Chinese Chemical Letters Vol. 11, No. 4, pp. 323–326, 2000

A New Phenylpropanoid Glycoside: Serratumoside A from *Clerodendrum serratum*

Hui YANG[1,2], Ai Jun HOU[1], Shuang Xi MEI[1], Li Yan PENG[1], Han Dong SUN[1]*

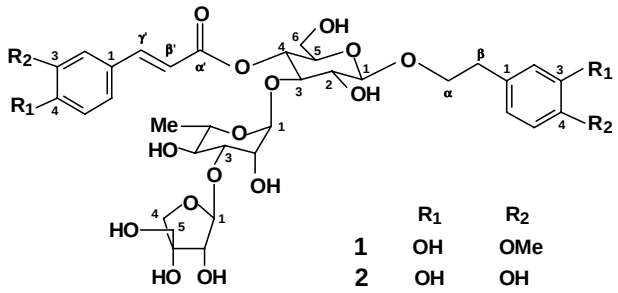
[1]Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204
[2]Chemistry Department, College of Life Science and Chemistry, Yunnan University, Kunming 650091

Abstract: A new phenylpropanoid glycoside, serratumoside A, was isolated from the aerial parts of *Clerodendrum serratum* var. *amplexifolium* Moldenke. Its structure was determined by spectral and chemical methods.

Keywerds: *Clerodendrum serratum*, Verbenaceae, phenylpropanoid glycoside, serratumoside A.

In the previous papers[1,2,3,4], we have reported some chemical constituents from *Clerodendrum serratum* var. *amplexifolium* Moldenke. A continuation of our studies on the same plant led to the isolation of a new phenylpropanoid, serratumoside A (**1**), which is reported in this paper.

Figure 1



Serratumoside A (**1**) with three known phenylpropanoid glycosides identified as acteoside[5], martinoside[6] and myricoside[7], respectively, were isolated from the *C. serratum*. Compound **1** was isolated as a brown amorphous powder, $[\alpha]_D^{19}$ + 89.42 (c 0.261, MeOH), the negative FABMS gave quasimolecular ion peak at *m/z* 783 $[M-1]^-$, suggesting the molecular formula as $C_{36}H_{48}O_{19}$, which was confirmed by the high resolution negative FABMS (found $[M-1]^-$ 783.2640, calcd. 783.2711) and the NMR

spectral data of **1**. Its UV [λ_{max} (log ε): 214.5 (5.15), 258 (4.73), 282.0 (4.59) and 325.5 (5.21) nm] and IR (ν: 3417 br., 1705, 1630 and 1595 cm^{-1}) spectra showed the presence of hydroxyl groups, α, β-unsaturated ester and aromatic rings. The ^{1}H and ^{13}C NMR spectral data (**Table 1** and **2**) of **1** showed that the signals were in good agreement with those of myricoside (**2**) except for the differences in the aglycone and acyl moieties, *i.e* the existence of two additional methoxy groups [δ_H 3.75 (3H, s); δ_C 55.8 (q) and δ_H 3.83 (3H, s); δ_C 55.8 (q)] in the aglycone and acyl moiety, respectively.

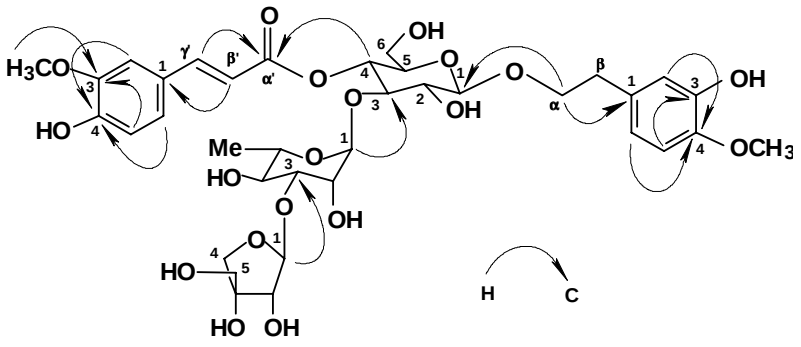
Table 1 ^{1}H NMR spectral data of compounds **1** and **2** in pyridine-d_5 (500MHz, δ in ppm from TMS and J in Hz)

Proton	1	2
Aglycone		
2	6.83 d (1.8)	6.62 d (1.7)
5	6.71 d (8.1)	6.63 d (7.6)
6	6.67 dd (8.1, 1.9)	6.50 dd (8.0, 1.8)
αa	3.89 m	3.84 m
αb	3.67 m	3.60 m
β	2.76 m	2.70 m
OMe	3.75 s	
Acyl moiety		
2	7.32 d (1.8)	7.04 d (1.8)
5	6.84 d (8.1)	6.76 d (8.0)
6	7.12 dd (8.0, 1.8)	6.99 dd (8.2, 1.8)
β'	6.44 d (15.8)	6.22 d (15.8)
γ'	7.58 d (15.8)	7.46 d (15.8)
OMe	3.83 s	
Glucosyl moiety		
1	4.41 d (7.6)	4.37 d (7.8)
2	3.20 m	3.17 m
3, 5	3.72 m	3.69 m
4	4.71 t (9.7)	4.68 t (9.7)
6		3.43 m
6a	3.45 m	
6b	3.40 m	
Rhamnosyl moiety		
1	5.06 br.s	5.02 br.s
2, 3	3.72 m	3.69 m
4	3.14 m	3.11 m
5	3.37 m	3.33 m
6	1.01 d (6.1)	0.96 d (6.1)
Apiosyl moiety		
1	4.81 d (2.7)	4.77 d (2.9)
2	3.72 m	3.69 m
4a	3.80 d (9.2)	3.78 d (9.4)
4b	3.58 d (9.2)	3.55 d (9.4)
5	3.32 m	3.27 m

Acidic hydrolysis of **1** gave glucose, rhamnose and apiose (identified by TLC

comparing with authentic samples). Additionally, its ^{1}H and ^{13}C NMR spectral data showed three anomeric signals at δ_H 4.41 (1H, d, J = 7.6 Hz) and δ_C 102.3 (d); δ_H 5.06 (1H, br. s) and δ_C 101.3 (d) and δ_H 4.81 (1H, d, J = 2.7 Hz) and δ_C 109.2 (d), which were attributed to glucose, rhamnose and apiose by the ^{1}H-^{1}H COSY, HMQC and HMBC spectra of **1**. Further analysis of HMBC, HMQC-TOCSY spectra and comparison of the NMR spectral data of **1** with those of **2**, the ^{1}H and ^{13}C NMR spectral signals of sugar moieties could be assigned. The negative FABMS produced the fragment (*m/z* 651 [M-Api-1]$^-$), which revealed the apiose as a terminal sugar. From the HMBC spectrum of **1**,

Figure 2 The key ^{1}H-^{13}C long-range correlations observed in the HMBC spectrum of **1**



1

some principal ^{1}H-^{13}C long range correlations (**Figure 2**) were clearly observed between the protons (δ3.75) of a methoxy group and C-3 (δ148.0) of acyl moiety; the protons (δ3.83) of a methoxy group and C-4 (δ145.9) of aglycone moiety; H-5 (δ6.84) of acyl moiety and C-3 (δ148.0) of acyl moiety; H-2 (δ7.32) and H-6 (δ7.12) of acyl moiety and C-4 (δ149.5) of acyl moiety, respectively; H-5 (δ 6.71) of aglycone and C-3 (δ146.2) of aglycone; H-2 (δ6.83), H-6 (δ6.67) of aglycone and C-4 (δ145.9) of aglycone, respectively; H-1 (δ4.41) of glucose and C-α (δ70.2) of aglycone; H-4 (δ4.71) of glucose and C-α' (δ166.0) of acyl moiety; H-1 (δ5.06) of rhamnose and C-3 (δ78.9) of glucose; and H-1 (δ4.81) of apiose and C-3 (δ76.1) of rhamnose. These facts indicated that the linkages among aglycone, acyl moiety, glucose, rhamnose and apiose of **1** were consistent with those of **2** and showed the two additional methoxy groups were attached to the C-3 position of acyl moiety and the C-4 position of aglycone, respectively. Therefore, serratumoside A was deduced to be 3-hydroxy-4-methoxy-β-phenethyl-O-β-D-apiofuranosyl-(1→3)-α-L-rhamnopyranosyl- (1→3)-4-O-feruloyl-β-D-glucopyranoside. Its structure was shown in **Figure 1**.

Table 2 ^{13}C NMR spectral data of compounds **1** and **2** in pyridine-d_5 (125.8 MHz, δ in ppm from TMS)

C	1	2	C	1	2
Aglycone			**Glc moiety**		
1	131.1 s	129.2 s	**1**	102.3 d	102.2 d
2	112.4 d	115.5 d	**2**	74.5 d	74.4 d
3	146.2 s	144.9 s	**3**	78.9 d	78.9 d
4	145.9 s	143.5 s	**4**	69.5 d	69.4 d
5	116.4 d	116.4 d	**5**	72.9 d	72.8 d
6	119.6 d	119.6 d	**6**	67.2 t	67.1 t
α	70.2 t	70.4 t	**Rha moiety**		
β	35.0 t	35.0 t	**1**	101.3 d	101.3 d
OMe	55.8 q		**2**	70.6 d	70.5 d
Acyl moiety			**3**	76.1 d	75.9 d
1	125.8 s	125.5 s	**4**	71.7 d	71.7 d
2	111.2 d	114.8 d	**5**	68.9 d	68.8 d
3	148.0 s	145.9 s	**6**	18.2 q	18.2 q
4	149.5 s	148.5 s	**Api moiety**		
5	115.6 d	115.8 d	**1**	109.2 d	109.2 d
6	123.3 d	121.6 d	**2**	76.1 d	75.9 d
α'	165.9 s	165.8 s	**3**	78.9 s	78.9 s
β'	114.0 d	113.4 d	**4**	73.5 t	73.4 t
γ'	146.3 d	145.6 d	**5**	63.2 t	63.2 t
OMe	55.8 q				

Acknowledgments

The authors are grateful for financial support from the National Natural Science Foundation of China (Grant No. 29772039).

References

1 H. Yang, A.J. Hou, B. Jiang, Z.W. Lin, H.D. Sun, *Acta Botanica Yunnanica* (in press).
2 H. Yang, J. Wang, A.J. Hou, Z.W. Lin, H.D. Sun, *Chinese Chemical Letters* (in press).
3 H. Yang, B. Jiang, Z. Na, Y.P. Guo, H.D. Sun, *Chinese Chemical Letters* (in press).
4 H. Yang,Q. Mu, Y.N. He, H.D. Sun, *Chinese Chemical Letters* (submitted).
5 S. Hiroko, S. Yutaka, O. Kazunoki, *et al*, *Phytochemistry*, **1987**, *26* (8), 1981.
6 S. Hiroshi, T. Heihachiro, E. Tohru, *et al*, *Chem. Pharm. Bull.*, **1978**, *26* (7), 2111.
7 Cooper Raymond, Snolomon Philippa H., Kubo Isao, *et al*, *J. Am Chem. Soc.*, **1980**, *102* (27), 7953.

Received 27 October 1999
Revised 21 December 1999