Pergamon

PII: S0031-9422(96)00737-6

Phytochemistry, Vol. 45, No. 1, pp. 141–148, 1997

0031-9422/97 $17.00+0.00

LIMONOIDS FROM *TRICHILIA ELEGANS* SSP. *ELEGANS*

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(*Received in revised form* 13 *September* 1996)

Key Word Index—*Trichilia elegans* ssp. *elegans*; Meliaceae; limonoids.

Abstract—From the seeds of *Trichilia elegans* ssp. *elegans*, six new limonoids, four of which possess the uncommon *seco*-A, B and D carbocyclic rings, have been isolated, together with two known limonoids–kihadanin A and B and 3-*O*-β-D-glucopyranosyl-sitosterol. The structures of these compounds have been established on the basis of 1D and 2D NMR spectroscopic techniques. © 1997 Elsevier Science Ltd. All rights reserved

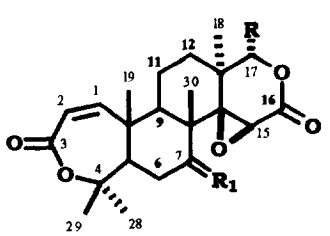
INTRODUCTION

We have recently reported the isolation of three *seco*-A-protolimonoids from *Trichilia elegans* ssp. *elegans* [1]. In continuing our investigations on the chemical constituents of this species, the composition of the ethanolic extract from the seeds has been further studied. Herein we report the isolation and structure elucidation of six new limonoids (**1**, **2**, **5**–**8**), together with kihadanins A and B (**3** and **4**), earlier described from two rutaceous plants [2–4], and 3-*O*-β-D-glucopyranosyl-sitosterol. The structures of the known and new compounds were established on the basis of spectroscopic methods, including ^{1}H–^{1}H COSY and HETCOR techniques and long range proton–carbon connectivity data from HMBC experiments.

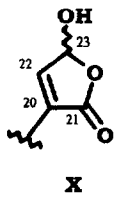
RESULTS AND DISCUSSION

After a combination of column and flash chromatography on silica gel, gel filtration and reversed phase HPLC separations of the dichloromethane solubles, obtained from partition of the ethanolic extract from the seeds, limonoids **1**–**8** were isolated, together with 3-*O*-β-D-glucopyranosyl-sitosterol.

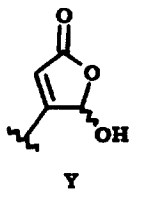
Compound **1** showed six methyl singlets in the ^{1}H NMR spectrum (Table 1) at δ 1.13, 1.19, 1.32, 1.34, 1.43 (tertiary C-methyl groups) and 2.11 (acetate methyl). The spectrum also showed a pair of doublets of a conjugated double bond at δ 5.87 and 6.44 (1H each, J = 12.2 Hz). Its ^{13}C NMR spectrum (Table 2) displayed signals for 28 carbon atoms, two of which related to an acetate group (δ 169.9 and 21.1). The remaining ^{13}C signals were attributed to three more ester carbonyls, four olefinic carbons, and, with the aid of a DEPT experiment, to five more quaternary carbons, six methines, three methylenes and five methyl carbons. This information led to the assumption that **1** possessed a tetranortriterpenoid carbon skeleton. However, the characteristic signals for a furan moiety at C-17, typical for limonoids of the Meliaceae, were absent in the NMR spectra of **1**. It showed instead, two broad one-proton singlets at δ 6.21 and 7.31, which were shown to be coupled in the ^{1}H–^{1}H COSY spectrum. This information, along with its ^{13}C NMR spectroscopic data, were in agreement with the presence of a γ-hydroxybutenolide function in **1**, wherein the hemicetal carbon appeared as a broad signal at δ 97.7. From the ^{1}H–^{13}C HETCOR spectrum, it was seen that this resonance showed connectivity to the broad one-proton singlet at δ 6.21. The signal at δ 169.6 was assigned to the α,β-unsaturated γ-lactone carbonyl and the remaining two carbon resonances at δ 133.3 and 150.8 were ascribed to the olefinic carbons C-20 and C-22, respectively. In the ^{1}H–^{13}C HETCOR spectrum a cross-peak correlation was observed between the latter carbon signal and the broad proton singlet at δ 7.31. The equilibrium between the two epimeric forms at C-23 of the γ-hydroxybutenolide ring accounts for the broadness of the ^{13}C signal of C-23. This effect is also observed at the neighbouring carbon (C-22) and, with a lesser intensity, at C-20. The occurrence of limonoids possessing γ-hydroxybutenolide side chains at C-17 has already been reported in several members of the Meliaceae [5–12], including the genus *Trichilia* [13, 14]. In the ^{1}H–^{1}H COSY spectrum, resonances at δ 6.21 (H-23) and 7.31 (H-22) showed further couplings to a broad singlet at δ 5.51 (1H). This signal was, therefore, attributed to H-17. Its chemical shift and multiplicity were in accordance with the presence of a ring D lactone moiety in **1** [15]. Another characteristic feature of the ^{1}H NMR spectrum of **1** was the one-proton singlet observed at δ 3.48, which was associated with the H-



	R	R_1
1	X	H, α OAc
2	Y	H, α OAc
3	Y	O
4	X	O



X



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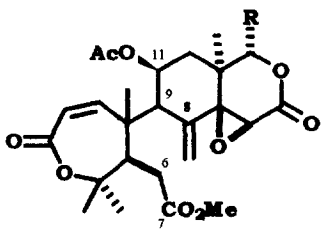

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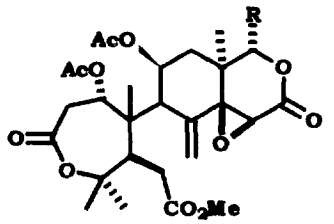
6 R = Y



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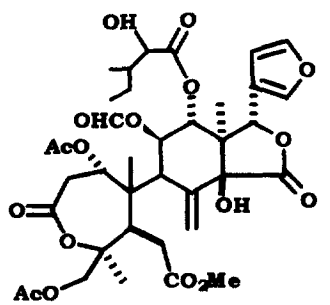
8 R = Y



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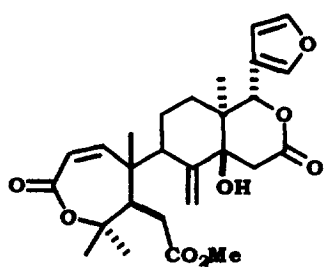

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15 resonance in a ring D-14,15-epoxy-δ-lactone [15].

On the basis of connectivities discernible from an HMBC experiment, unambiguous assignments of the C-16 and C-21 carbonyls were established (Table 3). Accordingly, two and three-bond proton-carbon correlations were observed between H-15 (δ 3.48) and C-16 (δ 167.1) and between H-17 (δ 5.51) and C-21 (δ 169.6), respectively. A prominent cross-peak between H-17 and C-14 (δ 69.6) and the above mentioned correlation between H-15 and C-16 supported the presence of a 14,15-epoxide function in **1**.

The chemical shifts and multiplicities of the two olefinic protons observed as a pair of doublets at δ 6.44 (*J* 12.2 Hz) and 5.87 (*J* 12.2 Hz) indicated that ring A in **1** is the same as that found in the obacunone-type limonoids [16–18]. These doublets were assigned to H-1 and H-2, respectively. The ^{13}C NMR signal at δ 84.8 could be attributed to the quaternary, oxygen bearing C-4 and HMBC correlations of H-1 and H-2 to the carbonyl at δ 167.4 allowed the assignment of C-3.

The broad singlet at δ 4.47 was ascribed to the equatorial proton on the acetate-bearing carbon. The location of this group was established by difference NOE studies. Thus, irradiation of the above mentioned singlet gave rise to a NOE enhancement at the signal due to H-15, indicating that the acetate group is attached to C-7. The α-orientation of the C-7 acetoxy substituent was based on biogenetic grounds, considering that, like all limonoids from the Meliaceae, **1** is derived from an *apo*-tirucallol (or *apo*-euphol) precursor [5, 19]. Limonoid **1** has a close structural relationship to 7-α-obacunyl acetate, which differs from **1** in possessing a furan ring at C-17 instead of a γ-hydroxybutenolide residue. The carbon and proton shifts of the rings A–D in **1** are comparable with those reported for 7-α-obacunyl acetate [20], although the chemical shifts of the methyl groups were not attributed in the latter. The methyl resonances in **1** were determined on the basis of ^{1}H–^{13}C HETCOR and HMBC data.

The ^{1}H and ^{13}C NMR spectral data of compounds

Table 1. ^{1}H NMR spectral data for compounds **1** and **2** in $CDCl_3$ (200 MHz) and **3** and **4** in $CDCl_3$/CD_3OD (**3**: 200 MHz, **4**: 300 MHz, TMS $\delta = 0$)

H	1	2	3	4
1	6.44 *d* (12.2)	6.47 *d* (12.1)	6.64 *d* (11.7)	6.47 *d* (11.7)
2	5.87 *d* (12.2)	5.92 *d* (12.1)	5.94 *d* (11.7)	5.87 *d* (11.7)
5	2.38–2.46 *m**	2.37–2.45 *m**	2.62 *dd* (14.1, 4.9)	2.53 *dd* (14.0, 4.7)
6	1.75–2.01 *m*†	1.69–1.96 *m*†	2.26 *dd* (13.7, 4.9) [6_{eq}]	2.21 *br dd* (13.8, 4.7)* [6_{eq}]
	[H_2-6]	[H_2-6]	3.00 *br t* (13.9) [6_{ax}]	2.90 *br t* (14.0) [6_{ax}]
7	4.47 *br s*	4.52 *br s*	—	—
9	2.38–2.46 *m**	2.37–2.45 *m**	2.01–2.14 *m**	2.21 *br dd* (13.8, 4.7)*
11	1.34–1.43 *m* [11_{ax}]	1.69–1.96 *m*†	1.88–1.93 *m*	1.17–1.32 *m* [11_{ax}]
	1.75–2.01 *m*† [11_{eq}]	[H_2-11]	[H_2-11]	1.74–1.84 *m*† [11_{eq}]
12	1.75–2.01 *m*†	1.69–1.96 *m*†	1.70 *br t* (10.4) [12_{ax}]	1.74–1.84 *m*† [12_{ax}]
	[H_2-12]	[H_2-12]	2.01–2.14 *m** [12_{eq}]	2.00–2.09 *m* [12_{eq}]
15	3.48 *s*	3.50 *s*	3.58 *s*	3.59 *s*
17	5.51 *br s*	5.50 *br s*	5.32 *br d* (1.4)	5.33 *br s*
18	1.19 *s*	1.32 *s*	1.09 *s*	1.04 *s*
19	1.32 *s*	1.32 *s*	1.47 *s*	1.36 *s*
21	—	6.08 *br s*	6.13 *br s*	—
22	7.31 *br s*	6.25 *br s*	6.25 *br s*	7.20 *br s*
23	6.21 *br s*	—	—	6.11 *br s*
28	1.34 *s*	1.35 *s*	1.42 *s*	1.41 *s*
29	1.43 *s*	1.43 *s*	1.48 *s*	1.42 *s*
30	1.13 *s*	1.11 *s*	1.21 *s*	1.17 *s*
OAc	2.11 *s*	2.11 *s*		

Coupling constants (J in Hz) are given in parentheses.
Assignments were confirmed by the ^{1}H–^{1}H COSY spectra.
*,†Overlapped signals.

1 and **2** showed that they have identical constituting rings A, B, C and D and differ only in the nature of the side chain attached at C-17 (Tables 1 and 2). This was shown to be a 21-hydroxybut-20(22)-ene-γ-lactone residue in **2**, by the presence of two broad singlets at δ 6.08 (H-21) and 6.25 (H-22) in the ^{1}H NMR spectrum. This information was corroborated by the ^{13}C NMR data, which indicated a hemicetal carbon at δ 98.9 (C-21) and an α,β-unsaturated γ-lactone [δ 163.3 (C-20), 122.8 (C-22) and 169.1 (C-23)]. Limonoid **2**, as well as **1**, exhibited in the negative ESI mass spectrum a pseudo-molecular ion at m/z 529 $[M-H]^-$ ($C_{28}H_{34}O_{10}$ requires m/z 530).

Comparison of the spectral properties of **2** with those of **3** indicated that these are closely related (Tables 1 and 2). However, the ^{1}H NMR spectrum of **3** lacked the acetate methyl signal, showing instead a pair of double doublets at δ 2.62 (1H, J = 14.1 and 4.9 Hz) and 2.26 (1H, J = 13.7 and 4.9 Hz) and an one-proton triplet at δ 3.00 (J = 13.9 Hz). These chemical shifts and multiplicities were in agreement with the presence of a keto group at C-7. In the ^{13}C NMR spectrum, the presence of a ketone function in **3** was inferred by the signal at δ 207.5. Accordingly, the negative ESI mass spectrum of **3** showed a $[M-H]^-$ ion at m/z 485 (44 mass units fewer than that of **2**). The two H-6 protons at δ 2.26 (H-6_{eq}) and 3.00 (H-6_{ax}) were shown to be coupled in the ^{1}H–^{1}H COSY spectrum and ^{1}H–^{13}C cross-peak correlations with the carbon resonance at δ 39.4 confirmed geminal coupling. Both exhibited further coupling to the single proton at δ 2.62 (H-5), which in turn displayed ^{1}H–^{13}C connectivity to C-5 at δ 56.9. Therefore, compound **3** was characterized as the corresponding 7-keto derivative of **2**, to which structure **3** was attributed. The carbon and proton shifts of **3** are very similar to those reported for kihadanin A, previously isolated from *Phellodendron amurense* (Rutaceae) [4], although the spectral characterization of the latter has not been fully described.

The structure of **4** was readily established by analogy with **3**, since the carbon and proton shifts of the rings A, B, C and D of both compounds correspond to each other. The only difference refers to the isomeric nature of the γ-hydroxybutenolide side chain in **4**, as already described for **1** (Tables 1 and 2). The ESI-mass spectrum of **4**, measured in the negative ion mode, gave a pseudo-molecular ion at m/z 485 $[M-H]^-$. Compound **4** has the same proposed structure as kihadanin B isolated from *P. amurense* [3, 4]. This limonoid has been also obtained, together with kihadanin A (**3**) as an unresolved mixture, from *Citrus natsudaidai* (Rutaceae) [2].

The ^{1}H NMR spectrum of **5** (Table 4) showed a three-proton singlet at δ 3.69 assignable to a carbomethoxy group and a multiplet at δ 5.39–5.45, integrating for four protons, assignable to an exocyclic methylene group and two oxymethine protons. The ^{13}C NMR spectrum (Table 2) provided further evidence for the presence of the first two groups by dis-

Table 2. ^{13}C NMR spectral data for compounds **1** and **5–8** in $CDCl_3$, **2** in $CDCl_3$/Py-d_5 and **3–4** in $CDCl_3$/CD_3OD (50 MHz, TMS $\delta = 0$)

C	1*	2	3*	4	5	6*	7	8
1	155.2	155.4	157.3	156.8	149.4	150.0	71.0/71.3	71.6
2	120.5	121.1	122.1†	122.3	121.8	121.8	36.5	36.5
3	167.4	166.9	167.5	167.3	167.7	168.5	171.0/171.8	171.6
4	84.8	84.2	84.3	84.2	84.4	85.3	84.5/85.0	84.6
5	49.0	48.9	56.9	57.0	49.5	49.3	45.5	45.7
6	26.6‡	26.7‡	39.4	39.7	34.7	34.5	34.7	34.7
7	72.8	72.6	207.5	207.8	173.5	173.4	173.0/173.1	173.0
8	44.1	43.4	52.8	52.8	136.6	135.9	136.1/136.4	136.0
9	41.3	41.0	48.7	49.1	52.7	52.6	51.4/51.8	51.5
10	42.1	41.9	42.8	43.2	46.5	46.4	48.2/48.7	48.0
11	16.2	16.2	19.0	19.0	68.7	68.6	68.8/69.3	68.5
12	25.4‡	25.9‡	31.7	30.1	33.4	33.4	34.3	34.1
13	39.2	38.7	37.3	37.7	38.9	38.9	38.9/39.0	39.0
14	69.6	69.2	64.7	64.9	66.3	66.3	67.3/67.4	67.4
15	56.3	55.3	52.3	53.0	54.9	54.9	54.9	55.0
16	167.1	165.8	165.9	166.7	165.7	164.9	165.6/165.8	164.9
17	76.1	77.8	78.1	75.4	74.5	76.4	74.7/75.4	76.6
18	17.3	17.8	20.8	20.2	14.6	15.8	15.0	15.7
19	16.3	15.8	16.0	16.3	22.8	22.8	24.4‡	24.4
20	133.3	163.3	162.7	132.5	132.5	161.8	132.7/133.6	161.7
21	169.6	98.9	98.9	169.9	169.5	97.7	168.8/169.0	98.1
22	150.8	122.8	122.1†	152.0	150.4	122.9	149.9/150.3	123.4
23	97.7	169.1	169.7	97.6	97.7	169.1	97.1/97.7	168.6
28	32.0	31.8	31.5	31.7	30.1	30.0	33.7/34.0	34.0
29	26.3	26.3	26.2	26.4	22.1	21.8	24.3/24.4‡	21.2
30	18.3	18.9	16.2	16.9	124.7	125.2	126.1/126.4	126.3
OAc	169.9	169.9			170.2	169.9	170.3/170.4	170.3
	21.1	20.8			20.7	20.6	21.2	21.4
							170.5/170.6	170.7
							21.5/21.6	21.5
OMe	—	—			52.4	52.4	52.2/52.3	52.4

Multiplicities were established from the DEPT and/or PENDANT pulse sequences.
*Assignments were confirmed by the ^1H–^{13}C HETCOR spectrum.
†Overlapped signals.
‡Interchangeable signals.

playing signals for an ester carbonyl at δ 173.5, a methoxyl at δ 52.4, a methylene carbon at δ 124.7 and a quaternary carbon at δ 136.6. From the above information and, considering that the ^1H NMR spectrum which showed signals for four tertiary methyl groups (δ 0.95, 1.05, 1.29 and 1.53) instead of the usual five of an intact limonoid carbocyclic skeleton, it was deduced that **5** consisted of a ring B-opened limonoid.

The presence of the same C-17 γ-hydroxybutenolide side chain in **5** as that found in **1** and **4** was established on the basis of characteristic ^1H and ^{13}C NMR resonances (Tables 1, 2 and 4). One of the four protons observed in the multiplet at δ 5.39–5.45 could be assigned to H-17. A correlation noted between the broad singlet at δ 7.28 (H-22) and the above multiplet in the ^1H–^1H COSY spectrum, as well as a ^1H–^{13}C connectivity between the latter and the carbon signal at δ 74.5 (C-17) confirmed this assignment. In the ^1H NMR spectrum, a signal at δ 4.01 (1H) was attributed to H-15 in a ring-D-14β,15β-epoxy-δ-lactone moiety, corroborated by a ^1H–^{13}C cross-peak correlation with the carbon resonance at δ 54.9 (C-15). In the HMBC spectrum (Table 3), a two-bond proton-carbon correlation of H-15 to δ 165.7 and a three-bond correlation of H-17 to δ 66.3 allowed the assignments of C-16 and C-14, respectively. As in compounds **1–4**, a ring A α,β-unsaturated-ε-lactone moiety was also seen to be present in the structure of **5** (Tables 2 and 4).

The two H-6 protons were characterized by the multiplet at δ 2.15-2.23, which in turn was shown to be coupled in the ^1H–^1H COSY spectrum to the one-proton double-doublet at δ 3.56, ascribed to H-5. It showed a cross-peak correlation in the ^1H–^{13}C HETCOR spectrum with the carbon signal at δ 49.5 (C-5), whereas the H-6 protons showed connectivity to the carbon at δ 34.7 (C-6). A three-bond correlation observed in the HMBC spectrum between H-1 (δ 6.71) and C-5 (δ 49.5) confirmed the former assignment.

The presence of an acetate group in **5** was indicated by the three-proton singlet at δ 2.11 and two carbon resonances at δ 20.7 and 170.2. The remaining proton

Table 3. ^{13}C–^{1}H long range correlations in the HMBC spectra of **1** and **5**

C	1	5
1	-	H-9
3	H-1, H-2	H-1
4	H-5	—
5	—	H-1, H-9
8	H-9	H-9
9	—	H-11
10	H-9	H-2, H-9
11	H-9	H-9, H-12$_{ax}$
12	—	H-9
13	—	H-12$_{ax}$
14	H-17	H-9, H-17, H-30
16	H-15	H-15
17	—	H-12$_{ax}$
18	H-17	H-12$_{ax}$
20	H-17	—
21	H-17	—
22	H-17	—
29	H-5	-
30	H-9	H-9

to be assigned in the multiplet at δ 5.39–5.45 was attributed to the one attached to the acetate bearing carbon. This was indicated by the presence of a cross-peak correlation in the ^{1}H–^{13}C HETCOR spectrum between the above multiplet and the signal at δ 68.7. The acetate group, in turn, could be located at C-11 or C-12. It was positioned at C-11 by the presence of a one-proton doublet at δ 2.97 (J = 6.7 Hz), which was ascribed to H-9. This was shown to be coupled to the multiplet at δ 5.39–5.45 in the ^{1}H–^{1}H COSY spectrum and displayed a ^{1}H–^{13}C connectivity with the carbon signal at δ 52.7 (C-9). Moreover, H-9 showed in the HMBC spectrum two-bond correlations with C-8 (δ 136.6), and with the carbon assigned to C-11 (δ 68.7) and three-bond connectivities with C-1 (δ 149.4), C-5 (δ 49.5), C-14 (δ 66.3), C-30 (δ 124.7) and the carbon attributed to C-12 (δ 33.4). A broad triplet at δ 2.39 (J = 13.3 Hz) and a double doublet at δ 1.38 (J = 13.8 and 4.7 Hz) were ascribed to H-12$_{ax}$ and H-12$_{eq}$, respectively. The former displayed two and three-bond correlations to C-11 (δ 68.7), C-17 (δ 74.5) and the methyl-18 (δ 14.6).

The value of 6.7 Hz for the vicinal coupling constant between H-9 and H-11 supported the β configuration of the acetoxyl substituent at C-11. This was shown to be the magnitude of the coupling constant for H-9/H-11 in B-ring opened limonoids with β-oriented substituents at C-11 [21, 22]. In α-oriented isomers, the signal for H-9 appears as a broad singlet in the ^{1}H NMR spectrum [10, 23].

The remaining quaternary carbons in the structure of **5** were assigned on the basis of the ^{1}H–^{13}C long range correlations listed in Table 3.

Compound **6** was found to be a limonoid with the same 21-hydroxy-20(22)-ene-γ-lactone moiety already described for **2** and **3** (Tables 1, 2 and 4). The remainder of the ^{1}H and ^{13}C NMR data were in complete agreement with the presence in **6** of identical constituting rings A–D to those reported for **5**. The negative ESI-mass spectra of the two isomeric limonoids **5** and **6** showed both a pseudo-molecular ion at m/z 573 $[M-H]^-$ ($C_{29}H_{34}O_{12}$ requires m/z 574).

The signals displayed in the ^{1}H NMR spectrum of compound **7** (Table 4) revealed the presence of the characteristic H-22 (br s, δ 7.27) and H-23 (br s, δ 6.14) protons of the γ-hydroxybutenolide residue in C-17, already reported for compounds **1**, **4** and **5**. Resonances due to the carbomethoxy group at δ 3.66 and the H-15 epoxy oxymethine proton at δ 3.87 were also observed.

The main difference with respect to the ^{1}H NMR spectrum of **5** was the absence of the two doublets ascribed to H-1 and H-2 of a ring A α,β-unsaturated lactone and the presence of two acetate methyl groups (δ 2.12 and 2.14), instead of one in that of **5**, together with an additional proton in the multiplet at δ 5.27–5.55, which, in compound **5**, was assigned to the superimposed H-11, H-17 and H$_2$-30 signals. From the foregoing data, it was concluded that **7** differs from **5** in that the olefinic bond at C-1/C-2 of the latter is replaced in **7** by an acetoxyl group at C-1. The additional proton in the above mentioned multiplet was therefore attributed to the one attached to the acetoxyl bearing C-1 carbon. The ^{13}C NMR spectrum of **7** (Table 2) showed a number of duplicated signals. The carbon resonances at δ 71.0/71.3, 36.5 and 171.0/171.8 were attributed to C-1, C-2 and C-3, respectively. The lack of the olefinic C-1 and C-2 carbon resonances, as those found in **5**, and the downfield shift of the C-3 ester carbonyl from **5** to **7** (Δ δ 3.3) supported the location of the acetoxyl substituent at C-1. It should be mentioned that the ^{1}H NMR spectrum of **7** also showed duplicated signals for H-15 and the tertiary methyl groups, as well as unresolved peaks in the δ 2.50–3.40 region. It was found that in prieurianin (**9**) and related compounds, the presence of multiple conformational isomers at ambient temperature, due to restricted rotation about the C-9/C-10 bond, accounts for the unresolved nature of their ^{1}H and ^{13}C NMR spectra, the resolution of which being therefore improved at higher temperatures [24]. Likewise, by recording the ^{1}H NMR spectrum of **7** at 60 C, a better resolution was achieved, which, with the aid of a ^{1}H–^{1}H COSY experiment, enabled establishment of the assignments listed in Table 4. We tentatively suggest an α-configuration for the acetoxyl group at C-1 by analogy with proposals for all known C-1 substituted limonoids and considering that an X-ray structure has confirmed this configuration in prieurianin (**9**) [24].

Compound **8** gave ^{1}H and ^{13}C NMR spectra which were extremely similar to those of **7** (Tables 2 and 4), the only difference being the absence of the signals attributed to the C-17 γ-hydroxybutenolide side chain in **7** and the presence instead of the signals relative to

Table 4. ^{1}H NMR spectral data for compounds **5**–**8** in $CDCl_3$ (200 MHz, TMS $\delta = 0$)

H	**5**	**6**	**7***	**8†**
1	6.71 *d* (12.9)	6.78 *d* (12.9)	5.53 *br d* (7.8)	5.34–5.56 *m*†
2	6.19 *d* (12.9)	6.11 *d* (12.9)	3.05 *br d* (16.5) [2A]	3.06 *dd* (16.5, 1.3) [2A]
			3.18–3.34 *m*‡ [2B]	3.25–3.47 *m*§ [2B]
5	3.56 *br dd* (6.4; 3.2)	3.66–3.72 *m*§	3.18–3.34 *m*‡	3.25–3.47 *m*§
6	2.15–2.23 *m*	2.10–2.33 *m*	2.03–2.19 *m*§, ¶ [6A]	2.03–2.17 *m* [6A]
	[H_2–6]	[H_2–6]	2.64–2.74 *m* [6B]	2.66 *dd* (18.3; 3.1) [6B]
9	2.97 *d* (6.7)	2.99 *d* (6.6)	3.18–3.34 *m*‡	3.19 *d* (6.8)
11	5.39–5.45 *m*‡	5.38–5.56 *m*‡	5.30 *dd* (6.0, 4.3)	5.34–5.56 *m*‡
12	2.39 *br t* (13.3) [12_{ax}]	2.43 *br t* (12.8) [12_{ax}]	2.03–2.19 *m*§, ¶ [12_{ax}]	1.94 *br t* (12.2) [12_{ax}]
	1.38 *dd* (13.8, 4.7) [12_{eq}]	1.65 *dd* (12.8, 5.2) [12_{eq}]	1.33–1.34 *m* [12_{eq}]	1.57–1.78 *m* [12_{eq}]
15	4.01 *s*	4.03 *s*	3.87 *br s*	3.91 *s*
17	5.39–5.45 *m*‡	5.38–5.56 *m*‡	5.44 *br s*	5.34–5.56 *m*‡
18	1.05 *s*	1.06 *s*	1.03–1.06 *br s***	1.12 *s*
19	0.95 *s*	0.97 *s*	1.17–1.22 *br s***	1.12 *s*
21	—	6.09 *brs*	—	6.01 *br s*
22	7.28 *br s*	6.27 *br s*	7.27 *br s*	6.23 *br s*
23	6.26 *br s*	—	6.14 *br s*	—
28	1.29 *s*	1.33 *s*	1.42 *br s*	1.44 *s*
29	1.53 *s*	1.57 *s*	1.57 *s*	1.57 *s*
30	5.39–5.45 *m*‡	5.38–5.56 *m*‡	5.38 *br s*	5.34–5.56 *m*‡
OAc	2.11 *s*	2.17 *s*	2.12 *s* 2.14 *s*	2.11 *s* 2.18 *s*
OMe	3.69 *s*	3.72 *s*	3.66 *s*	3.68 *s*

Coupling constants (*J* in Hz) are given in parentheses.
Assignments were confirmed by the ^{1}H–^{1}H COSY spectra.
*Recorded at 60°.
†Recorded at 50°.
‡, §Overlapped signals.
The signal for H-5 is partly obscured by that for the OMe group.
¶The signal for H-12_{ax} and H-6A is partly obscured by that for the two OAc groups.
**Duplicated signals.

the isomer already reported for **2**, **3** and **6**. In the negative ESI-mass spectra of **7** and **8**, a pseudo-molecular ion at *m/z* 633 $[M-H]^-$ was observed in both cases ($C_{31}H_{38}O_{14}$ requires *m/z* 634).

Finally, it should be mentioned that the skeletal type displayed by limonoids **5**–**8** is noteworthy for its chemosystematic relevance. Very few limonoids with seco-A, B and D carbocyclic rings have been reported in the literature. In the Meliaceae, they have only been described in species of the subfamily Swietenioideae, e.g. *Khaya ivorensis* [25] and *Soymida febrifuga* [8]. From *Neochamaelea pulverulenta* (Cneoraceae), was obtained cneorin R (**10**) [26], a limonoid structurally similar to **5** and **6**. This is, therefore, the first report of the occurrence of this unusual skeletal type in the meliaceous subfamily Melioideae, to which the genus *Trichilia* belongs.

EXPERIMENTAL

General. Mps: uncorr. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200 MHz) and DPX-300 (300 MHz) spectrometers, with TMS as int. standard. HMBC experiments were performed at 400 MHz on a Varian Unity-400 instrument. Standard pulse sequences were used for homo- and heteronuclear correlation experiments. ESI-MS data were obtained using a Micromass Platform II single quadrupole mass spectrometer. The samples were introduced using a loop injection method and ionized by electrospray in both positive and negative ion modes. Silica gel 60 was used for chromatography: 70–230 mesh for CC and 230–400 mesh for flash CC. Sephadex LH-20 was used for molecular exclusion chromatography. Semiprep. HPLC was performed using RP 18 (25ϕ × 250mm, 7μm particle size) and RP 8 (22ϕ × 250mm, 10 μm particle size,) columns, with a flow rate of 8 ml min^{-1} and monitoring at 250 nm.

Plant Material. Trichilia elegans ssp. *elegans* A. Juss. seeds were collected in Corumbá, Mato Grosso do Sul, Brazil, in February, 1990. The plant was identified by Prof. Humberto Barreiros, of the Jardim Botânico do Rio de Janeiro, RJ, where voucher specimens are deposited.

Extraction and isolation of compounds. As reported previously [1], the ethanolic extract of *T. elegans* ssp. *elegans* seeds (225 g) was partitioned between petrol and EtOH/H_2O (1:1). The hydroalcoholic soln. was then partitioned with CH_2Cl_2. The CH_2Cl_2 phase was subjected to CC on silica gel, eluted with increasing amounts of EtOAc in hexane and 5% MeOH–EtOAc. The residue of the latter eluate gave, after treatment with acetone, 3-*O*-β-D-glucopyranosyl-sitosterol (10 mg, 0.004% yield), mp 300° (dec.). Spectral data in

agreement with lit. values (^{13}C NMR, 50 MHz, $CDCl_3$/py d_5) [27, 28].

One of the frs eluted with EtOAc was sepd by CC over Sephadex LH-20, using hexane–CH_2Cl_2 (1:4) followed by CH_2Cl_2–$(Me_2)CO$ (3:2) as solvent. This step afforded six main frs (A→F). Fr. A consisted of **6** [30 mg, 0.013% yield].

Elegantin B (**6**). Mp 157–159°. $[\alpha]_D^{24}$ +41.2° ($CHCl_3$; *c* 0.422). IR ν_{max}^{KBr} cm^{-1}: 3439, 1745, 1690, 1263, 1127, 1039. ESI-MS (negative) *m/z* (rel. int.): 573 $[M-H]^-$ (100). ^1H and ^{13}C NMR (Tables 4 and 2, respectively).

Fr. B, eluted with hexane–CH_2Cl_2 (1:4) and containing a mixt. of **5**, **6**, **7** and **8** was again sepd by flash CC [CH_2Cl_2-isopropanol (18.0:0.5), followed by CH_2Cl_2-isopropanol (10.0:0.5) and EtOAc as eluents], collecting 10ml frs (frs 1–59) and 200ml frs (frs 60–61). Frs 27–41 provided **6** (26mg–0.012% yield). Purification of frs 52–55 by HPLC [RP 18, 7μm, ACN–MeOH–H_2O (11.5:38.5:50.0)] afforded **7** (12 mg–0.005% yield). Compd. **8** [10 mg, 0.004% yield] was obtained after HPLC [RP 8, ACN–MeOH–H_2O (22:26:52)] of frs 56–59 and **5** (9 mg, 0.004% yield), after HPLC [RP 8, ACN–MeOH–H_2O (22:26:52)] of fr. 60.

Elegantin A (**5**). Mp 165–167°. $[\alpha]_D^{24}$ +58.5° ($CHCl_3$; *c* 0.41). IR ν_{max}^{KBr} cm^{-1}: 3452, 1746, 1690, 1264, 1231, 1127, 1039. ESI-MS (negative) *m/z* (rel. int.): 573 $[M-H]^-$ (100). ^1H and ^{13}C NMR (Tables 4 and 2, respectively).

1,2-*Dihydro*-1α-*acetoxyelegantin A* (**7**). Mp 189–191°. $[\alpha]_D^{24}$ −9.7° ($CHCl_3$; *c* 0.6). IR ν_{max}^{KBr} cm^{-1}: 3445, 1740, 1254, 1194, 1123, 1026. ESI-MS (negative) *m/z* (rel. int.): 633 $[M-H]^-$ (100). ^1H and ^{13}C NMR (Tables 4 and 2, respectively).

1,2-*Dihydro*-1α-*acetoxyelegantin B* (**8**). Mp 175–178°. $[\alpha]_D^{24}$ −11.7° ($CHCl_3$; *c* 0.35). IR ν_{max}^{KBr} cm^{-1}: 3444, 1740, 1254, 1196, 1123, 1040, 1028. ESI-MS (negative) *m/z* (rel. int.): 633 $[M-H]^-$ (100). ^1H and ^{13}C NMR (Tables 4 and 2, respectively).

The fourth fr. from the Sephadex LH-20 column (fr. D), eluted with CH_2Cl_2–Me_2CO (3:2), contained a mixt. of **1**, **2**, **5** and **8**. Additional sepn was accomplished by flash CC, eluted with CH_2Cl_2–EtOAc–AcOH (9.0:2.0:0.1) with an increasing proportion of EtOAc, collecting 5 ml frs (frs 1–36), 2ml frs (frs 37–96) and 11 ml frs (frs 97–116). Further purification of frs 38–59 by HPLC [RP 8, ACN–MeOH–H_2O (22:30:48)] yielded **1** (8 mg, 0.004% yield) and **2** (12 mg, 0.005% yield). Frs 100–107 gave rise to **5** (30mg, 0.013% yield) and **8** (11mg, 0.005% yield), after purification by HPLC [RP 18, ACN–MeOH–H_2O (14:46:40)].

7-*Deoxo*-7α-*acetoxykihadanin B* (**1**). Mp 187–190°. $[\alpha]_D^{24}$ +48.7° ($CHCl_3$, *c* 0.575). IR ν_{max}^{KBr} cm^{-1}: 3442, 1747, 1697, 1275, 1260, 1235, 1130, 1024. ESI-MS (negative) *m/z* (rel. int.): 529 $[M-H]^-$ (100). ^1H and ^{13}C NMR (Tables 1 and 2, respectively).

7-*Deoxo*-7 α-*acetoxykihadanin A* (**2**). Mp 215–217°. $[\alpha]_D^{24}$ +37.6° (acetone; *c* 0.34). IR ν_{max}^{KBr} cm^{-1}: 3453, 1748, 1696, 1276, 1255, 1235, 1131, 1034. ESI-MS (negative) *m/z* (rel. int.): 529 $[M-H]^-$ (100). ^1H and ^{13}C NMR (Tables 1 and 2, respectively).

Fr. E from the Sephadex LH-20 column, also eluted with CH_2Cl_2–Me_2CO (3:2), afforded, after purification by HPLC [RP 8, ACN-MeOH–H_2O (21:29:50)], **1** (14mg, 0.006% yield), **2** (11mg, 0.005% yield), kihadanin A (**3**, 10 mg, 0.004% yield, mp 233–236° (dec.) [lit. [3] mp 232° (dec.), [4] mp 192–196° (dec.)]), and kihadanin B (**4**, 6mg, 0.003% yield, mp 255–258° (dec.) [lit. [3] mp 262–263° (dec.), [4] mp 260–263°C (dec.)]).

Kihadanin A (**3**). $[\alpha]_D^{24}$ −34.2° (MeOH; *c* 0.24). IR ν_{max}^{KBr} cm^{-1}: 3433, 1765, 1701, 1283, 1121, 1045. ESI-MS (negative) *m/z* (rel. int.): 485 $[M-H]^-$ (80). ^1H and ^{13}C NMR (Tables 1 and 2, respectively).

Kihadanin B (**4**). $[\alpha]_D^{24}$ −15.8° (acetone; *c* 0.1) [lit. [3] −7.4° (acetone)]. IR ν_{max}^{KBr} cm^{-1}: 3438, 1752, 1702, 1282, 1119, 1026. ESI-MS (negative) *m/z* (rel. int.): 485 $[M-H]^-$ (100). ^1H and ^{13}C NMR (Tables 1 and 2, respectively).

Acknowledgements—Thanks are due to CPq-PROPP/UFMS, CECITEC-MS and FAPESP for financial support and to CAPES-PICDT and CNPq for the award of scholarships. The authors are grateful to Mrs Vali J. Pott of the Centro de Pesquisa Agropecuária do Pantanal, EMBRAPA, MS, Brazil and to Prof. Humberto Barreiros of the Jardim Botânico do Rio de Janeiro, RJ, Brazil, for kindly collecting and identifying, respectively, the plant material. The authors also wish to express their sincere thanks to Dr Leslie Gunatilaka, of the Virginia Polytechnic Institute and State University, U.S.A., for the acquisition of the HMBC spectra and to Mr Mark Bayliss (Micromass UK Limited), for the ESI-MS spectra.

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