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FIVE TETRAHYDROISOQUINOLINE-MONOTERPENE GLYCOSIDES WITH A DISACCHARIDE MOIETY FROM *ALANGIUM LAMARCKII*

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Key Word Index—*Alangium lamarckii*; Alangiaceae; fruits; structure elucidation; tetrahydroisoquinoline-monoterpene glycosides; alangiside.

Abstract—Five novel tetrahydroisoquinoline-monoterpene glycosides, 6′-*O*-β-D-glucopyranosylalangiside, 3′-*O*-β-D-glucopyranosylalangiside, 6′-*O*-α-D-glucopyranosylalangiside, 6′-*O*-α-D-glucopyranosyl-3-*O*-demethyl-2-*O*-methylalangiside and 6′-*O*-α-D-xylopyranosylalangiside, were isolated from dried fruits of *Alangium lamarckii*. The structures of these new compounds were determined by spectroscopic means. © 1997 Elsevier Science Ltd

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INTRODUCTION

Alangium lamarckii Thwaites is a deciduous shrub of wide distribution in India and South East Asia, and has been used in Indian folk medicine for many years. It is known to contain the Ipecac alkaloids emetine and cephaeline, as well as benzopyridoquinolizine alkaloids [1-3]. On account of our interest in the tetrahydroisoquinoline-monoterpene glucosides closely related to Ipecac alkaloids, we have recently examined the fruits of *A. lamarckii* and isolated several new glucosides [4–7]. Further investigation of the more polar constituents of this plant has led to the isolation of five new tetrahydroisoquinoline-monoterpene glycosides (**1**–**5**) with a disaccharide moiety. We report here the structure elucidation of these compounds.

RESULTS AND DISCUSSION

Compound **1** was isolated as an amorphous powder. It showed UV maxima at 233 and 284 nm and IR bands at 3394, 1657, 1583, 1514 and 903 cm^{-1}. Its ^{1}H NMR spectrum exhibited a doublet for an olefinic proton at δ 7.41 ($J = 2.5$ Hz), a singlet for two aromatic protons at δ 6.69, signals for a terminal vinyl group at δ 5.20 (*dd*, $J = 10.0$ and 1.5 Hz), 5.30 (*dd*, $J = 17.0$ and 1.5 Hz) and 5.51 (*dt*, $J = 17.0$ and 10.0 Hz), a doublet for an acetal proton at δ 5.45 ($J = 1.5$ Hz), a doublet for an anomeric proton at δ 4.70 ($J = 8.0$ Hz) and a signal for a methoxyl group at δ 3.83, indicating the presence of an alangiside (**6**) moiety in the molecule. This was also supported by its SI mass spectrum which showed fragment ions at *m/z* 506 and 344 due to an alangiside moiety and an aglycone moiety, respectively [7]. Furthermore, the coupling constants between H_2-13 and H-13a ($J_{13\alpha,13a} = 12.0$ Hz, $J_{13\beta,13a} = 3.5$ Hz) and the chemical shifts of C-6, C-12a and C-13 indicated an *R*-configuration at C-13a [5, 6] and the chemical shifts of aromatic protons and carbons (Tables 1 and 2) indicated a methoxyl group at C-3 [6, 7]. Its HR SI mass spectrum showed a pseudomolecular ion $[M + H]^+$ at *m/z* 668.2563, consistent with a molecular formula $C_{31}H_{41}NO_{15}$, which was $C_6H_{10}O_5$ more than that of **6**, suggesting the presence of one additional hexose in **1**. The ^{1}H and ^{13}C NMR spectra showed, besides the signals due to an alangiside moiety, an anomeric proton signal at δ 4.37 (*d*, $J = 7.5$ Hz) and glucosyl carbon signals (Table 2). Thus, one additional hexose was assigned to β-glucose. The location of the glucose unit at C-6′ of the alangiside (**6**) moiety was determined by means of the following observations: (i) downfield shift of C-6′ (Δ 7.2 ppm) and upfield shift of C-5′ (Δ − 1.1 ppm) when compared with **6**; (ii) NOE interaction between H-1″ and H-6′ [(δ 3.80 (*dd*, $J = 11.5$ and 5.5 Hz)]; and (iii) HMBC correlations of H_2-6′ [δ 3.80, 4.18 (*dd*, $J = 11.5$ and 2.0 Hz)] to C-1″ (δ 104.9) and H-1″ to C-6′ (δ 69.9). Further, the β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside unit was substantiated by the agreement of ^{13}C NMR chemical shifts of the sugar moiety in **1** with those of 6′-*O*-β-D-glucosylgentiopicroside [8]. Thus, compound **1** was characterized as 6′-*O*-β-D-glucopyranosylalangiside.

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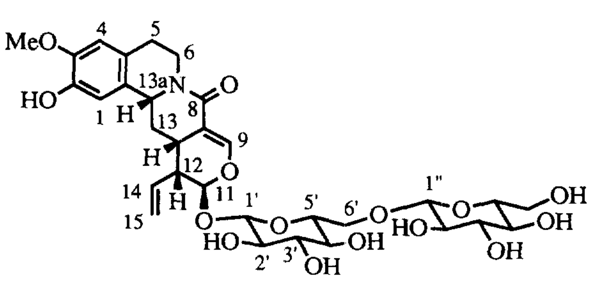

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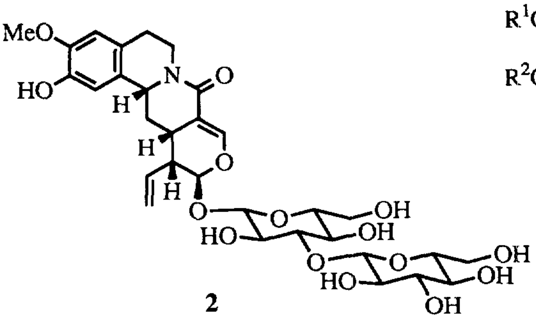

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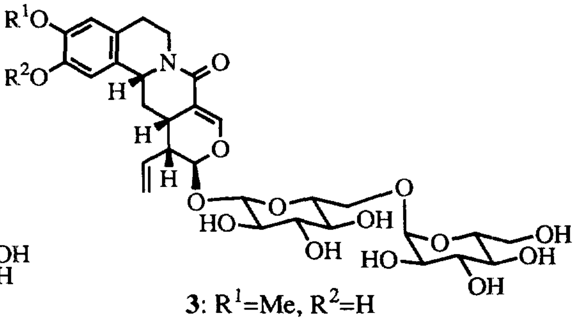

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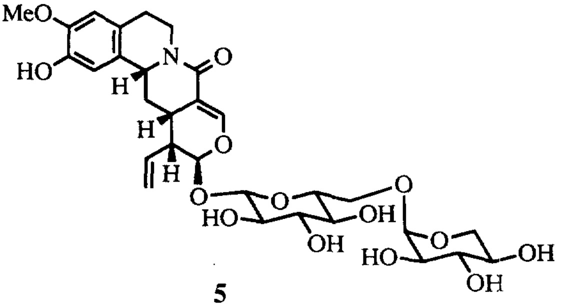

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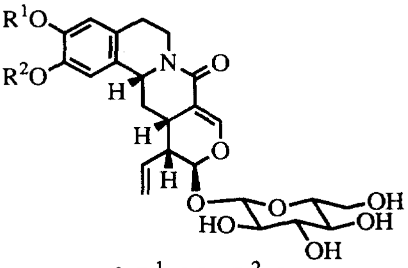

6: R^1=Me, R^2=H
7: R^1=H, R^2=Me

The second glycoside **2** had the same molecular formula as **1**. Its ^{1}H and ^{13}C NMR spectral features were closely similar to those of **1**, suggesting that compound **2** also consisted of an alangiside (**6**) moiety and another β-glucosyl unit. The attachment of the second glucosyl unit at C-3′ of the alangiside moiety was confirmed by the downfield shift of C-3′ and the upfield shifts of C-2′ and C-4′ as well as cross-peaks between H-3′ (δ 3.59) and C-1″ (δ 105.3) and between H-1″ (δ 4.57) and C-3′ (δ 87.5) in the HMBC spectrum. Accordingly, compound **2** was assigned to 3′-*O*-β-D-glucopyranosylalangiside.

Glycosides **3** and **4** were also obtained as amorphous powders. The HR-SIMS measurements of **3** and **4** revealed the same molecular formula $C_{31}H_{41}NO_{15}$, isomeric with **1** and **2**. The ^{1}H and ^{13}C NMR spectra of **3** and **4** were closely related to those of **6** and 3-*O*-demethyl-2-*O*-methylalangiside (**7**), respectively, except for the signals arising from the sugar moiety. Thus, glycosides **3** and **4** possessed **6** and **7** as a basic skeleton, respectively. The ^{13}C NMR spectra of **3** and **4** exhibited two glucose units, and the downfield shifts of C-6′ as well as the upfield shifts of C-5′ in each glycoside. Accordingly, the second glucosyl unit in **3** and **4** was located at C-6′ as in **1**, and this was also supported by the cross-peaks between H-6′ (**3**: δ 3.80; **4**: δ 3.80 and 3.97) and C-1″ (**3** and **4**: δ 99.9) in HMBC experiments. The second glucosyl linkage in each glycoside was determined to be α from the coupling constant (**3** and **4**: $J_{1'',2''}$ = 3.5 Hz) of the anomeric proton and the chemical shift of the anomeric carbon [9]. Furthermore, the chemical shifts of carbon signals arising from the glycosyl moiety of **3** and **4** were in good agreement with those of hunterioside (strictosidinic acid 6′-α-D-glucoside) [10]. Thus, glycosides **3** and **4** were characterized as 6′-*O*-α-D-glucopyranosylalangiside and 6′-*O*-α-D-glucopyranosyl-3-*O*-demethyl-2-*O*-methylalangiside, respectively.

The fifth new glycoside **5** was isolated as an amorphous powder. The ^{1}H and ^{13}C NMR spectra of its alangiside moiety were closely related to those of **3**. Its SI mass spectrum showed a $[M+H]^+$ ion at *m/z* 638, and fragment ion peaks at *m/z* 506 and 344 indicated that **5** consisted of **6** and one additional pentose. The residual sugar was determined to be α-xylose by its ^{1}H NMR [δ 4.80 (*d*, J = 3.5 Hz, H-1″), 3.36 (*dd*,

Table 1. ^{1}H NMR data for compounds **1**–**5** in CD_3OD

H	**1**	**2**	**3***	**4***	**5**
1	6.69 *s*	6.69 *s*	6.69^a *s*	6.79 *s*	6.69 *s*
4	6.69 *s*	6.70 *s*	6.70^a *s*	6.59 *s*	6.69 *s*
5	2.66 *dt* (15.5, 3.0)	2.67 *dt* (15.5, 3.5)	2.66 *dt* (15.5, 3.5)	2.60 *dt* (15.5, 3.0)	2.66 *dt* (15.5, 3.0)
5	2.76 *ddd* (15.5, 11.0, 4.0)	2.76 *ddd* (15.5, 11.0, 4.5)	2.77 *ddd* (15.5, 11.0, 4.5)	2.73 *ddd* (15.5, 11.5, 4.5)	2.76 *ddd* (15.5, 11.0, 4.5)
6	2.89 *ddd* (12.5, 11.0, 3.0)	2.89 *ddd* (12.0, 11.0, 3.5)	2.90 *ddd* (12.5, 11.0, 3.5)	2.87 *ddd* (12.5, 11.5, 3.0)	2.89 *ddd* (12.5, 11.0, 3.0)
6	4.71 *m*	4.68–4.75 *m*	4.69 *ddd* (12.5, 4.5, 3.5)	4.72 *ddd* (12.5, 4.5, 3.0)	4.70 *ddd* (12.5, 4.5, 3.0)
9	7.41 *d* (2.5)	7.41 *d* (2.5)	7.41 *d* (2.5)	7.41 *d* (2.5)	7.41 *d* (2.5)
11	5.45 *d* (1.5)	5.49 *d* (2.0)	5.42 *d* (1.5)	5.42 *d* (1.5)	5.42 *d* (1.5)
12	2.71 *br dd* (10.0, 5.5)	2.71 *ddd* (10.0, 5.5, 1.5)	2.71 *ddd* (10.0, 5.5, 1.5)	2.73 *ddd* (10.0, 5.5, 1.5)	2.71 *ddd* (10.0, 5.5, 1.5)
12a	3.18 *dddd* (13.0, 5.5, 3.5, 2.5)	3.17 *m*	3.18 *dddd* (13.0, 5.5, 3.5, 2.5)	3.20 *dddd* (13.0, 5.5, 3.5, 2.5)	3.18 *dddd* (13.0, 5.5, 3.5, 2.5)
13	1.35 *td* (13.0, 12.0)	1.35 *td* (13.0, 11.5)	1.38 *td* (13.0, 11.5)	1.39 *td* (13.0, 11.5)	1.36 *td* (13.0, 11.5)
13	2.31 *dt* (13.0, 3.5)	2.31 *dt* (13.0, 3.5)	2.31 *dt* (13.0, 3.5)	2.38 *dt* (13.0, 3.5)	2.31 *dt* (13.0, 3.5)
13a	4.72 *br d* (12.0)	4.68–4.75 *m*	4.72 *br d* (11.5)	4.77 *dd* (11.5, 3.5)	4.72 *dd* (11.5, 3.5)
14	5.51 *dt* (17.0, 10.0)	5.52 *dt* (17.0, 10.0)	5.52 *dt* (17.0, 10.0)	5.53 *dt* (17.0, 10.0)	5.51 *dt* (17.0, 10.0)
15	5.20 *dd* (10.0, 1.5)	5.19 *dd* (10.0, 2.0)	5.19 *dd* (10.0, 2.0)	5.20 *dd* (10.0, 1.5)	5.19 *dd* (10.0, 2.0)
15	5.30 *dd* (17.0, 1.5)	5.28 *dd* (17.0, 2.0)	5.30 *dd* (17.0, 2.0)	5.31 *dd* (17.0, 1.5)	5.30 *dd* (17.0, 2.0)
1′	4.70 *d* (8.0)	4.74 *d* (8.0)	4.72 *d* (8.0)	4.73 *d* (8.0)	4.71 *d* (8.0)
2′	3.21 *br t* (8.5)	3.41 *dd* (9.0, 8.0)	3.24 *dd* (9.0, 8.0)	3.23 *dd* (9.0, 8.0)	3.23 *dd* (9.0, 8.0)
3′	3.25–3.41 *m*	3.59 *t* (9.0)	3.40 *t* (9.0)	3.40 *t* (9.0)	3.39 *t* (9.0)
4′	3.25–3.41 *m*	3.42 *dd* (10.0, 9.0)	3.43 *t* (9.0)	3.43 *t* (9.0)	3.41 *t* (9.0)
5′	3.52 *ddd* (9.5, 5.5, 2.0)	3.37 *ddd* (10.0, 5.5, 2.0)	3.54 *ddd* (9.0, 5.0, 2.0)	3.54 *ddd* (9.0, 4.5, 2.0)	3.53 *ddd* (9.0, 5.5, 2.0)
6′	3.80 *dd* (11.5, 5.5)	3.70 *dd* (12.0, 5.5)	3.80 *dd* (11.0, 2.0)	3.80 *dd* (11.0, 2.0)	3.77 *dd* (11.0, 2.0)
6′	4.18 *dd* (11.5, 2.0)	3.91 *dd* (12.0, 2.0)	3.97 *dd* (11.0, 5.0)	3.97 *dd* (11.0, 4.5)	3.91 *dd* (11.0, 5.0)
OMe	3.83 *s*	3.83 *s*	3.83 *s*	3.84 *s*	3.83 *s*
1″	4.37 *d* (7.5)	4.57 *d* (8.0)	4.87 *d* (3.5)	4.87 *d* (3.5)	4.80 *d* (3.5)
2″	3.23 *br t* (8.5)	3.26 *dd* (9.0, 8.0)	3.40 *dd* (9.5, 3.5)	3.40 *dd* (9.5, 3.5)	3.36 *dd* (9.5, 3.5)
3″	3.25–3.41 *m*	3.38 *t* (9.0)	3.66 *t* (9.5)	3.66 *t* (9.5)	3.59 *dd* (9.5, 9.0)
4″	3.25–3.41 *m*	3.27 *dd* (10.0, 9.0)	3.33 *br t* (9.5)	3.33 *t* (9.5)	3.47 *ddd* (10.5, 9.0, 5.5)
5″	3.25–3.41 *m*	3.31 *m*	3.68 *ddd* (9.0, 5.0, 2.0)	3.69 *ddd* (9.5, 5.0, 2.0)	3.54 *dd* (10.5, 5.5)
5″	—	—	—	—	3.58 *t* (10.5)
6″	3.67 *dd* (12.0, 5.5)	3.63 *dd* (12.0, 6.0)	3.70 *dd* (11.0, 5.0)	3.70 *dd* (11.5, 5.0)	—
6″	3.87 *dd* (12.0, 2.0)	3.88 *dd* (12.0, 2.0)	3.82 *dd* (11.0, 2.0)	3.81 *dd* (11.5, 2.0)	—

Values in parentheses are coupling constants in Hz.

* Measured at 50°.

[a] Assignments are interchangeable.

Table 2. ^{13}C NMR data for compounds **1**–**7** in CD_3OD

C	**1**	**2**	**3**	**4**	**5**	**5***	**6**	**7**
1	113.3	113.3	113.3	110.3	113.3	112.9[i]	113.3	110.3
2	146.4	146.4	146.4	148.1	146.4	144.2	146.4	148.2
3	148.0	148.0	148.0	146.5	147.9	146.8	148.0	146.5
4	112.7	112.6	112.6	116.1	112.6	112.7[i]	112.6	116.1
4a	127.3	127.3	127.3	128.9[f]	127.2	127.6	127.3	128.9[k]
5	29.6	29.6	29.5	29.4	29.5	28.6	29.5	29.4
6	41.0	41.0	41.0	40.8	40.9	40.8	41.0	40.8
8	166.0	166.0	165.9	165.9	165.9	165.9	166.0	166.0
8a	109.3	109.3	109.3	109.3	109.3	108.7	109.3	109.3
9	148.8	148.8	148.7	148.7	148.7	148.0	148.8	148.8
11	97.7	97.6	97.8	97.9	97.9	97.8	97.5	97.6
12	44.5	44.5	44.5	44.4	44.5	43.1	44.5	44.5
12a	27.8	27.8	27.8	27.8	27.7	26.5	27.8	27.9
13	35.0	35.1	35.0	35.2	35.0	33.6	35.1	35.3
13a	57.0	57.0	57.0	57.3	57.0	56.5	57.0	57.3
13b	130.3	130.3	130.2	128.7[f]	130.2	129.5	130.3	128.8[k]
14	133.9	134.0	133.8	133.8	133.7	132.4	134.0	134.0
15	120.6	120.5	120.7	120.6	120.6	121.1	120.4	120.4
1′	99.8	99.4	100.1[d]	100.1[g]	100.0	98.9[j]	99.7	99.7
2′	74.8[a]	74.2	74.8	74.7	74.7	73.4	74.9	74.9
3′	77.9[b]	87.5	78.0	78.0	78.0	76.5	78.0	78.1
4′	71.4	70.1	71.4	71.4	71.5	70.1	71.6	71.6
5′	77.3	77.9[c]	76.7	76.7	76.7	75.4	78.4	78.4
6′	69.9	62.6	67.5	67.5	67.8	66.5	62.7	62.7
OMe	56.4	56.4	56.4	56.7	56.4	56.1	56.4	56.7
1″	104.9	105.3	99.9[d]	99.9[g]	100.4	99.1[j]	—	—
2″	75.1[a]	75.6	73.7[e]	73.7[h]	73.8	72.2	—	—
3″	78.1[b]	78.1[c]	75.3	75.3	75.3	73.9	—	—
4″	71.6	71.6	71.7	71.7	71.5	70.1	—	—
5″	78.1	78.2[c]	73.8[e]	73.8[h]	63.2	62.1	—	—
6″	62.8	62.7	62.7	62.6	—	—	—	—

* Measured in D_2O. Internal standard was MeOH (49.6 ppm).

[a–k] Values with same superscript are interchangeable.

$J = 9.5$ and 3.5 Hz, H-2″), 3.59 (*dd*, $J = 9.5$ and 9.0 Hz, H-3″), 3.47 (*ddd*, $J = 10.5$, 9.0 and 5.5 Hz, H-4″), 3.54 (*dd*, $J = 10.5$ and 5.5 Hz, H-5″) and 3.58 (*t*, $J = 10.5$ Hz, H-5″)], and ^{13}C NMR spectral features (Table 2). Additionally, attachment of the α-xylose unit at C-6′ of the alangiside moiety was shown by the downfield shift of C-6′ relative to **6**, and long range C-H coupling between H_2-6′ (δ 3.77 and 3.91) and C-1″ (δ 100.4) in HMBC experiments. That the sugar moiety was α-xylopyranosyl-(1 → 6)-β-D-glucopyranoside was also supported by the agreement of the glycosyl carbon signals of **5** with the corresponding signals of aucubigenin-1-*O*-β-serotinoside [11] in their ^{13}C NMR spectra in D_2O. Compound **5** was then deduced to be 6′-*O*-α-D-xylopyranosylalangiside.

This is the first isolation of tetrahydroisoquinoline-monoterpene glycosides with a disaccharide moiety.

EXPERIMENTAL

General. ^1H (500 MHz) and ^{13}C (125 or 75 MHz) NMR spectra were recorded at room temp. (unless otherwise specified), with TMS as int. standard (unless otherwise specified). SIMS: glycerol as matrix.

Plant material. The dried fruits of *Alangium lamarckii*, collected in India, were purchased from Mikuni, Osaka, Japan. A voucher specimen (KPFY-921) is deposited in our laboratory.

Extraction and isolation. Dried fruits (4.5 kg) of *A. lamarckii* were crushed and extracted with hot MeOH, and the extract was fractionated as described previously [6]. Fr. 8 in ref. [6] was chromatographed on silica gel and elution with $CHCl_3$–MeOH (9:1–17:3) afforded 5 frs, 8/a–8/e. Fr. 8/a was purified by prep. HPLC (μBondasphere 5μ C18-100 Å, MeOH–H_2O, 9:11), giving **6** (206 mg) [3] and **7** (30.5 mg) [4]. Frs 8/b and 8/c were also purified by prep. HPLC with MeOH–H_2O (9:11), giving demethylalangiside (1.3 mg) [12] and **6** (2.2 mg) as well as demethylalangiside (228.8 mg), 10-hydroxyvincoside lactam (17.7 mg) [6], demethylneoalangiside (10.6 mg) [6], **5** (15.2 mg) and **6** (11.9 mg). Fr. 8/d was further subjected to a reversed-phase MPLC with MeOH–H_2O (2:3) giving 2 frs, each of which was purified by prep. HPLC with MeOH–H_2O (1:1) to give **2** (9.1 mg) and **5** (6.5 mg), respectively. Fr. 8/e was purified by prep. HPLC with MeOH–H_2O (9:11) to afford loganic acid (233.8 mg) [3], demethylalangiside (5.8 mg) and **6** (5.4 mg). In the same way, the following frs were purified by a combination of reversed-phase MPLC with MeOH–H_2O (3:7–2:3) and prep. HPLC with MeOH–H_2O (1:1, 9:11, 2:3). Fr. 9 yielded demethylneoalangiside (0.9 mg), **6** (105.3 mg) and **7** (18.1 mg); fr. 10: demethylalangiside (32.6 mg), **1** (8.5 mg), **3** (119.3 mg), **4** (10.3 mg) and **6** (101 mg); fr. 11: demethylalangiside (29.7 mg), **1** (9.2 mg), **3** (20.7 mg), **6** (78.1 mg) and **7** (13 mg).

6′-O-β-D-*Glucopyranosylalangiside* (**1**). Amorphous powder, $[\alpha]_D^{26} - 81°$ (c = 0.67, MeOH). UV λ_{max}^{MeOH} nm (log ε): 233 (4.32), 284 (3.67); IR ν_{max}^{KBr} cm^{-1}: 3394 (OH), 1657 (NCO), 1583 (Ar), 1514 (Ar), 903 (C=C); ^{1}H NMR: Table 1; ^{13}C NMR: Table 2; NOESY: H-11/H-1′; H-6′ (δ 3.80)/H-1″; HMBC: H-11 → C-1′; H-1′ → C-11; H-6′ (δ 3.80) → C-1″; H-6′ (δ 4.18) → C-1″; H-1″ → C-6′; SIMS m/z: 690 $[M+Na]^+$, 668 $[M+H]^+$, 506, 344, 326, 274, 178; HR-SIMS Found: 668.2563 $[M+H]^+$; $C_{31}H_{42}NO_{15}$ requires 668.2556.

3′-O-β-D-*Glucopyranosylalangiside* (**2**). Amorphous powder, $[\alpha]_D^{26} - 107°$ (c = 0.52, MeOH). UV λ_{max}^{MeOH} nm (log ε): 233.5 (4.34), 284 (3.71); IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1653 (NCO), 1570 (Ar), 1516 (Ar), 903 (C=C); ^{1}H NMR: Table 1; ^{13}C NMR: Table 2; HMBC: H-11 → C-1′; H-1′ → C-11; H-3′ → C-1″; H-3′ → C-2′; H-3′ → C-4′; H-1″ → C-3′; SIMS m/z: 690 $[M+Na]^+$, 668 $[M+H]^+$, 506, 344, 326, 178; HR-SIMS Found: 668.2557 $[M+H]^+$; $C_{31}H_{42}NO_{15}$ requires 668.2556.

6′-O-α-D-*Glucopyranosylalangiside* (**3**). Amorphous powder, $[\alpha]_D^{26} - 33°$ (c = 1.0, MeOH), CD λ_{max}^{MeOH} nm (Δ ε): 236 (−14.4). UV λ_{max}^{MeOH} nm (log ε): 234 (4.34), 284 (3.69); IR ν_{max}^{KBr} cm^{-1}: 3394 (OH), 1655 (NCO), 1578 (Ar), 1514 (Ar), 903 (C=C); ^{1}H NMR: Table 1; ^{13}C NMR: Table 2; HMBC: H-11 → C-1′; H-1′ → C-11; H-6′ (δ 3.78) → C-1″; H-6′ (δ 3.97) → C-1″; SIMS m/z: 690 $[M+Na]^+$, 668 $[M+H]^+$, 506, 344, 326, 274, 178; HR-SIMS Found: 668.2580 $[M+H]^+$; $C_{31}H_{42}NO_{15}$ requires 668.2556.

6′-O-α-D-*Glucopyranosyl*-3-O-*demethyl*-2-O-*methylalangiside* (**4**). Amorphous powder, $[\alpha]_D^{30} + 2.4°$ (c = 0.69, MeOH), CD λ_{max}^{MeOH} nm (Δ ε): 239 (−12.3). UV λ_{max}^{MeOH} nm (log ε): 234 (4.32), 283 (3.65), 292 sh (3.55); IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1655 (NCO), 1578 (Ar), 1516 (Ar), 905 (C=C); ^{1}H NMR: Table 1; ^{13}C NMR: Table 2; NOESY: H-1/H-13 (δ 2.39); H-1/OMe; H-4/H-5 (δ 2.60); HMBC: H-11 → C-1′; H-1′ → C-11; H-6′ (δ 3.78) → C-1″; H-6′ (δ 3.98) → C-1″; SIMS m/z: 690 $[M+Na]^+$, 668 $[M+H]^+$, 506, 344, 326, 274, 178; HR-SIMS Found: 668.2576 $[M+H]^+$; $C_{31}H_{42}NO_{15}$ requires 668.2556.

6′-O-α-D-*Xylopyranosylalangiside* (**5**). Amorphous powder, $[\alpha]_D^{29} - 38°$ (c = 0.33, MeOH). UV λ_{max}^{MeOH} nm (log ε): 233.5 (4.32), 284 (3.68); IR ν_{max}^{KBr} cm^{-1}: 3410 (OH), 1655 (NCO), 1578 (Ar), 1514 (Ar), 903 (C=C); ^{1}H NMR: Table 1; ^{13}C NMR: Table 2; NOESY: H-11/H-1′; H-6′ (δ 3.77)/H-1″; HMBC: H-11 → C-1′; H-1′ → C-11; H-6′ (δ 3.77) → C-1″; H-6′ (δ 3.91) → C-1″; SIMS m/z: 660 $[M+Na]^+$, 638 $[M+H]^+$, 506, 344, 326, 178; HR-SIMS Found: 638.2425 $[M+H]^+$; $C_{30}H_{40}NO_{14}$ requires 638.2450.

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