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DITERPENE GLYCOSIDES FROM *GUTIERREZIA SPHAEROCEPHALA*

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Key Word Index—*Gutierrezia sphaerocephala*; Compositae; Asteraceae; labdane diterpene glycosides.

Abstract—Five new diterpene glycosides, two arabinopyranosides and three xylopyranosides were isolated from *Gutierrezia sphaerocephala*. One of the arabinosides contained a tiglate ester at the 3′-position of the sugar moiety.

INTRODUCTION

From the genus *Gutierrezia* a number of new diterpene derivatives [1–5], as well as some highly oxygenated new flavonoids [4, 5] were reported. Recently, a large number of unusual flavonols were encountered in *G. grandis* and *G. microcephala* [6, 7]. We report here several new diterpenoid glycosides from *G. sphaerocephala*; this is the first report of this class of compounds from the genus *Gutierrezia*.

RESULTS AND DISCUSSION

The aerial parts of *G. sphaerocephala* afforded two diterpene-aldehyde arabinosides (**1** and **2**), one diterpene-aldehyde xyloside (**3**) and two diterpene-methyl ester xylosides (**5** and **6**).

Electron impact mass spectrometry of all these glycosides gave no molecular ion. Even in their CI mass spectra, the fragments of highest molecular weight which could be observed were $[M+H-H_2O]^+$. The IR spectrum of **1** showed absorptions for hydroxyl groups (3450, 1080, 1020 cm^{-1}), double bond(s) (3090, 1650 cm^{-1}), aldehydic function (2720, 1700 cm^{-1}) and an ester group (1700, 1270 cm^{-1}). Together the spectral data indicated a bicyclic system of the *ent* or normal labdane type for **1** since the ^{1}H NMR and ^{13}C NMR of **1** eliminated the other rearranged labdane skeletons, for example the clereodane type. In the ^{1}H NMR spectrum of **1** (Table 1), an ABX pattern of the type exhibited by manool [8] appeared at δ5.91 (1H, *dd*, J = 11, 17 Hz), 5.22 (1H, *br d*, J = 17 Hz) and 5.08 (1H, *br d*, J = 11 Hz). The lack of another geminal methyl signal and the presence of a signal at δ9.17 were in accord with an equatorial aldehydic group attached to C-4 [1]. The fully substituted C-4 and C-10 positions could also be confirmed by the doublet H-5 signal, a conclusion which was settled by irradiation experiments. Instead of exocyclic methylene signals for protons at position C-17 as in **9** [1], compound **1** exhibited a vinylic methyl signal at δ1.74 (3H, *br s*) for an 8-methyl group and a vinylic proton signal at 5.80 (*br s*) assignable to a proton at C-7 in accord with a C-7, C-8 double bond system of either an *ent* or normal labdane type diterpene [3]. A tiglate side chain was unambiguously indicated in **1** by signals at δ6.98 (1H, *dq*, J = 2, 7 Hz), 1.80 (3H, *br d*, J = 7 Hz) and 1.87 (3H, *br s*) and mass spectral fragments at m/z 100 (35%), 83 (100%) and 55 (92%). In the region of δ3.61–4.86, there were seven proton signals (Table 1) including a typical one-proton doublet at 4.25 (J = 7 Hz), which together indicated a sugar moiety was present in compound **1**. In the ^{13}C NMR spectra of **1**, the above conclusions were confirmed by an anomeric carbon signal appearing at δ106.8 (*d*), six sp^2 carbon signals at 145.1 (*d*), 112.1 (*t*) (C-14, C-15 double bond), 123.3 (*d*), 138.7 (*s*) (C-7, C-8 double bond), 128.3 (*s*), 138.5 (*d*) (tigloyloxy double bond), an aldehydic carbon doublet at 208.1 and another six oxygen-bearing carbon signals between 66.2 and 79.5. Among the latter six signals, a singlet at 73.5 was attributable to C-13 and one of the other five signals could be assigned to a sugar-aglycone linkage. The other four signals, together with the anomeric signal, were consistent with a pentosyl moiety. That the sugar moiety was equatorially attached to C-6 of the aglycone was deduced by signals at δ1.91 (*d*, J = 11 Hz) and 4.08 (*br d*, J = 11 Hz) and by spin decoupling experiments. The fact that the tigloyloxy side chain was attached at the C-3′ position was confirmed by the well-separated signals of the pentosyl in the ^{1}H NMR spectrum (Table 1) as well as on the basis of spin decoupling experiments. Irradiation of a doublet at δ4.25 (anomeric proton) collapsed a double-doublet at δ3.09 for H-2′ into a doublet. Irradiation at the latter signal collapsed not only the anomeric signal into a singlet, but also the downfield signal (δ4.86, *dd*, J = 3, 9 Hz) into a doublet with small coupling constant (*ca* 3 Hz), thus confirming that this signal represents H-3′. Irradiation of the signal for H-3′ collapsed the signal for H-2′ into a doublet, and sharpened the H-4′ signal at δ4.02. The transformation of compound **1** into **2** (obtained as a natural product in this study) provided further evidence for a 3′-tigloyloxy ester. In the ^{1}H NMR spectrum of **2**, signals for the tigloyloxy side chain were not present. Consequently, the signal for H-3′ shifted from δ4.86 to 3.57. Acid hydrolysis of **2** gave arabinose (co-TLC). Comparison of the ^{13}C NMR and ^{1}H NMR spectral data of the sugar moieties of **2** and **1** with those reported [9–11] favoured an α-L-arabinopyranosyl group in both compounds. The relative stereochemistry at C-5 and C-6

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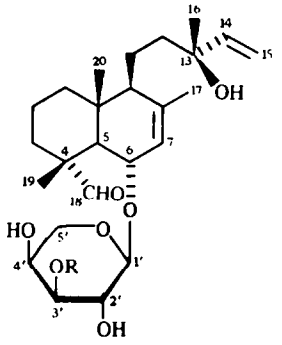
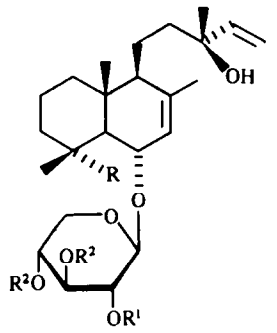


R

1 Tigloyl
2 H



	R	R^1	R^2
3	CHO	Ac	H
4	CHO	H	H
5	COOMe	Ac	H
6	COOMe	H	H
7	CH_2OH	H	H
8	COOMe	Ac	Ac

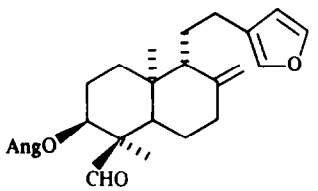


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Table 1. ^{1}H NMR spectral data of compounds 1–4 [recorded at 360 MHz in $CDCl_3$, TMS as internal standard (3 in C_5D_5N at 200 MHz)]*

H	1	2	3	3 C_5D_5N	4
5	1.91 *d* (11)	1.90	1.89	2.0	1.89
6	4.08 *br d* (11)	4.03	4.05	4.35	4.05
7	5.80 *br s*	5.78	5.66	6.08	5.77
14	5.91 *dd* (11, 17)	5.90	5.91	6.21	5.91
15a	5.22 *br d* (17)	5.21	5.22	5.60	5.22
15b	5.08 *br d* (11)	5.07	5.08	5.20	5.08
16†	1.30 *s*	1.29	1.30	1.33	1.29
17†	1.74 *br s*	1.73	1.74	1.82	1.74
18	9.17 *s*	9.16	9.09	9.45	9.16
19†	1.18 *s*	1.19	1.19	1.50	1.19
20†	0.85 *s*	0.85	0.84	0.85	0.86
		Arabinopyranosyl		Xylopyranosyl	
1′	4.25 *d* (7)	4.15	4.56 *d* (5)	4.90 *d* (7)	4.24
2′	3.69 *dd* (7, 9)	3.47	4.52 *dd* (5, 7)	5.47 *t* (7)	3.20 *dd* (7, 9)
3′	4.86 *dd* (3, 9)	3.57	3.58 *t* (7)	4.10	3.44 *t* (9)
4′	4.02 *br s*	3.90	3.67 *m*	4.17 *ddd* (5, 7, 11)	3.67 *ddd* (4, 9, 11)
5′a	3.99 *br d* (12)	4.01	4.11 *dd* (4, 12)	4.85 *dd* (5, 11)	4.00 *dd* (4, 11)
5′b	3.61 *br d* (12)	3.52	3.36 *dd* (6, 12)	3.71 *t* (11)	3.27
	tigloyl		acetyl	acetyl	
3″	6.98 *dq* (2, 7)		2.21 *s*†	2.41†	
4″†	1.80 *br d* (7)				
5″†	1.87 *br s*				

*Coupling pattern, coupling constants (in parentheses) are not repeated if they are identical with those in the preceding column.

†Intensity is for three protons.

could be followed from the downfield shifted signal of H-5 which indicated that the oxygen functions at C-6 and C-18 and the H-5 must be on the same side; thus, the C-4 and C-6 oxygen functions must be equatorially substituted [2]. The NOE results conducted on compound **5** also confirmed this conclusion. If these new glycosides form a labdane series, the 6α-*O*-substituent in **1** follows from the large coupling (11 Hz) of H-6 and H-5, a result confirmed by spin decoupling. The ^{13}C NMR data for **2** were in accord with the structures proposed for **1** and **2**. The ^{13}C NMR spectra of **1–4** gave unexpected doublet signals for C-4 when the off resonance decoupled spectra were recorded in the usual manner (high-field, −8.3 ppm) due to the aldehydic proton at C-18 [12]. The APT and low-field (9.4 ppm) single frequency off-resonance decoupling experiments confirmed these assignments.

The ^{1}H NMR spectrum of **5** (and also of **6**) gave signals for a diterpene derivative (Table 2) similar to those of **1**. But the aldehydic group at C-18 in **1** was replaced by a methyl ester group (δ3.62, 3H, *s*) in **5**. Also, instead of a tigloyloxy side chain an acetoxy group was present (δ2.19, 3H, *s*). Signals attributable to a sugar moiety in the δ3.44–4.68 region were observed, but the chemical shifts and coupling constants were different from those observed for **1**. Upon acid hydrolysis compound **6**, the alkaline hydrolysis product of **5**, afforded xylose which confirmed **5** and **6** were xylosides. A two-dimensional *J*-correlation experiment located H-1′, H-2′, H-5′a, H-5′b, H-3′ and H-4′. Irradiation experiments on **5** at 200 MHz also supported the above findings. The downfield signal of H-2′ at δ4.52 (1H, *t*, J = 4 Hz in $CDCl_3$) confirmed that the acetyl group was attached at the C-2′ position. The observation of $J_{1',2'}$ = 4 Hz (in $CDCl_3$) at first suggested an α-configuration for a xyloside. However, when the spectrum was recorded in C_5D_5N (Table 2), $J_{1',2'}$ = 7 Hz, or when the acetyl group was removed to give **6**, the spectrum (in $CDCl_3$) of **6** exhibited normal β-coupling, namely $J_{1',2'}$ = 7 Hz. The ^{13}C NMR data (Table 3) of the xylose moiety in **5** and **6** were also in accord with β-xyloside [13, 14]. $LiAlH_4$ reduction of **5** afforded the diol xyloside **7** and acetylation gave triacetate **8**. As found for compound **1**, the 6α-configuration could also be suggested for **5** on the basis of the $J_{6,5}$ (11 Hz) value. In order to establish the relative stereochemistry for all these new glycosides, further 2D COSY and NOE experiments were conducted at 500 MHz on compound **5**. The NOE results clearly indicated a *trans*-fused A-B ring system and that H-19, H-20 and H-6 were on the same side since irradiation on the H-6 signal dramatically enhanced the signals for H-19, H-20 and H-7 but not the signal for H-5 (other reciprocal irradiations also supported this conclusion). From all the available data, compound **5** was deduced to be the 2′-acetyl derivative of compound **6**.

The ^{1}H NMR spectrum of compound **3** also exhibited the same ABX pattern and a signal for an aldehydic proton. Instead of signals for a tigloyloxy group as observed for compound **1**, a 3-proton singlet appeared at δ2.21 in the spectrum of compound **3**. Comparison of the signals for **3** with those for **1** and **5** indicated that **3** may have the same aglycone as **1** but with the sugar moiety of compound **5**. This was supported by the ^{13}C NMR data of **3** and **4** (the alkaline hydrolysis product of **3**) when

Table 2. ^{1}H NMR spectral data of compounds **5–7** [recozded at 200 MHz (**5** at 360 MHz), with TMS as internal standard]*

H	**5** $CDCl_3$	**5** C_5D_5N	**6** $CDCl_3$	**7** C_5D_5N
5	2.44 *d* (11)	2.80	2.38	2.31
6	4.05 *br d* (11)	4.35	4.09	4.54
7	5.66 *br s*	6.19	5.77	6.18
14	5.90 *dd* (11, 17)	6.21	5.91	6.21 *dd* (10, 17)
15a	5.20 *br d* (17)	5.60 *dd* (1, 17)	5.21	5.57 *dd* (2, 17)
15b	5.07 *br d* (11)	5.20 *dd* (1, 11)	5.08	5.18 *dd* (2, 10)
16†	1.28 *s*	1.50	1.30	1.49
17†	1.73 *br s*	1.77	1.72	1.83
18a	—	—	—	4.31 *d* (11)
18b	—	—	—	3.35 *d* (11)
19†	1.28 *s*	1.49	1.29	1.02
20†	0.82 *s*	0.92	0.83	0.90
OMe†	3.62 *s*	3.74	3.64	—
		xylopyranosyl		
1′	4.68 *d* (4)	5.00 *d* (7)	4.25	5.05
2′	4.52 *t* (4)	5.32 *t* (7)	3.14 *dd* (7, 9)	4.01 *dd* (7, 8)
3′	3.63 —	4.14 *t* (7)	3.48 *t* (9)	4.20 —
4′	3.63 —	4.19 *ddd* (5, 7 11)	3.70 —	4.20 —
5′a	4.14 *dd* (3, 12)	4.45 —	4.00 *dd* (5, 11)	4.42 *dd* (4, 10)
5′b	3.44 *dd* (5, 12)	3.75 —	3.29 *t* (11)	3.79 *dd* (9, 10)
Ac†	2.19 *s*	2.39	—	—

*Coupling pattern, coupling constants (in parentheses) are not repeated if identical with those in the preceding column.

†Intensity is for three portions.

Table 3. ^{13}C NMR spectral data of compounds 1–7 [recorded at 22.6 MHz (2 at 90 MHz), in $CDCl_3$ (7 in C_5D_5N) with TMS as internal standard]*

C	1	2	3	4	5	6	7
1	38.4 *t*	38.4 —	38.3 *t*	38.4	38.2	38.3	38.8
2	21.0 *t*	21.0 *p*	21.0 *t*	21.1	20.6	20.9	21.4
3	31.5 *t*	31.5 *p*	32.6 *t*	31.6	26.7	37.4	38.0
4	47.7 *d*	47.7 *p*	47.0 *d*	47.8	43.5 *s*	44.2	40.8
5	49.0 *d*	49.0 *n*	49.7 *d*	49.0	48.5	49.8	49.0
6†	74.5 *d*	73.0 *n*	73.4 *d*	73.6	73.6	73.7	75.2
7	123.3 *d*	123.4 *n*	123.6 *d*	123.4	123.3	123.5	126.5
8	138.7 *s*	138.3 —	138.7 *s*	138.8	138.7	138.7	137.7
9	55.0 *d*	55.0 *n*	54.7 *d*	55.0	54.8	55.2	54.3
10	37.6 *s*	37.7 —	38.7 *s*	37.7	38.2	38.3	38.5
11	16.6 *t*	16.7 *p*	16.9 *t*	16.8	17.2	17.5	18.7
12	44.5 *t*	44.5 *p*	44.5 *t*	44.6	44.3	44.6	45.7
13	73.5 *s*	73.5 —	73.6 *s*	73.6	73.3	73.6	72.8
14	145.1 *d*	145.0 *n*	145.0 *d*	145.2	144.8	145.1	147.2
15	112.1 *t*	112.0 *p*	112.1 *t*	112.2	111.8	112.1	111.3
16	27.7 *q*	27.8 *n*	27.6 *q*	27.8	27.3	27.7	28.2
17	22.1 *q*	22.1 *n*	22.1 *q*	22.2	22.0	22.2	22.1
18	208.2 *d*	208.3 —	204.9 *d*	208.6	179.4 *s*	183.5	72.4 *t*
19	14.4 *q*	14.2 —	14.8 *q*	14.3	17.0	17.0	19.0
20	15.1 *q*	15.1 *n*	15.0 *q*	15.2	14.7	15.0	15.6
OMe					51.8 *q*	52.6	
	arabinopyranosyl		xylopyranosyl		xylopyranosyl		
1′	106.8 *d*	106.1 *n*	101.6 *d*	106.3	101.6	106.4	105.1
2′†	67.0 *d*	67.8 *n*	74.4 *d*	76.4	72.6	76.5	78.2
3′	79.5 *d*	79.4 *n*	78.2 *d*	79.4	80.0	80.4	78.4
4′†	69.0 *d*	71.5 *n*	69.7 *d*	69.3	69.2	69.3	71.0
5′	66.2 *t*	65.9 *p*	64.1 *t*	65.6	63.3	65.5	67.0
	tigloyl	—	acetyl	—	acetyl	—	—
1″	167.5 *s*	— *p*	171.8 *s*	—	171.4 *s*	—	—
2″	128.3 *s*	— *p*	21.3 *q*	—	21.1 *q*	—	—
3″	138.5 *d*	— *n*	—	—	—	—	—
4″	14.2 *q*	— *n*	—	—	—	—	—
5″	12.1 *q*	— *n*	—	—	—	—	—

*Multiplicities were obtained from high-field (−8.3 ppm) single frequency off resonance decoupling experiments and are not repeated if identical with those in the preceding column. APT (attached proton test) experiments were also conducted on compounds **1** and **2**. Results of both compounds were the same and were given under compound **2**: *p* = positive signal (no proton or two protons attached); *n* = negative signal (one proton or three protons attached).

†These signals might be interchanged within each column.

comparing with those of **5** and **6** (Table 3). The acetoxy group at C-2′ in **3** could be deduced by irradiation experiments. Acid hydrolysis of compound **4** afforded xylose. The ^{13}C NMR data of **3** and **4** were also in accord with the structure assignments.

We have previously observed small differences between manool and 13-epimanool for the C-14 and C-16 signals in their ^{13}C NMR spectra.

The absolute configuration for the five new glycosides (**1–3**, **5**, **6**) could not be assigned with confidence on the basis of the available spectral data. Therefore, one compound (**6**) was submitted for X-ray analysis. These results [W. H. Watson, personal communication], which became available when page proofs were received, established **6** to be a normal labdane; since the xylosyl moiety in **6** is a β-D-xylose (determined by NMR coupling constants and standard comparison), **6** has the absolute configuration as shown. We assigned the new compounds **1–3** and **5** the same configuration as **6**.

Although the tigloyloxy side chain is commonly found in the family Compositae, compound **1** is the first report where it is attached to a sugar moeity. It is also of interest that the coupling constants of the anomeric proton signals in **3**, **5** and **8** in their ^{1}H NMR spectra recorded in $CDCl_3$ were found to be strongly affected by the acetoxy group attached to the adjacent position. Although methoxyl groups in diterpenoids are not commonly found in nature, it is considered to be of natural occurrence in this extract since methanol was not involved in the extraction and separation procedures used to obtain compounds **5** and **6**.

EXPERIMENTAL

Gutierrezia sphaerocephala Gray was collected in Brewster County, Texas, 3.5 miles south of Ft. Davis on the road to Alpine, on Sept. 7, 1984. The plant was identified by Richard Hilsenbeck and Michael Powell of Sul Ross State University, Alpine, Texas. A voucher specimen (Barrie No. 971) is on deposit in the Herbarium of the University of Texas at Austin.

Mps were uncorr. Determination of sugars was made by co-chromatography on cellulose plates (solvent: pyridine–EtOAc–HOAc–H_2O, 36:36:7:21) and PC [15], aniline hydrogen phthalate was used as developer.

Isolation of the compounds. The aerial parts of *G. sphaerocephala* (630 g) were extracted with CH_2Cl_2 (6 L × 2) for 30 min. The extracts were combined and evaporated under red. pres. to yield 71 g of residue. The residue was dissolved in 1.3 l. Me_2CO and kept in a refrigerator overnight. After filtering to remove the ppt, the soln was evaporated to give 66.2 g of material which was charged onto a silica gel column. The column was eluted with a hexane–EtOAc gradient solvent system. Finally, it was washed with MeOH–EtOAc (10–20% MeOH). Further separations and purifications were made over a Sephadex LH-20 column (cyclohexane–CH_2Cl_2–MeOH, 7:4:1) to give **1**, **3**, **5** (from the hexane–EtOAc eluate) and **2** (from the MeOH–EtOAc eluate). Compound **6** was obtained by using a combination of a Sephadex LH-20 column and prep. TLC (C_6H_6–HOAc, 1:2).

Compound **1**. 105 mg; $[\alpha]_D^{30}$ + 40.4° (MeOH; *c* 1.93). IR ν_{max}^{KBr} cm^{-1}: 3450, 1080, 1020 (OH), 3090, 1650 (C=C), 2720, 1700 (CHO), 1700, 1270 (tiglate). EIMS (probe), 70 eV, *m/z* (rel. int.): 302 [M − tigloylarabinosyl − OH]$^+$ (1), 284 [302 − H_2O]; (6), 269 [284 − Me]$^+$ (6), 255 [284 − CHO]$^+$ (32), 100 [$C_5H_8O_2$]$^+$ (35), 83 [C_5H_7O]$^+$ (100), 55 [C_4H_7]$^+$ (92). CIMS (methane, probe) 70 eV, *m/z* (rel. int.): 517 [M + H − H_2O]$^+$ (0.5), 499 [M + H − 2 × H_2O]$^+$ (0.2), 285 [M + H − H_2O − tigloylarabinosyl − OH]$^+$ (40), 215 (100), 101 [MeCH=C(Me)CO_2H + H]$^+$ (12), 83 [C_5H_7O]$^+$ (55).

Alkali hydrolysis of **1**. Compound **1** (79 mg) was hydrolysed with 10% KOH–EtOH under N_2 at room temp. for 1 hr. The usual work-up gave 40 mg of **2**. $[\alpha]_D^{30}$ + 62.8° (MeOH; *c* 0.78). IR ν_{max}^{KBr} cm^{-1}: 3420, 1090 (OH), 3100, 1640 (C=C), 2730, 1700 (CHO). EIMS (probe) 70 eV, *m/z* (rel. int.): 284 [M − H_2O − arabinosyl − OH]$^+$ (4), 269 [284 − Me]$^+$ (10), 255 [284 − CHO]$^+$ (40), 173 (92), 43 (100).

Acid hydrolysis of compound **2**. A soln of **2** (13 mg in 1 ml MeOH and 2 ml 10% HCl) was stirred for 3 hr at room temp. The mixture was extracted with EtOAc (the EtOAc extract yielded decomposed complex aglycones). Arabinose was identified in the H_2O layer of the hydrolysate.

Compound **2**. The ^{1}H NMR, mass and IR spectra of **2** (60 mg) showed that it was identical to the compound obtained by alkaline hydrolysis of **1**.

Compound **3**. Colourless plates (85 mg), mp 145–146° (cyclohexane–CH_2Cl_2–MeOH). $[\alpha]_D^{32}$ + 70.7° (MeOH; *c* 0.82). IR ν_{max}^{KBr} cm^{-1}: 3440, 1080, 1050 (OH), 3100, 1640 (C=C), 2740, 1730 (CHO), 1730, 1250 (MeCOOR). EIMS (probe) 70 eV, *m/z* (rel. int.): 284 [M − H_2O − acetylxylosyl − OH]$^+$ (4), 269 [284 − Me]$^+$ (5), 255 [284 − CHO]$^+$ (39), 173 (91), 43 (100). CIMS (methane, probe) 70 eV, *m/z* (rel. int.): 477 [M + H − H_2O]$^+$ (1), 459 [477 − H_2O]$^+$ (2), 285 [M + H − H_2O − acetylxylosyl − OH]$^+$ (100).

Alkali hydrolysis of **3**. Compound **3** (60 mg) when hydrolysed in the same manner as described for **1** gave compound **4** (48 mg). $[\alpha]_D^{32}$ + 54.9° (MeOH; *c* 0.82). EIMS (probe) 70 eV, *m/z* (rel. int.): 284 [M − H_2O − xylosyl − OH]$^+$ (3), 269 [284 − Me]$^+$ (6), 255 [284 − CHO]$^+$ (39), 173 (82), 43 (100). When **4** was hydrolysed with acid in the manner described for **6**, a decomposed aglycone and xylose were detected.

Compound **5**. White prisms (780 mg) from EtOAc–hexane, Mp 133.5–134°. $[\alpha]_D^{29}$ + 76.7° (MeOH; *c* 0.73). IR ν_{max}^{KBr} cm^{-1}: 3450, 1090, 1050 (OH), 3100, 1640 (C=C), 1730, 1250 (COOMe and AcOR). EIMS (probe) 70 eV, *m/z* (rel. int.): 332 [M − acetyl − xylosyl − OH]$^+$ (1), 314 [332 − H_2O]$^+$ (14), 299 [314 − Me]$^+$ (14), 255 [314 − COOMe]$^+$ (39), 239 [299 − HCOOMe]$^+$ (69), 173 (100).

Partial hydrolysis of **5** *with alkali.* Compound **5** (230 mg) was dissolved in a small amount of EtOH, then 10 ml of 2% KOH–EtOH were added. The mixture was stirred at room temp. for 1 hr. The usual work-up gave 191 mg of **6**. The material was repeatedly crystallized in EtOAc to give colourless prisms, mp 198°. $[\alpha]_D^{30}$ + 113.5° (MeOH; *c* 0.52). IR ν_{max}^{KBr} cm^{-1}: 3450, 1080, 1040 (OH), 3100, 1640 (C=C), 1705, 1270 (COOMe). EIMS (probe), 70 eV, *m/z* (rel. int.): 332 [M − xylosyl − OH]$^+$ (2), 314 [332 − H_2O]$^+$ (6), 299 [314 − Me]$^+$ (7), 255 [314 − COOMe]$^+$ (43), 239 [299 − HCOOMe]$^+$ (32), 173 (100).

Compound **6**. The ^{1}H NMR, MS and TLC of **6** (11 mg) showed that it was identical to the compound obtained from **5** by alkaline hydrolysis.

Acid hydrolysis of **6**. Compound **6** (56 mg) was dissolved in 5 ml MeOH and 5 ml 10% HCl. The mixture was stirred at room temp. for 3 hr; then the solvent was evaporated to remove MeOH and part of the HCl. The remaining soln was extracted with CH_2Cl_2. The CH_2Cl_2 extract afforded decomposed aglycone material (four major spots, unidentified), while the H_2O layer yielded xylose.

Acetylation of **5** *and* **6**. Compound **5** (37 mg) was acetylated with Ac_2O–pyridine in the usual manner to give 42 mg of triacetate **8**. When compound **6** was acetylated, **8** was obtained. ^{1}H NMR (200 MHz, $CDCl_3$): δ0.85 (3H, *s*, H-20), 1.27 (3H, *s*, H-19), 1.30 (3H, *s*, H-16), 1.74 (3H, *br s*, H-17), 2.49 (1H, *d*, *J* = 11 Hz, H-5), 3.49 (1H, *dd*, *J* = 8, 12 Hz, H-5'b), 3.55 (3H, *s*, OMe), 4.09 (1H, *br d*, *J* = 11 Hz, H-6), 4.15 (1H, *dd*, *J* = 5, 12 Hz, H-5'a), 4.66 (1H, *s*, H-1'), 4.68 (1H, *d*, *J* = 5 Hz, H-2'), 4.96 (1H, *ddd*, *J* = 5, 8, 12 Hz, H-4'), 5.1 (1H, H-3'), 5.09 (1H, *br d*, *J* = 11 Hz, H-15b), 5.22 (1H, *br d*, *J* = 17 Hz, H-15a), 5.70 (1H, *br s*, H-7), 5.92 (1H, *dd*, *J* = 11, 17 Hz, H-14), 2.03 (3H, *s*, OAc), 2.05 (3H, *s*, OAc), 2.13 (3H, *s*, OAc). ^{1}H NMR (360 MHz, C_6D_6): δ0.80 (3H, *s*, H-20), 1.12 (3H, *s*, H-19), 1.35 (3H, *s*, H-16), 1.69 (3H, *br s*, H-17), 2.71 (1H, *d*, *J* = 11 Hz, H-5), 3.15 (1H, *dd*, *J* = 8, 12 Hz, H-5'b), 3.58 (3H, *s*, OMe), 3.98 (1H, *dd*, *J* = 5, 12 Hz, H-5'a), 4.08 (1H, *br d*, *J* = 11 Hz, H-6), 4.57 (1H, *d*, *J* = 7 Hz, H-1'), 4.97 (1H, *d*, *J* = 11 Hz, H-15b), 5.09 (2H, H-3', 4' obscured), 5.19 (1H, *d*, *J* = 17 Hz, H-15a), 5.41 (1H, *t*, *J* = 7 Hz, H-2'), 5.75 (1H, *dd*, *J* = 11, 17 Hz, H-14), 5.90 (1H, *br s*, H-7), 1.60 (3H, *s*, OAc), 1.82 (3H, *s*, OAc), 2.15 (3H, *s*, OAc).

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