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HUMIRIANTHENOLIDES, NEW DEGRADED DITERPENOIDS FROM *HUMIRIANTHERA RUPESTRIS**

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Key Word Index—*Humirianthera rupestris*; Icacinaceae; degraded diterpenoids; humirianthenolides.

Abstract—The tuber of *Humirianthera rupestris* (Icacinaceae) contains the degraded diterpenoids 3β,20-epoxy-3α-hydroxy-14-oxo-9β-podocarpan-19,6β-olide (humirianthenolide A), 3β,20-epoxy-3α,14α-dihydroxy-9β-podocarpan-19,6β-olide (humirianthenolide B), 3β,20; 16,14-diepoxy-3α-hydroxy-17-nor-15-oxo-9β-abiet-13-en-19,6β-olide (humirianthenolide C), 3β,20-epoxy-3α,14-dihydroxy-13-oxo-9β-podocarp-8(14)-en-19,6β-olide (humirianthenolide D), 3β,20-epoxy-3α-hidroxy-14-oxo-8α,9β-podocarpan-19,6β-olide (humirianthenolide E) and 3β,20-epoxy-3α,14β-dihydroxy-8α,9β-podocarpan-19,6β-olide (humirianthenolide F). ^{1}H NMR and ^{13}C NMR spectroscopy were effective for the determination of the humirianthenolide structures.

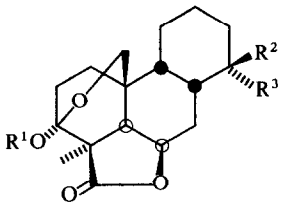
INTRODUCTION

Humirianthera rupestris (Icacinaceae) is a shrub whose tuber, weighing about 40 kg, is eaten like flour after several water washings [1]. A chemical investigation of a tuber collected in Manaus (Amazon) Brazil revealed the presence of six new degraded diterpenoids.

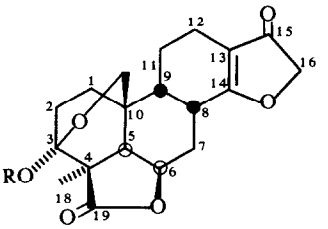
RESULTS

The benzene and ethanol extracts from the tuber of *Humirianthera rupestris* contained sitosterol and six crystalline substances, for which the names humirianthenolide A (**1a**), B (**1b**), C (**2a**), D (**3**), E (**4a**) and F (**4b**) are proposed.

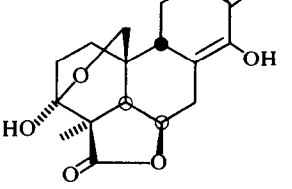
Humirianthenolide A (**1a**), $C_{17}H_{22}O_5$, possessed a γ-lactone (IR: 1766 cm^{-1} and ^{13}C NMR: δ 179.9), hemiacetal (^{13}C NMR: δ 96.8), saturated ketone (IR: 1710 cm^{-1} and ^{13}C NMR: δ 212.4) and C—Me (^{1}H NMR *s*, 3H, δ 1.37) functions, and contained, therefore, five rings. Catalytic dehydrogenation yielded a



1a R^1 = H, $R^2 + R^3$ = O
1b $R^1 = R^2$ = H, R^3 = OH
1c $R^1 = R^2$ = H, R^3 = OAc
1d R^1 = Me, R^2 = H, R^3 = OH
1e R^1 = Me, R^2 = H, R^3 = OAc



2a R = H
2b R = Ac



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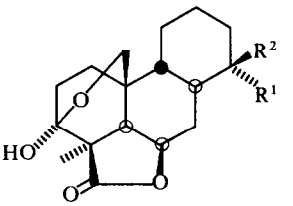


4a $R^1 + R^2$ = O
4b R^1 = H, R^2 = OH

*Based on part of the doctorate thesis presented by M. G. B. Zoghbi to Universidade de São Paulo (1979). Sponsored by Fundação de Amparo à Pesquisa do Estado de São Paulo.

phenanthrene derivative (as determined by its UV spectrum), suggesting that the natural product was a degraded diterpenoid. The presence of only one methyl, as well as the hydrogen bond between the hemiacetal hydroxyl and the γ-lactone carbonyl groups indicated an A/B ring pattern as shown in structure **1**. This assumption was confirmed by the strong similarity between the ^1H and ^{13}C NMR spectral data of **1a** and those of momilactone B [2] and annonalide [3], both of which share these same features.

The ^1H NMR spectrum at 270 MHz, with couplings unambiguously established by comprehensive double-irradiation experiments, was instrumental in the determination of the stereochemical features of the humirianthenolides (Tables 1 and 2). Thus, for **1a**, the two protons on C-20 showed $^4J_{H,H}$ values of relatively large magnitudes implying *W*-type arrangements. The highest field of the two signals was split by H-5 (1.5 Hz), indicating the *trans* junction between rings A and B and that the proton giving rise to this signal was *cisoid* to C-1. The

Table 1. ^1H NMR chemical shifts of humirianthenolides and their derivatives*

	1a†	1b†	1c†	1d†	1e†	2a‡	2b‡	3‡	4a†	4b†
2β		2.33				2.19	2.41			
5	2.13	2.04				2.12		2.23	2.22	2.18
6	4.80	4.79	4.80	4.75	4.70	4.70	4.66	4.78	4.84	4.90
7α								3.56	2.67	
7β	2.26					2.31	2.64			
8	2.68	2.22				2.73	2.76			
12β							3.11			
13α	2.49									
13β	2.30								2.42	
14		3.78								3.93
16						4.59	4.48			
18	1.37	1.35	1.35	1.31	1.30	1.23	1.42	1.24	1.39	1.36
20′	3.58	3.57	3.55	3.55	3.50	3.47	3.76	3.72	3.72	3.75
20	4.27	4.41	4.40	4.45	4.40	4.16	4.44	4.13	3.92	3.95
MeCO			2.00		2.00		2.13			
OMe				3.42	3.40					

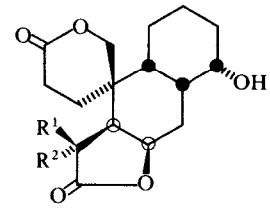
*The spectra of compound **1c**, **1d** and **1e** were determined at 60 MHz, the remainder were determined at 270 MHz.
†$CDCl_3$; TMS internal standard.
‡DMSO; TMS internal standard.

Table 2. ^1H NMR coupling constants ($J_{H,H}$ Hz) of humirianthenolides and their derivatives

	1a	1b	1c	1d	1e	2a	2b	3	4a	4b
1α–20	3.5	3.5	3.0	3.0	3.0	3.0	3.5	3.0	3.5	3.5
1β–2β		5.0				5.0	6.0			
2α–2β		16.0				16.0	17.0			
5–6	5.5	5.5	5.0	5.0	5.0	5.0	5.0	8.0	7.5	7.5
5–20′	1.5	1.5	2.0	2.0	2.0		1.5		2.0	2.0
6–7α	5.5	5.5	5.0	5.0	5.0	5.0	5.0	8.0	9.5	7.5
6–7β	1.0		1.0	1.0	2.0		1.0	8.0	9.5	9.5
7α–7β	15.5					16.0	16.0	12.0	14.0	
7α–8	12.0	13.0				12.0	13.0			
7β–8	5.5	4.5				5.0	5.0		2.0	
8–9	5.5	4.5				5.0	5.0			
8–14		4.5								
11α–12β							11.5			
11β–12β							2.0			
12α–12β							13.5			
12α–13α	6.5									
12α–13β	3.0									
12β–13α	13.0								1.5	
12β–13β	3.0								3.5	
13α–13β	15.0								13.5	
13α–14		11.5								
13β–14		4.5								
20–20′	9.5	9.5	10.0	10.0	10.0	9.0	9.5	9.5	9.5	9.5

other proton of the oxymethylene was located over ring B and showed an even larger $^4J_{H,H}$ coupling (3.5 Hz), presumably with H-1α. H-6 appeared as a broad triplet, with almost no coupling with H-7β. This observation is best explained by a chair-ring B with the lactonic oxygen substituent in an axial position. The saturated ketone function must be located at C-14, in view of the low-field absorption of H-8. The coupling pattern of this hydrogen showed only one proton in an *anti* relationship and this must be H-7α (axial). Therefore, the B/C ring junction was *cis*, with both H-8 and H-9 β-orientated. In the ^{13}C NMR spectrum (Table 3) this arrangement was reflected by the high-field position of C-11, which was axial to ring B in addition to the *gauche* relationship with C-1 (three γ-effects). Thus this compound has structure **1a**.

Humirianthenolide B (**1b**) had two more mass units than **1a** and was converted to the latter by Jones oxidation. The stereochemistry of the alcohol function was defined by the ^{1}H and ^{13}C NMR spectral data. Thus, the carbinolic proton signal had splittings consistent with an equatorial hydroxyl group (Table 2). This was confirmed by the invariance of the C-12 absorption and the shelding of the C-7 by the *gauche* hydroxyl group. The IR spectral data showed that the lactone carbonyl of **1b** had both intra- and inter-molecular hydrogen bonds (with 3-OH and 14-OH, respectively, giving a band at 1760 cm^{-1} that was eliminated by conversion to derivative **1e**, which had no free hydroxyl groups). The β-arrangement of the γ-lactone and hemiacetal functions was also indicated by an alkaline hydrolysis of **1b**, which resulted in a retro-aldol reaction, in agreement with previous observations [2, 3]. In our case, a 2:1 mixture of the isomers **5a** and **5b**, respectively, was obtained. The characteristic feature of the ^{1}H NMR spectrum of these compounds was the splitting of the methyl signal into a



5a R^1 = H, R^2 = Me
5b R^1 = Me, R^2 = H

doublet, and therefore indicating the presence of a 4-H. In the major compound, the signal of the latter proton was not split further than a quartet, indicating an approximately 90° dihedral angle with H-5. In the minor product, such a coupling existed (7.5 Hz). This is consistent with the configurations shown in formula **5**.

Humirianthenolide C (**2a**), with the same ring A and B pattern as compound **1**, had two additional carbon atoms. IR (1700, 1640 cm^{-1}), UV (λ_{max}^{MeOH} 267 nm, ε 20 000), ^{13}C NMR (three singlets at δ 200.6, 191.4 and 111.2) and ^{1}H NMR (δ 3.78, *s*, 2 H) spectra define a dihydrofuran-4-one moiety. The allylic nature of H-8 (δ 2.73) and the high-

Table 3. ^{13}C NMR chemical shifts of humirianthenolides A (**1a**), B (**1b**), C (**2a**), D (**3**) and acetyl humirianthenolide B (**1c**)*

	1a†,‡	**1b**†	**1b**§	**1c**§	**2a**§	**3**§
1	30.3	29.6	30.3	29.8	30.0	29.1
2	27.7	27.0	28.4	28.8	28.8	27.8
3	96.8	96.3	96.4	96.1	96.2	96.4
4	51.8	51.3	51.7	51.3	51.3	48.8
5	44.9	45.2	45.4	44.5	43.7	45.4
6	74.4	75.9	75.1	74.2	73.1	73.9
7	25.0	19.0	19.4	18.7	26.0	25.2
8	44.2	27.3	29.3	24.5	29.0	129.0
9	40.7	38.7	39.4	38.7	36.7	37.1
10	32.1	32.5	32.8	32.2	31.3	33.5
11	19.7	19.8	20.5	20.4	16.4	26.6
12	24.6	23.2	23.9	23.1	17.7	36.9
13	36.9	32.6	33.2	29.8	111.2	192.8
14	212.4	71.2	70.9	74.2	191.4	144.9
15	—	—	—	—	200.6	—
16	—	—	—	—	75.0	—
18	17.3	17.0	17.2	16.7	16.8	19.3
19	179.9	179.8	178.4	178.0	177.9	178.2
20	72.8	72.7	72.8	72.2	72.3	73.5
MeCO	—	—	—	20.9	—	—
MeCO	—	—	—	169.7	—	—

*Residual couplings in the single frequency off-resonance decoupled spectra were used in some cases to help assignment. Spectra for **1a**, **2a** and **3** were measured at 22.6 MHz, for **1b** at 25.2 MHz and for **1c** at 20 MHz.

†$CDCl_3$; TMS internal standard.

‡A few drops of MeOH were added to improve solubility.

§DMSO-d_6; the solvent peak was taken as δ 39.5.

field position of C-12 (17.7), shielded by a γ-effect on the carbonyl oxygen, located the side-chain as shown in **2**.

Humirianthenolide D (**3**) had an enolized α-diketone system, as shown by IR (1670 and 1650 cm^{-1}), UV (λ_{max}^{MeOH} 272 nm, ε 10 500) and ^{13}C NMR (three singlets at δ 192.8, 144.9 and 129.0). C-8 was part of this system, since one of the hydrogens on C-7 was strongly deshielded by the π-system and its signal showed only coupling to H-6, in addition to the geminal splitting. The signals in the ^1H and ^{13}C NMR spectra due to the A- and B-ring nuclei were slightly changed in **3** relative to compounds **1** and **2**. A very diagnostic feature was the shape of the H-6 signal, a quartet with three couplings (to H-5, H-7α and H-7β) of 8 Hz. The sp^2 nature of C-8, a bridgehead carbon, forces ring B into a boat conformation, with different dihedral angles between its peripheral protons. H-9 remains β-orientated, since the alternative configuration would entail more drastic changes, e.g. a γ-effect between C-20 and C-11. Instead, C-11 is deshielded by the loss of a *gauche* interaction with C-7, now above the plane of the boat-shaped ring B.

Humiroanthenolide E (**4a**) was an isomer of **1a** and, indeed, its IR spectrum showed the presence of a saturated ketone (1700 cm^{-1}). However, it differed from **1a** in the geometry of rings B and C, H-6 being split by large coupling constants by all its three neighbours. This pattern was strongly reminiscent of the one described for **3**, suggesting a *trans* junction between rings B and C, and a boat-like ring B, similar to **3** where C-8 was sp^2-hybridized. One of the two protons on C-7 absorbed at low-field (δ 2.67), indicating that the ketone was probably located at C-14. The small coupling between this proton and H-8 was in agreement with a *quasi*-equatorial and axial positioning, respectively, for these two hydrogen atoms.

Humirianthenolide F (**4b**) had the same molecular weight as **1b** and its molecular ion in the MS lost two molecules of water, as was the case with **1b** (but not with **1a** or **4a**, which lost only one water molecule), indicating the presence of an hydroxyl group other than the one located at C-3. The *trans* nature of the B/C ring junction was determined by the shape of the ^1H NMR signal of H-6 which was very similar to that in the spectrum of **4a**. The proton spectrum showed also a carbinolic hydrogen as a multiplet with $W_{1/2} = 7$ Hz, which was only consistent with an axial secondary alcohol. Biogenetic considerations would suggest that the hydroxyl is located at C-14.

The configurations shown in formulae **1–4** are meant to be relative. The fact that they also may represent absolute configurations follows from the similarity of the ORD curve of **1b** (see Experimental) and the ORD curves of momilactones A and B [3].

DISCUSSION

Only four diterpenoids with the phenanthrene skeleton feature a *trans–syn* stereochemistry, i.e. with H-9 and C-20 in a *cis* relationship. These are annonalide [3] and momilactones A, B [2] and C [4], all of which are Δ^7 compounds. This work, therefore, constitutes the first example of diterpenoids with *trans–syn–cis* and *trans–syn–trans* arrangements. While the former stereochemistry predominates in this species, an interconversion of the two forms by the enolization of a 14-carbonyl function, as shown in compound **3**, could be visualized. The apparently lower stability of the B/C *trans* ring junction may be a result of the boat-like forms of ring B that must be assumed in these compounds.

The humirianthenolides may derive from successive oxidative degradations of a precursor with an abietane skeleton. This sequence could start with the removal of one of the methyls of the isopropyl side-chain, leaving a carbonyl group in its place, as in compound **2a**. Since this product contains a masked β-diketone functionality, a retro-aldol reaction would lead to compounds oxidized in ring C only at C-14, such as **1** and **5**.

EXPERIMENTAL

Extraction and isolation. A tuber of *Humirianthera rupestris* Ducle (40 kg) collected in Manaus (Amazon) and classified by Dr. W. Rodrigues (Herbaria INPA, Manaus: 46811) was oven dried at 60°. The ground material (2.4 kg) was extracted with C_6H_6 and EtOH successively. The C_6H_6 extract (47 g) was directly chromatographed on Si gel using a C_6H_6–MeOH gradient. Elution with C_6H_6–MeOH (99:1) gave sitosterol (875 mg); C_6H_6 MeOH (98:2) gave **1a** (47 mg), **1b** (2.6 g), **2a** (1.3 g), **3** (177 mg), **4a** (25 mg) and **4b** (17 mg) in different fractions. Compounds **1a**, **1b**, **2a** and **3** were purified by successive crystallizations; **4a** and **4b** by prep. TLC ($CHCl_3$ MeOH, 95:5). The EtOH extract (65 g) was worked up in the same way to give **1a** (80 mg), **1b** (150 mg), **2a** (500 mg) and **3** (160 mg).

Humirianthenolide A (**1a**). Mp 209–211° ($CHCl_3$–EtOH) (MW: Found 306.1432; $C_{17}H_{22}O_5$ requires: 306.1467). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (infl.), 3530, 1766, 1710. MS *m/z* (rel. int.): 306 (M^+, 62), 288 (33), 247 (20), 242 (21), 215 (20), 209 (24), 196 (72), 195 (28), 191 (33), 178 (28), 163 (21), 161 (23), 159 (20), 149 (21), 147 (23), 145 (23), 137 (100), 135 (20), 131 (26), 123 (28), 121 (40), 119 (20), 117 (21), 111 (27), 107 (21), 105 (34). For ^1H NMR and ^{13}C NMR see Tables 1–3.

Humirianthenolide B (**1b**). Mp 187–189° (C_6H_6) (MW: Found: 308.1635; $C_{17}H_{24}O_5$ requires: 308.1624). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3604, 3526, 1760. MS *m/z* (rel. int.): 308 (M^+, 72), 290 (58), 272 (25), 244 (20), 217 (39), 199 (24), 193 (75), 192 (20), 191 (21), 180 (100), 175 (40), 173 (29), 162 (25), 149 (20), 147 (30), 145 (32), 133 (42), 131 (26), 121 (34), 119 (24), 111 (36), 107 (30), 105 (40). For ^1H NMR and ^{13}C NMR see Tables 1–3. $[\alpha]_D^{20}$ −200° (*c* 0.5, $CHCl_3$). ORD (*c* 1.7 mM, $CHCl_3$) $[\phi]_{238}$ 0, $[\phi]_{240}$ −2400, $[\phi]_{245}$ −1800, $[\phi]_{250}$ −1200, $[\phi]_{260}$ −600, $[\phi]_{270}$ −540, $[\phi]_{280}$ −450, $[\phi]_{290}$ −660, $[\phi]_{300}$ −900, $[\phi]_{310}$ −1080, $[\phi]_{320}$ −1200, $[\phi]_{330}$ −1200, $[\phi]_{340}$ −1140, $[\phi]_{350}$ −1080. ORD (*c* 5.1 mM, MeOH): $[\phi]_{230}$ +700, $[\phi]_{238}$ 0, $[\phi]_{240}$ +100, $[\phi]_{250}$ +900, $[\phi]_{260}$ +1250, $[\phi]_{270}$ +1150, $[\phi]_{280}$ +1050, $[\phi]_{290}$ +900, $[\phi]_{300}$ +740, $[\phi]_{310}$ +640, $[\phi]_{320}$ +620, $[\phi]_{350}$ +600.

Acetylation of **1b**. A mixture of **1b** (200 mg), Ac_2O (2 ml) and pyridine (2 ml) was left at room temp. for 72 hr. Treatment in the usual manner afforded a solid (219 mg) which was eluted through a Si gel column ($CHCl_3$–MeOH, 95:5) to give **1c** (134 mg), mp 202–204° (C_6H_6). (MW: Found: 350.1694; $C_{19}H_{26}O_6$ requires: 350.1729). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1730; ν_{max}^{KBr} cm^{-1}: 3420, 1766, 1716. MS *m/z* (rel. int.): 350 (M^+, 15), 235 (34), 234 (67), 219 (100), 217 (17), 195 (15), 193 (17), 180 (24), 133 (18). For ^1H NMR and ^{13}C NMR see Tables 1–3.

Jones oxidation of **1b**. The Jones reagent was added to an ice-cooled soln of **1b** (53 mg) in Me_2CO. The usual work-up afforded a solid (56 mg) which was eluted through a Si gel column with $CHCl_3$–EtOH (8:2) to give **1a** (32 mg).

Methylation of **1b**. Compound **1b** (102 mg) was dissolved in MeOH (5 ml) and TsOH (5 mg) was added. This mixture was maintained in an 80° oil bath for 8 hr with agitation. The usual work-up afforded a solid (100 mg) which was purified by prep. TLC, $CHCl_3$–MeOH (95:5) giving **1d** (39 mg), mp 222–4° (EtOAc) (MW: Found: 322.1857; $C_{18}H_{26}O_5$ requires 322.1780).

IR ν_{max}^{KBr} cm^{-1}: 3500, 1760. MS *m/z* (rel. int.): 322 (M^+, 100), 304 (17), 290 (29), 272 (23), 249 (28), 231 (22), 217 (29), 207 (26), 199 (24), 194 (48), 193 (23), 175 (46), 162 (36), 161 (24), 147 (50), 145 (51), 137 (22), 135 (25), 134 (28), 133 (66), 131 (36), 123 (23), 121 (48), 120 (24), 119 (37), 117 (23), 111 (32), 109 (24), 107 (36), 105 (52). For ^{1}H NMR see Tables 1 and 2.

Acetylation of **1d**. A mixture of **1d** (28 mg), Ac_2O (1 ml) and pyridine (1 ml) was left at room temp. for 72 hr. Treatment in the usual manner afforded a solid (34 mg). Recrystallization from MeOH yielded **1e** (20 mg), mp 183–185° (MW: Found: 364.1910; $C_{20}H_{28}O_6$ requires: 364.1886). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1774, 1730; ν_{max}^{KBr} cm^{-1}: 3450, 1769, 1734. MS *m/z* (rel. int.): 364 (M^+, 17), 272 (17), 207 (25), 194 (20), 175 (20), 147 (23), 145 (25), 131 (17), 121 (21), 120 (17), 119 (17), 105 (22). For ^{1}H NMR see Tables 1 and 2.

Hydrolysis of **1b**. Compound **1b** (216 mg) was stirred in 1 M NaOH (6 ml) under N_2 at room temp. for 72 hr. After acidification and extraction with $CHCl_3$ a mixture of the isomers **5a** and **5b** (188 mg) was obtained. IR ν_{max}^{KBr} cm^{-1}: 3500, 1770, 1718. ^{1}H NMR of **5a** ($CDCl_3$, 270 MHz): δ 4.84 (*t*, J = 5 Hz, H-6), 4.43 (*d*, J = 12 Hz, H-20, 4.14 (*d*, J = 12 Hz, H-20), 3.83 (*dt*, J = 11.5 and 4 Hz, H-14), 2.71 (*q*, J = 7.5 Hz, H-4), 1.97 (*d*, J = 4.5 Hz, H-5), 1.34 (*d*, J = 7.5 Hz, Me).

Dehydrogenation of **1b**. Compound **1b** (42 mg) was heated in a sealed tube at 300° with Pd/C 10% (85 mg) for 4 hr. The mixture was washed with EtOAc and filtered through celite. The product (3.8 mg) was purified by prep. TLC (C_6H_6): IR λ_{max}^{MeOH} (3.8 × 10^{-1} g/l.) cm^{-1}: 349, 341, 332, 323, 316; (7.8 × 10^{-3} g/l.): 298, 286, 276, 255, 247, 231, 225, 211.

Humirianthenolide C (**2a**). Mp 220° (EtOH–Me_2CO) (MW: Found: 346.1416; $C_{19}H_{22}O_6$ requires: 346.1416). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (infl.), 3524, 1768, 1698, 1630. MS *m/z* (rel. int.): 346 (M^+, 74), 273 (10), 250 (16), 249 (100), 231 (32), 177 (14), 137 (14), 136 (20), 123 (46). For ^{1}H NMR and ^{13}C NMR see Tables 1–3. ORD (*c* 0.42 mM, MeOH) $[\phi]_{220}$ +17 500, $[\phi]_{233}$ +12 500, $[\phi]_{250}$ +14 000, $[\phi]_{260}$ +2500, $[\phi]_{265}$ +11 500, $[\phi]_{270}$ 0, $[\phi]_{272}$ −7000, $[\phi]_{275}$ −3500, $[\phi]_{278}$ +1800, $[\phi]_{280}$ −5300, $[\phi]_{284}$ −7000, $[\phi]_{300}$ −4000, $[\phi]_{310}$ −2000, $[\phi]_{318}$ 0, $[\phi]_{330}$ +500, $[\phi]_{340}$ +100, $[\phi]_{350}$ +100.

Acetylation of **2a**. A mixture of **2a** (300 mg), Ac_2O (2, 5 ml) and pyridine (2, 5 ml) was refluxed for 2 hr. Treatment in the usual manner gave a residue (347 mg) which was eluted through a Si gel column. The crystalline fraction (C_6H_6–$CHCl_3$, 1:1) was purified by prep. TLC (C_6H_6–EtOH, 4:1) to give **2b** (12 mg), mp 195–198° (C_6H_6–EtOH) (MW: Found: 388.1545; $C_{21}H_{24}O_7$ requires 388.1515). IR ν_{max}^{KBr} cm^{-1}: 3450, 1780, 1750, 1700, 1650, 1625. MS *m/z* (rel. int.): 388 (M^+, 15), 347 (30), 346 (100), 250 (32), 249 (97), 231 (49), 138 (37), 137 (63), 123 (76). For ^{1}H NMR see Tables 1 and 2.

Humirianthenolide D (**3**). Mp 216° ($CHCl_3$–MeOH) (MW: Found: 320.1260; $C_{17}H_{20}O_6$ requires: 320.1260). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590 (infl.), 3560 (infl.), 3490 (infl.), 3456, 1755, 1677, 1652. MS *m/z* (rel. int.): 320 (M^+, 100), 302 (23), 260 (20), 256 (20), 247 (25), 205 (24), 201 (26), 195 (43), 177 (34), 175 (25), 173 (23), 163 (30). For ^{1}H NMR and ^{13}C NMR see Tables 1–3.

Humirianthenolide E (**4a**). Mp 198–203° ($CHCl_3$–MeOH) (MW: Found: 306.1480; $C_{17}H_{22}O_5$ requires: 306.1467). IR ν_{max}^{KBr} cm^{-1}: 3500, 1740, 1700. MS, *m/z* (rel. int.): 306 (M^+, 14), 288 (25), 196 (47), 178 (22), 131 (16), 123 (19), 121 (27), 111 (22), 105 (26). For ^{1}H NMR: Tables 1–3.

Humirianthenolide F (**4b**). Mp 127–32° ($CHCl_3$–MeOH) (MW: Found: 308.1628; $C_{17}H_{24}O_5$ requires: 308,1624). IR ν_{max}^{KBr} cm^{-1}: 3500, 3470, 1740. MS *m/z* (rel. int.): 308 (M^+, 36), 290 (60), 272 (26), 244 (20), 217 (36), 199 (20), 180 (100), 162 (30), 147 (34), 145 (36), 133 (48), 131 (30), 121 (40), 119 (32), 111 (40), 107 (36), 105 (38). For ^{1}H NMR see Tables 1–3.

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