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DISTRIBUTION OF IRIDOID GLYCOSIDES IN *CLERODENDRUM* SPECIES

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Key Word Index—*Clerodendrum* species; Verbenaceae; chemotaxonomy; iridoid glycosides; ugandoside.

Abstract—Twelve *Clerodendrum* species have been examined for iridoids. Eight of them contain iridoid glycosides. Besides the several known compounds (melittoside, aucubin, 8-*O*-acetylharpagide, harpagide, ajugoside, 8-*O*-acetylmioporoside, reptoside, euphroside, plantarenaloside) a new iridoid, ugandoside, was isolated. The structure and relative configuration was determined. *Clerodendrum* species, which belong to the section Cyclonema, show a good correlation of morphological and chemical results. They contain iridoid glycosides with a C-4 formyl group which have not been found previously in Verbenaceae. The taxonomic significance of our results is discussed.

INTRODUCTION

The genus *Clerodendrum* belongs to the subfamily Viticoideae. It is the largest genus of the Verbenaceae and comprises *ca* 560 species and varieties according to Moldenke [1]. Suggestions to classify it came from Schauer [2], Briquet [3], Lam [4], Thomas [5] and Moldenke [6]. The classification of Thomas [5] is obviously different from that of the other authors, for it is based on different morphological criteria. Since all these classifications confine themselves to either African or Asian representatives of the genus, there is no standard set of parameters up to now which is suited for a natural classification of the whole genus.

None of the following groups of substances occurring in *Clerodendrum* species seem to be of great taxonomic importance: diterpenes (clerodendrins A and B, clerodin, epicaryoptin), the widely spread phytosterols and triterpenes and also the numerous flavone derivatives. However, (24*S*)-ethylcholesta-5,22,25-triene-3β-ol is claimed to be typical for at least some *Clerodendrum* species [7, 8].

Hegnauer [9] and Wieffering [10] realized the general systematical importance of iridoid glycosides but up to now only Kooiman [11] has looked for the distribution of iridoids within the genus *Clerodendrum*. He examined 13 species by PC. Our own work on *Verbena* species [12] showed that the distribution of iridoids can be a useful character at the generic level. We, therefore, tried to examine the distribution of iridoids in this genus more closely. This paper comprises the results of examining 12 *Clerodendrum* species.

RESULTS

From *Clerodendrum thomsonae* Balf.f., a species in which Kooiman [11] detected three iridoid glycosides, we isolated six different iridoid glycosides; the five known compounds, melittoside, aucubin, 8-*O*-acetylharpagide, ajugoside, reptoside and a new iridoid glycoside which we identified as the 6-epimer of ajugoside, 8-*O*-acetylmioporoside [13]. According to the structure proposed for ajugol (**2**) [14] and mioporoside (**1**) [15] we assigned structure **1a** to our compound. Soon after publication of these results, detailed papers on ^{13}C NMR spectroscopy of iridoids were published by Bianco *et al.* [16] and Damtoft *et al.* [17]. By comparison with other pairs of epimers both groups suggested a change of the structures of ajugol to **1** and of mioporoside to **2**, which was confirmed by subsequent papers of Guiso *et al.* [18], Trogolo *et al.* [19] and Damtoft *et al.* [20]. Therefore, 8-*O*-acetylmioporoside must now be represented by **2a** rather than **1a**. Our NOE experiments with **2b** are in agreement with this structure. By irradiating the signal of H-5 the intensities of the H-9 and especially of the H-6 increased; by irradiating the signal of H-9 the intensities of the H-1, H-5 and H-6 signals increased. The intensity increase of the H-6 signal was a little weaker than that of the first experiment. These results show that H-5, H-6 and H-9 are located on the same (β) side of the molecule, thus confirming the α-position of the 6-hydroxy group in 8-*O*-acetylmioporoside. In addition the α-position of the methyl group, H_3-10 was proved by irradiating the signal of H_3-10. The intensity of H-1, but not the intensity of H-9, was increased.

From *Clerodendrum ugandense* Prain we isolated two iridoid glycosides. One of them was identified as euphroside [21] by comparison with the authentic substance. Due to poor resolution in HPLC and to the scarcity of material the second compound could not be isolated in a pure state. Nevertheless, the spectra were interpretable without restrictions. The UV ($\lambda_{max}^{H_2O}$ nm: 240, log ε, 3.9), IR (ν cm^{-1}: 1655, 1615) and ^1H NMR data indicated a close structural relationship between euphroside and the second compound, for which we suggest the name ugandoside (**3a**). Like most iridoids, this substance was quickly converted by acid hydrolysis into glucose and insoluble black products due to the decomposition of the aglycone. Glucose was formed by hydrolysis with β-glucosidase. The IR spectrum of the acetylated compound (**3b**) showed characteristic bands belonging to an exocyclic methylene group (3090, 890 cm^{-1}). Further functional groups were identified as follows: the H-11 signal shows a chemical shift value

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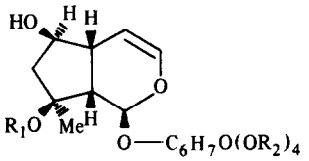
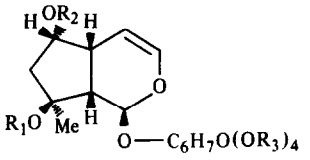


1 $R_1=R_2=H$

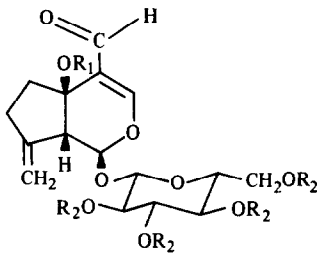
1a $R_2=H$, $R_1-C(=O)-Me$



2 $R_1=R_2=R_3=H$

2a $R_2=R_3=H$, $R_1=C(=O)-Me$

2b $R_1=R_2=R_3=-C(=O)-Me$



3a $R_1=R_2=H$

3b $R_1=H$, $R_2=-C(=O)-Me$

3c $R_1=R_2=-SiMe_3$

typical for aldehyde protons (δ9.23). The sharp singlet at δ7.55 was assigned to the H-3; it is highly deshielded by the presence of the carbonyl group at C-4. The lack of coupling showed that the carbon atom at C-5 must be completely substituted. According to the chemical shift and the integration, the broad signal occurring at δ5.19 was assignable to an exocyclic methylene group. For biosynthetic reasons this methylene group should be attached to C-8. Four protons were attributable to the three multiplets at δ2.00, 2.19 and 2.47. These are the H_2-6 and H_2-7 protons. Spin decoupling experiments confirmed the assignment. The irradiation of the H_2-10 signal simplified the multiplet at δ2.19, while the multiplet at 2.00 was not altered. Therefore, the quasi axial H-7β was assigned to the multiplet at lower field. Several coupling constants were available from these multiplets. The two greatest values have to be interpreted as geminal couplings of the methylene protons at C-6 and C-7. Obviously the neighbourhood of a π orbital enlarges the coupling constant of H_2-7 [22]. The three smaller values represent the vicinal couplings of the protons mentioned above. Since the signal of H-9 appeared as a broad singlet and a signal for H-5 was missing, there was an additional confirmation that C-5 is substituted with a hydroxyl group. The very small value for the coupling constant $J_{1,9}$ was in agreement with a *trans* relationship between these protons. A comparison of the ^{1}H NMR spectrum of **3b** with that of other iridoid glucosides confirmed the presence of a β-D-glucose moiety; chemical shift values and the intensity of the signals were in a good agreement. The mass spectral data of **3a–3c** were also in agreement with the structure deduced from the other spectral data.

From six other *Clerodendrum* species we isolated several iridoid glycosides and identified them by comparison with authentic substances and the data given in the summary of El-Naggar and Beal [23].

In four *Clerodendrum* species no iridoids could be found. The results of our investigation are listed in Table 1.

The paper of El-Gazzar and Watson [24] was the base for own morphological examinations. We used some of the varying characters of their group 782. There are several new arguments for separating the section Cyclonema from the section Euclerodendrum (Table 2).

DISCUSSION

Considering the distribution of iridoid glycosides in *Clerodendrum* species, it is conspicuous that there are two species containing exclusively C-4 formyl-type iridoids, so far unknown in Verbenaceae. They form a small but homogenous group with regard to iridoid accumulation. All the other *Clerodendrum* species may accumulate, harpagide- and/or aucubin-type iridoids. Although the number of *Clerodendrum* species examined up to now is small compared with the large genus, some conclusions can be drawn. (1) The only two species accumulating C-4 formyl-type iridoids show a good correlation between

Table 1. Occurrence and identification of iridoid glycosides in *Clerodendrum* species

Species	Method of identification	Concn (%)
C. ugandense	Ugandoside (**3a**)	
Leaves	UV, IR, ^{1}H NMR, MS	
	as **3b**: ^{1}H NMR, MS	0.07
	as **3c**: MS	
	Euphroside TLC, HPLC, IR	0.1
C. serratum var. *dentatum*	Plantarenaloside [27] TLC, IR, ^{1}H NMR, ^{13}C NMR,	
Leaves	MS	0.05
	Euphroside TLC, HPLC, IR, ^{1}H NMR, ^{13}C NMR, MS	0.03
C. inerme	Melittoside TLC, HPLC,	
Leaves	IR, MS	0.1
C. thomsonae	Melittoside TLC, HPLC,	
Leaves	IR, ^{1}H NMR, MS	0.18
	Aucubin TLC, HPLC; as aucubinhexa-acetate: IR	0.1
	8-O-Acetylharpagide TLC HPLC, IR	0.1
	Ajugoside (**1a**) TLC, HPLC, IR, MS	0.05
	8-O-Acetylmioporoside (**2a**) TLC, HPLC, IR, UV, ^{1}H NMR, ^{13}C NMR, MS	
	As **2b**: TLC, HPLC, IR, ^{1}H NMR, ^{13}C NMR, MS	0.05
	Reptoside TLC, HPLC, IR, ^{1}H NMR, MS	0.1
C. tomentosum	Harpagide TLC, HPLC, IR	0.01
Leaves		
C. trichotomum		
Leaves	Harpagide TLC, HPLC, IR	0.01
Fruits	Harpagide TLC	0.05
Fruits	Melittoside TLC, HPLC, IR, MS	0.19
C. colebrokianum		
Leaves	Melittoside TLC, HPLC	0.1
Fruits	Harpagide TLC, HPLC; as harpagidehexa-acetate: IR	0.02
Fruits	Melittoside TLC, HPLC, IR	0.2
C. indicum		
Leaves	Harpagide TLC, HPLC; as harpagidehexa-acetate: TLC, HPLC	0.02

Quantitative data are related to the dry wt of the plant material.

chemical and morphological characters (Table 3). Our results support the separation of the section Cyclonema according to Briquet [3], Thomas [5] and Junell [25]. Moldenke's suggestion [1] to exclude Cyclonema from the genus *Clerodendrum* and raise it to the level of an individual genus, as Schauer did, also agrees with our results. (2) Chemical as well as morphological characters indicate that *C. serratum* var. *dentatum* H. J. Lam belongs to the section Cyclonema rather than to Euclerodendrum (Tables 2 and 3). Further criteria for a classification of the sections Euclerodendrum and Siphonanthus are not derivable from our investigations. (3) In Table 4, all genera of the Lamiaceae–Verbenaceae complex, belonging to El-Gazzar and Watson's group 790 [24], are listed together with iridoid glycoside types found in each genus. Obviously, several genera contain the same iridoid glycosides which very often occur in Schrophulariales. Although a few genera of the group 790 have not been examined with regard to the occurrence of iridoid glycosides, small differences between the subgroups 779 and 782 are noticeable. The observation that amongst the subgroup 779 no genus has so far been found with iridoids, while at least parts of the genera *Callicarpa* [26; Rimpler, H., unpublished results] and *Clerodendrum* do not contain appreciable amounts of iridoids, points to a less marked tendency of iridoid accumulation amongst the subgroup 782. Although lack of iridoids in this group must be a derived state, we suppose that subgroup 782 is more primitive than subgroup 779, for the genera of the subgroup 779 mainly accumulate C-9 iridoids, while in genera of the subgroup 782 more often both, C-9 iridoids and C-10 iridoids, their biogenetic precursors are found.

EXPERIMENTAL

As far as possible plant material was cultivated and identified at the Institut für Pharmazeutische Biologie, Freiburg. Seeds were obtained from other Botanical Gardens. The plant material from *C. serratum* var. *dentatum* H.J. Lam, *C. inerme* (L.) Gaertn. and *C. paniculatum* L. originates from wild growing plants in Sri Lanka, the material of *C. colebrokianum* Walp. and *C. indicum* (L.) Kuntze from wild growing plants in India; *C. bungei* Steud. was obtained from cultivated plants in California, U.S.A. The plant material coming from overseas was available only air-dried, while material cultivated in Freiburg was lyophilized. We always collected stems or twigs and leaves from flowering plants and fruits in a mature status, except for *C. tomentosum* (Vent.) R. Br. and *C. ugandense* Prain which did not flower. Voucher specimens are deposited in the Herbarium of the Institut für Pharmazeutische Biologie, Freiburg, the numbers are as follows: *C. buchanani* (Roxb.) Walp. 76.04.02, *C. bungei* Steud. 80.02.07, *C. colebrokianum* Walp. 76.04.01, *C. indicum* (L.) Kuntze 79.06.22, *C. inerme* (L.) Gaertn. 79. 2615, *C. paniculatum* L. 80. 2745, *C. serratum* var. *dentatum* H. J. Lam 80. 2762, *C. splendens* G. Don 76.04.03, *C. thomsonae* Balf.f. 76.04.04, *C. tomentosum* (Vent.) R.Br. 76.04.05, *C. trichotomum* Thunb. 76.04.06, *C. ugandense* Prain 78.01.02.

Column chromatography. Si gel (Merck), solvents CH_2Cl_2–MeOH–H_2O (90:10:1)–(70:30:3); Servachrom XAD 7 (Serva), solvent H_2O; Sephadex G-15 (Pharmacia) solvent H_2O.

TLC. Si gel 60, solvents CH_2Cl_2–MeOH–H_2O (90:10:1)–(70:30:3), *n*-BuOH–MeOH–H_2O (4:1:5)–(9:1:10), toluene–Me_2CO (80:20)–(70:30) (iridoidglycoside acetates), MeCN–CS_2–H_2O (85:5:10) (glucose).

PC. M + N 261, solvent EtOAc–pyridine–H_2O (3:1:2). Spray reagents for iridoid glycosides and their acetates: Vanillin 3% and H_2SO_4 1% in 100 ml EtOH followed by heating at 110° for 5–10 min. Spray reagents for glucose: thymol 0.5% and H_2SO_4 5% in EtOH; 1.6 g aniline, 0.93 g phthalic acid in 100 ml *n*-BuOH satd with H_2O.

GC/MS. For the trimethylsilylated iridoids we used the following columns: 3% OV-17 1.2 m × 2 mm i.d., 1.5% OV-101 1.2 m × 2 mm i.d., 3% OV-225 2 m × 2 mm i.d. Voltage 70 eV, temp. of injector, column, separator, source, flow of the carrier gas and stationary phase were as follows: (1) melittoside: 280°, 290°, 265°, 220°, 30 ml/min, OV-17; (2) plantarenaloside, euphroside: 250°, 250°, 222°, 210°, 30 ml/min, OV-101; (3) ajugoside, 8-*O*-acetylmioporoside: 250°, 210°, 247°, 210°, 25 ml/min, OV-225; (4) reptoside: 250°, 240°, 250°, 210°, 25 ml/min, OV-225;

Table 2. Diagnostic characters of the sections Euclerodendrum and Cyclonema and of *C. serratum* var. *dentatum* based on our own observations and on descriptions of the literature for five species of Cyclonema and 12 species of Euclerodendrum

Characters	*C. serratum* var. *dentatum*	Sections	
		Cyclonema	Euclerodendrum
Appearance of the corolla	As described in section Cyclonema	Corolla strongly zygomorphic, 2-lipped, anterior segment decurved forward, concave spoonshaped, concave face upwards, the other segment pairwise arising between the two posterior corolla segments. Corolla tube short, 0.6–1.2 cm long, bellied with a deep cleft on the not-bellied side. [5]	Corolla ± zygomorphic, not two-lipped, corolla lobes subequal; corolla tube narrow, 0.3–17 cm long, straight or curved, mostly below the throat and often at the base ± extended [5].
Colour of the corolla	The anterior lobe violet-blue, the others lighter blue	Multicoloured, often bluish-violet [5]	Only one colour, often white, but also red, yellowish white, greenish [5].
Gynoecium	*	Placentas not furrowed [5].	Placentas ± deep furrowed [5].
Relation of length of style-arms	Unequal	Unequal	Equal or subequal
Length of the style-arms	Shorter style-arm: 3 mm; longer style-arm: 6 mm	Length of the shorter style-arm 2–3 mm, the longer one 3–6 mm	Length 0.5–1.8 mm, most of the species ± 1 mm.
Hairiness of the filaments	Filaments hairy at the base	Filaments hairy at the base	Filaments glabrous at the base

*This character has not been examined.

Table 3. Distribution of iridoid glycoside types in *Clerodendrum* species belonging to different sections

Section/subsection according to Schauer [2], Lam [4] Junell [25]	Species	Iridoid type occurring
Siphonanthus [2]	*C. indicum*	Harpagide-type
Euclerodendrum		
Axilliflora [4]	*C. thomsonae*	Harpagide-type, aucubin-type
Axilliflora [2]	*C. inerme*	Aucubin-type
Axilliflora [2]	*C. tomentosum*	Harpagide-type
Axilliflora [2]	*C. splendens*	*
Paniculata [2]	*C. trichotomum*	Harpagide-type; aucubin-type
Paniculata [4]	*C. colebrokianum*	Harpagide-type; aucubin-type
Squamata [2]	*C. paniculatum*	*
†	*C. buchanani*	*
†	*C. bungei*	*
Cyclonema [25]	*C. ugandense*	C-4 formyl-type
‡	*C. serratum* var. *dentatum*	C-4 formyl-type

*No iridoids detected.

†In our opinion belonging to the section Euclerodendrum, but not definitively included in Schauer's system.

‡*C. serratum* was classified [2–4] in the section Euclerodendrum, subsection Racemiflora until now.

Table 4. Distribution of iridoid glycoside types in genera of the Lamiaceae–Verbenaceae complex according to El-Gazzar and Watson [24]

	Group 790
Group 779	
Ajuga	Harpagide-type [14, 28, 29]
Amethystea	Harpagide-type [26]
Teucrium	Harpagide-type [30]
Leucosceptrum	*
Trichostema	Harpagide-type [31]
Isanthus	*
Synandra	*
Salazaria	Catalpol-type [31]
Melittis	Harpagide-type, aucubin-type [15, 32–34]
Physostegia	C-4 carboxyl-type [35]
Brazoria	*
Phyllostegia	*
Gomphostemma	*
Prasium	Aucubin-type [31]
Premna	Catalpol-type, C-4 carboxyl-type [36, 37]
Gmelina	Catalpol-type [26]
Holmskioldia	Harpagide-type, catalpol-type [36]
Group 782	
Clerodendrum	Harpagide-type, aucubin-type, C-4 formyl-type
Caryopteris	Harpagide-type, C-4 carboxyl-type [11, 38, 39]
Aegiphila	*
Amasonia	*
Callicarpa	No iridoids detected [26; Rimpler, H., unpublished results]
Vitex	Aucubin-type, C-4 carboxyl-type [40–44]

*These genera have not been examined previously.

(5) ugandoside: 250°, 220°, 260°, 230°, 40 ml/min, OV-225.

HPLC. μ-Bondapak phenyl, MeOH–THF–H_2O (10:5.8:84.2), μ-Bondapak NH_2, MeCN–H_2O (85:15)–(90:10), sometimes with 1–5% THF, μ-Bondapak C_{18} MeOH (10–60%), μ-Porasil, CH_2Cl_2–MeOH–H_2O (80:20:2)–(70:30:3); all columns 300 × 3.9 mm i.d. Partisil 10 ODS column (Whatman) 500 × 9.4 mm i.d., MeOH (15–60%). The flow rate varied from 1.0 to 2.5 ml/min.

Isolation procedure. The ground plant materials were extracted in three steps by refluxing for 30 min with EtOH 96%, 80% and 70% [step (1) 1 l/100 g, steps (2) and (3) 0.5 l/100 g]. The combined ethanolic extracts were evaporated *in vacuo* and subsequently chromatographed on a Celite column. Elution with *n*-hexane–CH_2Cl_2 (1:1) afforded the lipophilic fractions, elution with CH_2Cl_2–MeOH (1:1) the hydrophilic fractions. In every case the hydrophilic fractions were adsorbed on Celite once more, dried and rechromatographed successively on Si gel, XAD and Sephadex. Iridoid containing fractions were identified by TLC. It was necessary to purify most of them by HPLC and/or further CC for spectroscopic examinations. Only melittoside was purified by cristallization from MeOH. Quantities of plant material worked-up and detection of iridoid glycosides in TLC are as follows [R_f values are related to CH_2Cl_2–MeOH–H_2O (70:30:3) as solvent]: *C. colebrokianum* 1 kg, one spot, R_f, 0.10; *C. colebrokianum* fruits 440 g, two spots, R_fs, 0.10, 0.26; *C. indicum* 100 g, one spot, R_f, 0.26; C. inerme 500 g, one spot, R_f, 0.10; *C. serratum* var. *dentatum* 575 g, two spots, R_fs, 0.43, 0.33; *C. thomsonae* 700 g, six spots, R_fs, 0.10, 0.35, 0.5, 0.58, 0.60, 0.66; *C. tomentosum* 500 g, one spot, R_f, 0.26; *C. trichotomum* 500 g, one spot, R_f, 0.26; *C. trichotomum* fruits 100 g, two spots, R_f, 0.10, 0.26; *C. ugandense* 164 g, two spots, R_fs, 0.43, 0.33.

The following *Clerodendrum* species were worked-up as described above: *C. bungei* Steud. 100 g, *C. paniculatum* L. 100 g, *C. buchanani* (Roxb.) Walp. 100 g, *C. splendens* G. Don 500 g. The occurrence of one of the cited iridoid glycosides could be excluded by TLC of the purified fractions of *C. bungei*. The chromatographic pattern of the three latter species showed very weak spots, similar to those of harpagide and 8-*O*-acetylharpagide, respectively. Therefore, they were submitted to HPLC analysis, but none of the peaks recorded with a 3% solution corresponded to the peaks of a 1% iridoid solution, recorded with the highest UV detector sensitivity.

Ugandoside (**3a**). 4-Formyl-1-(β-D-glucopyranosyloxy)-4a-hydroxy-7-methylene-1,4a,5,6,7,7a-hexahydro-cyclopenta (*c*)pyran. HPLC was performed under several sets of conditions (see above). We also tried to optimize strength and selectivity of the solvent by using tertiary and quarternary mixtures [45] of MeOH, MeCN, THF and H_2O on a μ-Bondapak C_{18} column. All these efforts did not improve the purity of **3a**. The ^1H NMR spectrum showed two pairs of singlets for H-11 and H-3, respectively, in a ratio of 9:1; therefore, we assume that **3a** is accompanied by *ca* 10% of a very similar compound.

IR ν_{max}^{KBr} cm^{-1}: 3400, 2920, 2880, 1655, 1615, 1265, 1240, 1160, 1070, 930. ^1H NMR (250.10 MHz, D_2O): δ9.23 (1H, *s*, H-11), 7.55 (1H, *s*, H-3), 6.00 (1H, *d*, $J_{1,9}$ = 2Hz, H-1), 5.19 (2H, *s**, H_2-10), 4.82 (1H, *d*, H-1'), 3.07 (1H, *s**, H-9), 2.47 (2H, *m*, H-6α, H-7α), 2.19 (1H, *m*, $J_{7\alpha,7\beta}$ = −16.5 Hz, $J_{6\beta,7\beta}$ = 7.5 Hz, $J_{7\beta,6\alpha}$ = 3 Hz, H-7β), 2.00 (1H, *m*, $J_{6\beta,6\alpha}$ = −13 Hz, $J_{6\beta,7\alpha}$ = 11 Hz, H-6β). EIMS (solid probe 360°, source 230°) 70 eV, *m/z* (rel. int.): 196 (2.14), 179 (5.31), 178 (5.48), 161 (7.80), 160 (14.49), 150 (16.38).

Penta-(trimethylsilyl)-ugandoside (**3c**). Compound **3c** was obtained by silylation of **3a** with TMSI-S (Serva) for 2 hr at room temp. EIMS, 70 eV, *m/z* (rel. int.): 340 (0.84), 251 (9.02), 250 (1.12), 222 (2.13), 197 (1.00), 169 (14.34), 161 (16.25), 133 (15.61), 132 (2.32).

Ugandosidetetra-acetate (**3b**). Compound **3a** was acetylated (Ac_2O–pyridine) for 22 hr at room temp. and the residue chromatographed on Si gel afforded a tetra-acetate (25 mg), needles from EtOH, mp 162–163°. IR ν_{max}^{KBr} cm^{-1}: 3550, 3090, 2960, 1741, 1672, 1619, 1430, 1370, 1220, 1163, 1117, 1058, 980, 960, 905, 890, 860, 690. ^1H NMR (250.10 MHz, $CDCl_3$): δ9.42 (1 H, *s*, H-11), 7.15 (1 H, *s*, H-3), 5.59 (1 H, *d*, $J_{1,9}$ = 2 Hz, H-1), 4.9 (1 H, *d*, $J_{1',2'}$ = 8 Hz, H-1'), 3.76 (1 H, *m*, H-5'), 3.0 (1 H, *br s*, H-9), 5.35–4.82 (5H, *m*, H_2-10 and three glucose protons), 4.11–4.36 (2 H, *m*, H_2-6'). EIMS (solid probe 340°, source 230°) 70 eV, *m/z* (rel. int.): 196 (0.21), 179 (4.39), 178 (1.44), 161 (15.4), 160 (2.05), 150 (16.39).

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