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MALABARICANE TRITERPENE GLUCOSIDES FROM *ADESMIA ACONCAGUENSIS*

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Key Word Index—*Adesmia aconcaguensis*; Leguminosae; triterpene glucosides; malabaricane derivatives.

Abstract—Three new triterpenes, belonging to the rare malabaricane class, have been isolated from *Adesmia aconcaguensis* and assigned the structures, 3β,12α,25,30-tetrahydroxy-14*R*,17*R*,20*R*,24*S*-diepoxy-malabaricane-3-*O*-β-glucopyranoside, 3β,12α,14,17,25-pentahydroxy-20*R*,24*S*-epoxymalabaricane-3-*O*-β-glucopyranoside and 3β,12α, 20*R*,24*S*,25-pentahydroxy-14*R*,17*R*-epoxymalabaricane-3-*O*-β-glucopyranoside.

INTRODUCTION

The Leguminosae have been studied extensively because of their pharmacological and nutritional importance. However, a great number of tribes still lack any chemical and biological data. The genus *Adesmia* (tribe Adesmieae), which includes 230 species, is distributed in arid or semi-arid zone of South America and is found along the Cordillera de Los Andes from northern Peru to the Tierra del Fuego [1]. Only one chemical study, dealing with the flavonoids present in species from Argentina, has been hitherto reported on this genus [2]. We report herein on the structural elucidation of three new malabaricane-type triterpene glucosides (**1**–**3**), which were isolated from *A. aconcaguensis* Burk., a perennial herbaceous species endemic to the central Chilean Andes.

RESULTS AND DISCUSSION

The fragmentation of compound **1** in the FAB-mass spectrum was characterized by the losses of one to three molecules of H_2O from the quasi-molecular ion at *m/z* 671 and by prominent ions at *m/z* 227 and 143 (base peak). The presence of two fragments at *m/z* 509 and 491, corresponding to the losses of 162 and 180 mu from the $[M + H]^+$ suggested a glycosidic structure for **1**, in accordance with its high polarity. This was confirmed by ^1H and ^{13}C NMR spectra which showed signals for a glucopyranosyl moiety (Table 1). In particular, the chemical shifts of H-1′ and C-1′ (δ4.95 with $J = 8.0$ Hz and δ107.5, respectively), required the glucosyl moiety to be β-oriented [3].

The ^1H and ^{13}C NMR data (Tables 2 and 3, respectively) and the results obtained from decoupling, COSY and HETCOR experiments gave support for the aglycone **1a**, in agreement with an M_r of 508 and an empirical formula of $C_{30}H_{52}O_6$. The following groups were revealed to be present in the triterpene: seven methyls, 10 methylenes (one of which was connected to an oxygen), seven methines (four CH–O) and six quaternary carbons (three C–O). These findings, to be consistent with the formula $C_{30}H_{52}O_6$, require the triterpene moiety **1a** to contain five rings (no double bonds being present), four hydroxyl groups and two ether bridges. A complete proton and carbon chemical-shifts assignment was achieved by the use of FLOCK [4] and selective long-range INEPT [5] measurements; these results are summarized in Table 4. For instance, the isopropyloxy grouping (C-25,C-26 and C-27 in Table 3) was connected by the FLOCK experiment ($^3J_{26,24}$ and $^3J_{27,24}$) to a trisubstituted tetrahydrofuran ring (C-20 to C-24), as represented by the partial structure **a** (Scheme 1). The chemical-shift values for carbon and proton signals reported in the literature for the partial structure **a** of dammarane [6–13] or cycloartane [14–16] triterpenes are in general agreement with those of **1**. In the mass spectra of the above mentioned triterpenes, the loss of the side-chain **a**, by the characteristic α-fission of α-substituted tetrahydrofurans [17], yields the ion $[a]^+$ at *m/z* 143, which in general is the base peak and is flanked by a fragment at *m/z* 125 (loss of H_2O) [8, 13]. In the mass spectrum of **1**, the presence of $[\mathbf{a}]^+$ as the base peak (*vide supra*) and its companion ion

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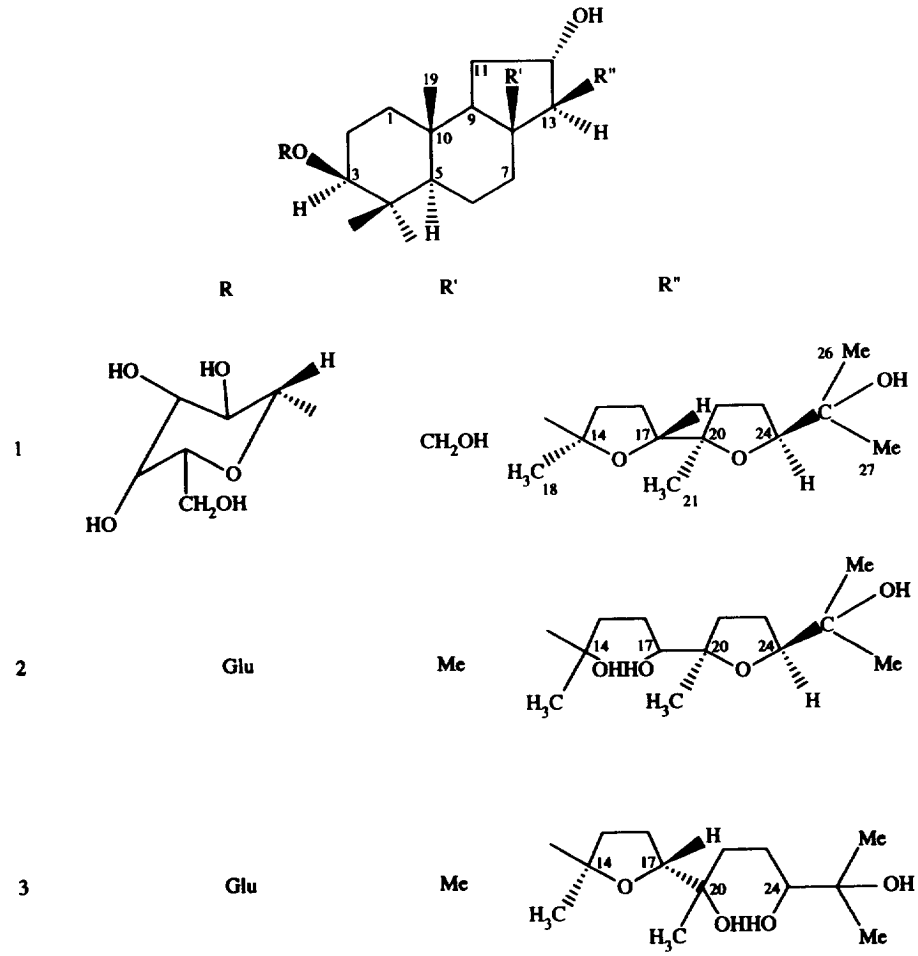


Table 1. Carbon and proton signals of the glucose moiety in compounds 1–3*

	1		2		3	
Position	[δ_C]	δ_H**	[δ_C]	δ_H**	[δ_C]	δ_H**
1′	107.5	4.95	107.6	4.98	107.5	4.97
2′	76.4	4.05	76.4	4.09	76.4	4.08
3′	78.9	4.27	78.8	4.28	78.8	4.27
4′	72.3	4.24	72.4	4.25	72.4	4.25
5′	79.3	3.98	79.4	4.01	79.3	3.99
6′a	63.6	4.59	63.6	4.61	63.6	4.59
6′b	63.6	4.42	63.6	4.43	63.6	4.42

*100 and 400 MHz, respectively, in C_5D_5N; TMS as internal standard. Assignments supported by decoupling, COSY and HETCOR experiments.

**$J_{H,H}$ coupling constants (Hz): $J_{1',2'} = 8.0$; $J_{2',3'} = 8.5$; $J_{3',4'} = 9.0$; $J_{4',5'} = 9.0$; $J_{5',6'a} = 2.5$; $J_{5',6'b} = 5.5$; $J_{6'a,6'b} = 11.0$.

(see Experimental) confirms the presence of partial structure **a**.

The ^{13}C NMR spectra of compounds with a 24*R*-configuration show for the C-26 and C-27 methyls different (*ca* 3 ppm) chemical shifts [8, 9, 12, 13], due to a strong hydrogen bond between the tertiary hydroxyl group and the tetrahydrofuran oxygen [9]. By contrast, in the ^{13}C NMR spectra of the 24*S*-series the two methyls exhibit very close values (< 1 ppm). As a consequence, an *S*-configuration was assigned to the C-24 carbon in **1**. The 20*R*-24*S* configuration was then attributed to structure **a**, because selective irradiation of the C-21 methyl protons in a DIFNOE experiment caused enhancement of the H-24 signal.

The remaining proton and carbon signals of compound **1** did not fit, however, with those reported in the literature for the tetracarbocyclic skeleton of dammarane [6–13] and cycloartane [14–16] triterpenes. Moreover, the signals in the ^{13}C NMR spectrum of **1** at δ87.2(*s*), 37.1(*t*), 25.1(*t*) and 84.3(*s*) revealed the presence of a second similar tetrahydrofuran ring. The $^3J_{H\text{-}21/C\text{-}17}$ and $^2J_{H\text{-}17/C\text{-}20}$ connections (Table 4) allowed us to link the two rings as in the partial structure **b**. Accordingly, a fragment [b]$^+$ at *m/z* 227, which yields in turn the ion at *m/z* 209 by the loss of H_2O (m* at 192.4), is present in the mass spectrum of **1**. The stereochemistry 14*R*-17*S* was attributed to structure **b**, since the H-17 proton did not show any NOE effect on the C-18 and C-21 methyl

Table 2. ^{1}H NMR spectra of aglycone moietes **1a**, **2a**, **3a**; δ_H (J in Hz)*

Position	**1a**	**2a**	**3a**
1a	1.26 *dt* (13, 3 × 2)	1.28 *dt* (13, 3 × 2)	1.31 *dt* (13, 3 × 2)
1b	0.91 *dd* (13, 3.5)	0.86 *dd* (13, 7)	0.95 *m*
2a	2.27 *m*	2.26 *dddd* (12, 7, 4.5, 3)	2.30 *m*
2b	1.80 *dt* (11 × 2.3)	1.96 *m*	1.87 *dt* (12 × 3, 3.5)
3	3.46 *dd* (11.5, 4.5)	3.49 *dd* (11.5, 4.5)	3.48 *dd* (11.5, 4.5)
5	0.84 *dd* (8, 6)	0.79 *dd* (9, 6)	0.83 *dd* (10, 4.5)
6a	1.56 *m*	1.55 *m*	1.53 *m*
6b	1.53 *m*	1.52 *m*	1.49 *m*
7a	2.62 *dt* (12, 2.5 × 2)	2.18 *dt* (12, 3 × 2)	2.11 *ddd* (12, 6, 2)
7b	0.97 *m*	1.15 *dt* (12 × 2, 6)	1.17 *dt* (12 × 2, 6)
9	0.99 *m*	0.91 *m*	0.90 *m*
11a	2.02 *ddt* (12, 7.5 × 2, 5)	2.04 *ddd* (13, 6, 3)	2.06 *m*
11b	1.66 *m*	1.76 *dt* (13 × 2, 5)	1.71 *dt* (13 × 2, 3.5)
12	4.71 *ddd* (8, 6, 3)	5.02 *m*	4.75 *ddd* (9, 7, 3.5)
13	1.33 *m*	1.35 *d* (7)	1.33 *d* (7)
15a	2.34 *dt* (11 × 2, 7)	2.71 *dt* (12 × 2, 6)	2.39 *m*
15b	1.69 *m*	2.12 *m*	1.58 *m*
16a	2.18 *m*	2.09 *m*	2.19 *dddd* (13, 11, 5, 1.5)
16b	1.94 *m*	1.92 *m*	1.95 *m*
17	4.02 *t* (7)	3.93 *br d* (10)	4.09 *dd* (7.5, 6)
18	1.44 *s*	1.55 *s*	1.34 *s*
19	0.92 *s*	0.89 *s*	0.88 *s*
21	1.34 *s***	1.41 *s*	1.58 *s*
22a	1.75 *m*	2.49 *ddd* (12, 9, 5.5)	2.37 *m*
22b	1.54 *m*	1.67 *dt* (12, 8 × 2)	1.77 *ddd* (13, 10, 5)
23a	1.99 *m*	2.29 *m*	2.04 *m*
23b	1.88 *m*	1.88 *ddt* (13 × 2, 7, 3)	1.64 *m*
24	3.89 *dd* (9, 5.5)	4.01 *t* (7)	3.78 *dd* (10.5, 1.5)
26	1.33 *s***	1.31 *s*	1.55 *s*
27	1.46 *s*	1.49 *s*	1.51 *s*
28	1.35 *s***	1.39 *s*	1.37 *s*
29	1.00 *s*	1.05 *s*	1.03 *s*
30a	4.29 *br d* (11)	1.59 *s*	1.47 *s*
30b	4.13 *br dd* (11, 6)	—	—

*400 MHz, in C_5D_5N, TMS as internal standard. Assignments supported by COSY spectra.
**Signals can be distinguished by FLOCK experiments or in a $CDCl_3$–C_5D_5N (1:1).

signals. A literature search revealed that groupings similar to the partial structure **b** are found in teurilene, a tricyclic ether with a squalene carbon skeleton [18] and in momensin, a polyetherin antibiotic [19]. Conversely, one of the minor components of *Ailanthus malabarica* was reported to have a side-chain identical to partial structure **b** [20]. The compound belongs to a rare class of tricarbocyclic triterpenes named malabaricanes [20–23]. The proton and carbon chemical shifts (Tables 2 and 3, respectively), as well as the connectivities revealed by Table 4, agree well with the values and results expected for a tricarbocyclic malabaricane skeleton with hydroxyl groups at positions 3,12 and 30. A DIFNOE experiments confirmed the β position of 19-Me and 30-CH_2OH.

The attachment of the sugar moiety at the C-3 position of **1a** was suggested by the lowfield chemical-shift value of C-3 [3] and was confirmed by selective irradiation of the H-3 proton, which showed a long-range correlation with C-1′ (Table 4). Moreover, the coupling constants of H-3 with H-2a and H-2b (11 and 5 Hz, respectively) revealed the C-3(O) substituent, that is the glucosyl moiety, to be equatorial [24].

Finally, the link between the side-chain **b** and the tricyclic skeleton was substantiated by the $^3J_{H3\text{-}18/C\text{-}13}$ correlation (Table 4). Therefore, compound **1** was assigned the structure 3β,12α,25,30-tetrahydroxy-14*R*, 17*R*,20*R*,24*S*-diepoxymalabaricane-3-*O*-β-glucopyranoside.

The other isolated glucosides, **2** and **3**, showed molecular peaks at m/z 673 in their FAB mass spectra. The ^{1}H and ^{13}C NMR spectra of the aglycones **1a**, **2a** and **3a** are compared in Tables 2 and 3, respectively. The signals belonging to the tricarbocyclic skeleton are almost coincident for the three compounds, but the CH_2OH group at C-8 of **1** is substituted in **2** and **3** by a methyl group. This finding is supported by the upfield shift of the signal for C-8 and the downfield shift of that for C-7 and the ^3J connection of H_3-30 protons with carbons 7, 9 and 13 (Table 4). Considering that no other qualitative change occurred in the carbon frameworks (Table 3), the M_rs of

Table 3. ^{13}C NMR spectra of aglycone moietes **1a**, **2a**, **3a**; δ_C*

Carbon	1a	2a	3a
1	39.4 (*t*)	39.3	39.3
2	27.3 (*t*)	27.8	27.1
3	89.9 (*d*)	89.9	90.0
4	40.0 (*s*)	40.0	40.0
5	57.4 (*d*)	57.0	57.1
6	19.9 (*t*)	19.6	19.7
7	38.3 (*t*)	[43.6]	[43.7]
8	50.2 (*s*)	[45.0]	[45.0]
9	62.2 (*d*)	61.7	61.6
10	37.0 (*s*)	37.0	37.1
11	33.3 (*t*)	34.3	33.9
12	72.8 (*d*)	73.7	72.9
13	62.5 (*d*)	61.8	63.0
14	87.2 (*s*)	[77.0]	86.7
15	37.1 (*t*)	[42.8]	37.7
16	25.1 (*t*)	[28.5]	24.6
17	84.3 (*d*)	[78.5]	85.1
18	26.4 (*q*)	26.9	26.7
19	16.5 (*q*)	16.5	16.4
20	84.0 (*s*)	87.5	[73.3]
21	25.3 (*q*)	24.3	25.1
22	35.0 (*t*)	33.8	[38.4]
23	27.3 (*t*)	27.1	27.0
24	86.1 (*d*)	86.2	[80.3]
25	71.4 (*s*)	72.0	[73.3]
26	27.4 (*q*)	27.2	26.8
27	27.5 (*q*)	28.2	26.4
28	28.8 (*q*)	28.8	28.9
29	17.1 (*q*)	17.1	17.2
30	63.2 (*t*)	[18.1 (*q*)]	[18.3]

*100 MHz, in C_5D_5N, TMS as internal standard. Multiplicities, in parentheses, are given only once. Square brackets denote the most significant changes in chemical-shift values compared with those of **1**.

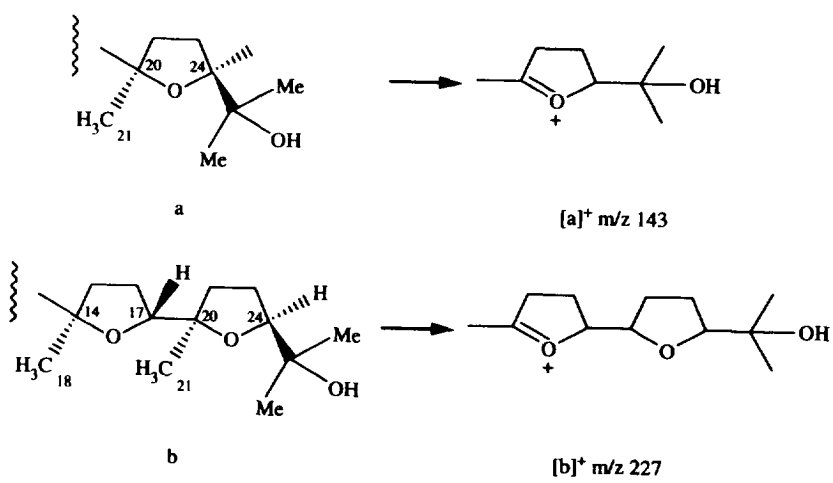
Table 4. Long-range heterocorrelations* for compounds **1–3**

Proton**	Long-range connected carbons**		
	1	**2**	**3**
3	1′	1′	1′
11b	(12)	(12)	(12)
13	(12)	(12)	(12)
17	—	(20)	—
18	13,(14),15	13,(14),15	13,(14),15
19	1,9,(10)	1,5,9,(10)	1,9,(10)
21	20,(22)	17,(20),22	17,(20),22
26	24,(25),27	24,(25),27	24,(25),27
27	24,(25),26	24,(25),26	24,(25),26
28	(4),5,29	3,(4),5,29	3,(4),5,29
29	(4),5,28	3,(4),5,29	(4),5,28
30	—	7,(8),9,13	7,(8),9,13
3′	—	4′	—
4′	—	3′	—
3	1′,(4),28,29	—	—
5	(4),(10),19	—	—
12	8	—	—
18	13,(14),15	—	—
19	5,9,(10)	—	—

*Determined by FLOCK (upper part) and selective INEPT (lower part) experiments. Carbons related by $^2J_{H,C}$ are given in parentheses.

**Values of proton and carbon signals relative to each compound are reported in Tables 2 and 3, respectively.

2 and **3** are expected to be 654. The measured values of 672 may be formally derived by the addition of a molecule of H_2O, combined with ring-opening of one of the tetrahydrofuran rings. In compound **2**, the signals of C-20 to C-27 in the ^{13}C NMR spectrum (Table 3) and the signals of the relative protons in the ^1H NMR spectrum (Table 2) appeared at chemical-shift values very close to those of compound **1** (Table 3 and 2, respectively). By contrast, the carbons and protons relative to C-15, C-16 and C-17 (still two methylenes and an oxygenated methine) showed resonances quite different from those of **1**. These results were in agreement with the postulated opening and hydration of one tetrahydrofuran ring, which thus occurred at C-14 and C-17. In conclusion, the



Scheme 1.

second glucoside was assigned the structure 3β,12α,14,17,25-pentahydroxy-20*R*,24*S*-epoxymalabaricane-3-*O*-β-glucopyranoside (**2**).

In the third compound, C-20, C-22, C-24 and C-25 (and the protons relative to the last three) showed changed chemical-shift values, which suggested the structure **3**. In agreement with this, a fragment at *m/z* 245 was found in the mass spectrum of **3** only. Notably, this ion originated by α-fission at C-14 [17] of the side-chain, yielding again the fragment at *m/z* 227 by the loss of a molecule of H_2O $[M]^+$ at *m/z* 210.3). C-14 in compound **2** is not included in a tetrahydrofuran ring and the ion at *m/z* 245, in spite of the presence of a structural unit having the same weight as in **3**, is not formed. Therefore, the third glucoside was assigned the structure 3β,12α,20*R*,24*S*,25-pentahydroxy-14,17-epoxy-malabaricane-3-*O*-β-glucopyranoside (**3**).

This is the first report on the presence of malabaricane-type triterpenes in the Leguminosae. Compounds with a tricyclic malabaricane skeleton, in addition to those above mentioned from the Simaroubaceae [20, 21], have been previously isolated from Compositae [22] and Polypodiaceae [23]. For the malabaricane-trienes isolated from marine sources [25, 26], which feature a different ring-fusion (*trans-syn-trans* instead a *trans-anti-trans*) of the tricyclic skeleton, the name *iso*-malabaricanes has been proposed [26].

EXPERIMENTAL

Plant material. Adesmia aconcaguensis Burk. was collected in January 1990 at Farellones Sky Center, in the Metropolitan Region of Chile. Voucher specimens are deposited at the herbarium of the Faculty of Sciences, University of Chile, Santiago, Chile.

Extraction and fractionation. Air-dried and finely powdered whole plants (0.34 kg) were defatted with petrol and macerated with EtOH at room temp. The residue of the extract was partitioned between H_2O and $CHCl_3$ (×3). The pooled $CHCl_3$ extracts gave a residue of 9 g, a part of which (2.9 g) after silica gel CC (CH_2Cl_2–MeOH mixts of increasing polarity) afforded compounds **1** (824 mg), **2** (78 mg) and **3** (121 mg).

3β-12α-25,30-*Tetrahydroxy*-14R,17S,20R,24S-*diepoxy-malabaricane*-3-*O*-β-*glucopyranoside* (**1**). $C_{36}H_{62}O_{11}$. $[\alpha]_D = -36.1$ (EtOH, *c* 0.52). Mp 210–212°. IR ν_{max} cm^{-1}: 3400, 2940, 2860, 1730, 1640, 1460, 1370, 1070, 1020, 920, 890, 700. ^1H and ^{13}C NMR in Tables 1–3. FABMS *m/z* (rel. int.): 671 $[MH]^+$ (50), 653(1), 635(2), 617(1), 537(2), 509(2), 507(1), 491(4), 473(2), 469(7), 455(5), 437(7), 227 $[\mathbf{b}]^+$ (34), 209 $[\mathbf{b} - H_2O]^+$ (30), 143 $[\mathbf{a}]^+$ (100), 125 $[\mathbf{a} - H_2O]^+$ (75); $[M]^+$: 635.5 (671 → 653), 192.4 (227 → 209), 109.3 (143 → 125), 91.3 (125 → 107).

3β,12α,14,17,25-*Pentahydroxy*-20R,24S-*epoxymalabaricane*-3-O-β-*glucopyranoside* (**2**). $C_{36}H_{64}O_{11}$. $[\alpha]_D = 1.4$ (EtOH, *c* 0.2). Mp 243–245°. IR ν_{max} cm^{-1} 3380, 2940, 2860, 1650, 1450, 1390, 1370, 1080, 1020, 950, 700. ^1H and ^{13}C NMR in Tables 1–3. FABMS *m/z* (rel. int.): 673 $[MH]^+$ (10), 655(3), 637(2), 619(1), 493(3), 469(7), 457(7), 439(12), 227 $[\mathbf{b}]^+$ (39), 209 $[\mathbf{b} - H_2O]^+$ (29), 185(62), 143 $[\mathbf{a}]^+$ (100), 125 $[\mathbf{a} - H_2O]^+$ (66); $[M]^+$: 637.5 (673 → 655), 192.4 (227 → 209), 109.3 (143 → 125).

3β,12α,20,24,25-*Pentahydroxy*-14R,17S-*epoxymalabaricane*-3-O-β-*glucopyranoside* (**3**). $C_{36}H_{64}O_{11}$. $[\alpha]_D = -12.6$ (MeOH, *c* 0.51). mp 255 – 257°. IR ν_{max} cm^{-1}: 3400, 2950, 2860, 1630, 1460, 1390, 1370, 1070, 1020, 920, 890, 700. ^1H and ^{13}C NMR in Tables 1–3. FABMS *m/z* (rel. int.): 673 $[MH]^+$ (31), 655(4), 637(2), 619(3), 511 $[MH-162]^+$ (4), 493(4), 475(4), 469(5), 457(13), 439(7), 245 $[\mathbf{b}']^+$ (16), 227 $[\mathbf{b}]^+$ (40), 209 $[\mathbf{b} - H_2O]$ (75), 143 $[\mathbf{a}]^+$ (100), 125 $[\mathbf{a} - H_2O]^+$ (60); $[m]^+$, 637.5 (673 → 655), 210.3 (245 → 227), 192.4 (227 → 209), 109.3 (143 → 125).

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