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FURTHER GUAIANOLIDES AND 5-ALKYLCOUMARINS FROM *GUTENBERGIA* AND *BOTHRIOCLINE* SPECIES

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Key Word Index—*Gutenbergia marginata*; *Bothriocline longipes*; *B. eupatorioides*; *B. ripensis*; Compositae; sesquiterpene lactones; guaianolides; 5-alkylcoumarins.

Abstract—From *Gutenbergia marginata* ten new guaianolides were isolated. Two guaianolides isolated previously from *Erlangea inyangana* are identical with two further lactones and their structures have been revised. From *Bothriocline ripensis* ethulia coumarin and two further 5-alkylcoumarin derivatives, one being a chromone, were isolated, while *B. longipes* and *B. eupatorioides* gave nine 5-alkylcoumarins and two related compounds. The structures were elucidated by highfield NMR techniques and a few chemical transformations.

INTRODUCTION

From the African *Erlangea* group (Compositae, tribe Vernonieae) so far only a few species have been studied chemically. Germacranolides of cordifolin type are reported from *E. cordifolia* [1], from *E. remifolia* guaianolides [2] and from the closely related *Bothriocline* and some *Erlangea* species 5-methylcoumarins [3–5]. We now have investigated further species of this group. The results are discussed in this paper.

RESULTS AND DISCUSSION

The aerial parts of two collections of *Gutenbergia marginata* (Oliv. et Hiern) Wild. et Pope afforded the guaianolides **1**–**12**. Two of these lactones (**7** and **8**) showed identical ^{1}H NMR spectra (Table 1) with those of two guaianolides previously reported from *E. inyangana* [2]. The ^{13}C NMR spectrum of **8** (Table 2) indicated that the structure has to be revised. The 400 MHz ^{1}H NMR spectra of **7** and **8** (Table 1) now could be assigned completely by spin decoupling which showed that the exomethylene signals (H-15) in the spectra of **7** and **8** were coupled with H-3 (δ5.53 and 5.49 *br dd*). This excluded the ester groups proposed previously (in lit. [2] compounds **2** and **5**). NOE difference spectroscopy indicated effects between H-7 and H-5, between H-1, H-2α, H-3 and H-5, between H-9 and H-14 as well as between H-6 and H-2β. These observations established the stereochemistry of all chiral centres. The fragmentation pattern in the mass spectrum of **7** also supported the structure, though no molecular ion was detected. However, elimination of the acyloxy radical led to *m/z* 287 ($M - C_7H_{12}O_5$). The acyl cation (*m/z* 159) was of low intensity but the base peak (*m/z* 131) was formed by loss of CO from *m/z* 159. Furthermore *m/z* 89 (131 − ketene) and *m/z* 71 (131 − HOAc) were strong fragments.

The ^{1}H NMR spectra of **4** and **5** (Table 1) clearly showed that the corresponding 4′-and 5′-acetoxyangelates were present, while that of **6** showed the typical signals of a 4′,5′-diacetoxyangelate. The configuration of the $\Delta^{2'}$ double bond was confirmed by a NOE of H-5′ with H-3′. This excluded a diacetoxy tiglate.

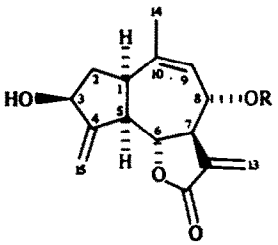
The ^{1}H NMR spectra of **1**–**3** (Table 1) were close to those of **4**, **5** and **8**. The presence of a free 3-hydroxy group caused, as expected, an upfield shift of the H-3 signal and for H-1 and H-2 no more first order signals were visible.

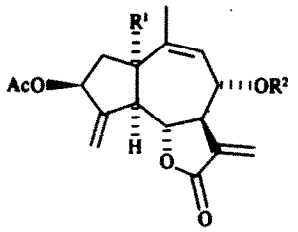
The ^{1}H NMR spectra of **9** and **10** (Table 1) indicated by the absence of a H-1 signal that a substituent must be at C-1. In agreement with the ^{13}C NMR spectrum of **9** (Table 2), which showed an additional signal (δ80.9 *s*) in the region of the oxygen-bearing carbons, and with the mass spectrum this only could be a hydroxy group. NOE difference spectroscopy indicated that the stereochemistry was the same as in **1**–**8** and that the hydroxy group was *cis* to H-5. From the signals of the ester residues in the spectra of **9** and **10** the presence of a 5′-acetoxy- and a 4′,5′-diacetoxyangelate, respectively, could be deduced.

The ^{1}H NMR spectra of **11** and **12** (Table 1) differed in a pronounced fashion from those of **1**–**8**. The typical signals of an angelate indicated the nature of the ester group while the chemical shifts of the exomethylene signals showed that now 10(14)-double bonds were present. A pair of doublets around δ4.0 and a signal at δ4.19 indicated a 3β,4α-dihydroxy-15-chloro derivative, especially when compared with the spectra of similar guaianolides [6]. This was supported by the molecular formula of **11** ($C_{20}H_{25}O_6Cl$). The ^{1}H NMR spectrum of **12** indicated the presence of a 11,13-dihydro derivative of **11** as the exomethylene signals of H-13 were replaced by a methyl doublet at δ1.18. The signal of H-11, however, overlapped with that of H-7 and, hence, the couplings could not be observed. In deuteriobenzene H-11 was a clear *dq* at δ2.38. The coupling $J_{7,11}$ indicated an 11α-proton.

The aerial parts of *Bothriocline ripensis* (Hutch) Wild. et Pope (= *Volkensia ripensis*) afforded a polar fraction which gave by further separation the known 5-methylcoumarin **13** [7], the corresponding 5-ethyl derivative **14** and the ketone **15**.

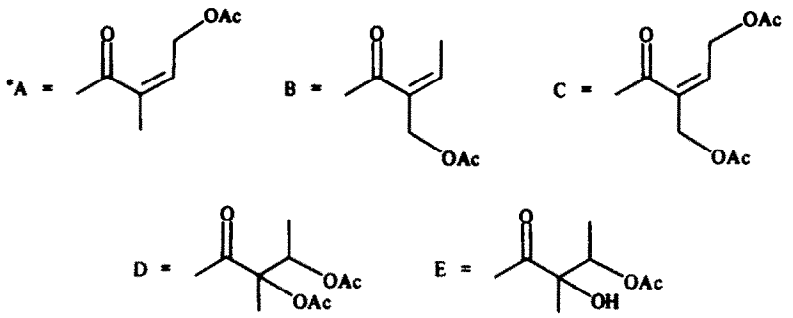
The structure of **14** clearly followed from the ^{1}H NMR

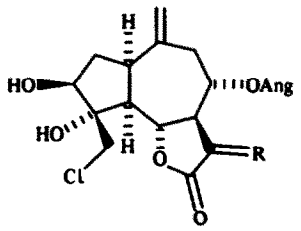




	1	2	3
R	A*	B*	D*

	4	5	6	7	8	9	10
R^1	H	H	H	H	H	OH	OH
R^2	A*	B*	C*	E*	D*	B*	C*





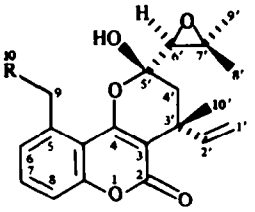
11 R = CH_2
12 R = βMe,H

spectrum (see Experimental) which was very close to that of **13**, only the aromatic methyl signal being replaced by the signals of an ethyl group. The stereochemistry was deduced from the observed NOEs. Clear effects were present between H-8′ and H-4′$_2$, between H-9′ and H-6′ as well as between H-10′, H-4′$_2$, H-2′ and H-1t′. This configuration agrees with that obtained by X-ray crystallography for a closely related coumarin [8].

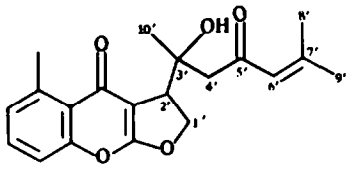
The structure of **15** also followed from the ^{1}H NMR spectrum (Table 1) which clearly showed that again a similar aromate linked with a monoterpene was present. Spin decoupling indicated a dihydrofuran system formed by addition of 5-oxolinalol to 4-hydroxy-5-methylcoumarin leading to a chromone as followed from the chemical shift of H-9. The position of the keto group followed from the typical chemical shift of the senecioyl residue. The configurations at C-2′ and C-3′ could not be determined. Compound **15** we have named volkensiachromone.

The aerial parts of *B. longipes* (Oliv. et Hiern.) N. E. Br. and of *B. eupatorioides* (Hutch. et B. L. Burtt) Wild. et Pope afforded a very complex mixture of further 5-alkylcoumarins and related compounds. Finally nine prenylated 5-alkylcoumarins (**16–24**) and two degraded compounds, the ketones **25** and **27** were isolated. However, the mixture of **16–20** could only be separated after preparing the *O*-methyl ethers. As in similar cases [9] mixtures of 2- and 4-*O*-methyl ethers were obtained.

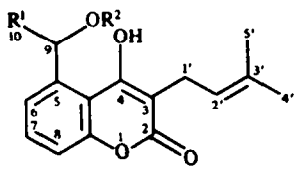
The structure of **22**, $C_{16}H_{16}O_3$, followed from the ^{1}H NMR spectral data (see Table 3). The presence of a prenyl group clearly followed by the typical signals and the aromatic protons led to a pattern very similar to that of other 5-substituted coumarins [7]. A NOE between H-10 and H-6 allowed the assignment of the aromatic protons. The remaining signals (δ6.06 *br q*, 1.77 *d*, 3H) and the presence of a chiral carbon required an additional five-membered ring. The ^{13}C NMR spectrum further supported the proposed structure (Table 3). The data were in part close to those of similar 5-alkylcoumarins [3–5]. In the ^{1}H NMR spectrum of **21** the signals of H-9 and H-10



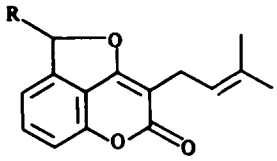
13 R = H
14 R = Me



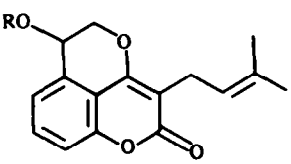
15



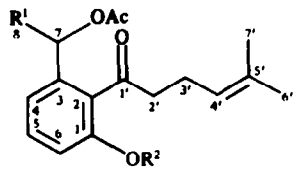
	16	17	18	19	20
R^1	H	H	Me	Me	Me
R^2	Ac	Prop	H	Ac	Prop



21 R = H
22 R = Me



23 R = Ac
24 R = Prop



	25	26	27	28
R^1	H	H	Me	Me
R^2	H	Me	H	Me

*16a–20a = 2-OMe
16b–20b = 4-OMe

were replaced by a broadened singlet at δ5.75. In agreement with the changed molecular formula therefore the 9-desmethyl derivative of **22** was present which we have named cyclolongipesin.

The spectral data of **23** (Table 3) indicated the presence of an acetate. Most signals were close to those of **21**, however, a pair of double doublets at δ4.59 and 4.45 as well as double doublet at δ6.13 indicated an additional oxygen function and a pyran ring. A NOE between H-9 and H-6 allowed the assignment of H-9 and the two aromatic doublets. The chemical shift of H-9 and the allylic coupling with H-6 also supported the structure. The ^{1}H NMR data of **24** (Table 3) clearly showed that we were dealing with the corresponding propionate. Due to the chiral centre the propionate methylene showed an ABX_3 pattern. The corresponding desacyl derivative we have named homocyclolongipesin.

The ^{1}H NMR spectra of **16a** and **16b** (Table 3), which were obtained by reaction with diazomethane, showed that isomeric 2- and 4-*O*-methyl ethers were present. As in similar cases [9] the 2-*O*-methyl signal was shifted further downfield. The singlets at δ5.51 (2H) and 2.14 (3H) indicated a benzylacetate. In agreement with the molecular formula therefore the structure was settled. The desacetyl derivative of **16** we have named longipesin. The ^{1}H NMR spectrum of **17a** (Table 3) showed that the corresponding propionate was present. The ^{1}H NMR spectral data of **18a–20a** as well as those of **19b** and **20b** (Table 3) showed that we were dealing with the 2-*O*-and 4-*O*-methyl ethers, respectively, of 9-methyllongipesin, its acetate and its propionate, respectively. Again in the spectrum of **20a** and **20b** the signal of the propionate methylene was an ABX_3 system. If the ^{1}H NMR data of **18a–20a** were compared with those of **22** the shift differences of H-10 were obvious. However, ring closure also led to an upfield shift of H-6. As expected the position

Table 1. ^{1}H NMR spectral data of 1–12 (400 MHz, $CDCl_3$, TMS as internal standard, multiplicity last column if no exception is marked)

	1	2	3	4	5	6	7	8	9	10	11	12*	Multiplicity
H-1	2.61†	2.60†	2.61	2.65	2.66	2.65	2.64	2.62	—	—	3.61	3.43	*ddd*
H-2α	2.61†	2.60†	2.66	2.79	2.77	2.78	2.80	2.76	2.71	2.71	1.61	1.71	*ddd*
H-2β	1.66†	1.63†	1.63	1.64	1.64	1.64	1.58	1.59	1.98‡	2.01‡	2.44	2.54	*ddd*
H-3	4.52†	4.51†	4.56	5.53	5.52	5.52	5.53	5.49	5.63	5.64	4.18	4.19	*br dd*
H-5	2.86	2.82	2.82	2.83	2.81	2.82	2.81	2.79	2.89§	2.90§	2.33	2.32	*dd*
H-6	4.79	4.67	4.76	4.69	4.67	4.64	4.68	4.59	4.51	4.49	4.73	4.67	*dd*
H-7	3.11	3.07	3.05	3.10	3.10	3.10	3.08	3.03	3.47	3.51	3.14	2.70†	*dddd*
H-8	5.83	5.86	5.59	5.77	5.88	5.85	5.72	5.56	5.95	5.95	5.14‖	5.05‖	*dd*
H-9	5.78	5.77	5.88	5.81	5.79	5.76	5.79	5.84	5.70	5.68	2.65‡ 2.46§	2.75‡ 2.28‡	*br d* *br d*
H-13	6.28	6.27	6.31	6.29	6.29	6.29	6.25	6.27	6.29	6.30	6.20	1.18	*d*
H-13′	5.54	5.59	5.58	5.56	5.59	5.56	5.56	5.55	5.58	5.57	5.63		*d*
H-14 H-14′	1.90¶	1.88	1.88¶	1.88	1.88¶	1.88¶	1.88	1.84¶	1.97¶	1.98¶	5.14 4.84	5.13 4.97	*d* *d*
H-15	5.51	5.47	5.45	5.50	5.49	5.49	5.49	5.45	5.57	5.58	4.35**	4.23**	*br s*
H-15′	5.49	5.45	5.41	5.43	5.42	5.42	5.43	5.38	5.51	5.52	3.97**	3.90**	*br s*
OAc	2.08	1.97	2.04	2.07	2.08	2.08	2.08	2.04	2.07	2.10	—	—	*s*
			1.95	2.04	1.98	2.07	1.95	1.99	1.97	2.08			
						1.98		1.92		2.00			
OCOR	6.12	6.49	5.12	6.02	6.46	6.37	4.96	5.03	6.47	6.39	6.21	6.14	
	tq	*q*	*q*	*tq*	*q*	*t*	*q*	*q*	*q*	*t*	*qq*	*qq*	
	4.94	4.89	1.54	4.98	4.63	5.07	3.11 (OH)	1.49	4.62	5.07	2.04	1.99	
	dq	*d*	*s*	*dq*	*br s*	*br d*	*br s*	*s*	*br s*	*d*	*dq*	*dq*	
	1.90	4.43	1.11	1.84	2.09	4.63	1.27	1.06	2.06	4.63	1.93	1.88	
	br s	*d*	*d*	*dt*	*d*	*s*	*s*	*d*	*d*	*s*	*dq*	*dq*	
		2.11					1.19		2.20 (OH)	2.26 (OH)			
		q					*d*		*s*	*s*			

*H-11 2.70 *m*, in C_6D_6 2.38 *dq* J = 8, 7.5 Hz.
†*m*.
‡*dd*.
§*br d*.
‖*ddd*.
¶*br s*.
**d*.
††*tq*.

J (Hz): compounds **1–10**: 1,2α = 1, 5 = 2α, 3 = 2β, 3 = 7; 1,2β = 2α, 2β = 13; 5,6 = 11.5; 6,7 = 9.5; 7,8 = 2; 7,13 = 3.7; 7,13′ = 3.2; 8,9 = 7.5; 9,14 = 1 (compounds **9** and **10**: 2α, 2β = 14.5; 2α, 3 = 6; 2β, 3 = 8; 2α, 5 = 1; 3,15 = 3, 15′ = 15, 15′ = 1.5; 8,9 = 6.5); compounds **11** and **12**: 1,2α = 8; 1,2β = 11; 1, 5 = 9; 2α, 2β = 15; 2α, 3 = 1.5; 2β, 3 = 6.5; 5,6 = 11; 6,7 = 9; 7,8 = 10; 7,13 = 3.5; 7,13′ = 3; 8,9 = 5; 9,9′ = 15; 9,14 = 2; 15,15′ = 12 (compound **12**: 7,11 = 8; 8,9 = 5; 9,9′ = 14; 11,13 = 7.5); OCOR: A: 3,4 = 5; 4,5 = 1; B: 3,4 = 7; 5,5′ = 12; C: 3,4 = 5; D/E: 3,4 = 6.5.

of the methoxy group caused clear shift differences of H-9. In the 2-*O*-methyl ethers the 4-keto group led to a downfield shift of H-9.

The ^{1}H NMR spectra of **25** and **27** and of the methyl ethers **26** and **28** obtained with diazomethane (see Experimental) differed in a pronounced fashion from those of **16–24**. The nature of one side chain clearly followed from the signals at δ2.95 *t* (2H), 2.42 *br q* (2H), 5.09 *br t* (1H), 1.68 and 1.62 *br s* (each 3H). The signals of the aromatic protons indicated the presence of a vicinal trisubstituted benzene derivative. Again the aromatic proton signals were assigned by a NOE between OH and H-6 as well as between H-8 and H-4. The signals of the olefinic methyls were assigned by NOEs between H-6′ and H-4′ as well as between H-7′ and H-3′. The remaining signals differed in the spectra of **25–28**. While **25** and **26** obviously were benzyl acetates, **27** and **28** showed the typical signals of a α-phenyl ethyl acetate. All data agreed nicely with the proposed structures which were further supported by the ^{13}C NMR of **27** (see Experimental). It is remarkable that the chemical shift of the hydroxy proton differed in **25** and **27**. Perhaps this is due to steric hindrance of the hydrogen bond formation. Most likely **25** and **27** are derived from **16** and **19**, respectively, by decarboxylation of the corresponding β-keto acid formed by hydrolysis of the lactone ring. Similar compounds have been isolated from Compositae cooccurring with 5-alkylcoumarins [9]. Compound **25** we have named *seco*-longipesin 9-*O*-acetate. The absolute configuration of **15–20** and **22–28** could not be determined.

Morphologically the closely related genera *Erlangea*, *Bothriocline* and *Gutenbergia* are not very well delimited.

Table 2. ^{13}C NMR data of **3**, **4**, **8** and **9** ($CDCl_3$, 67.8 MHz)

	3	4	8	9
C-1	44.0 *d*	44.0 *d*	44.0 *d*	80.9 *s*
C-2	41.2 *t*	38.6 *t*	38.4 *t*	46.2 *t*
C-3	72.1 *d*	73.5 *d*	73.2 *d*	72.6 *d*
C-4	152.2 *s*	147.3 *s*	147.3 *s*	147.0 *s*
C-5	51.1 *d*	51.5 *s*	51.3 *d*	60.9 *d*
C-6	77.2 *d*	76.9 *d*	76.4 *d*	76.6 *d*
C-7	48.8 *d*	49.2 *d*	48.6 *d*	47.6 *d*
C-8	67.2 *d*	65.6 *d*	67.1 *d*	65.5 *d*
C-9	119.9 *d*	120.6 *d*	120.1 *d*	120.9 *d*
C-10	145.2 *s*	144.1 *s*	144.6 *s*	144.6 *s*
C-11	134.6 *s*	135.5 *s*	134.4 *s*	134.9 *s*
C-12	168.9 *s*	168.9 *s*	168.7 *s*	168.9 *s*
C-13	122.1 *t*	121.3 *t*	122.1 *t*	121.9 *t*
C-14	28.4 *q*	28.3 *q*	28.2 *q*	24.8 *q*
C-15	115.2 *t*	117.7 *t*	117.6 *t*	118.2 *t*
OR	168.6 *s*	165.8 *s*	168.4 *s*	164.8 *s*
	81.7 *s*	128.0 *s*	81.6 *s*	127.0 *s*
	72.4 *d*	139.9 *d*	71.8 *d*	146.1 *d*
	16.3 *q*	62.8 *t*	16.5 *q*	16.0 *q*
	14.6 *q*	19.7 *q*	14.5 *q*	65.3 *t*
OAc	169.5 *s*	170.8 *s*	170.8 *s*	170.9 *s*
	170.0 *s*	170.7 *s*	169.4 *s*	170.4 *s*
	21.0 *q*	20.9 *q*	169.2 *s*	20.7 *q*
	20.9 *q*	21.1 *q*	20.8 *q*	21.2 *q*
			20.9 *q*	
			21.1 *q*	

They differ in cypsilas and in the trichomes of the vegetative parts [10]. For *Erlangea* hair-like trichomes with an erect terminal subulate cell are usually present. *Bothriocline* species have trichomes on vegetative parts which are also hair-like and T-shaped but with one arm very short and the other long while in *Gutenbergia* these trichomes are simple and hair-like with T-shaped arms of equal length [10]. The chemistry of *Gutenbergia* clearly differs from that of *Bothriocline* where 5-alkylcoumarins are characteristic. These compounds have been reported from *Erlangea rogersii* [4] which is, however, also placed in *Bothriocline* [10] and from *E. fusca* [3], which may be also better placed in *Bothriocline*. The chemistry of the genus *Erlangea* and *Gutenbergia* seem to be characterized by sesquiterpene lactones of different types. Further investigations may show whether these preliminary results are valid for a clear separation of these closely related genera.

EXPERIMENTAL

The air dried aerial parts from species grown in the greenhouse from seeds collected in Malawi were extracted and worked-up as reported previously [11].

The extract from 60 g of *Gutenbergia marginata* (voucher Jones 76–169) was separated into four CC fractions (1: Et_2O–petrol, 1:1, 2: Et_2O, 3: Et_2O–MeOH, 9:1 and 4: Et_2O–MeOH, 4:1). Fraction 1 gave by PTLC (SiO_2, PF 254) 10 mg lupeol and fraction 2 80 mg **8**. PTLC of fraction 3 (Et_2O–petrol, 7:3, three developments) gave 80 mg **8** (R_f 0.45), 10 mg **6** (R_f 0.38) and a mixture which afforded by repeated PTLC (toluene–CH_2Cl_2–Et_2O, 3:3:4, 3 ×) 20 mg **7** (R_f 0.63) and a mixture (3/4). PTLC of fraction 4 (same solvent) gave 40 mg **8** and a mixture which was combined with 3/4 and separated by HPLC (RP 8, MeOH–H_2O, 3:2) affording 30 mg **9** (R_t 8.0 min) and 50 mg **3** (R_t 8.7 min). The extract of 230 g of a second collection of *Gutenbergia marginata* (voucher Jones 76-168) gave polar CC fractions (Et_2O and Et_2O–MeOH, 9:1) which were combined and separated by HPLC (RP, MeOH–H_2O, 3:2) affording 5 mg loliolide (R_t 4.7 min), 22 mg **10** (R_t 8.2 min), 24 mg **9** (R_t 8.7 min), 23 mg **2** (R_t 10.3 min), 4 mg **1** (R_t 11.7 min), 5 mg **12** (R_t 13.0 min), 4.5 mg **11** (R_t 14.7 min), 20 mg **6** (R_t 16.2 min), 13 mg **5** (R_t 16.9 min) and 6 mg **4** (R_t 21.2 min).

The extract of the air dried aerial parts of *Bothriocline ripensis* (240 g, voucher Jones 76-193, originally collected near Mzuzu, Malawi by Pawek, voucher 11687) gave a polar CC fraction (Et_2O) which afforded by PTLC (SiO_2, PF 254, EtOAc–petrol, 1:4, two developments) 4 mg **14** (R_f 0.52), 2 mg **13** (R_f 0.44) and 2 mg **15** (R_f 0.09).

Table 3. ^1H NMR spectral data of **16–24** (400 MHz, $CDCl_3$, TMS as internal standard)

	16a	16b	17a	18a	19a	19b	20a	20b	21	22	23	24	Multiplicity
H-6	7.32	7.31	7.32	7.34	7.07	7.26	7.28	7.26	7.11	7.05	7.14	7.14	*br d*
H-7	7.53	7.46	7.53	7.53	7.52	7.46	7.52	7.46	7.49	7.48	7.52	7.51	*dd*
H-8	7.37	7.31	7.37	7.38	7.47	7.42	7.47	7.42	7.13	7.11	7.18	7.17	*br d*
H-9	5.92*	5.51*	5.93*	5.29	7.31	6.74	7.33	6.76	5.75	6.06	6.13†	6.13†	*q*
H-10	—	—	—	1.60	1.56	1.50	1.57	1.50	—	1.71	4.59† / 4.45†	4.59† / 4.50†	*t*
H-1′	3.15	3.32	3.15	3.19	3.15	3.33	3.15	3.33	3.19	3.17	3.21	3.20	*br t*
H-2′	5.19	5.24	5.19	5.19	5.21	5.25	5.21	5.25	5.31	5.32	5.32	5.32	*br d*
H-4′	1.65	1.71	1.68	1.67	1.67	1.72	1.67	1.71	1.68	1.68	1.70	1.70	*br s*
H-5′	1.75	1.76	1.76	1.76	1.75	1.78	1.75	1.77	1.74	1.74	1.76	1.75	*br s*
OR	2.28	2.14	2.47	6.33 (OH)§	2.10	2.13	2.38‡	2.42‡	—	—	2.07	2.31‡	*s*
			1.22				1.15	1.17				1.07	*t*
OMe	4.10	3.93	4.10	4.14	4.08	3.98	4.09	3.99	—	—			*s*

* *s*.
† *dd*.
‡ ABX_3.
§ *dq*.

J (Hz): 6,7 = 7,8 = 8; 1′,2′ = 7; compounds **18a**, **19a**, **19b**, **20a**, **20b** and **22**: 9,10 = 7; compound **23**: 9,10 = 4; 9,10′ = 6.5; 10,10′ = 13; OProp: 2,3 = 7.

The extract of the air dried aerial parts of *Bothriocline longipes* (180 g, voucher 76-160, originally collected near Mzuzu, Malawi) gave two fractions (1: Et_2O–petrol, 1:1, 1.2 g and 2: Et_2O, 1.1 g). PTLC of 100 mg of fraction 1 (Et_2O–petrol, 3:7, three developments) gave 15 mg **22** (R_f 0.35), 10 mg **21** (R_f 0.31), 10 mg **27** (R_f 0.25), 8 mg **25** (R_f 0.22) and 40 mg of a mixture of **23** and **24** (R_f 0.15). To 300 mg of fraction 1 diazomethane was added. PTLC (Et_2O–petrol, 1:1, three developments) gave 25 mg **28** (R_f 0.85), 20 mg **26** (R_f 0.79), 60 mg of **21** and **22**, 80 mg **23** (R_f 0.30) and 5 mg **24** (R_f 0.34). Repeated PTLC of the mixture of **21/22** (Et_2O–petrol, 3:7, three developments) gave 25 mg **22** (R_f 0.35) and 15 mg **21** (R_f 0.30). The ^1H NMR of fraction 2 showed no methoxy signal. After addition of CH_2N_2 PTLC of 300 mg (Et_2O–petrol, 1:1) gave four bands (2/1–2/4). HPLC (MeOH–H_2O, 4:1) of 2/1 gave 50 mg **19b** (R_t 4.6 min), a mixture (2/1/2, R_t 5.0 min) and 2 mg **20a** (R_t 5.4 min). PTLC of 2/1/2 (Et_2O–petrol, 1:1) gave 15 mg **20b** (R_f 0.65), 5 mg **20a** (R_f 0.53) and 5 mg **19b** (R_f 0.50). HPLC (MeOH–H_2O, 4:1) of 2/2 gave 40 mg **16b** (R_t 3.1 min), 20 mg **19a** (R_t 4.2 min) and 10 mg **17a** (R_t 5.3 min). PTLC of 2/3 and 2/4 (Et_2O–petrol, 1:1, three developments) gave 8 mg **16a** (R_f 0.44) and 5 mg **18a** (R_f 0.41), respectively.

The extract of 80 g of the aerial parts of *Bothriocline eupatorioides* (voucher 76-194, collected originally in Malawi, Mzuzu) gave also **16–25** and **27** in slightly different concentrations.

3β-Hydroxy-8α-[4-acetoxyangeloyloxy]-eremanthin (**1**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3575 (OH), 1770 (γ-lactone), 1740, 1250 (OAc), 1725, 1645 (C=CCO_2R); MS *m/z* (rel. int.): 402.168 $[M]^+$ (0.4) (calc. for $C_{22}H_{26}O_7$: 402.168), 244 $[M - RCO_2H]^+$ (21), 226 $[244 - H_2O]^+$ (28), 141 $[RCO]^+$ (40), 99 $[141 - ketene]^+$ (100).

3β-Hydroxy-8α-[5-acetoxyangeloyloxy]-eremanthin (**2**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1732 (CO_2R); MS *m/z* (rel. int.): 402.168 $[M]^+$ (0.1) (calc. for $C_{22}H_{26}O_7$: 402.168), 384 $[M - H_2O]^+$ (0.2), 342 $[M - HOAc]^+$ (0.2), 324 $[342 - H_2O]^+$ (0.3), 244 $[M - RCO_2H]^+$ (17), 226 $[244 - H_2O]^+$ (28), 141 $[RCO]^+$ (100), 99 $[141 - ketene]^+$ (32), 81 $[141 - HOAc]^+$ (66).

3β-Hydroxy-8α-[2,3-diacetoxy-2-methylbutyryloxy]-eremanthin (**3**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1765 (γ-lactone), 1740 (OAc, CO_2R); MS *m/z* (rel. int.): 402.168 $[M - HOAc]^+$ (0.5) (calc. for $C_{22}H_{26}O_7$: 402.168), 244 $[M - RCO_2H]^+$ (23), 226 $[244 - H_2O]^+$ (24), 201 $[RCO]^+$ (26), 159 $[201 - ketene]^+$ (46), 131 $[159 - CO]^+$ (100); $[\alpha]_D^{24°}$ −190 ($CHCl_3$; *c* 0.36).

3β-Acetoxy-8α-[4-acetoxyangeloyloxy]-eremanthin (**4**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770 (γ-lactone), 1740 (OAc), 1720, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 444.178 $[M]^+$ (0.15) (calc. for $C_{24}H_{28}O_8$: 444.178), 384 $[M - HOAc]^+$ (1.5), 324 $[384 - HOAc]^+$ (0.7), 226 $[384 - RCO_2H]^+$ (82), 141 $[RCO]^+$ (18), 99 $[141 - ketene]^+$ (100).

3β-Acetoxy-8α-[5-acetoxyangeloyloxy]-eremanthin (**5**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780 (γ-lactone), 1735 (OAc, CO_2R); MS *m/z* (rel. int.): 444.178 $[M]^+$ (0.5) (calc. for $C_{24}H_{28}O_8$: 444.178), 384 (1.3), 324 (1.6), 226 (93), 141 (100), 81 $[141 - HOAc]^+$ (71).

3β-Acetoxy-8α-[4,5-diacetoxyangeloyloxy]-eremanthin (**6**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770 (γ-lactone), 1740 (OAc, CO_2R); MS *m/z* (rel. int.): 442.163 $[M - HOAc]^+$ (0.7) (calc. for $C_{24}H_{26}O_8$: 442.163), 286 $[M - RCO_2H]^+$ (2), 226 $[286 - HOAc]^+$ (100), 199 $[RCO]^+$ (14), 157 $[199 - ketene]^+$ (48), 115 $[157 - ketene]^+$ (62); $[\alpha]_D^{24°}$ −138 ($CHCl_3$; *c* 0.57).

3β-Acetoxy-8α-[3-acetoxy-2-hydroxy-2-methylbutyryloxy]-eremanthin (**7**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH), 1785 (γ-lactone), 1750 (OAc, CO_2R); MS *m/z* (rel. int.): 402.168 $[M - HOAc]^+$ (2) (calc. for $C_{22}H_{26}O_7$: 402.168), 287 $[M - OCOR]^+$ (10), 227 $[287 - HOAc]^+$ (92), 226 $[402 - RCO_2H]^+$ (60), 159 $[MeCH(OAc)CH(OH)CO]^+$ (20), 131 $[159 - CO]^+$ (100), 89 $[131 - ketene]^+$ (98), 71 $[131 - HOAc]^+$ (60); $[\alpha]_D^{24°}$ −185 ($CHCl_3$; *c* 0.61).

3β-Acetoxy-8α-[2,3-diacetoxy-2-methylbutyryloxy]-eremanthin (**8**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780 (γ-lactone), 1740 (OAc, CO_2R); MS *m/z* (rel. int.): 444.178 $[M - HOAc]^+$ (2.5) (calc. for $C_{24}H_{28}O_8$: 444.178), 287 $[M - OCOR]^+$ (3.5), 286 $[M - RCO_2H]^+$ (3.8), 226 $[286 - HOAc]^+$ (100), 201 $[RCO]^+$ (27), 159 (26), 131 (84), 71 (11); $[\alpha]_D^{24°}$ −159 ($CHCl_3$; *c* 0.54).

3β-Acetoxy-1α-hydroxy-8α-[5-acetoxyangeloyloxy]-eremanthin (**9**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone), 1740 (OAc, CO_2R); MS *m/z* (rel. int.): 400.152 $[M - HOAc]^+$ (7) (calc. for $C_{22}H_{24}O_7$: 400.152), 340 $[400 - HOAc]^+$ (0.7), 242 $[400 - RCO_2H]^+$ (38), 141 $[RCO]^+$ (61), 81 $[141 - HOAc]^+$ (100).

3β-Acetoxy-1α-hydroxy-8α-[4,5-diacetoxyangeloyloxy]-eremanthin (**10**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770 (γ-lactone), 1735 (OAc, CO_2R); MS *m/z* (rel. int.): 458.158 $[M - HOAc]^+$ (0.4) (calc. for $C_{24}H_{26}O_9$: 458.158), 302 $[M - RCO_2H]^+$ (0.2), 242 $[302 - HOAc]^+$ (7.5), 224 $[242 - H_2O]^+$ (1.3), 157 $[RCO - ketene]^+$ (6), 144 (100), 115 $[157 - ketene]^+$ (39).

Desacylchlorojanerin 8-O-*angelate* (**11**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1770 (γ-lactone), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 396.134. $[M]^+$ (3) (calc. for $C_{20}H_{25}O_6Cl$: 396.134), 296 $[M - RCO_2H]^+$ (3), 278 $[296 - H_2O]^+$ (2.5), 260 $[296 - HCl]^+$ (2), 242 $[260 - H_2O]^+$ (2), 83 $[RCO]^+$ (100), 55 $[83 - CO]^+$ (47).

Desacyl-11,13-dihydrochlorojanerin 8-O-*angelate* (**12**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1775 (γ-lactone), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 298.097 $[M - RCO_2H]^+$ (3) (calc. for $C_{15}H_{19}O_4Cl$: 298.097), 280 $[298 - H_2O]^+$ (1.5), 262 $[298 - HCl]^+$ (3.5), 244 $[262 - H_2O]^+$ (6), 83 $[RCO]^+$ (100), 55 $[83 - CO]^+$ (61).

5-Methylethuliacoumarin (**14**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1705, 1600 (coumarin); MS *m/z* (rel. int.): 356.162 $[M]^+$ (4) (calc. for $C_{21}H_{24}O_5$: 356.162), 341 $[M - Me]^+$ (2), 285 $[M - CH(O)CMe_2]^+$ (5), 284 $[M - C_4H_8O]^+$ (6), 269 $[284 - Me]^+$ (8), 149 $[C_9H_9O_2]^+$ (42); ^1H NMR ($CDCl_3$): δ 7.05 (*br d*, H-6), 7.38 (*t*, H-7), 7.16 (*dd*, H-8), 2.35 (*q*, H-9), 0.97 (*t*, H-10), 5.15 (*d*, H-1c'), 5.10 (*d*, H-1t'), 6.11 (*dd*, H-2'), 2.23 and 2.02 (*d*, H-4'), 3.12 (*s*, H-6'), 1.49 (*s*, H-8'), 1.38 (*s*, H-9'), 1.71 (*s*, H-10') (*J* [Hz]: 6,7 = 7,8 = 8; 6,8 = 1.5; 9,10 = 7; 1'c,2' = 10; 1't',2' = 17; 4',4' = 14).

Volkensiachromone (**15**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1720 (chromone), 1690 (C=CC=O); MS *m/z* (rel. int.): 342.147 $[M]^+$ (10) (calc. for $C_{20}H_{22}O_5$: 342.147), 205 (26), 176 (20), 135 (17), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (43); ^1H NMR ($CDCl_3$): δ 7.12 (*br d*, H-6), 7.45 (*t*, H-7), 7.23 (*br d*, H-8), 2.85 (*s*, H-9), 4.51 and 4.18 (*dd*, H-1'), 3.23 (*dd*, H-2'), 2.92 and 2.51 (*d*, H-4'), 6.08 (*qq*, H-6'), 2.17 (*br s*, H-8'), 1.92 (*br s*, H-9'), 1.42 (*s*, H-10') (*J* [Hz]: 6,7 = 7,8 = 8; 1',1' = 11; 1'$_t$,2' = 3.5; 1'$_t$,2' = 7; 4',4' = 16; 6',8' = 6',9' = 1).

Longipesin 9-O-*acetate* (**16**). Isolated as methyl ethers **16a** and **16b**. **16a**: colourless crystals, mp 115°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (OAc), 1645 (C=O); MS *m/z* (rel. int.): 316.131 $[M]^+$ (22) (calc. for $C_{18}H_{20}O_5$: 316.131), 286 $[M - CH_2O]^+$ (34), 256 $[M - HOAc]^+$ (32), 242 $[M - Me, OAc]^+$ (66), 227 $[286 - OAc]^+$ (100), 187 $[256 - C_5H_9]^+$ (93). **16b**: colourless crystals, mp 33°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735 (OAc, C=O); MS *m/z* (red. int.): 316.131 $[M]^+$ (17) (calc. for $C_{18}H_{20}O_5$: 316.131), 257 $[M - OAc]^+$ (35), 201 $[257 - C_4H_8]^+$ (100).

Longipesin 9-O-*propionate* (**17**). Isolated as 2-*O*-methyl ether (**17a**). Colourless crystals, mp 84°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745 (CO_2R),

1630 (C=O); MS *m/z* (rel. int.): 330.147 $[M]^+$ (37) (calc. for $C_{19}H_{22}O_5$: 330.147), 256 $[M-RCO_2H]^+$ (68), 241 [256 − Me]$^+$ (100), 227 [256 − CHO]$^+$ (93), 187 [256 − C_5H_9]$^+$ 88).

9-*Methyllongipesin* (**18**). Isolated as 2-*O*-methyl ether **18a**. Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH), 1630 (C=O); MS *m/z* (rel. int.): 288.136 $[M]^+$ (14) (calc. for $C_{17}H_{20}O_4$: 288.136), 271 $[M-OH]^+$ (11), 270 $[M-H_2O]^+$ (13), 256 [271 − Me]$^+$ (60), 241 [256 − Me]$^+$ (71), 201 [256 − C_4H_7]$^+$ (100), 187 [256 − C_5H_9]$^+$ (18); $[\alpha]_D^{24°}$ + 17 ($CHCl_3$; *c* 0.47).

9-*Methyllongipesin* 9-O-*acetate* (**19**). Isolated as methyl ethers **19a** and **19b**. **19a**: colourless crystals, mp 104°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (OAc), 1630 (C=O); MS *m/z* (rel. int.): 330.147 $[M]^+$ (12) (calc. for $C_{19}H_{22}O_5$: 330.147), 270 $[M-HOAc]^+$ (12), 241 [270 − CHO]$^+$ (100), 187 [241 − C_4H_6]$^+$ (44). **19b**: colourless crystals, mp 116°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735 (OAc, C=O); MS *m/z* (rel. int.): 330.147 $[M]^+$ (14) (calc. for $C_{19}H_{22}O_5$: 330.147), 270 $[M-HOAc]^+$ (46), 255 [270 − Me]$^+$ (100), 227 [255 − CO]$^+$ (31), 201 [255 − C_4H_6]$^+$ (48).

9-*Methyllongipesin* 9-O-*propionate* (**20**). Isolated as methyl ethers **20a** and **20b**. **20a**: colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R), 1635 (C=O); MS *m/z* (rel. int.): 344.162 $[M]^+$ (11) (calc. for $C_{20}H_{24}O_5$: 344.162), 270 $[M-RCO_2H]^+$ (28), 255 [270 − Me]$^+$ (100), 201 [255 − C_4H_6]$^+$ (78). **20b**: Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (CO_2R, C=O); MS *m/z* (rel. int.): 344.162 $[M]^+$ (59) (calc. for $C_{20}H_{24}O_5$: 344.162), 270 $[M-RCO_2H]^+$ (30), 255 [270 − Me]$^+$ (100), 227 [255 − CO]$^+$ (21), 201 [255 − C_4H_6]$^+$ (44); $[\alpha]_D^{24°}$ − 11 ($CHCl_3$; *c* 0.92).

Cyclolongipesin (**21**). Colourless crystals, mp 124°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730, 1680 (C=O); MS *m/z* (rel. int.): 242.094 $[M]^+$ (22) (calc. for $C_{15}H_{14}O_3$: 242.094), 227 $[M-Me]^+$ (100), 187 $[M-C_4H_7]^+$ (38).

9-*Methylcyclolongipesin* (**22**). Colourless crystals, mp 85°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730, 1680 (C=O); MS *m/z* (rel. int.): 256.110 $[M]^+$ (66) (calc. for $C_{16}H_{16}O_3$: 256.110), 241 $[M-Me]^+$ (82), 201 $[M-C_4H_7]^+$ (100); ^{13}C NMR ($CDCl_3$, C-2–C-10): 165.8 *s*, 100.0 *s*, 165.7 *s*, 142.0 *s*, 115.4 *d*, 133.0 *d*, 113.5 *d*, 89.8 *d*, 20.8 *q*; C-4a: 119.0 *s*; C-8a: 149.4 *s*; C-1′–C-5′: 23.1 *t*, 120.5 *d*, 133.2 *s*, 25.7 *q*, 17.8 *q*.

Homocyclolongipesin 9-O-*acetate* (**23**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (OAc), 1730 (C=O); MS *m/z* (rel. int.): 314.115 $[M]^+$ (32) (calc. for $C_{18}H_{18}O_5$: 314.115), 299 [M − Me]$^+$ (8), 255 $[M-OAc]^+$ (25), 254 $[M-HOAc]^+$ (24), 239 [254 − Me]$^+$ (38), 199 [254 − C_4H_7]$^+$ (100).

Homocyclolongipesin 9-O-*propionate* (**24**). Colourless oil; IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1740 (CO_2R, C=O); MS *m/z* (rel. int.): 328.131 $[M]^+$ (31) (calc. for $C_{19}H_{20}O_5$: 328.131), 273 $[M-C_4H_7]^+$ (24), 255 $[M-OCOR]^+$ (30), 254 $[M-RCO_2H]^+$ (27), 239 [254 − Me]$^+$ (44), 199 [254 − C_4H_7]$^+$ (100).

seco-*Longipesin* 7-O-*acetate* (**25**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (OAc), 1640 (C=O); MS *m/z* (rel. int.): 276 $[M]^+$ (3.5), 216.115 $[M-HOAc]^+$ (22) (calc. for $C_{14}H_{16}O_2$: 216.115), 201 [216 − Me]$^+$ (23), 134 [216 − C_6H_{10}]$^+$ (100), 69 [C_5H_9]$^+$ (40); ^{1}H NMR ($CDCl_3$): 6.97 (*br d*, H-4), 7.35 (*t*, H-5), 6.94 (*d*, H-6), 5.29 (*br s* H-7), 2.95 (*t*, H-2′), 2.42 (*br q*, H-3′), 5.09 (*br t*, H-4′), 1.68 (*br s*, H-6′), 1.62 (*br s*, H-7′), 2.10 (*s*, OAc), 10.67 (*s*, OH) (*J* [Hz]: 4,5 = 5,6 = 8; 2′,3′ = 3′4′ = 7). Addition of CH_2N_2 gave **26**. Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (OAc), 1640 (C=O); MS *m/z* (rel. int.): 290.151 $[M]^+$ (1.5) (calc. for $C_{17}H_{22}O_4$: 290.152), 230 $[M-HOAc]^+$ (20), 215 [230 − Me]$^+$ (11), 161 [230 − C_5H_9]$^+$ (23), 148 [230 − C_6H_{10}]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ6.97 (*br d*, H-4), 7.31 (*t*, H-5), 6.88 (*d*, H-6), 5.01 (*s*, H-7), 2.85 (*t*, H-2′), 2.37 (*br q*, H-3′), 5.12 (*br t*, H-4′), 1.67 (*br s*, H-6′), 1.62 (*br s*, H-7′), 3.81 (*s*, OMe), 2.05 (*s*, OAc) (*J* [Hz]: 4,5 = 5,6 = 8; 2′,3′ = 3′,4′ = 7).

7-*Methyl*-seco-*longipesin* 7-O-*acetate* (**27**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745 (OAc), 1700 (C=O); MS *m/z* (rel. int.): 290.152 $[M]^+$ (1) (calc. for $C_{17}H_{22}O_4$: 290.152), 230 $[M-HOAc]^+$ (21), 162 [230 − C_5H_8]$^+$ (37), 161 [230 − C_5H_9]$^+$ (32), 148 [230 − C_6H_{10}]$^+$ (100); ^{1}H NMR ($CDCl_3$): δ7.03 (*br d*, H-4), 7.31 (*t*, H-5), 6.83 (*dd*, H-6), 6.03 (*q*, H-7), 1.54 (*d*, H-8), 3.04 and 2.93 (*dt*, H-2′), 2.43 (*br q*, H-3′), 5.12 (*br t*, H-4′), 1.68 (*br s*, H-6′), 1.63 (*br s*, H-7′), 2.07 (*s*, OAc), 8.23 (*s*, OH) (*J* [Hz]: 4,5 = 5,6 = 8; 4,6 = 1; 7,8 = 7; 2′,2′ = 16.5; 2′,3′ = 3′,4′ = 7); ^{13}C NMR ($CDCl_3$, C-1–C-8): 155.2 *s*, 125.5 *s*, 141.6 *s*, 117.6 *d*, 131.9*d*, 116.2*d*, 69.8 *d*, 22.9 *q*; (C-1′–C-7′): 208.0 *s*, 44.4 *t*, 23.1 *t*, 122.7 *d*, 132.9 *s*, 25.7 *q*, 17.7 *q*; OAc: 170.2 *s*, 21.2 *q*. Addition of CH_2N_2 gave **28**. Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1250 (OAc), 1700 (C=O); MS *m/z* (rel. int.): 304.167 $[M]^+$ (1) (calc. for $C_{18}H_{24}O_4$: 304.167), 244 $[M-HOAc]^+$ (25), 229 [244 − Me]$^+$ (10), 175 [244 − C_5H_9]$^+$ (22), 162 [244 − C_6H_{10}]$^+$ (100), 161 [244 − C_6H_{11}]$^+$ (44); ^{1}H NMR ($CDCl_3$): δ7.02 (*br d*, H-4), 7.22 (*t*, H-5), 6.82 (*d*, H-6), 5.59 (*q*, H-7), 1.51 (*d*, H-8), 2.95 and 2.89 (*dt*, H-2′), 2.41 (*br q*, H-3′), 5.16 (*br t*, H-4′), 1.69 (*br s*, H-6′), 1.65 (*br s*, H-7′), 3.81 (*s*, OMe), 2.04 (*s*, OAc) (*J* [Hz]: 4,5 = 5,6 = 8; 7,8 = 7; 2′,2′ = 17; 2′,3′ = 3′,4′ = 7).

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