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DARUTOSIDE, A DITERPENOID FROM *SIEGESBECKIA PUBESCENS* AND ITS STRUCTURE REVISION

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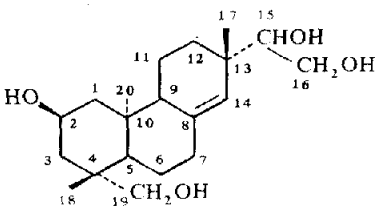
Key Word Index—*Siegesbeckia pubescens*; *S. orientalis*; Compositae; ^{13}C NMR; *ent*-pimarane-type glucoside; darutoside.

From *Siegesbeckia pubescens* (Compositae), which is an Asian folk medicine 'Hi-cheom', several *ent*-kaurane-type diterpenes and an *ent*-pimarane-type diterpene (**1**) have been isolated [1–3]. In addition, a diterpene glucoside (**2**), $C_{26}H_{44}O_8 \cdot H_2O$, mp 225–226°, $[\alpha]_D$ −48° (MeOH; *c* 1.0) which gave an aglycone (**3**), $C_{20}H_{34}O_3$, mp 163°, $[\alpha]_D$ −10° (MeOH; *c* 1.0) by hydrolysis with β-D-glucosidase, was also isolated and the structures **2a** and **3a** were tentatively proposed for this glucoside and its aglycone, respectively [3].



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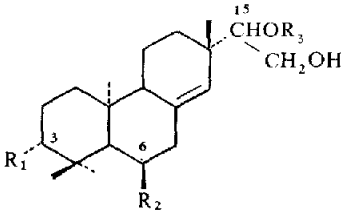
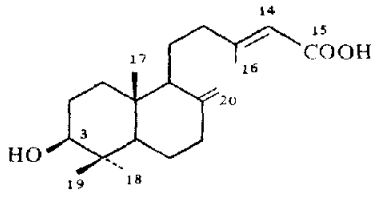


	R_1	R_2	R_3
2	OGlc*	H	H
2a	H	OGlc	H
2b	OH	H	Glc
3	OH	H	H
3a	H	OH	H



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* Glc = β-D-Glucopyranosyl

Table 1. ^{13}C-Chemical shifts (δ_C) for **1**, **2**, **3** (in C_5D_5N) and **4** (in $CDCl_3$)

Carbon No.	Compounds 1	2	3	4*
1	49.2	36.9	37.5	37.1
2	63.9	23.9	28.5	27.8
3	45.5	85.1	78.2	78.9
4	39.7	38.5	39.5	39.2
5	55.5	54.8	54.7	54.7
6	22.6	22.5	22.8	24.0
7	36.7	36.3	36.5	38.2
8	138.0	138.1	138.5	147.7
9	51.3	50.6	51.0	56.0
10	40.9	37.9	38.3	39.5
11	19.0	18.6	18.8	21.7
12	32.7	32.7	32.9	40.0
13	37.9	37.8	37.6	163.7
14	129.7	129.3	129.6	114.9
15	76.5	76.5	76.7	171.4
16	63.9	63.8	64.0	19.2
17	23.2	23.2	23.3	14.6
18	28.2	28.8	29.0	28.3
19	64.8	14.7	14.9	15.4
20	16.9	17.1	16.6	106.9
Glc-1		102.2		
2		74.9		
3		77.9		
4		71.8		
5		78.3		
6		63.0		

* Quoted from ref. [8].

The assignments of ^{13}C NMR spectra of pimarane-type diterpenes have been reported [4–7]. Referring to these results, we assigned the carbon resonances of **1**, reconfirming the structure proposed by Murakami *et al.* [2]. On the basis of these assignments, the spectrum of **3** was compared with those of the 3β-(equatorial)-hydroxy-labdane-type diterpene (**4**) [8] and the 3β-(equatorial)-hydroxy-triterpenes [9]. As shown in Table 1, signals due to the A-ring carbons (C-1, -2, -3, -4 and -5) of **3** were found at almost the same positions as those of **4**, and a signal at δ 22.8 (triplet) of **3** must be attributable to the unsubstituted methylene group of C-6. It follows that the former proposal of the allocation of the third hydroxyl group of **3** at C-6 must be revised to be located at C-3 (equatorial).

The stereochemistry of carbon signal displacements of both aglycone and sugar moieties of glycosides has been reported [10]. On going from **3** to **2**, a β-D-glucoside of **3**, a signal due to C-3 was deshielded by +6.9

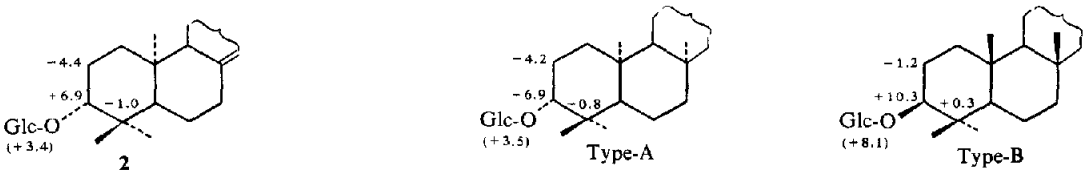

Fig. 1. β-D-Glucosylation NMR chemical shifts. Each value indicates the glucosylation shift ($\Delta\delta = \delta_{\text{glucoside}} - \delta_{\text{aglycone}}$). Values in parentheses indicate the glucosylation shift of anomeric carbon ($\Delta\delta = \delta_{\text{glucoside}} + \delta_{\beta\text{-glucose}}$). Glc = β-D-Glucopyranosyl.

ppm and signals attributable to C-2 and C-4 were displaced upfield by −4.2 and −0.8 ppm, respectively, while other carbon signals including C-15 and C-16 remained almost unshifted. Comparison of the magnitude of these displacements with those of β-D-glucopyranosides, types-A and -B (Fig. 1) [10] led to the conclusion that in the structure of **2**, the β-D-glucosyl linkage must be located at the 3-equatorial hydroxyl group and the chirality of this hydroxyl group should be represented by the *R* configuration. This means that the absolute configuration of **3** should be the *ent*-type, the same as for type-A. With regard to the carbon resonances of the sugar residue, the spectrum of **2** exhibited signals corresponding to a β-D-glucopyranosyl moiety at almost the same positions as those of type-A. It should be noted that the anomeric carbon signal of type-B appears at a remarkably higher field than that of type-A [10]. Consequently, the structure of **2** can be now formulated as illustrated.

Previously, Diara *et al.* [11] isolated a glucoside named darutoside from *Siegesbeckia orientalis*, for which the structure **2b** was proposed. Direct comparison of the ^{13}C NMR spectrum, mp and optical rotation of **2** with those of an authentic sample of darutoside definitely indicated the identity of both glucosides, leading to the revision of the structure of darutoside from **2b** to **2**.

EXPERIMENTAL

^{13}C NMR spectra were recorded on a JEOL PFT-100 spectrometer, equipped with EC-6 computer, operating at 25.15 MHz (pulse flip angle of 90°, at pulse interval of 1–2 sec). Samples were studied as 0.2–0.5 M soln in C_5D_5N with TMS as internal standard; 500–15000 accumulations with 8192 data points for 4 KHz were used.

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