d* (8.4)	7.71 *d* (7.2)
4'	70.09	70.11	3", 5"	7.54 *d* (8.8)	7.40 *d* (8.8)
5'	75.61	75.62	4"		7.41m
6'	61.17	61.20	α	6.37 *d* (16)	6.63 *d* (16)
C=O	166.45	166.12	β	7.53 *d* (16)	7.63 *d* (16)
α	113.67	117.69	OH	10.66 *s*	
β	145.23	145.05			
1"	125.04	134.01			
2",6"	130.46	128.52			
3",5"	114.93	129.01			
4"	159.95	130.65			

*Assignments based on HMBC and HMQC

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