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LANTANOSIDE, A MONOCYCLIC C_{10} IRIDOID GLUCOSIDE FROM *VIBURNUM LANTANA**

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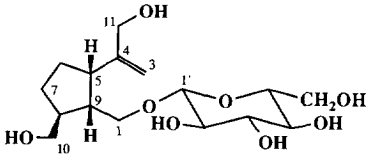
Key Word Index—*Viburnum lantana*; Caprifoliaceae; iridoid glucosides; lantanoside; dihydropenstemide; monoterpene glucoside; betulalbuside A.

Abstract—A new monocyclic C_{10} iridoid glucoside was isolated from the leaves of *Viburnum lantana*, together with the two known glucosides, dihydropenstemide and betulalbuside A. The structure of the new compound, lantanoside, was established from extensive ^1H and ^{13}C NMR, 1D and 2D homo-and heteronuclear correlation experiments.

INTRODUCTION

The genus *Viburnum* L. is represented by three species in the flora of Turkey; *V. opulus* L., *V. orientale* Pallas, and *V. lantana* L. [1]. In the course of an investigation into the chemical constituents of *Viburnum* species, we reported a series of acyclic monoterpene glycosides, anatoliosides [2, 3], and a valeriana type iridoid glucoside, viborientoside, from *V. orientale* [4]. As a result of continuing research into the genus *Viburnum*, we now report on the isolation and structure elucidation of a novel C_{10} iridoid glucoside, lantanoside (**1**), as well as dihydropenstemide (**2**) [5–7], and the acyclic monoterpene glucoside, betulalbuside A (**3**) [3, 8] from *V. lantana*. In the previous studies, 2′-*O*-acetylpatrinoside, 2′-*O*-acetyldihydropenstemide [9] and decapetaloside [10] have also been reported from the same plant.



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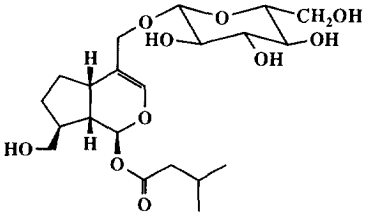

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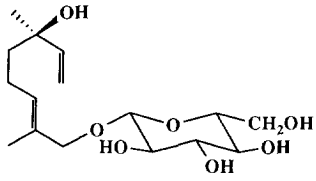

(3)

RESULTS AND DISCUSSION

Compound **1** was obtained as an amorphous powder. Its molecular formula, $C_{16}H_{28}O_8$, was established by FAB-MS ($[M+Na]^+$, *m/z* 371). The ^1H and ^{13}C NMR spectral data for **1** were assigned from the results of 2D ^1H, ^1H homo- and 2D ^1H–^{13}C heteronuclear COSY experiments. The ^1H and ^{13}C NMR spectra of **1** showed resonances for two methylene (δ1.80/1.72 and 1.94/1.30: H_2-6 and H_2-7; δ29.7 and 28.7: C-6 and C-7) and three oxymethylene groups (δ3.69/3.37, 3.54 and 4.16/4.03: H_2-1, H_2-10 and H_2-11; δ71.9, 67.2 and 66.2: C-1, C-10 and C-11), together with the resonances for an exocyclic double bond (δ5.17 and 4.93: H_2-3; 108.1 and 150.4: C-3 and C-4). Additionally, three methine protons were observed (δ2.54, 2.03 and 2.24: H-5, H-8 and H-9). The remaining protons and corresponding carbon signals were consistent for the presence of a glucose unit. The β-glycosidic linkage was derived from the $J_{1',2'}$ (7.8 Hz).

When the sugar unit was substracted from the molecular formula of **1**, the aglycone was found to have the

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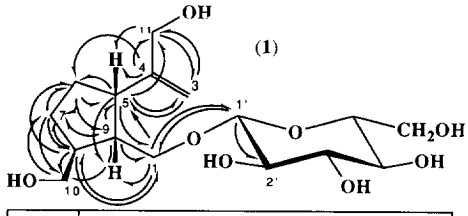

C-1	H-1', H-1, H-5, H-8, H-9
C-3	H-3a,b, H-11a,b, H-5
C-4	H-3a,b, H-11a,b, H-5, H-6a,b
C-5	H-3a,b, H-11a,b, H-1a,b, H-9, H-6a,b
C-6	H-5, H-7, H-9
C-7	H-6, H-8, H-10
C-8	H-1a,b, H-6, H-7, H-10
C-9	H-1a,b, H-5, H-10
C-10	H-7a,b, H-5
C-11	H-3a,b, H-5
C-1'	H-1a,b, H-1', H-2'

Fig. 1. Schematic representation of heteronuclear multiple bond correlations for lantanoside (1). Arrows point from carbon to proton resonances, whose shift values are given in the Experimental

formula $C_{10}H_{18}O_3$, indicating it to be a monocyclic C_{10} moiety. All connectivities, especially the inerglycosidic linkage between the glucose unit and the aglycone moiety were established from the results of a 2D ^1H–^{13}C heteronuclear long range COSY experiment (HMBC), which showed correlations between C-1 (δ71.9) of the aglycone and H-1' (δ4.18) of the glucose and C-1' (δ104.2) of the glucose and H-1a and H-1b (δ3.69 and 3.37) of the aglycone. 2D NOESY of **1** clearly showed H-5, H-9 and H_2-10 to be β. The other correlations are shown in Fig. 1 and confirmed the proposed structure for **1**.

Compound **1**, which has a similar structure to those of eucommioside [11], ajureptoside [12], gelsemiol 1- and 3-glucosides [13], in which the pyran rings are opened, is only the third example of a monocyclic cyclopentanoid-triol C_{10} iridoid glucoside. Menzetriol [14], a non-glucosidic iridoid, has a similar structure to the aglycone moiety of lantanoside (**1**).

Based on their spectral data, **2** and **3** were identified as dihydropenstemide [5–7] and betulalbuside A [3, 8], respectively.

EXPERIMENTAL

General experimental procedures were as reported in ref. [2].

Plant material. Viburnum lantana L. was collected in May 1992 from Beynam Forest, Ankara, Central Anatolia, Turkey. A voucher specimen has been deposited in the Herbarium of Hacettepe University, Faculty of Pharmacy, Department of Pharmacognosy (HUEF 92-001).

Extraction and isolation of **1–3**. The air-dried leaves (300 g) were extracted twice with MeOH. The methanolic extract was evapd to dryness and H_2O (0.5 l) was added. This soln was successively extracted with petrol, Et_2O, EtOAc and 1-BuOH (petrol extract, *ca* 25 g; Et_2O extract, 5.6 g; EtOAc extract, 7.0 g; BuOH extract, 23 g). A portion of the butanolic extract (10 g) was chromatographed over silica gel (200 g) with $CHCl_3$–MeOH–H_2O (9:1:0.1 → 3:2:0.2) and the frs obtained were combined into 10 main frs, A–J (A, 164 mg; B, 1600 mg; C, 1500 mg; D, 880 mg; E, 190 mg; F, 480 mg; G, 363 mg; H, 515 mg; I, 377 mg; J, 705 mg). Fr. D was subjected to MPLC (Sepralyte 40 μm, MeOH–H_2O gradient, 35–40% MeOH) to give **3** (20 mg) and **2** (480 mg). Fr. F was also applied to MPLC (Sepralyte 40 μm, MeOH–H_2O gradient, 25–30% MeOH) to yield crude **1** (70 mg) which was finally purified over silica gel (20 g) using $CHCl_3$–MeOH–H_2O (4:1:0.05).

Lantanoside (**1**). $[\alpha]_D^{20}$ −28° (MeOH; *c* 0.41). FAB-MS *m/z* (rel. int.): 371 (100) $[M+Na]^+$, 387 (9) $[M+K]^+$ (calcd for $C_{16}H_{28}O_8$: M_r 348); UV λ_{max}^{MeOH} nm: 205; IR ν_{max}^{KBr} cm^{-1}: 3392, 2929, 1608, 1163, 1083 and 1044; ^1H NMR (500 MHz, MeOH): aglycone moiety: δ3.69 and 3.37 (each *m*, H-1a and H-1b), 5.17 and 4.93 (each *d*, J_{AB} = 1.0 Hz, H-3a and H-3b), 2.54 (*m*, H-5), 1.80 and 1.72 (each *m*, H-6a and H-6b), 1.94 and 1.30 (each *m*, H-7a and H-7b), 2.03 (*m*, H-8), 2.24 (*m*, H-9), 3.54 (*m*, H-10), 4.16 and 4.03 (each *br d*, J_{AB} = 14.6 Hz, H-11a and H-11b), glucose moiety: δ4.18 (*d*, *J* = 7.8 Hz, H-1'), 3.18 (*dd*, *d*, *J* = 7.8 and 9.1 Hz, H-2'), 3.38 (*dd* '*t*', *J* = 9.0 Hz, H-3'), 3.30 (*dd* '*t*', *J* = 9.0 Hz, H-4'), 3.27 (*m*, H-5'), 3.70 (*dd*, *J* = 12.0 and 4.8 Hz, H-6'a), 3.89 (*dd*, *J* = 12.0 and 2.2 Hz, H-6'b); ^{13}C NMR (125 MHz, MeOH): aglycone moiety: δ71.9 *t* (C-1), 108.1 *t* (C-3), 150.4 *s* (C-4), 45.2 *d* (C-5), 29.7 *t* (C-6), 28.7 *t* (C-7), 46.4 *d* (C-8), 43.9 *d* (C-9), 67.2 *t* (C-10), 66.2 *t* (C-11); glucose moiety: 104.2 *d* (C-1'), 75.2 *d* (C-2'), 78.0 *d* (C-3'), 71.6 *d* (C-4'), 77.9 *d* (C-5'), 62.7 *t* (C-6').

Dihydropenstemide (**2**). $[\alpha]_D^{20}$ −83° (MeOH; *c* 0.87). UV λ_{max}^{MeOH} nm: 211; IR ν_{max}^{KBr} cm^{-1}: 3401, 2959, 2930, 1750, 1668, 1148, 1078 and 1017; ^1H NMR (300 MHz, MeOH): aglycone moiety: δ6.01 (*d*, *J* = 4.7 Hz, H-1), 6.43 (*br s*, H-3), 2.87 (*d* '*t*', *J* = 6.0 Hz, H-5), 1.75 and 1.98 (each *m*, H-6a and H-6b), 1.44 and 1.75 (each *m*, H-7a and H-7b), 2.03 (*m*, H-8), 2.05 (*m*, H-9), 3.57 (*d*, *J* = 6.0 Hz, H-10), 4.30 and 4.13 (each *d*, J_{AB} = 11.6 Hz, H-11a and H-11b), glucose moiety: δ4.33 (*d*, *J* = 7.8 Hz, H-1'), 3.23 (*dd*, *d*, *J* = 7.8 and 9.1 Hz, H-2'), 3.40 (*dd* '*t*', *J* = 9.0 Hz, H-3'), 3.32 (*dd*, '*t*', *J* = 9.0 Hz, H-4'), 3.31 (*m*, H-5'), 3.68 (*dd*, *J* = 12.0 and 4.8 Hz, H-6'a), 3.92 (*dd*, *J* = 12.0 and 2.2 Hz, H-6'b), acyl moiety: δ 2.28 (*d*, *J* = 6.6 Hz, -CH_2), 2.3 (*m*, -CH), 1.01 (6H, *d*, *J* = 6.6 Hz, Me × 2); ^{13}C NMR (75 MHz, MeOH): aglycone moiety: δ93.1 *d* (C-1), 140.7 *d* (C-3), 115.1 *s* (C-4), 36.9 *d* (C-5), 30.9 *t* (C-6), 28.1 *t* (C-7), 43.8 *d* (C-8), 44.9 *d* (C-9), 66.5 *t* (C-10), 69.6 *t* (C-11); glucose moiety: 103.1 *d* (C-1'), 75.1 *d* (C-2'), 78.1 *d* (C-3'), 71.7 *d* (C-4'), 77.9 *d* (C-5'), 62.8 *t* (C-6'), acyl moiety: δ44.2 *t* (CH_2), 26.8 *d* (CH), 22.6 *q* (Me × 2), 173.5 *s* (C=O).

Betulabuside A (**3**). ^1H NMR (75 MHz, MeOH): aglycone moiety: δ 4.07 and 4.24 (each *d*, J_{AB} = 11.6 Hz, H-1a and H-1b), 5.52 (*dd* '*br t*', *J* = 7.2 Hz, H-3), 2.12 (2H, *m*, H_2-4), 1.60 (2H, *m*, H_2-5), 5.95 (*dd*, *J* = 17.4 and 10.8 Hz, H-7), 5.23 (*dd*, *J* = 17.4 and 1.5 Hz, H-8a), 5.07 (*dd*, *J* = 10.8 and 1.5 Hz, H-8b), 1.72 (3H, *s*, Me-9), 1.30 (3H, *s*, Me-10), glucose moiety: δ4.28 (*d*, *J* = 7.8 Hz, H-1'), 3.23 (*dd*, *J* = 7.8 and 9.1 Hz, H-2'), 3.38 (*dd*, '*t*', *J* = 9.0 Hz, H-3'), 3.35

(*dd*, '*t*', $J = 9.0$ Hz, H-4'), *ca* 3.33 (*m*, H-5'), 3.70 (*dd*, $J = 12.0$ and 5.5 Hz, H-6'a), 3.90 (*dd*, $J = 12.0$ and 2.2 Hz, H-6'b); ^{13}C NMR (75 MHz, MeOH): aglycone moiety: δ76.0 *t* (C-1), 132.9 *s* (C-2), 130.2 *d* (C-3), 23.5 *t* (C-4), 43.0 *t* (C-5), 73.8 *s* (C-6), 146.3 *d* (C-7), 112.2 *t* (C-8), 14.1 *q* (C-9), 23.5 *q* (C-10); glucose moiety: 102.7 *d* (C-1'), 75.1 *d* (C-2'), 78.2 *d* (C-3'), 71.8 *d* (C-4'), 77.9 *d* (C-5'), 62.8 *t* (C-6').

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