Chinese Chemical Letters Vol. 11, No. 4, pp. 333–336, 2000

A New Triterpenoid Saponin: Se-saponin A

Hui YANG[1,2], Qin MU[1], Yi Neng HE[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 triterpenoid saponin, se-saponin A, was isolated from the aerial parts of *Clerodendrum serratum* var. *amplexifolium* Moldenke. Its structure was determined by spectral and chemical methods. Only one triterpenoid saponin has been isolated from *Clerodendrum* genus before. Se-saponin A is the second instance.

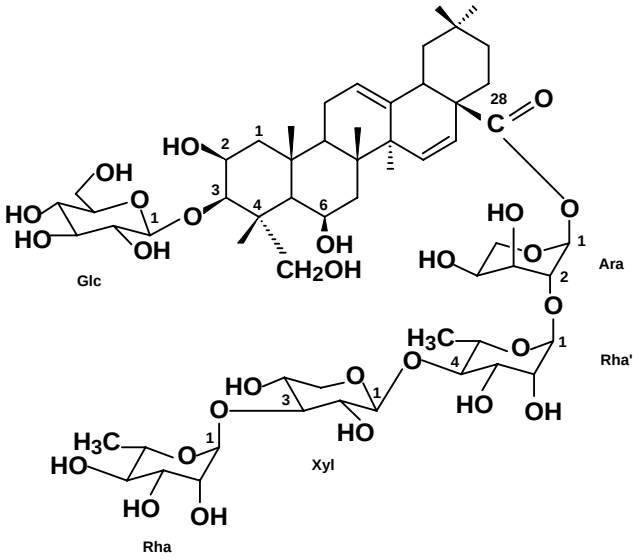
Keywerds: *Clerodendrum serratum*, Verbenaceae, triterpenoid saponin, se-saponin A.

In continuation of our studies on the constituents of *Clerodendrum serratum* var. *amplexifolium* Moldenke[1,2,3], a new triterpenoid saponin, se-saponin A (**1**), was isolated. To the best of our knowledge, it is the second instance of triterpenoid saponin from the *Clerodendrum* genus. This paper deals with the structural elucidation of the new compound.

Se-saponin A (**1**) an amorphous powder, gave positive Liebermann-Burchard reaction. It was deduced to have a molecular formula of $C_{58}H_{92}O_{27}$ by high resolution negative FABMS (found $[M-1]^-$ 1219.5751, calcd. 1219.5748) and NMR spectra. The IR spectrum showed absorption bands (3414 br., 1735, 1630 and 918 cm^{-1}) which corresponded to hydroxyl groups, carboxyl group and olefinic bonds, respectively. The ^1H NMR spectrum exhibited the presence of four angular methyl group signals [δ1.22, 1.55, 1.90 and 2.10 (each 3H, s)], two geminal tertiary methyl groups [δ0.84 and 0.91 (each 3H, s)], two secondary methyl group signals [δ1.65 (3H, d, J = 6.2 Hz) and 1.71 (3H, d, J = 6.2 Hz)] , three olefinic proton signals [δ5.76 (1H, br.s), 5.86 (1H, d, J = 9.9 Hz) and 5.98 (1H, d, J = 9.9 Hz)] in the aglycone moiety, and five anomeric proton signals [δ4.96 (1H, d, J = 7.30 Hz), 5.21 (1H, d, J = 7.7 Hz), 5.98 (1H, br.s), 6.15 (1H, br.s) and 6.27(1H, br.s)]. The ^{13}C NMR spectrum gave 58 carbon signals including one carbonyl carbon [δ174.7 (s)], four olefinic carbons [δ123.6 (d)], 140.5 (s), 137.1 (d) and 129.1 (d)], three methines bearing oxygen (δ70.8, 83.6 and 68.3), one methylene group adjacent to oxygen (δ65.7) and five anomeric carbon signals (δ94.3, 101.4, 102.6, 105.5 and 107.4). These ^1H and ^{13}C NMR spectral data were assigned by 2D NMR spectra as shown in **Table 1** and **2**, and they suggested **1** to be a triterpenoid saponin with five

glycosyl groups.

Figure 1



1

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

Proton	1	Proton	1
Aglycone		**1**	5.98 br.s
2	4.19 m	**2**	4.55 m
3	4.31 m	**3**	4.88 m
5	1.93 m	**4**	4.48 m
6	4.17 m	**5a**	4.33 m
9	1.93 m	**5b**	4.48 m
12	5.76 br.s	**Rha′**	
15	5.98 d (9.9)	**1**	6.15 br.s
16	5.86 d (9.9)	**2**	4.33 m
18	3.30 dd (15.6, 4.7)	**3**	4.33 m
23a	3.57 d (9.2)	**4**	4.33 m
23b	4.05 d (9.2)	**5**	4.48 m
24	1.90 s	**6**	1.65 d (6.2)
25	1.55 s	**Xyl**	
26	2.10 s	**1**	4.96 d (7.3)
27	1.22 s	**2**	4.12 m
29	0.84 s	**3**	4.24 m
30	0.91 s	**4**	4.12 m
3 - O - Glc		**5a**	3.44 m
1	5.21 d (7.7)	**5b**	4.24 m
2	4.05 m	**Rha**	
3	4.24 m	**1**	6.27 br.s
4	4.24 m	**2**	4.33 m
5	3.93 m	**3**	4.33 m
6a	4.33 m	**4**	4.55 m
6b	4.48 m	**5**	4.88 m
28 - O - Ara		**6**	1.71 d (6.2)

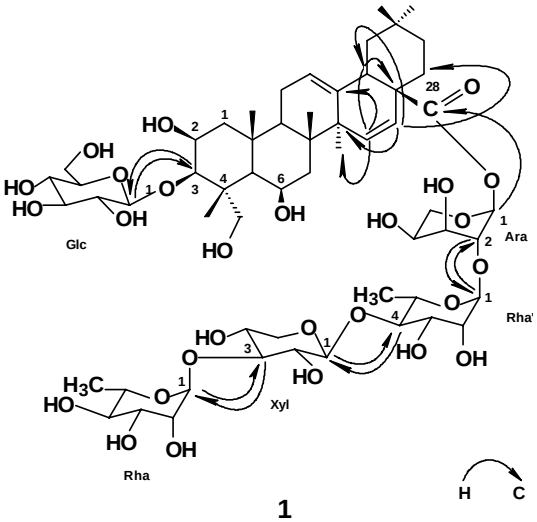
Table 2 ^{13}C NMR spectral data of compound **1** in pyridine-d_5 (125.8 MHz, δ in ppm from TMS)

C	1	C	1	C	1
Aglycone		**22**	33.1 t	**Rha′**	
1	44.0 t	**23**	65.7 t	**1**	101.4 d
2	70.8 d	**24**	16.8 q	**2**	72.4 d
3	83.6 d	**25**	18.4 q	**3**	72.7 d
4	43.7 s	**26**	18.9 q	**4**	84.4 d
5	49.2 d	**27**	24.9 q	**5**	68.6 d
6	68.3 d	**28**	174.7 s	**6**	18.7 q
7	40.6 t	**29**	33.3 q	**Xyl**	
8	37.2 s	**30**	23.3 q	**1**	107.4 d
9	49.2 d	**3 - O - Glc**		**2**	76.6 d
10	40.1 s	**1**	105.5 d	**3**	83.2 d
11	23.9 t	**2**	75.6 d	**4**	70.0 d
12	123.6 d	**3**	78.7 d	**5**	67.4 t
13	140.5 s	**4**	71.7 d	**Rha**	
14	45.4 s	**5**	78.3 d	**1**	102.6 d
15	137.1 d	**6**	62.8 t	**2**	72.6 d
16	129.1 d	**28 - O - Ara**		**3**	72.3 d
17	47.9 s	**1**	94.3 d	**4**	74.2 d
18	42.6 d	**2**	74.3 d	**5**	69.4 d
19	46.1 t	**3**	69.4 d	**6**	18.7 q
20	30.7 s	**4**	68.3 d		
21	34.9 t	**5**	65.7 t		

By comparison of the NMR data, the aglycone of **1** was very similar to protobassic acid[4,5] except for the difference in an additional olefinic bond, and the additional olefinic bond was determined to be located between C-15 and C-16 in D-ring (*i.e.* $\Delta^{15,16}$) by ^1H-^1H COSY and HMBC analysis. Hence, the aglycone of **1** was formulated as 2β,3β,6β,23-tetrahydroxy-olean-12,15-dien-28-oic acid. Acidic hydrolysis of **1** afforded glucose, arabinose, rhamnose and xylose identified by TLC comparing with authentic samples. Thus, the oligosaccharide moiety of **1** was composed of them. The negative FABMS gave the fragments (*m/z* 1074 $[M\text{-}Rha]^-$, 941 $[M\text{-}Rha\text{-}Xyl]^-$ and 1057 $[M\text{-}Glc]^-$, indicating that rhamnose and glucose were the terminal sugars, respectively. Sugar proton and carbon signals in the NMR spectra (**Table 1** and **2**) were assigned by 2D NMR techniques (especially by HMQC-TOCSY NMR technique) and compared with those of Mi-saponin A[4,6] for the saccharide chain. These signals revealed that the structure of the oligosaccharide moiety of **1** was the same as that of Mi-saponin A. The sugar linkages were decided by HMBC spectrum. In HMBC spectrum, ^1H-^{13}C long range correlations (**Figure 2**) were observed between the anomeric proton signal at δ5.21 (H-1 of Glc) and the carbon signal at δ83.6 due to C-3 of aglycone; between the anomeric proton signal at δ6.27 (H-1 of Rha) and the carbon signal at δ83.2 due to C-3 of Xyl; between the anomeric proton signal at δ4.96 (H-1 of Xyl) and the carbon signal at δ84.4 due to C-4 of Rha'; between the anomeric proton signal at δ6.15 (H-1 of Rha') and the carbon signal at δ74.3 due to C-2 of Ara and between the anomeric proton signal at δ5.98 (H-1 of Ara) and the carbon signal at δ174.7 due to C-28 of aglycone. These facts exhibited that the sequence of the monosaccharide units of **1** was identical with that of Mi-saponin A. Consequently, the structure of Se-saponin A (**1**) was characterized to be 3-O-β-D-glucopyranosyl-2β, 3β, 6β, 23-tetrahydroxy-olean-12, 15-

dien-28-oic acid 28-O-[α-L-rhamnopyranosyl (1→3)-β-D-xylopyranosyl (1→4)-α-L-rhamnopyranosyl (1→2)]-α-L-arabinopyranoside, Its structure was shown in **Figure 1**.

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



1

Acknowledgment

The authors are grateful for the 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* (submitted).
4. M. Toyota, J.D. Msonthi, K. Hostettmonn, *Phytochemistry*, **1990**, *29* (9), 2849.
5. I. Kitagawa, A. Inada, I. Yoshioka, R.Somananthan, M.U.S. Sultanbawa, *Chem. Pharm. Bull.*, **1972**, *20* (3), 630.
6. I. Kitagawa, A. Inada, I. Yoshioka, *Chem. Pharm. Bull.*, **1975**, *23* (10), 2268.

Received 27 October 1999
Revised 3 January 2000