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Two New Diterpenoid Glucosides from *Clerodendrum serratum*

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

Keywords: *Clerodendrum serratum*, Verbenaceae, diterpenoid glucoside, cleroserraoside A, cleroserraoside B.

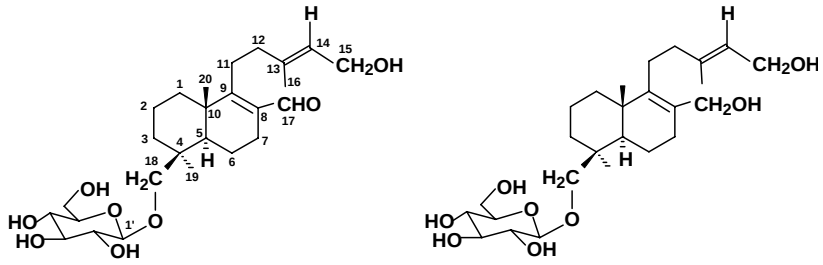
We reported some constituents from the plant of *C. serrartum* var. *amplexifolium* Moldenke[1]. Further study on the aerial parts of the plant resulted in the isolation of two new labdane type diterpenoid glucosides, cleroserraoside A (**1**) and cleroserraoside B (**2**). In this paper we describe the structural elucidation of the compounds.

Cleroserroside A (**1**), $[\alpha]_D^{16.2}$ - 97.22 (c 0.289, MeOH), was obtained as white amorphous powders. It exhibited an $[M-1]^-$ ion peak at m/z 481 in the negative ion FABMS indicating its molecular weight to be 482. The molecular formula was determined as $C_{26}H_{42}O_8$ by high resolution negative ion FABMS ($[M-1]^-$ 481.2714, calcd. 481.2801). The UV spectrum of **1** showed absorption maxima at 202 (logε 4.86) and 257.5 (logε 5.03) nm indicating the presence of an α, β - unsaturated carbonyl skeleton. The IR spectrum of **1** displayed strong absorption bands due to hydroxyl groups (3400 cm^{-1}, br.) and a carbonyl group (1661 cm^{-1}, sh.). Its ^1H NMR spectrum (**Table 1**) revealed the signals of three tertiary methyl groups (δ1.68, 1.22 and 1.04), two oxymethylenes (δ4.49 and δ4.29, 3.62), one olefinic proton (δ 5.78), one aldehydic proton (δ10.27) and one anomeric proton (δ4.83). The ^{13}C NMR spectrum (**Table 2**) gave 26 carbon signals including one aldehydic carbonyl group (δ 193.0), four olefinic carbons (δ167.2, 136.3, 132.1 and 126.7) and one glucopyranosyl group (δ105.3, 75.4, 78.9, 71.9, 78.5 and 63.0)[2], whose glycosidic linkage was shown to be β by the coupling constant (J = 8.0 Hz) of the anomeric proton signal (δ4.38). These ^1H and ^{13}C NMR signals were assigned with the aid of ^1H - ^1H COSY, HMQC and HMBC spectra. Additionally, the molecular formula of **1** suggested that **1** had 6 degrees of unsaturation, which indicated that **1** possessed two rings as well as an aldehydic carbonyl group, two olefinic bonds and one glucosyl group. According to the discussion mentioned above and the 2D NMR spectra, **1** was presumed

to be a monoglucoside of labdane - type diterpene. The connectivities of the glucosyl unit, aldehydic group and double bonds were determined by the HMBC spectrum (**Figure 2**).

Exhaustive acidic hydrolysis of **1** gave glucose which was identified by TLC comparison with the authentic sample. The relative stereochemistry of the aglycone moiety of **1** was determined by the NOESY spectrum . From the NOESY spectrum, three pairs of significant ^{1}H-^{1}H correlation between H-18 and H-20, H-15 and H-16, and H-5α and H-19 could be clearly observed. Consequently, the structure of **1** was deduced to be 15,18-dihydroxy-labda-8E,13E-dien-17-al-18-O-β-D-glucopyanoside. Its structure was shown in **Figure 1**.

Figure 1 The structures of **1** and **2**



Cleroserroside B (**2**) was established to have a molecular formula of $C_{26}H_{44}O_8$ by high resolution negative ion FABMS ($[M-1]^-$ 483.2913, calcd. 483.2957) and NMR spectra. The analysis of ^{1}H and ^{13}C NMR data (**Table 1** and **2**) revealed **2** resembled closely that of cleroserroside A (**1**). The only difference between **2** and **1** was that the carbon signal at δ193.0 ppm assigned to –CHO group in **1** was replaced by that at δ 62.70 ppm arising from methylene adjacent to oxygen (-OCH_2 -). The proton signal at δ10.27ppm corresponding to -CHO group in **1** was absent in **2**, whereas, two new proton signals at δ4.49 and 4.28 ppm ascribed to methylene group in **2**. All these facts showed the presence of oxymethylene group instead of -CHO group in **2**, *i.e* -CHO group of **1** was hydrogenated to oxymethylene group of **2**. The results from IR and UV spectra further demonstrated the conclusion. The strong absorption at 1661cm^{-1} owing to -CHO group in IR spectrum of **1** disappeared in that of **2**, and no absorption signals was observed in UV spctrum of **2**. Furthermore, the acidic hydrolysis of **2** gave the same sugar moiety - glucosyl group - as in **1**, and the 2D NMR spectra (including ^{1}H-^{1}H COSY, HMQC, HMBC and NOESY) also comfirmed that **2** had the same carbon skeleton and stereochemical sturcture as **1**. Therefore, cleroserroside B (**2**) was identified as 15,17,18-trihydroxy-labda-8E,13E-dien- 18-O-β-D-glucopyanoside. Its structure was shown in **Figure 1**.

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

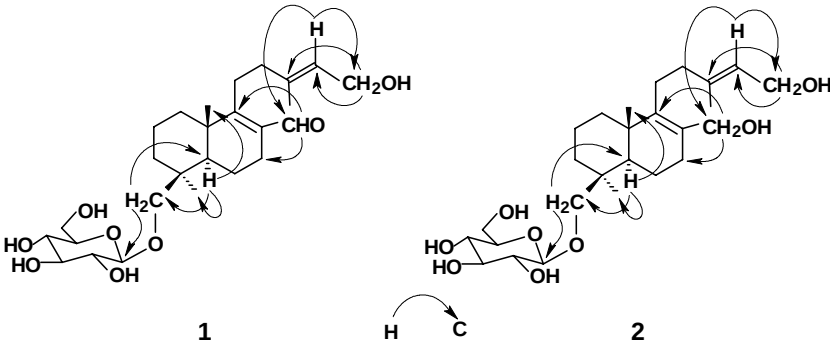


Table 1 The ^{1}H NMR spectra data of compounds 1 and 2 in pyridine-d_5 (400MHz, δ in ppm from TMS and *J* in Hz)

H	1	2
1α	1.23 m	1.25 m
1β	1.78 br.d(12.4)	1.08 br.d(12.3)
2α	1.40 br.d(14.0)	1.38 br.d(14.0)
2β	1.66 m	1.66 m
3α	0.96 m	0.96 m
3β	2.00 br.d(13.6)	2.08 br.d(13.0)
5α	1.18 d(13.0)	1.30 d(12.7)
6α	1.90 m	1.90 m
6β	1.55 m	1.64 m
7α	2.15m	2.26 m
7β	2.49 dd(17.6, 5.6)	2.59 dd(17.5, 5.8)
11a	2.81 m	2.39 m
11b	2.29 m	2.06 m
12	2.12 m	2.26 m
14	5.78 t(6.4)	5.80 t(6.5)
15	4.49 d(6.4)	4.47 d(6.5)
16	1.68 s	1.69 s
17a	10.27 s	4.49 d(12.2)
17b		4.28 d(12.2)
18a	4.29 d(9.6)	4.36 d(9.4)
18b	3.62 d(9.6)	3.63 d(9.4)
19	1.22 s	1.22 s
20	1.04 s	1.04 s
1'	4.83 d(8.0)	4.83 d(7.7)
2'	4.04 t(8.0)	4.05 t(7.9)
3', 4'	4.25 m	4.25 m
5'	3.97 m	3.95 m
6'a	4.57 dd(11.6, 2.0)	4.55 dd(11.7, 2.2)
6'b	4.38 dd(11.6, 5.2)	4.37 dd(11.4, 5.2)

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

Carbon	1	2	Carbon	1	2
1	36.54 (t)	37.18 (t)	**14**	126.7 (d)	125.8 (d)
2	18.69 (t)	19.30 (t)	**15**	58.98 (t)	59.06 (t)
3	35.60 (t)	36.75 (t)	**16**	16.47 (q)	16.49 (q)
4	38.50 (s)	38.54 (s)	**17**	193.0 (d)	62.66 (t)
5	52.02 (d)	53.03 (d)	**18**	73.34 (t)	73.24 (t)
6	18.95 (t)	19.75 (t)	**19**	28.10 (q)	28.16 (q)
7	25.43 (t)	29.88 (t)	**20**	20.51 (q)	21.05 (q)
8	132.1 (s)	131.7 (s)	**1'**	105.3 (d)	105.4 (d)
9	167.2 (s)	142.6 (s)	**2'**	75.40 (d)	75.44 (d)
10	41.22 (s)	39.61 (s)	**3'**	78.87 (d)	78.85 (d)
11	25.43 (t)	26.75 (t)	**4'**	71.87 (d)	72.01 (d)
12	43.64 (t)	42.15 (t)	**5'**	78.48 (d)	78.31 (d)
13	136.3 (s)	137.7 (s)	**6'**	62.96 (t)	63.05 (t)

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