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Chlorophytoside A, a New Labdane Diterpene Glycoside from *Chlorophytum laxum*

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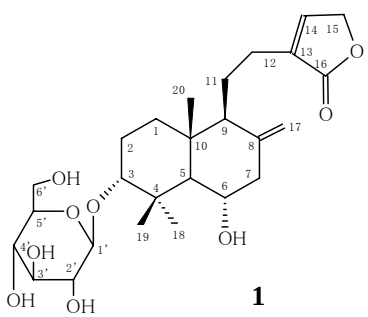
Abatract: A new labdane-type diterpene glycoside **1** , chlorophytoside A, had been isolated from *Chlorophytum laxum* R.Br. The structure had been elucidated as (10S)-6α-hydroxy-labda-8,13-dien-15,16-olide 3R-O-β-D-glucopyranoside on the basis of chemical and spectroscopic data.

Keywords: *Chlorophytum laxum*, labdane-type diterpene glycoside, chlorophytoside A.

Chlorophytum laxum R.Br is mainly distributed in south China. The aerial part of the plant is used as a folk medicine for the treatment of traumatic injury, poisonous snake bites, swelling and pain[1]. In order to find out bioactive constituents, from ethanolic extract of this plant we isolated a new labdane diterpene glucoside, named chlorophytoside A (**1**). The present paper describes the isolated and structure elucidation of compound **1**.

The EtOAc soluble fraction of ethanolic extract from the aerial part of the plant was applied to column chromatography over silica gel and Sephadex LH-20, respectively, to yield compound **1**.

Figure 1 Chemical structure of compound **1**



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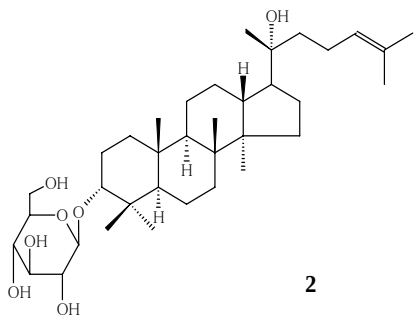

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Compound **1** was a powder. It showed quasi-molecular ion peaks at *m/z* 497 $[M+1]^+$, *m/z* 519$[M+Na]^+$ and *m/z* 535$[M+K]^+$ in the positive FAB-MS, consistent with a molecular formula of $C_{26}H_{40}O_9$, which suggestes seven degrees of unsaturation. The IR spectrum of compound **1** exhibited strong absorption bands due to hydroxyl group (3381cm^{-1}) and α, β-unsaturated lactone (1751 and 1645 cm^{-1}). The ^{1}HNMR spectrum of **1** showed the signals of three tertiary methyl groups (δ 0.77, 1.19, 1.86) and one anomeric proton (δ 4.90). The ^{13}CNMR spectrum of **1** gave 26 carbon signals including a diterpene moiety and one glucopyranosyl group (δ 101.5, 75.3, 78.8, 72.2, 78.4, 63.2)[2], its glycosidic linkage showed to be in β comfigulation by the coupling constant (*J*=8.0 Hz) of the anomeric proton signal. These ^{1}H and ^{13}CNMR signals were assigned with the aid of ^{1}H-^{1}H COSY, HMQC and HMBC spectra as shown in **Table 1**, and suggested compound **1** to be a labdane-type diterpene glucoside. The linkage position of the glucosyl unit was determined by the HMBC spectrum as shown in **Figure 2**.

Acidic hydrolysis of compound **1** gave glucose,which was detected as D-glucose by comparison with the authentic sample on paper chromatography.

The relative configurations of the aglycone moiety of compound **1** was achieved by the analysis of NOESY spectrum, and the key correlations were shown in **Figure 3**.

The absolute configuration of C-3 was established to be *R* by the comparison of the chemical shifts of the signals of C-2, C-3, C-4 and C-1′ (anomeric carbon) between **1** and dammarenediol-I 3*R*-O-β-D-glucopyranoside(2), because the chemical shifts of α-, β- and β'-carbons of secondary alcohols to which β-D-glucopyranose was attached and

Table 1 ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectral data for compound **1** (in pyridine-d_5, δ ppm)

H/C	δ_H (J_{Hz})	δ_C	H/C	δ_H (J_{Hz})	δ_C
1	1.44 (1H, dd, 13.0,3.5)	32.5 (t)	13		134.1 (s)
	2.06 (1H, br s)		14	7.11 (1H, t, 1.5)	145.1 (d)
2	1.82 (1H, m)	21.7 (t)	15	4.72 (2H, s)	70. 6 (t)
	2.0 8 (1H, t, 12.0)		16		174.6 (s)
3	3.77 (1H, br s)	82.7 (d)	17	4.74 (1H, s)	107.8 (t)
4		38.4 (s)		4.95 (1H, s)	
5	1.96 (1H, d, 9.5)	55.5 (d)	18	1.86 (3H, s)	32.6 (q)
6	4.02 (1H, t, 8.0)	70.2 (d)	19	1.19 (3H, s)	23.0 (q)
7	2.28 (1H, t, 11.0)	49.9 (t)	20	0.77 (3H, s)	16.6 (q)
	2.91 (1H, dd, 11.5,		1′	4.90 (1H, d, 8.0)	101.4 (d)
8	4.5)	146.7 (s)	2′	4.09 (1H, d, t, 10.5, 6.0)	75.2 (d)
9		55.7 (d)	3′	4.24 (1H, dd, 8.5, 8.5)	78.8 (d)
10	1.61 (1H, s)	39.1 (s)	4′	4.20 (1H , dd, 8.5, 8.5)	72.2 (d)
11		22.1 (t)	5′	3.95 (1H, ddd,9.0,5.5,	78.3 (d)
	1.61 (1H, br s)		6′	2.5)	63.2 (t)
12	1.79 (1H, m)	24.9 (t)		4.37 (1H, dd, 11.5, 5.5)	
	1.90 (1H, m)			4.55 (1H, dd, 11.5, 3.0)	
	2.41 (1H, t, 12.5)				

Assignment was deduced by analysis of 1D and 2D NMR spectra

anomeric carbon reflect the absolute configuration of the alcohols[2,3]. The chemical shifts of C-2, C-3, C-4 and C-1' of compound **1** were similar to those of compound **2** [δ 23.8 (C-2), 84.8 (C-3), 38.6 (C-4) and 102.0 (C-1'), while different from those of dammarenediol-I 3*S*-O-β-D-glucopyranoside [δ 26.8 (C-2), 88.8 (C-3), 39.7 (C-4) and 106.9 (C-1')[3]. Therefore, the structure of **1** was elucidated as (10*S*)-6α-hydroxylabda-8,13-dien-15,16-olide 3*R*-O-β-D-glucopyranoside.

Figure 2 The key correlations in HMBC spectrum of **1**

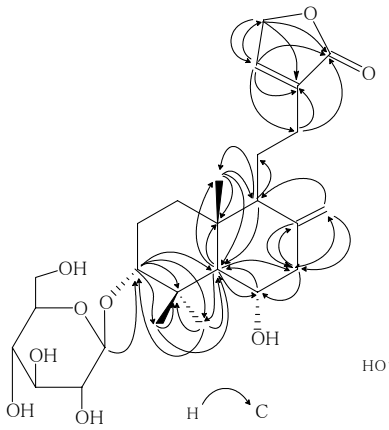
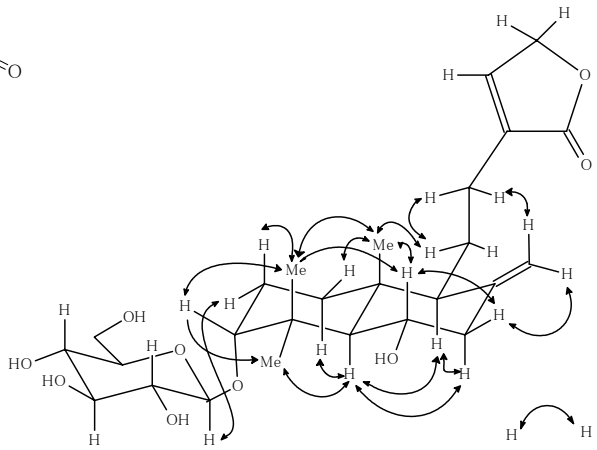


Figure 3 The key correlations in NOESY spectrum of **1**



Acknowledgment

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References

1. Jiangsu New Medicinal college, *Dictionary of Chinese Medicinal Materials*; Shanghai Scientific and Technological Press; Shanghai, **1977**, vol. *1*, 62
2. R. Kasai , M. Suzuo , J. Asaskawa, and O. Tanaka , *Tetrahedron Lett.*, **1977**, *2*, 175.
3. K. Tori , S. Seo , Y. Yoshimura , H. Arita, and Y. Tomita , *Tetrahedron Lett.*, **1977**, *2*, 179.

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