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HEMIALBOSIDE, A HEMITERPENE GLUCOSIDE FROM *LAMIUM ALBUM*

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Abstract—Hemialboside, (*S*)-1-hydroxy-3-methylbut-3-en-2-yl-*β*-D-glucopyranoside, was isolated from *Lamium album* and its structure elucidated from ^{1}H and ^{13}C NMR spectral data.

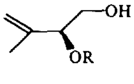
INTRODUCTION

As part of an ongoing phytochemical investigation of Lamiaceae, we have previously reported on the presence of iridoid glucosides in *Lamium album* L. [1, 2]. The present paper deals with the structure elucidation of a new hemiterpene glucoside from this plant.

RESULTS AND DISCUSSION

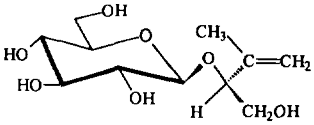
Fresh, aerial parts of *Lamium album* contained, in addition to the earlier reported iridoid glucosides [1, 2], 0.01% of the fresh weight of another glucoside (**1**). Elemental analysis showed the molecular formula to be $C_{11}H_{20}O_7$ and acetylation gave a pentaacetate (**1a**) with the molecular formula $C_{21}H_{30}O_{12}$ in agreement with the composition of the glucoside. The ^{13}C NMR spectrum of **1** in D_2O showed 11 signals of which six could be assigned to a *β*-glucopyranosyl moiety. Of the remaining five signals one methyl group was at high field while a signal at *δ*62.7 indicated the presence of a CH_2OH unit. Furthermore, a CH group at *δ*85.2 indicated the presence of a CHOGlc unit and the last two carbons, a CH_2 at *δ*115.5 and a quaternary carbon at *δ*143.4 indicated a double bond. An analysis of the ^{1}H NMR spectrum was in accordance with the structure **1**. We have named the hemiterpene glucoside hemialboside.

The only remaining question in the structure elucidation was the absolute configuration. It has been shown [3] that the absolute configuration of a chiral secondary allylic alcohol can be determined using the ^{13}C NMR glucosidation shifts. In the work cited [3], three pairs of acyclic allylic alcohols were used as model compounds. Drawing the preferred conformation of the molecules, the double bond was in a *syn*-position to the ring oxygen of the glucopyranosyl moiety in the *R*-series (as shown) and *anti* in the *S*-series. The glucosidation shifts found for the two series are listed in Table 1 together with the values calculated from the pair **1**/**2**. A good fit is seen between the latter and the series with the double bond in the *syn*-position to the ring oxygen. An exception to this good fit is seen for one *β*-carbon, but the model compounds are obviously insufficient since none of them carry a hydroxy group in the *β*-position. Consequently, we can draw the tentative conclusion that hemialboside (**1**) has the 2*S*-stereochemistry.



1 R=Glc

2 R=H



EXPERIMENTAL

The experimental details of the isolation of the hemiterpene glucoside (**1**) have been described [2].

Hemialboside (**1**). Crystallized from Me_2CO, mp 117–119°; $[\alpha]_D^{20}$ $-8.7°$ (MeOH; *c* 0.7); ^{1}H NMR (500 MHz, D_2O): *δ*5.13 (*b s*, H-4a), 5.07 (*b s*, H-4b), 4.57 (*d*, $J = 7.9$ Hz, H-1′), 4.29 (*b t*, $J = 5.5$ Hz, H-2) 3.7–3.8 (3H, *m*, 2 × H-1 + H-6′a), 1.77 (*b s*, 3H, Me-5); ^{13}C NMR: Table 1. (Found: C, 49.78; H, 7.60. $C_{11}H_{20}O_7$ requires, C, 49.99; H, 7.63%).

Hemialboside pentaacetate (**1a**). Prepd by acetylation with pyridine-Ac_2O (2:1, 2 hr at room temp.). Crystallized from EtOH after prep. TLC (silica gel; Et_2O) mp 78.5–79.5°; $[\alpha]_D^{20}$ $+4.7°$ ($CHCl_3$; *c* 1.1); ^{1}H NMR (500 MHz, $CDCl_3$): *δ*5.01 (*br s*, H-4a obscured by H-2′), 4.96 (*br s*, H-4b), 4.60 (*d*, $J = 7.9$ Hz, H-1′), 4.23 (*dd*, $J = 7.9$ and 3.7 Hz, H-2), 4.17 (*dd*, $J = 11.6$ and 7.9 Hz, H-1a), 4.09 (*dd*, $J = 11.6$ and 3.7 Hz, 1b), 1.75 (3H, *br s*, Me-5); ^{13}C NMR: Table 1. (Found: C, 53.20; H 6.39. $C_{21}H_{30}O_{12}$ requires: C, 53.16; H, 6.37%.)

Table 1. ^{13}C NMR spectral data of compounds **1**, **1a** and **2**

	1		**2**	**1a**	Ring oxygen/C = C bond in model [3]	
C	(D_2O)	(pyridine-d_5)		($CDCl_3$)	*syn*	*anti*
1	62.7	64.9 (− 1.4)*	66.3	64.6	− 3.4	− 4.3
2	85.2	85.8 (+ 7.3)	78.5	81.4	7.5	6.0
3	143.4	144.4 (− 2.8)	147.2	141.6	− 3.0	1.0
4	115.5	112.6 (+ 1.5)	111.1	114.3	1.7	4.3
5	16.4	19.5	19.0	17.5		
1′	102.6	105.2		99.6		
2′	74.2	75.7		70.9		
3′	76.7	78.5		72.2		
4′	70.5	71.5		67.9		
5′	76.7	78.4		71.2		
6′	61.5	62.6		61.5		

*Glucosidation shifts $\delta_1 - \delta_2$.

Enzymatic hydrolysis of compound **1**. Hemialboside (**1**, 7 mg) was dissolved in H_2O (1 ml) and β-glucosidase (*ca* 1 mg) was added. After 3 days the water was evapd and the ^{13}C NMR spectrum of the crude mixture was recorded in pyridine-d_5 with TMS as int. standard. The signals of the aglucone **2** were seen (Table 1) in addition to signals from α- and β-glucose.

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