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TWO BIBENZYL GLUCOSIDES FROM *PLEIONE BULBOCODIOIDES*

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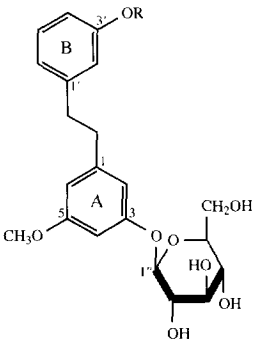
Key Word Index—*Pleione bulbocodioides*; Orchidaceae; tubers; bibenzyls; bibenzyl glucosides.

Abstract—From the tubers of *Pleione bulbocodioides*, two novel bibenzyl glucosides, together with their known aglycones, batatasin III and 3′-*O*-methylbatatasin III, were isolated. The new glycosides were 3′-hydroxy-5-methoxybibenzyl-3-*O*-β-D-glucopyranoside and 3′, 5-dimethoxybibenzyl-3-*O*-β-D-glucopyranoside on the basis of their spectroscopic data. Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

The isolation and structural determination of some stilbenoids and lignans in *Pleione bulbocodioides* were described in our previous papers [1–3]. Further investigation of the same source has resulted in the isolation of two new bibenzyl glucosides, batatasin III-3-*O*-glucoside and 3′-*O*-methylbatatasin III-3-*O*-glucoside, together with their known aglycones, batatasin III and 3′-*O*-methylbatatasin III. Herein, we report the isolation and characterization of the two new glucosides.



1 R = H
2 R = CH_3

RESULTS AND DISCUSSION

Compound **1** showed UV absorption maxima at 238, 269 and 286 nm. The IR spectrum exhibited absorptions at 3250 (hydroxyl) and 1580 cm^{-1} (benzenoids). The FAB-mass spectrum exhibited a $[M]^+$ at *m/z* 406($C_{21}H_{26}O_8$) and a base peak at *m/z* 244 $[M-C_6H_{10}O_5]^+$. From these data, it was assumed to be a bibenzyl glycoside. Acetylation of compound **1** yielded a pentaacetate ($[M+1]^+$ *m/z* 617), which showed four aliphatic acetyls and one aromatic acetyl group in its ^1H NMR spectrum, suggesting the presence of one hydroxyl group in the aglycone. The ^1H NMR spectrum (Table 1) exhibited the signals for an anomeric proton at δ 4.81 (J = 7.3 Hz) and six protons at δ 3.36–3.88 due to the sugar residue and a singlet at δ 3.73 due to one methoxyl group and multiplets at δ 2.83 for four protons of an ethylene linkage of bibenzyl derivatives, along with signals for seven aromatic protons on two benzene rings of bibenzyl, for the aglycone. The three last appeared as three triplets at δ 6.52, 6.51 and 6.40 due to H-2, -4, and -6 in the 1,3,5-trisubstituted A ring, and the remaining four protons appeared as signals at δ 7.05, 6.63, 6.61 and 6.59 assignable to H-5′, -6′, -4′ and 2′ in the 1′,3′-disubstituted B ring. The hydroxyl group was attached to the C-3′ position, which was confirmed by comparison with the spectral data of known 3′-hydroxybibenzyls [2, 4, 5] and by the presence of the fragment peak at *m/z* 107 in the mass spectrum due to the hydroxytropylium resulting from cleavage of the benzylic linkage. Thus, the position of the sugar moiety and the methoxyl group should be at C-3 and C-5 on the A ring, respectively. Enzymic hydrolysis of compound **1** yielded the aglycone, 3, 3′-dihydroxy-5-methoxybibenzyl (batatasin III [6]), which was identified by comparison with an authentic sample, and a sugar residue which was identified as D-glucopyranose by HPLC (see Experimental). Therefore, compound **1** was assigned as 3′-hydroxy-5-methoxybibenzyl-3-*O*-β-D-glucopyranoside (batatsin III-3-*O*-glucoside). The ^{13}C NMR spectral data (Table 2) also supported the structure of compound **1**.

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Table 1. ^{1}H NMR spectral data of compounds **1** and **2** and their acetates*

H	**1**	**1**-Pentaacetate	**2**	**2**-Tetraacetate
2	6.52 *t* (2.0)	6.45 *t* (2.0)	6.52 *t* (2.0)	6.45 *t* (1.7)
4	6.51 *t* (2.0)	6.38 *t* (2.0)	6.50 *t* (2.0)	6.39 *t* (1.7)
6	6.40 *t* (2.0)	6.35 *t* (2.0)	6.40 *t* (2.0)	6.34 *t* (1.7)
2′	6.59 *t* (2.0)	6.90† *m*	6.70 *br d* (1.7)	6.67 *t* (2.5, 1.7)
4′	6.61 *dd* (7.5, 2.8)	7.01 *br d* (7.3)	6.73 *dd* (8.6, 1.7)	6.74 *dd* (8.1, 1.7)
5′	7.05 *t* (7.7, 7.5)	7.26 *t* (8.1)	7.14 *t* (8.6, 7.7)	7.16 *t* (8.1, 7.7)
6′	6.63 *br d* (7.7)	6.90† *m*	6.74 *br d* (7.7)	6.73 *dd* (7.7, 2.5)
-CH_2CH_2-	2.83 *m*	2.87 *m*	2.84 *m*	2.85 *m*
OMe	3.73 *s* C-5	3.72 *s* C-5	3.74 *s* C-3′	3.74 *s* C-3′
			3.72 *s* C-5	3.73 *s* C-5
$COCH_3$	–	2.26 *s*	–	–
Glucose				
1″	4.81 *d* (7.3)	5.17 *d* (7.7)	4.80 *d* (7.3)	5.14 *d* (8.1)
2″–5″	3.36–3.47 *m*	4.02–5.15 *m*	3.35–3.47 *m*	4.00–5.13 *m*
		5.36 *t* (9.4)		5.34 *t* (9.2)
6″	3.71 *dd* (12.0, 5.6)	4.25 *dd* (12.3, 5.4)	3.69 *dd* (12.0, 5.6)	4.26 *dd* (12.4, 5.6)
	3.88 *dd* (12.0, 2.1)	4.14 *dd* (12.3, 2.6)	3.88 *dd* (12.0, 2.1)	4.15 *dd* (12.4, 2.6)
$COCH_3$	–	2.03 *s* 9H	–	2.03 *s* 9H
		1.99 *s* 3H		1.99 *s* 3H

*Coupling constants (*J* in Hz) are given in parentheses.
†Unresolved.

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

C	**1**	**2**
1	144.6	144.6
2	110.6	110.5
3	158.4	160.2
4	102.7	102.6
5	162.2	162.1
6	109.7	109.7
1′	145.6	145.4
2′	116.6	115.4
3′	160.2	161.2
4′	114.0	112.5
5′	130.3	130.3
6′	121.0	122.1
-CH_2CH_2-	38.6	38.8
-CH_2CH_2-	39.0	39.1
5-OMe	55.9	55.8
3′-OMe	–	55.7
Glucose		
1″	102.0	102.0
2″	75.1	75.0
3″	78.2	78.2
4″	71.7	71.6
5″	78.1	78.1
6″	62.8	62.7

Compound **2** was isolated as needles, mp 154–158° (methanol). The FAB-mass spectrum exhibited a $[M]^+$ at *m/z* 420 ($C_{22}H_{28}O_8$), 14 mu more than that of compound **1** and a peak at *m/z* 258[M − sugar]$^+$. Furthermore, the fragment ion at *m/z* 121, corresponding to the methoxytropylium, was observed instead of the peak at *m/z* 107 in compound **1**. The ^{1}H NMR spectrum showed that the signals of the aromatic protons depend on the same substitution patterns as those of compound **1**. On comparing the ^{1}H and ^{13}C NMR spectra of compound **2** with those of compound **1**, the additional signal due to the methoxyl group appeared at δ_H 3.74 and δ_C 55.7, respectively. Thus, compound **2** was concluded to be a 3′-methylether of compound **1**. Enzymic hydrolysis gave glucose and the aglycone, 3′, 5-dimethoxy-3-hydroxybibenzyl(3′-*O*-methylbatatasin III) which was identical to an authentic sample. From the above data, the structure of compound **2** was concluded to be 3′, 5-dimethoxybibenzyl-3-*O*-*β*-D-glucopyranoside.

EXPERIMENTAL

General. Mps, uncorr. IR: KBr. UV: MeOH. ^{1}H NMR and ^{13}C NMR: 500 and 125 MHz, respectively, MeOH-d_4 with TMS. CC and TLC were performed using Merck silica gel. HPLC: column, Waters Associates, *μ*Bondapak CH, 1/4″ × 1′; eluent: MeCN–H_2O(80:20); flow rate, 0.8 ml min^{-1}; RI detector.

Plant materials. See ref. [1].

Extraction and isolation. See ref. [1]. Fr. 8 was rechromatographed over silica gel, LH-20, HP-20 and Cosmosil C_{18} to give compounds **1** (150 mg) and **2** (100 mg).

Compound **1**. Powder. IR ν_{max}^{KBr} cm^{-1}: 3250, 1580. UV λ_{max}^{MeOH} nm (log *ε*): 238(4.07), 269(4.04), 286(3.88). ^{1}H NMR: Table 1; ^{13}C NMR: Table 2. FAB-MS *m/z* (rel. int.): 406[M]$^+$(7), 244(100), 137(50), 107(36).

Pentaacetate. Powder. ^{1}H NMR: Table 1. FAB-MS *m/z* (rel. int.): 617[M+1]$^+$(3), 407(5), 137(89), 107(99).

Compound **2**. Needles, mp 154–158° (MeOH). IR ν_{max}^{KBr} cm^{-1}: 3380, 1580, 1455. UV λ_{max}^{MeOH} nm (log ε): 225(3.20), 272(2.53), 280(2.50). ^{1}H NMR: Table 1; ^{13}C NMR: Table 2. FAB-MS *m/z* (rel.int.): 420[M]$^+$(8), 258(100), 136(78), 121(43).

Tetraacetate. Powder. ^{1}H NMR: Table 1. FAB-MS *m/z* (rel.int.): 589[M+1]$^+$(8), 136(100), 121(45).

Enzymic hydrolysis of glucosides. Each compound (10 mg) was dissolved in 5 ml H_2O–MeOH (10:1) and treated with β-glucosidase at 37° for 5 hr. After evapn to dryness, the residue was dissolved in 5 ml H_2O, then extracted with EtOAc to give an aglycone; it was compared with the authentic sample by TLC and the redissolved residue in H_2O was detected by HPLC as glucose.

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