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Two New Iridoid Glucosides from *Clerodendrum serratum*

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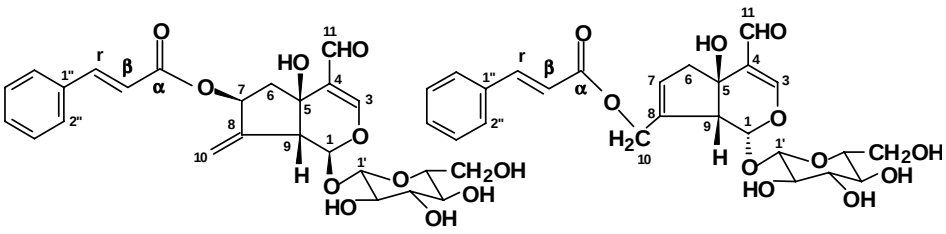
Abstract: Two new iridoid glucosides, serratoside A and serratoside B, were isolated from the aerial parts of *Clerodendrum serratum var. amplexifolium* Moldenke. Their structures were elucidated by spectral and chemical methods.

Keywords: *Clerodendrum serratum*, Verbenaceae, iridoid glucoside, serratoside A, serratoside B.

In our previous paper[1,2], we have reported some constituents from the extract of *C. Serratum var. amplexifolium* Moldenke. Further investigation on the same plant led to the isolation of two new iridoid glucosides, serratoside A (**1**) and serratoside B (**2**). In this communication, we describe the structural elucidation of the two new compounds.

Figure 1



1 **2**

Serratoside A (**1**) (**Figure 1**) was obtained as brown gum. The positive FABMS established a molecular formula of $C_{25}H_{28}O_{11}$ for **1** (*m/z* 505 $[M+1]^+$), which was confirmed by its high resolution positive FABMS (found $[M+1]^+$ 505.1714, calcd. 505.1710) and ^1H and ^{13}C NMR spectra (**Table 1** and **2**). The UV (MeOH) [λ_{max} (log ε): 203.5 (5.15), 216.5 (5.13), 222.5 (5.14), 243.5 (5.13), 256.5 (5.09), 278 (5.20) nm] and the IR (ν: 3391 br., 1712, 1675, 1624, 1450, 1355, 1276, 1171, 859 cm^{-1}) showed the

presence of the hydroxyl groups, carbonyl group, carboxyl group, α, β-unsaturated skeleton and aromatic ring. Especially, the UV (λ_{max}: 222.5 nm), IR (ν: 1624 cm^{-1}) and ^1H NMR spectral data for H-3 (δ 7.48, s) indicated the existence of a 4-substituted enol ether system of iridoid[3]. Inspection of ^1H and ^{13}C NMR spectra of **1** showed that the signals were in good agreement with those of ugandoside[4] except for the additional *trans*-cinnamoyloxy group [δ_H 6.68 (1H, d, *J* = 16.0 Hz, H-β), 7.88 (1H, d, *J* = 16.0 Hz, H-γ), 7.35 (1H, br.s, H-4"), 7.36 (2H, br.d, *J* = 7.5 Hz, H-3" and 5") and 7.59 (2H, br.d, *J* = 7.5 Hz, H-2" and 6"); δ_C 166.76 (s, C-α), 118.89 (d, C-β), 145.33 (d, C-γ), 134.95 (s, C-1"), 128.68 (d, C-2" and 6"), 129.40 (d, C-3" and 5") and

Table 1 The ^1H NMR spectral data of **1** and **2** in pyridine-d_5 (400MHz, δ in ppm from TMS and *J* in Hz)

Proton	1	2
1α	6.38 d, 2.3	
1β		5.83 d, 7.5
3	7.48 s	7.50 s
6α	3.56 dd, 13.2, 7.6	2.88 br.d, 17.3
6β	2.60 dd, 13.0, 8.3	3.27 br.d, 17.3
7		5.78 br.s
7α	5.76 t, 5.8	
9β	3.62 d, 2.3	3.47 d, 7.5
10a	5.28 br.s	5.11 d, 13.9
10b	5.49 br.s	5.22 d, 13.9
11	9.45 s	9.50 s
1'	5.37 d, 7.8	5.43 d, 7.8
2'	4.05 t, 8.3	4.14 t, 8.0
3', 4'	4.23 m	4.28 m
5'	4.02 m	4.03 m
6'a	4.55 dd, 11.8, 2.0	4.54 dd, 11.8, 2.0
6'b	4.37 dd, 11.8, 5.5	4.35 dd, 11.8, 5.7
2", 6"	7.59 br.d, 7.5	7.55 d, 6.4
3", 5"	7.36 br.d, 7.5	7.34 d, 6.4
4"	7.35 br.s	7.33 s
β	6.68 d, 16.0	6.67 d, 16.0
γ	7.88 d, 16.0	7.86 d, 16.0

130.81 (d, C-4")]. Exhaustive acid hydrolysis of **1** afforded glucose and *trans*-cinnamic acid (identified by comparing with authentic samples in TLC). All conclusions mentioned were demonstrated by the ^1H-^1H COSY, HMQC and HMBC spectra of **1**, and some significant ^1H-^{13}C long range correlations between H-7 with C-α, H-1 with C-1' and H-1' with C-1 could be clearly observed from the HMBC (**Figure 2**). Thus, it was confirmed that the *trans*-cinnamoyloxy group and glucosyl unit were attached to C-7 and C-1 positions of iridoid moiety, respectively. Meanwhile, the glycosidic linkage was shown to be β by the coupling constant (*J* = 7.8 Hz) of the anomeric proton signal. The relative stereochemistry of **1** was determined by the NOESY spectrum (**Figure 3**) and comparison of the ^1H and ^{13}C NMR data and coupling constants of **1** with those of ugandoside. Accordingly, the structure of serratoside A (**1**) was elucidated to be

7β-cinnamoyloxy-ugandoside.

Figure 2 The key ^{1}H-^{13}C long-range correlations observed in **1** and **2**

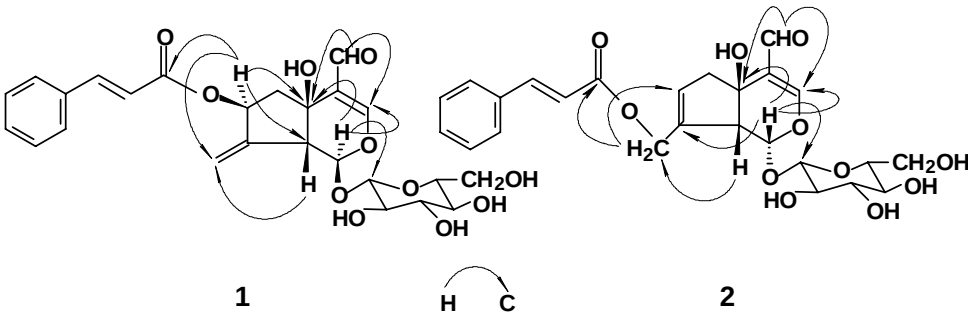
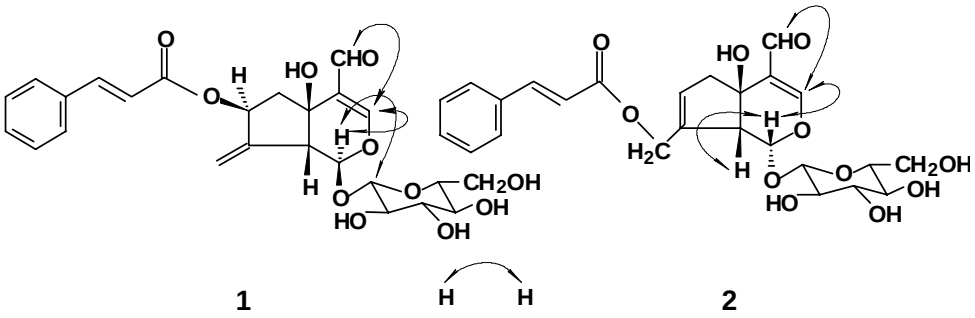


Figure 3 Some principal results observed in the NOESY spectra of **1** and **2**



Serratoside B (**2**) (**Figure 1**) was also obtained as a brown gum. It had the same molecular formula ($C_{25}H_{28}O_{11}$) as **1**, which was also confirmed by the high resolution positive FABMS (found $[M+1]^+$ 505.1666, calcd. 505.1709) and ^{1}H and ^{13}C NMR spectral data (**Table 1** and **2**). The spectral data of ^{1}H, ^{13}C NMR, IR and UV were quite similar to those of serratoside A (**1**). Moreover, exhaustive acidic hydrolysis of **2** gave glucse and *trans*-cinnamic acid, too. These facts indicated that they had similar structures. The main differences between **2** and **1** were that the signals at δ_C 73.70 [δ_H 5.76 (1H, t, J = 5.8 Hz)] due to a methine bearing an oxygen and δ_C 114.38 [δ_H 5.28 (1H, br.s) and 5.49 (1H, br.s)] assigned to an exomethlyene in **1** were replaced by those at δ_C 129.30 [δ_H 5.78 (1H, br.s)] arising from an olefinic bond group and δ_C 62.82 [δ_H 5.11 (1H, d, J = 13.9 Hz) and 5.22 (1H, d, J = 13.9 Hz)] owing to a methylene connected to oxygen in **2**, respectively. It means that the exocyclic olefinic bond ($\Delta^{8, 10}$) in **1** was converted to the cyclic one ($\Delta^{7, 8}$) in **2**. Meanwhile, the *trans*-cinnamoyloxy group was moved from the C-7 position of **1** to the C-10 position of **2**. These presumptions were demonstrated by the ^{1}H-^{1}H COSY, HMQC and HMBC spectra of **2**. Especially, the connectivity of the *trans*-cinnamoyloxy group was determined by the HMBC spectrum (**Figure 2**). In

addition, according to the NOESY spectrum (**Figure 3**), the H-1 of **2** was in the β-orientation instead of the α-orientation. Comparison of the coupling constant between H-1 and H-9 of **2** (J = 7.5 Hz) with that of **1** (J = 2.3 Hz) gave strong evidence to confirm the orientation of H-1. Therefore, the structure of serratoside B (**2**) was established as **2** shown in **Figure 1**.

Table 2 The ^{13}C NMR spectral data of **1** and **2** in pyridine-d_5 (100.6 MHz, δ in ppm from TMS)

C	1	2	C	1	2
1	97.27 (d)	99.64 (d)	**3'**	79.13 (d)	78.99 (d)
3	162.77 (d)	161.46 (d)	**4'**	71.52 (d)	71.52 (d)
4	123.98 (s)	126.59 (s)	**5'**	78.39 (d)	78.41 (d)
5	70.39 (s)	75.34 (s)	**6'**	62.70 (t)	62.82 (t)
6	42.91 (t)	46.76 (t)	**1"**	134.95 (s)	134.96 (s)
7	73.70 (d)	129.30 (d)	**2", 6"**	128.68 (d)	128.66 (d)
8	146.57 (s)	136.71 (s)	**3", 5"**	129.40 (d)	129.30 (d)
9	52.94 (d)	57.21 (d)	**4"**	130.81 (d)	130.68 (d)
10	114.38 (t)	62.82 (t)	**α**	166.76 (s)	166.63 (s)
11	190.58 (s)	190.57 (s)	**β**	118.89 (d)	118.76 (d)
1'	100.82 (d)	101.21 (d)	**γ**	145.33 (d)	145.19 (d)
2'	74.63 (d)	74.80 (d)			

Acknowledgments

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