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Diterpene esters of aristolochic acids from *Aristolochia pubescens*

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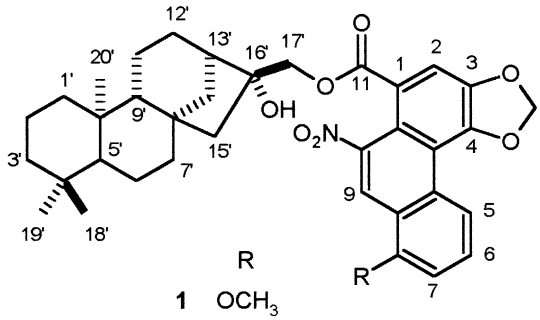
Abstract

From the acetone and ethanol extracts of the tubercula of *Aristolochia pubescens*, two diterpene esters of aristolochic acids were isolated, together with 23 known compounds. The structures of the compounds were determined on the basis of spectroscopic analysis.

Keywords: *Aristolochia pubescens*; Aristolochiaceae; Diterpene esters; Aristolochic esters; Aristolochic acids; Kaurane diterpenes; Lignans

1. Introduction

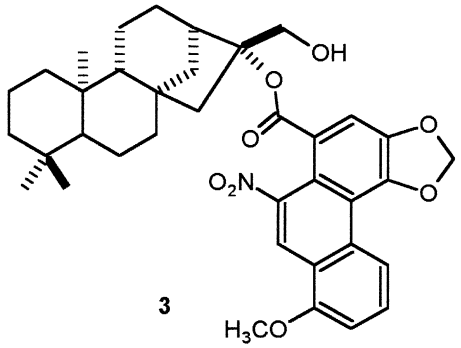
The interest in phytochemical studies of the Aristolochiaceae family is due to the widespread use of its species in traditional medicine and homeopathy (Lopes et al., 2001). As part of an ongoing study of the chemical constituents of *Aristolochia pubescens* (Aristolochiaceae) (Nascimento and Lopes, 1999, 2000), the isolation and structural elucidation of 25 compounds from the tubercula of this species are reported. Three of these compounds (**1**–**3**) present an unusual carbon skeleton in which an aristolochic acid derivative is bound to a kaurane diterpene, and two of them are new: 16α-hydroxy-*ent*-17-kauranyl aristolochate I (aristoloin I, **1**) and 16α-hydroxy-*ent*-17-kauranyl aristolochate II (aristoloin II, **2**). The structures of the new compounds were determined on the basis of spectroscopic methods, mainly using ^{1}H and ^{13}C NMR spectroscopy. The known compounds (**3**–**25**) were identified by comparing their physical and spectroscopic data with those of authentic samples and/or data reported in the literature. The known compounds 16α,17-*ent*-kauranediol (**15**) and (−)-cubebin (**18**) were also isolated from the stems and the roots of this species (Nascimento and Lopes, 1999, 2000), whereas (−)-isocorydine (**13**) and (−)-dihydrocubebin (**17**) were isolated for the first time from the Aristolochiaceae. The ^{13}C NMR spectroscope data of aristolochic acid VIIa (**5**), four sodium aristolochates (**6**–**9**), and two *N*-β-glucoside aristolactams (**11** and **12**) are described for the first time in this work.



R

1 OCH_3

2 H



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2. Results and discussion

Compounds **1**–**25** were isolated from the acetone and ethanol extracts of the tubercula by chromatography column, followed by preparative TLC, HPLC, and/or recrystallization. The known compounds were identified

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as aristolin (**3**) (Wu et al., 2002), aristolochic acid I (**4**), aristolochic acid VIIa (**5**), sodium aristolochate I (**6**) (Leu et al., 1998a), sodium aristolochate II (**7**), sodium aristolochate IIIa (**8**), sodium aristolochate IVa (**9**) (Chiang et al., 1998), aristolactam I *N*-β-glucoside (**10**) (Achari et al., 1984), aristolactam Ia *N*-β-glucoside (**11**) (Leu et al., 1998b), aristolactam IIIa *N*-β-glucoside (**12**) (Achari et al., 1981), (−)-isocorydine (**13**) (Guinaudeau et al., 1975), *trans*-*N*-feruloyltyramine (**14**) (Navickiene and Lopes, 2001), 16α,17-*ent*-kauranediol (**15**), *ent*-kaur-15-en-17-ol (**16**) (Lopes et al., 1990), (−)-dihydrocubebin (**17**) (Anjaneyulu et al., 1981), (−)-cubebin (**18**), (−)-hinokinin (**19**) (Navickiene and Lopes, 2001), kusunokinin (**20**), bursehernin (**21**) (Lopes et al., 1983), *trans*-methyl *p*-coumarate (**22**), and *cis*-methyl *p*-coumarate (**23**) (Chiang et al., 1998). In addition, allantoin (**24**) and glucose (**25**) were identified by comparison of their physical and spectroscopic data with those of authentic samples.

From *g*COSY, *g*HMQC, and *g*HMBC experiments, it was possible to assign more feasible δ values for carbons and hydrogens, including C-1′, C-7′, and C-14′, than those previously described in the literature (Kitajima et al., 1982) for **15**. These assignments were based mainly on the correlation between C-1′ (δ 40.3) and H_3-20′ (δ 0.95) and between C-16′ (δ 81.9) and H-14′ (δ 1.90) observed by *g*HMBC experiments. The ^1H and ^{13}C NMR, *g*COSY, *g*HMQC, and *g*HMBC data obtained for compounds **1**–**3** were very similar to those observed for aristolochic acids I (**4**) or II (**26**) and 16α,17-*ent*-kauranediol (**15**) (Tables 1 and 2).

The ESI-MS of alkaloid **1** displayed a *quasi*-molecular ion $[M+H]^+$ at *m*/*z* 630, which was consistent with the molecular formula $C_{37}H_{43}NO_8$. The ^1H NMR spectrum of **1** showed signals for five aromatic hydrogens at δ 8.86 (*s*), 8.72 (*d*, *J* = 7.5 Hz), 7.75 (*s*), 7.74 (*dd*, *J* = 7.5 and 8.0 Hz), and 7.13 (*d*, *J* = 8.0 Hz) similar to aristolochic acid I (**4**) (Table 1). It also showed signals for aliphatic hydrogens comparable to those observed for 16α,17-*ent*-kauranediol (**15**) (Kitajima et al., 1982), including three methyl groups at δ 1.04 (*s*), 0.87 (*s*), and 0.82 (*s*). However, it was observed that the carbinolic hydrogens (H_2-17′) absorbed at higher frequency (Δδ = +0.74 and +0.85) than in **15**. The ^{13}C NMR spectrum of **1** showed 14 carbons for the phenanthrene moiety and 20 carbons for the diterpene moiety (Table 2). The *g*HMBC spectrum showed correlations of a carbonyl carbon at δ 167.2 (C-11) with H-2 (δ 7.75) and H_2-17′ (δ 4.50 and 4.54) establishing that the two moieties were joined by an ester, which was confirmed by an absorption band at 1710 cm^{-1} in the IR spectrum. The *g*HMBC spectrum also allowed unambiguous establishment of the chemical shifts for C-1′, C-7′, and C-14′. The effects of the esterification observed on C-17′ (Δδ = +3.2) and C-16′ (Δδ = −1.8) were analogous to those reported for 16α,17-*ent*-kauranediol acetyl derivatives (Elliger et al., 1992; Fatope et al., 1996), which corroborated the proposed structure. Compound **1** exhibited optical rotation. Although aristolochic acid I also shows optical activity ($[\alpha]_D^{25}$ +12.5°; MeOH; c. 0.4), it is suggested that **1** belongs to the *ent*-kaurane series due to its negative specific rotation ($[\alpha]_D^{25} = -42.1°$), which is characteristic of the *ent* series (Velandia et al., 1998), and since to date, only *ent*-kauranes were isolated from *A. pubescens* and the Aristolochiaceae (Lopes et al., 2001). Thus, **1** was characterized as 16α-hydroxy-*ent*-17-kauranyl aristolochate I (named aristoloin I).

The UV, ESI-MS, IR, ^1H and ^{13}C NMR, *g*HMQC and *g*HMBC data obtained for compound **2** (Tables 1 and 2) showed that this compound differed from **1** only by the absence of a methoxyl substituent at C-8. This difference was supported by a $[M+H]^+$ at *m*/*z* 600, the number and multiplicities of the hydrogens in the C-ring as evidenced by the ^1H and ^{13}C NMR spectra data, as well as by the *g*HMBC and *g*HMQC data. The NMR spectra data for the aromatic hydrogens and carbons of **2** were comparable with those of aristolochic acid II (**26**). Compound **2** exhibited a specific rotation ($[\alpha]_D^{25} = -53.4°$) comparable to that for **1**. Therefore, compound **2** was characterized as 16α-hydroxy-*ent*-17-kauranyl aristolochate II (named aristoloin II).

A detailed analysis of the spectroscopic data obtained for compound **3** indicated that it is an isomer of **1**, and that the aristolochic and kaurane moieties were linked through C-11→O→C-16′, mainly due to the chemical shifts of C-17′ (δ 63.7) and H_2-17′ (δ 4.42, *d*, *J* = 13.5 Hz and 4.08, *d*, *J* = 13.5 Hz). In addition, the *g*HMBC spectrum of **3** did not show a correlation between C-11 and H_2-17′. Thus, compound **3** was identified as aristolin, recently isolated from *Aristolochia elegans* (Wu et al., 2002).

3. Experimental

3.1. General experimental procedures

The NMR spectra were measured on a Varian spectrometer (11.7 T) at 500 MHz (^1H) and 126 MHz (^{13}C), using the solvents as an internal standard. The mass spectra were obtained on a Fisons Platform II by flow injection into the electrospray source (ESI–MS). The IR spectra were obtained on a Nicolet-730 FT-IR spectrometer using KBr discs. UV absorption were measured in a Hewlett Packard 8452A diode array spectrophotometer. Optical rotations were measured on a Polamat A Carl Zeiss Jena. HPLC analyses were carried out using a Shimadzu liquid chromatograph 10 Avp equipped with a UV-vis detector. The employed column was RP 18 (Shimadzu, 250×20 mm) and the chromatograms were acquired at 254 nm.

3.2. Plant material

The plant was collected in Ituiutaba, MG, Brazil, and identified as *A. pubescens* Will. ex Duch. by Dr. Con-

Table 1
^{1}H NMR spectral data for compounds **1**, **2**, **4**, and **26** (500 MHz, δ)[a,b]

H	**1** ($CDCl_3$)	**2** ($CDCl_3$)	**4** ($CDCl_3$)	**26**[c] (DMSO-d_6)
2	7.75 *s*	7.76 *s*	7.80 *s*	7.80 *s*
5	8.72 *d* (7.5)	9.17 *d* (8.0)	8.66 *d* (8.5)	9.07 *d* (8.0)
6	7.74 *dd* (7.5, 8.0)	7.83 *t* (8.0)	7.68 *t* (8.5)	7.90 *t* (8.0)
7	7.13 *d* (8.0)	7.74 *t* (8.0)	7.07 *d* (8.5)	7.81 *t* (8.0)
8		8.01 *d* (7.5)		8.25 *d* (8.0)
9	8.86 *s*	8.36 *s*	8.81 *s*	8.57 *s*
1′	0.76 *dt* (3.0, 13.0), 1.80 *br d* (13.0)	0.76 *m*, 1.80 *m*		
2′	1.42 *m*	1.40 *m*		
3′	1.15 *dt* (4.0, 13.5), 1.64 *m*	1.15 *m*, 1.64 *m*		
5′	0.80 *m*	0.80 *m*		
6′	1.56 *m*	1.56 *m*		
7′	1.40 *m*, 1.52 *m*	1.38 *m*		
9′	1.06 *br d* (7.5)	1.07 *d* (7.4)		
11′	1.62 *m*	1.62 *m*		
12′	1.62 *m*	1.62 *m*		
13′	2.12 *br s*	2.13 *br s*		
14′	1.66 *m*, 1.98 *d* (11.5)	1.66 *m*, 1.99 *br d* (11.7)		
15′	1.54 *br d* (14.5), 1.72 *dd* (1.8, 14.5)	1.54 *m*, 1.72 *m*		
17′	4.50 *d* (11.5), 4.54 *d* (11.5)	4.51 *d* (11.5), 4.54 *d* (11.5)		
18′	0.87 *s*	0.87 *s*		
19′	0.82 *s*	0.82 *s*		
20′	1.04 *s*	1.04 *s*		
OCH_2O	6.39 *s*	6.42 *s*	6.34 *s*	6.49 *s*
OCH_3	4.08 *s*		4.01 *s*	

[a] The chemical shifts of the respective hydrogens between δ 1.68 and 0.80 were taken from *g*HMQC data and the multiplicities were not resolved.
[b] Multiplicity (*J* in Hz).
[c] Data obtained from the literature (Chiang et al., 1998).

dorcet Aranha (Secretaria do Meio Ambiente da Prefeitura de Joinville, Joinville, SC, Brazil). A voucher specimen was deposited at the herbarium of the Instituto Agronômico de Campinas, Campinas, SP, Brazil. The fresh tubercula (782.1 g) of *A. pubescens* were dried, ground and extracted exhaustively at room temp. with hexane, Me_2CO, and EtOH successively, and the extracts individually concentrated.

3.3. Isolation

The crude acetone extract (6.5 g) was washed with $CHCl_3$, MeOH, and Et_2O successively, and the extracts individually concentrated. The residue yielded allantoin (**24**, 220 mg). The $CHCl_3$ fraction (2.72 g) was fractionated by CC (silica gel, 50 g, hexane–EtOAc gradient) and yielded 19 fractions. Fractions 6, 9, and 13 gave **16** (118 mg), **19** (68 mg), and **18** (881 mg), respectively. Fraction 15 (260 mg) by CC (silica gel, 8 g, CH_2Cl_2–MeOH gradient) gave **17** (10 mg) and **18** (32 mg). One-third of the MeOH fraction (871 mg) was fractionated by CC (Lobar C-8 Merck, 240×10 mm, MeOH–H_2O gradient) and yielded 13 fractions. Fraction 3 after prep. TLC ($CHCl_3$–MeOH–H_2O 14:6:1) gave **22** (3 mg), **23** (2 mg), and **25** (4 mg). Fraction 6 was subjected to HPLC [MeOH–H_2O (HOAc 1%) 3:2] to give **11** (2 mg). Fraction 7 was subjected to HPLC [MeOH–H_2O (HOAc 1%) 1:1] to give **8** (1 mg) and **12** (3 mg). Fraction 10 gave **10** (37 mg). Fractions 11, 12, and 13 were subjected to HPLC [MeOH–H_2O (HOAc 1%) 3:2] to give **9** (2 mg), **7** (5 mg), **6** (4 mg), and **4** (3 mg). The Et_2O fraction (125 mg) was subjected to HPLC [MeOH–H_2O (HOAc 1%) 13:7] to give **4** (13 mg), **7** (4 mg), and **9** (2 mg). The crude ethanol extract (13.4 g) was washed with hot ethanol. After freezing, a precipitate was separated and yielded allantoin (**11**, 4.60 g). The ethanol solution was concentrated (7.70 g), dissolved in MeOH–H_2O 1:1 (400 ml), and extracted with $CHCl_3$ (3×100 ml). The organic phase was concentrated (2.0 g), fractionated by CC (silica gel, 40 g, $CHCl_3$–MeOH gradient), and yielded 33 fractions. After prep. TLC (hexane–EtOAc 7:3), fraction 3 (243 mg) gave **16** (80 mg) and **19** (21 mg). Fraction 4 after prep. TLC ($CHCl_3$–EtOAc 9:1) gave **20**+**21** (12 mg) and two sub-fractions that were also subjected to prep. TLC (hexane–EtOAc 7:3) to give **1** (4 mg), **2** (2 mg), and **3** (2 mg). Fractions 5, 13, and 20 gave **18** (258 mg), **15** (66 mg), and **14** (4 mg), respectively. Fraction 24 after prep. TLC [$CHCl_3$–MeOH–NH_4OH (19:1:0.1)] gave **13** (6 mg). Fractions 26 and 28 were subjected to prep. TLC [$CHCl_3$–MeOH–NH_4OH (3:2:0.25)] and [$CHCl_3$–MeOH–NH_4OH (7:3:0.5)] to give **6** (4 mg) and **5** (5 mg), respectively.

3.3.1. 16α-Hydroxy-ent-17-kauranyl aristolochate I (aristoloin I, 1)

Amorphous yellow solid. $[\alpha]_D^{25}$ −42.1° ($CHCl_3$; c. 0.20). (Found: C, 70.4; H, 7.0. $C_{37}H_{43}O_8N$ requires: C,

Table 2
^{13}C NMR spectral data for compounds **1**–**4**, **15** (126 MHz, δ) and **26** (20 MHz, δ)

C	**1** ($CDCl_3$) ^{13}C (δ)	*g*HMBC	**2**[a] ($CDCl_3$) ^{13}C (δ)	*g*HMBC	**3**[a] ($CDCl_3$) ^{13}C (δ)	*g*HMBC	**4** (DMSO-d_6) ^{13}C (δ)	**26**[c] (DMSO-d_6) ^{13}C (δ)	C	**15** ($CDCl_3$) ^{13}C (δ)
1	[b]		[b]		[b]		124.5	124.6		
2	112.7		112.8		112.5		112.2	112.0		
3	143.1		[b]		[b]		146.0	146.1		
4	147.5	H-2	146.8	H-2, $OC\underline{H}_2O$	146.2	H-2, $OC\underline{H}_2O$	146.2	146.3		
4a	[b]		[b]		[b]		116.9	116.8		
4b	131.0	H-6, H-9	[b]		131.0	H-6, H-9	129.8	[b]		
5	119.2		127.4		119.2		118.4	126.6		
6	131.0		130.5		[b]		131.5	130.5		
7	108.0	H-5	[b]		108.0	H-5	108.7	128.8		
8	156.9	H-6, $OC\underline{H}_3$	130.2	H-6, H-9	156.9	H-6, $OC\underline{H}_3$	156.3	130.5		
8a	120.2	H-5, H-7	128.5	H-7	120.2	H-5, H-7	118.8	128.9		
9	121.2		126.5		121.1		119.5	126.0		
10	145.9	H-9	[b]		[b]		145.7	146.0		
10a	[b]		118.3	H-2, H-9	119.2	H-2	117.3	117.4		
11	167.2	H-2, H-17′	167.5	H-2, H-17′	167.2	H-2	167.9	168.0		
1′	40.3	H-20′	40.4	H-20′	40.4	H-20′			1	40.3
2′	18.6		[b]		[b]				2	18.6
3′	41.9	H-18′, H-19′	42.0	H-18′, H-19′	42.0	H-18′, H-19′			3	41.9
4′	33.3		[b]		[b]				4	33.2
5′	56.0		56.1		56.2	H-18′, H-19′, H-20′			5	56.2
6′	20.5		[b]		20.5				6	20.4
7′	42.1	H-15′	42.0	H-15′	42.0				7	42.0
8′	44.9		[b]		[b]				8	44.7
9′	56.7	H-15′, H-20′	56.6	H-15′, H-20′	56.5	H-15′, H-20′			9	56.7
10′	39.4		[b]		[b]				10	39.4
11′	18.3		[b]		[b]				11	18.3
12′	26.3		27.1		27.4				12	26.3
13′	46.3	H-14′, H-17′	46.5	H-14′	43.5				13	45.5
14′	37.2		37.5		38.1				14	37.3
15′	53.3		53.4		51.0				15	53.4
16′	80.1	H-15′, H-17′	80.0	H-12′	[b]				16	81.9
17′	69.6	H-15′	70.2	H-15′	63.7				17	66.4
18′	33.6	H-19′	33.6	H-19′	33.6	H-19′			18	33.5
19′	21.5	H-18′	22.0	H-18′	21.6	H-18′			19	21.5
20′	17.8		18.0		17.8				20	17.8
OCH_2O	102.4		103.0		102.4		103.0	103.2		
OCH_3	56.2				56.2		56.2			

[a] The ^{13}C NMR data were obtained from *g*HMQC and *g*HMBC.
[b] Data not observed.
[c] Data obtained from the literature (Priestap, 1989).

70.6; H, 6.9%). UV λ_{max}^{MeOH} nm (log ε): 223 (4.42), 256 (4.24), 289 (4.06), 316 (3.86), 389 (3.68). IR ν_{max}^{KBr} cm^{-1}: 3600, 1710, 1599, 1432, 1352. Positive ESI–MS (probe) 70 eV, *m*/*z* (rel. int.): 630 $[M+H]^+$ (100). For ^1H and ^{13}C NMR, see Tables 1 and 2.

3.3.2. 16α-Hydroxy-ent-17-kauranyl aristolochate II (aristoloin II, **2**)

Amorphous yellow solid. $[\alpha]_D^{25}$ −53.4° ($CHCl_3$; c. 0.16). (Found: C, 72.0; H, 6.7. $C_{36}H_{41}O_7N$ requires: C, 72.1; H, 6.9%). UV λ_{max}^{MeOH} nm (log ε): 219 (4.28), 250 (4.19), 314 (3.80), 387 (3.50). Positive ESI-MS (probe) 70 eV, *m*/*z* (rel. int.): 600 $[M+H]^+$ (100). For ^1H and ^{13}C NMR, see Tables 1 and 2.

3.3.3. Aristolochic acid VIIa (**5**)

Amorphous brownish solid. UV, IR, and ^1H NMR data are in agreement with those reported in the literature (Leu et al., 1998a). ^{13}C NMR (126 MHz, DMSO-d_6): δ 61.0 (OCH_3-8), 102.7 (OCH_2O), 111.0 (C-2), 115.6 (C-10a), 117.9 (C-4a), 119.2 (C-9), 121.6, 122.9 (C-5, C-6), 122.0 (C-8a), 124.2 (C-1), 131.7 (C-4b), 142.9 (C-10), 145.9, 147.0 (C-3, C-4), 149.0 (C-7), 149.0 (C-8), 168.2 (COOH).

3.3.4. Sodium aristolochate I (**6**)

Amorphous brownish solid. UV, IR, ^1H NMR data are in agreement with those reported in the literature (Leu et al., 1998a). Positive ESI–MS (probe) 70 eV, *m*/*z*

(rel. int.): 364 $[M+H]^+$ (100). ^{13}C NMR (126 MHz, DMSO-d_6): δ 56.1 (OCH_3-8), 101.8 (OCH_2O), 108.1 (C-7), 111.6 (C-2), 116.2 (C-9), 116.4 (C-10a), 116.9 (C-4a), 118.5 (C-5), 119.1 (C-8a), 130.1 (C-4b), 130.3 (C-6), 136.7 (C-1), 142.7 (C-4), 145.7 (C-3), 148.2 (C-10), 156.0 (C-8), 169.1 (COONa).

3.3.5. Sodium aristolochate II (7)

Amorphous brownish solid. UV, IR, and ^1H NMR data are in agreement with those reported in the literature (Chiang et al., 1998). Positive ESI–MS (probe) 70 eV, *m*/*z* (rel. int.): 334 $[M+H]^+$ (100). ^{13}C NMR (126 MHz, DMSO-d_6): δ 101.9 (OCH_2O), 111.4 (C-2), 116.8 (C-10a), 122.5 (C-9), 126.4 (C-5), 127.8 (C-7), 128.9 (C-4b), 129.0 (C-8a), 129.3 (C-6), 129.8 (C-8), 142.5 (C-4), 145.6 (C-3), 148.6 (C-10).

3.3.6. Sodium aristolochate IIIa (**8**)

Amorphous brownish solid. UV, IR, and ^1H NMR data are in agreement with those reported in the literature (Chiang et al., 1998). Positive ESI–MS (probe) 70 eV, *m*/*z* (rel. int.): 350 $[M+H]^+$ (100). ^{13}C NMR (126 MHz, DMSO-d_6): δ 101.9 (OCH_2O), 111.1 (C-5), 111.6 (C-2), 118.2 (C-7), 122.6 (C-8a), 131.0 (C-4b), 131.7 (C-8), 145.3 (C-3), 159.2 (C-6).

3.3.7. Sodium aristolochate IVa (**9**)

Amorphous brownish solid. UV, IR, and ^1H NMR data are in agreement with those reported in the literature (Chiang et al., 1998). Negative ESI–MS (probe) 35 eV, *m*/*z* (rel. int.): 356 $[M\text{-}Na]^-$ (100). ^{13}C NMR (126 MHz, DMSO-d_6): δ 56.0 (OCH_3-8), 99.2 (C-7), 101.7 (OCH_2O), 103.6 (C-5), 111.5 (C-2), 112.2 (C-8a), 116.4 (C-4a), 117.4 (C-9), 131.7 (C-4b), 143.9 (C-4), 145.1 (C-10), 145.3 (C-3), 157.6 (C-8), 160.3 (C-6).

3.3.8. Aristolactam Ia N-β-glucoside (**11**)

Amorphous brownish solid. UV, IR, MS, and ^1H NMR data are in agreement with those reported in the literature (Leu et al., 1998b). ^{13}C NMR (126 MHz, DMSO-d_6): δ 60.8 (C-6′), 69.5 (C-2′), 70.2 (C-3′), 77.0 (C-4′), 80.0 (C-5′), 81.6 (C-1′), 100.8 (C-9), 103.2 (OCH_2O), 105.6 (C-2), 112.2 (C-7), 117,0 (C-5), 122.6 (C-8a), 124.1 (C-10a), 125.2 (C-4b), 126.1 (C-6), 133.1 (C-10), 148.2 (C-4), 154.2 (C-8).

3.3.9. Aristolactam IIIa N-β-glucoside (**12**)

Amorphous brownish solid. IR, MS, and ^1H NMR data are in agreement with those reported in the literature (Achari et al., 1981). ^{13}C NMR (126 MHz, DMSO-d_6): δ 62.1 (C-6′), 70.8 (C-2′), 70.8 (C-3′), 78.1 (C-4′), 80.7 (C-5′), 82.4 (C-1′), 104.2 (OCH_2O), 106.2 (C-2), 108.2 (C-9), 111.4 (C-4a), 111.8 (C-5), 118.2 (C-7), 125.6 (C-10a), 126.0 (C-4b), 127.0 (C-8a), 131.3 (C-8), 131.8 (C-10), 148.2 (C-4), 149.5 (C-3), 156.2 (C-6), 166.1 (CO).

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