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HIRSUTINOLIDES, GLAUCOLIDES AND SESQUITERPENE LACTONE FROM *VERNONIA* SPECIES

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Key Word Index – *Vernonia* spp.; *Pseudoelephantopus spicatus*; Compositae; sesquiterpene lactones; hirsutinolides; glaucolides; vernoallenolides; jalcaguaianolides; vernojalcanolides.

Abstract—The investigation of nine *Vernonia* species afforded in addition to known sesquiterpenes 28 new ones. The structures were elucidated by high field ^{1}H NMR spectroscopy and the configurations were determined by NOE difference spectroscopy and, in one case, by X-ray analysis. The results indicated that configurations of several previously reported sesquiterpene lactones have had to be revised. In addition to known types two new ones, the jalcaguaianolides and the vernojalcanolides, are described. Furthermore some unusual reaction products are presented which, in part, led to some natural occurring lactones.

INTRODUCTION

From the large genus *Vernonia* (Compositae, tribe Vernonieae) with more than 1000 species many highly oxygenated sesquiterpene lactones have been reported [1]. Glaucolides and hirsutinolides are especially widespread. These sesquiterpene lactones with a 7,11-double bond and an oxygen function at C-13 so far only have been isolated from representatives of the tribe Vernonieae though some other types have been reported. We now have investigated two species from Peru, four species from Central America and three species from Brazil, as well as *Pseudoelephantopus spicatus*.

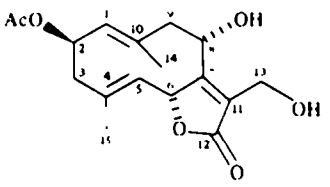
RESULTS AND DISCUSSION

The aerial parts of *Vernonia patens* H.B.K., collected in Peru, afforded stilpnotomentolide 8-*O*-angelate (**3**), 8-desacylvernonataloide 8-*O*-angelate (**4c**), vernonataloide (**4d**) [6], 8α-methacryloyloxycompactifloride (**5a**), the corresponding angeloyloxy derivative **5b**, vernopatensolide 8-*O*-angelate (**7a**), 8α-angeloyloxy-10α-hydroxy-1-desoxyhirsutinolide 13-*O*-acetate (**8a**), 8α-angeloyloxy-hirsutinolide 13-*O*-acetate (**8b**), 8α-angeloyloxy-4α,5α-epoxyjalcaguaianolide (**10a**), 8α-angeloyloxy-4α,5α-epoxy-13-*O*-methyljalcaguaianolide (**10c**) and 8α-angeloyloxy-4α,5α-epoxyjalcaguaianolide 13-*O*-acetate (**10e**).

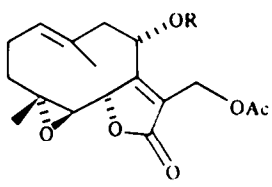
The structure of **3** followed from the ^{1}H NMR spectrum (Table 1) which was close to that of the corresponding tiglate [2]. The relative position of the ester groups was established by mild reaction of **3** with potassium carbonate which led to **7a** and **7b**. The ^{1}H NMR spectrum of the latter (Table 1) clearly indicated a free 13-hydroxy group while the angelate at C-8 was still present. Most likely the formation of **7a**, which also was isolated as a natural product, came about by way of a C-11 enolate, a reaction which would have to be more rapid than saponification of the allylic acetate. The configuration at C-10 previously assigned to analogues of **3** (in lit. [2] compounds **1–6**, **10** and **11**, see Table 9) has to be changed as NOE difference spectroscopy showed that a 10α-methyl group was present. Thus clear NOEs were observed in the spectrum of **3** between H-10 and H-8 and between H-15, H-6 and H-8 (always in Table 8). Similarly in the spectrum of **7a** NOEs were observed between H-14 and H-9β, between H-5, H-10 and H-15, between H-10, H-5 and H-8 and between H-15, H-3β and H-5. The NOEs with H-5 further indicated that the Δ^5 double bond of lactone **7a** had the *Z*-configuration. Although peaks in the spectrum of **7a** at room temperature were very broad and even at 90° in benzene only a few of the signals became clear, all signals could be interpreted at −40°. The data required a conformation with both H-5 and H-10 above and the keto group below the plane while the methyls were *quasi*-equatorial. This conformation did not allow hemi acetal formation which between the ketone and the C-4 hydroxyl group was observed in isomer **8b** where the Δ^5 double bond had the *E*-configuration (see below).

The structure of **4c** could be deduced easily from the ^{1}H NMR spectrum (Table 2) which was close to that of the corresponding methacrylate [6, 7]. NOE difference spectroscopy led to a conformation with the methyls at C-4 and C-10 above the plane as in the crystalline state [7]. Accordingly, NOEs were observed between H-14, H-8 and H-9β and between H-15, H-6 and H-8 as well as between H-5 and H-3α.

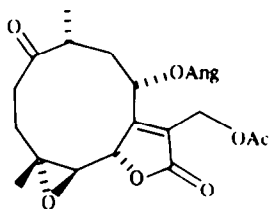
The ^{1}H NMR spectra of **5a** and **5b** (Table 2) showed that these lactones differed from 8α-caproyloxycompactifloride [5] only by the ester groups. NOE difference spectroscopy showed that the Δ^5 double bond had the *E*-configuration. Clear effects were observed between H-14, H-8 and H-9β and between H-15 and H-8. Inspection of a



1



2a R = Ac
2b R = Tigl



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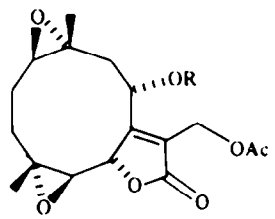
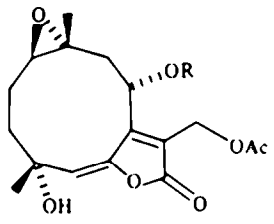
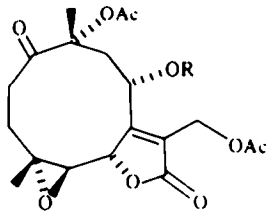


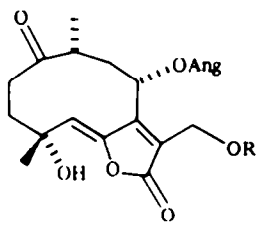
4a R = Ac **4b** R = iBu
4c R = Ang **4d** R = Meacr



5a R = Meacr
5b R = Ang



6a R = Ac
6b R = Meacr



7a R = Ac
7b R = H

model showed that this required a change in the configuration assigned to the Δ^5 double bond in some esters reported previously (compounds **4** and **5** in lit. [5]).

The lactones **10a**, **10c** and **10e** differed only by the nature of the oxygen function at C-13. The presence of guaianolides was deduced from the results of spin decoupling which led to the sequences H-1–H-3 and H-8–H-9. As a singlet around δ 5.30 (Table 3) obviously was due to H-6 all data agreed with the proposed structure which was further supported by NOE difference spectroscopy. Clear effects were observed between H-14, H-6 and H-8, between H-15 and H-6 and between H-6 and H-8. Acetylation of **10a** and **10e** gave the corresponding diacetates which excluded the possibility that the guaianolides were 4,5-dihydroxylated.

The aerial parts of *Vernonia jalcana* Cuatr. gave after repeated TLC and HPLC **2a**, the vernonataloides **4a**, **4b** and **4d** [6, 7], the glaucolides **6a** [8] and **6b** [8], the hirsutinolides **8c**, **8d**, **8e**, **8f**, **8g** and **8h** [9], the guaianolides **10b**, **10d** and **11**, as well as four cadinanolides (**12a–12d**).

The structure of **2a**, which most likely is the precursor of **4a**, followed from the ^{1}H NMR spectrum in deuteriobenzene at 77° (Table 2) where spin decoupling was possible, while in deuteriochloroform at 20° most signals were broadened. The data were close to those of the corresponding 8-*O*-methacrylate [10]. Similarly the structures of **4a** and **4b** could be deduced easily from the ^{1}H NMR spectra (Table 2) which were close to that of **4c** (see above). The changed nature of the ester residue at C-8 clearly followed from the typical ^{1}H NMR signals.

The structure of **8b** followed from the ^{1}H NMR spectral data (Table 1) which was close to those of similar lactones which differ only in the nature of the ester groups [2, 4]. X-ray analysis of **8b** (see Fig. 1) showed that the 10-methyl group was α-orientated and the ether ring was below the plane. Accordingly, this configuration has to be changed in esters reported previously [2, 4] (see Table 9).

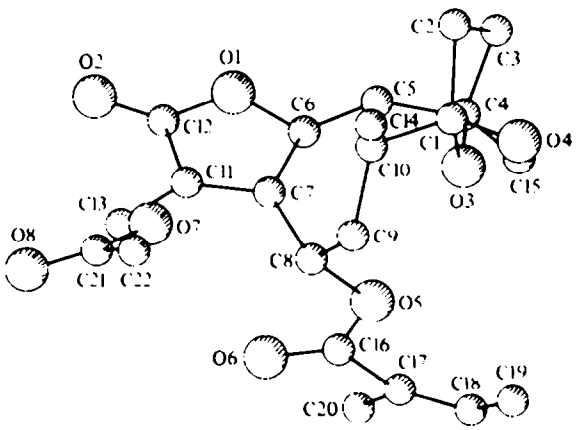


Fig. 1.

Table 1. ^{1}H NMR spectral data of sesquiterpene lactones **3**, **7a**, **7b**, **8a** and **8b** (400 MHz, $CDCl_3$, TMS as int. standard)

	3	7a (−40°)	7b	8b	8a (C_6D_6, 77°)*
H-1					3.99 *dd br*
H-2	2.69 *ddd*	2.50 *m*	2.3–2.5 *m*	2.33 *dd br*	1.55 *m*
H-2′	2.64 *ddd*	2.36 *m*		—	
H-3	2.30 *ddd*	2.36 *m*		—	—
H-3′	1.72 *ddd*	2.05 *m*	2.00 *m*	—	—
H-5	2.57 *d*	5.48 *s*	5.38 *br*	5.88 *s*	5.67 *s*
H-6	4.90 *d br*				
H-8	4.90 *dd br*	5.46 *dd*	5.50 *d br*	6.21 *d br*	6.37 *d br*
H-9	2.19 *ddd*	1.88 *ddd*	1.90 *m*	—	1.83 *d br*
H-9′	2.53 *ddd*	2.48 *dd br*	2.40 *m*	—	2.35 *dd*
H-10	2.97 *ddq*	2.93 *dq br*	2.92 *m*	—	
H-13	4.90 *d br*	4.99 *d*	4.62 *s br*	5.09 *d*	5.22 *d*
H-13′	4.83 *d br*	4.95 *d*		5.02 *d*	5.08 *d*
H-14	1.14 *d*	1.10 *d*	1.08 *d*	0.94 *d*	0.98 *s*†
H-15	1.62 *s*	1.56 *s*	1.51 *s br*	1.47 *s*	1.14 *s*†
OAc	2.07 *s*	2.06 *s*		2.07 *s*	1.71 *s*
OR	6.22 *qq*	6.28 *qq*	6.21 *qq*	6.08 *qq*	5.76 *qq*
	1.99 *dq*	2.05 *dq*	2.03 *dq*	1.98 *dq*	1.92 *dq*
	1.87 *dq*	1.91 *dq*	1.96 *dq*	1.89 *dq*	1.83 *dq*
OH		3.18 *s*	3.05 *s*		

*In $CDCl_3$: H-2β 2.55 *m*; H-3β 2.41 *m*.

†May be exchangeable.

—, Unassigned multiplets.

J (Hz): Compound **3**: 2, 2′ = 15; 2, 3 = 4.5; 2, 3′ = 9.5; 2′, 3 = 2′, 3′ = 6; 3, 3′ = 13.5; 5, 6 = 9; 8, 9 = 3.5; 8, 9′ = 5; 9, 9′ = 15.5; 9, 10 = 3.5; 9′, 10 = 11.5; 10, 14 = 7; 13, 13′ = 13; compounds **7a** and **7b**: 8, 9 = 2.5; 8, 9′ = 11.5; 9, 9′ = 13.5; 9, 10 = 11; 10, 14 = 7; 13, 13′ = 12.5; compound **8a**: 1, 2 = 7; 1, 2′ = 9; 8, 9′ = 8; 9, 9′ = 15; 13, 13′ = 13; compound **8b**: 2, 2′ = 16.5; 2, 3 = 12.5; 8, 9′ = 7; 10, 14 = 7; 13, 13′ = 13.

Table 2. ^{1}H NMR spectral data of sesquiterpene lactones **2a**, **4a–4c**, **5a** and **5b** (400 MHz, $CDCl_3$, TMS as int. standard)

	2a (C_6D_6, 77°)	4a	4b	4c	5a	5b
H-1	4.90 *m*	2.68 *d br*	2.68 *d br*	2.69 *d br*	3.06 *dd*	3.06 *dd*
H-2	•	2.11 *dd br*	2.13 *dd br*	2.13 *dd br*	2.15 *m*	2.15 *m*
H-2′	•	1.52 *m*	1.55 *m*	1.55 *m*	1.57 *m*	1.56 *m*
H-3	•	2.29 *ddd*	2.30 *ddd*	2.31 *ddd*	2.28 *ddd*	2.28 *ddd*
H-3′	•	1.33 *ddd*	1.34 *ddd*	1.35 *ddd*	2.07 *ddd*	2.10 *ddd*
H-5	2.07 *d br*	2.57 *d*	2.58 *d*	2.59 *d*	6.38 *s*	6.39 *s*
H-6	4.62 *d br*	4.92 *d br*	4.94 *d br*	5.02 *d br*	—	—
H-8	4.98 *dd*	5.17 *d br*	5.20 *d br*	5.25 *d br*	5.91 *d*	5.91 *d*
H-9	2.50 *m*	2.68 *d br*	2.66 *d br*	2.75 *d br*	2.62 *d*	2.60 *d*
H-9′		1.97 *dd br*	2.01 *dd br*	2.03 *dd br*	1.88 *dd*	1.87 *dd*
H-13	6.18 *dd*	5.02 *dd*	5.01 *dd*	4.91 *dd*	5.02 *d*	5.00 *d*
H-13′	4.95 *dd*	4.77 *dd*	4.79 *dd*	4.80 *dd*	4.89 *d*	4.90 *d*
H-14	1.38 *s br*	1.50 *s*	1.52 *s*	1.54 *s*	1.48 *s*	1.49 *s*
H-15	1.04 *s br*	1.46 *s*	1.47 *s*	1.50 *s*	1.78 *s*	1.78 *s*
OAc	1.76 *s*	2.06 *s*	2.10 *s*	2.02 *s*	2.04 *s*	2.06 *s*
OR	1.65 *s*	2.10 *s*	2.56 *qq*	6.24 *qq*	6.16 *s br*	6.23 *qq*
			1.18 *d*	2.00 *dq*	5.72 *dq*	2.02 *dq*
			1.14 *d*	1.87 *dq*	1.96 *dd*	1.90 *dq*

•Unassigned multiplets.

J (Hz): Compound **2a**: 5, 6 = 8.5; 6, 13 = 6, 13′ = 1; 8, 9 = 4; 8, 9′ = 10.5; 13, 13′ = 12.5; compounds **4a**, **4b** and **4c**: 1, 2′ = 10.5; 2, 2′ = 14; 2, 3 = 2; 2, 3′ = 6; 2′, 3 = 5; 2′, 3′ = 3, 3′ = 13.5; 5, 6 = 8.5; 8, 9′ = 9; 9, 9′ = 14; 13, 13′ = 13; compounds **5a** and **5b**: 1, 2 = 2.5; 1, 2′ = 10.5; 2, 3′ = 4.5; 2′, 3′ = 11; 3, 3′ = 14.5; 8, 9′ = 9.5; 9, 9′ = 14; 13, 13′ = 13.

Table 3. ^{1}H NMR spectral data of sesquiterpene lactones **10a**–**10e**, **10e**-acetate and **11** (400 MHz, $CDCl_3$, TMS as int. standard)

	10a	10b	10c	10d	10e	10e-acetate	11
H-1	2.32 *d br*	2.28 *d br*	2.30 *d br*	2.31 *d br*	2.31 *d br*	2.30 *d br*	2.62 *m*
H-6	5.28 *s*	5.24 *s*	5.30 *s*	5.26 *s*	5.32 *s*	5.34 *s br*	
H-8	5.76 *dd*	5.63 *dd*	5.70 *dd*	5.72 *dd*	5.76 *dd*	5.84 *dd br*	5.33 *dd*
H-9	1.49 *dd*	1.49 *dd*	1.50 *dd*	1.49 *dd*	1.49 *dd*	1.50 *dd br*	1.50 *dd*
H-9′	2.64 *dd*	2.59 *dd*	2.63 *dd*	2.57 *dd*	2.63 *dd*	2.61 *dd*	2.32 *m*
H-13	4.58 *s*	4.32 *d*	4.26 *d*	5.09 *d*	4.98 *d*	5.00 *d br*	4.35 *d*
H-13′		4.20 *d*	4.22 *d*	4.88 *d*	4.87 *d*	4.86 *d br*	4.23 *d*
H-14	1.43 *s*	1.43 *s*	1.43 *s*	1.43 *s*	1.43 *s*	1.65 *s*	1.31 *s*
H-15	1.50 *s*	1.46 *s*	1.49 *s*	1.47 *s*	1.49 *s*	1.50 *s*	1.53 *s*
OAc		2.16 *s*		2.15 *s*	2.03 *s*	2.11 *s*	
				2.07 *s*		2.01 *s*	
OMe		3.34 *s*	3.30 *s*				3.40 *s*
OR	6.26 *qq*		6.24 *qq*		6.26 *qq*	6.21 *qq*	2.62 *m*
	2.04 *dq*		2.04 *dq*		2.04 *dq*	2.02 *dq*	1.21 *d*
	1.97 *dq*		1.97 *dq*		1.92 *dq*	1.89 *dq*	1.24 *d*

J (Hz): Compounds **10a**–**10e**: 1, 2 = 8; 8, 9 = 10; 8, 9′ = 2; 9, 9′ = 13; 13, 13′ = 12; compound **11**: 8, 9 = 3.5; 8, 9′ = 12; 9, 9′ = 12; 13, 13′ = 11.

Most likely identical stereochemistry at C-4 is present in all similar lactones from *Vernonia* (see below). Furthermore the conformation indicated that the downfield shift of the H-8 signal in hirsutinolide is not caused by a deshielding effect of the ether oxygen but is due to the effect of the 7,11-double bond.

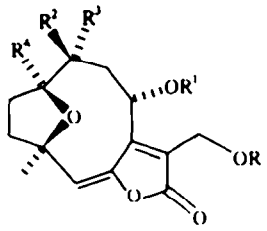
The structure of **8a** also could be deduced from the ^{1}H NMR spectrum (Table 1) which was close to that of the corresponding capronate [5]. NOE difference spectroscopy indicated that the stereochemistry at C-10 differed from that of **8b** as the methyl group in **8a** was β-orientated. Accordingly, clear NOEs were observed between H-14, H-1, H-2β, H-8 and H-9β, and between H-8, H-2β and H-3β. The ^{1}H NMR spectra of the hirsutinolides **8c**–**8g** (Table 4) again only could be interpreted at elevated temperature. Spin decoupling and the signals of the oxygen functions indicated that we were dealing with lactones which were closely related to **8b** [9]. The presence of a free 13-hydroxyl group in **8c** followed from the upfield shift of the H-13 signal if compared with that of **8b**. As **8d** could not be acetylated under mild conditions the methoxy group was at C-13. The same was true in case of **8f** with an additional methoxy group at C-1. Comparison of the ^{1}H NMR spectra of **8e** with those of **8d** and **8g** with **8f** clearly showed that these compounds were the corresponding methacrylates. As already discussed in the case of **8b** (see above) all hirsutinolides most likely have the same stereochemistry which now is represented in an uniform manner following the conventions enunciated by Rogers *et al.* [11]. Most likely in all cases the configurations at C-1, C-4 and C-8 are identical. The methyl group at C-10 mostly is α-orientated but changed to 10β if an oxygen function is present at C-10 (Table 9).

The formulae of many previously reported hirsutinolides have to be revised (in lit. [4] compounds **21**–**23**, **29**–**31** and **36**, in lit. [5] compounds **7** and **8**, in lit. [9] compounds **8**–**13**, in lit. [12] compounds **13a**–**13c** and **14**, in lit. [14] compounds **3**, **4** and **7**, in lit. [15] compounds

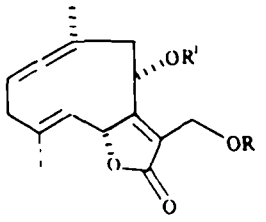
Table 4. ^{1}H NMR spectral data of sesquiterpene lactones **8c**–**8g**

	8c		8d		8f	8e	8g	
	$CDCl_3$	C_6D_6(75°)	$CDCl_3$	C_6D_6(72°)	$CDCl_3$	$CDCl_3$	$CDCl_3$	C_6D_6(72°)
H-5	5.92 *s br*	5.62 *s*	5.86 *s br*	5.66 *s*	5.91 *s br*	5.84 *s br*	5.88 *s br*	5.55 *s*
H-8	6.45 *m*	6.11 *d br*	6.36 *m*	6.31 *d br*	6.29 *m*	6.56 *d br*	6.50 *m*	6.62 *dd*
H-9	2.58 *m*	2.14 *dd*	2.53 *m*	2.36 *dd*	2.46 *d br*	2.58 *d br*	2.51 *dd*	2.44 *dd*
H-9′	2.12 *m*	1.69 *d br*	2.07 *m*	1.92 *dd*	2.07 *d br*	2.09 *d br*	2.09 *d br*	1.96 *dd*
H-13	4.61 *s br*	4.55 *d*	4.50 *d br*	4.48 *d*	4.47 *d br*	4.58 *d br*	4.53 *d br*	4.53 *d*
H-13′		4.45 *d*	4.24 *d br*	4.24 *d*	4.23 *d br*	4.27 *d br*	4.28 *d br*	4.31 *d*
H-14	1.60 *s br*	1.36 *s*	1.57 *s*	1.30 *s*	1.62 *s*	1.57 *s br*	1.61 *s*	1.29 *s*
H-15	1.26 *s br*	1.09 *s*	1.22 *s br*	1.12 *s*	1.24 *s*	1.22 *s br*	1.25 *s*	1.19 *s*
OAc	2.14 *s*	1.60 *s*	2.10 *s*	1.70 *s*	2.11 *s*		-	—
OMe	—		3.38 *s*	3.17 *s*	3.51 *s*	3.40 *s*	3.55 *s*	3.49 *s*
		—		—	3.38 *s*		3.40 *s*	3.16 *s*
OR		-	--		-	6.28 *s br*	6.33 *s br*	6.29 *s br*
						5.67 *dq*	5.69 *dd*	5.31 *dq*
						1.94 *s br*	1.97 *s br*	1.86 *s br*

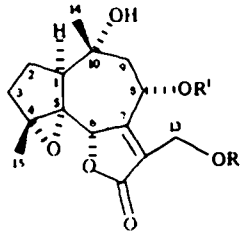
J (Hz): 8, 9 = 9; 8, 9′ = 2.5; 9, 9′ = 15.5; 13, 13′ = 12.5.



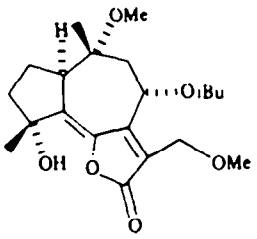
	8a	8b	8c	8d	8e	8f	8g	8h	8i	8k	8l
R	Ac	Ac	H	Me	Me	Me	Me	Ac	Ac	Ac	Ac
R¹	Ang	Ang	Ac	Ac	Meacr	Ac	Meacr	Ac	Ac	Ac	Meacr
R²	Me	H	Me	Me	Me	Me	Me	Me	Me	Me	Me
R³	OH	Me	OH	OH	OH	OH	OH	OH	OAc	OAc	OH
R⁴	H	OH	OH	OH	OH	OMe	OMe	OH	OH	OMe	OH



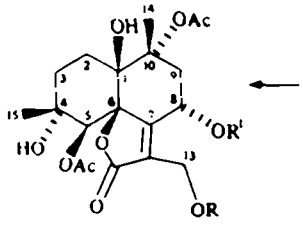
	9a	9b	9c
R	H	Ac	Ac
R¹	H	H	Ac



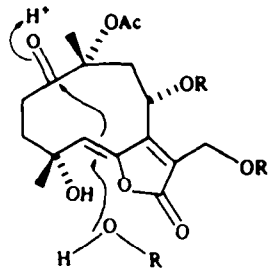
	10a	10b	10c	10d	10e
R	H	Me	Me	Ac	Ac
R¹	Ang	Ac	Ang	Ac	Ang



11



	12a	12b	12c	12d
R	H	Me	Me	Me
R¹	Ac	Ac	iBu	Meacr



12e

3–7, in lit. [16] compounds **1** and **2**, in lit. [17] compounds **1g** and **1h**, in lit. [18] compounds **1a–1f**) (see Table 9).

The spectrum of **10b** was very similar to that of **10c** and that of **10d** was close to that of **10e** as in these pairs of lactones the 8-*O*-angelates were replaced by 8-*O*-acetates (Table 3). Another guaianolide **11** most likely had been formed via the corresponding 4,5-epoxide of type **10**, which, however, was not isolated. The ^{1}H NMR spectrum (Table 3) fully agreed with the proposed structure. The configuration at C-4 was deduced from the chemical shift of H-15 and from biogenetic considerations, while that of the other chiral centres obviously was the same as in the lactones of types **10a–10e** where the stereochemistry was established by NOE difference spectroscopy.

The structural elucidation of **12a–12d** caused some problems. However, in deuteriobenzene all signals of the acetate of **12b** could be assigned by spin decoupling (Table 5). The absence of a proton at C-6 and a lowfield singlet at δ6.28 as well as the couplings of H-2, H-3, H-8 and H-9 indicated that cadinanolides were present. Biogenetic considerations also supported this assumption as these lactones most likely are formed via enol lactones of type **12e**. The position of the free hydroxyls was deduced from the shift differences in the ^{1}H NMR spectra of **12b** and its acetylation product (Table 5). As the H-15 signals were shifted downfield a 4-*O*-acetate was formed while acetylation of the hydroxy at C-1 most likely was sterically hindered. The stereochemistry was determined by NOE difference spectroscopy. Clear NOEs were

Table 5. ^{1}H NMR spectral data of sesquiterpene lactones **12a–12d** (400 MHz, $CDCl_3$, TMS as int. standard)

	12a	**12a**-acetate	**12b**	**12b**-acetate	(C_6D_6)	**12c**	**12d**-acetate
H-2	2.36 *m*	2.36 *m*	2.38 *m*	2.35 *ddd*	1.88 *dd*	2.39 *m*	2.38 *m*
H-2′	1.65 *m*	1.73 *m*	1.67 *m*	1.72 *m*	1.32 *ddd*	1.67 *m*	1.74 *m*
H-3	2.30 *m*	2.41 *ddd*	2.33 *m*	2.41 *ddd*	2.30 *ddd br*	2.34 *m*	2.38 *m*
H-3′	1.85 *m*	2.70 *ddd*	1.86 *m*	2.69 *ddd*	2.65 *ddd*	1.86 *m*	2.72 *m*
H-5	5.85 *s*	6.14 *s*	5.92 *s*	6.14 *s*	6.28 *s*	5.91 *s*	6.13 *s*
H-8	5.82 *dd*	5.85 *dd*	5.87 *dd*	5.85 *dd*	5.87 *dd*	5.81 *dd*	5.70 *dd*
H-9	3.30 *dd*	3.28 *dd*	3.32 *dd*	3.27 *dd*	3.25 *dd*	3.36 *dd*	3.43 *dd*
H-9′	2.05 *dd*	2.06 *dd*	2.03 *dd*	2.06 *dd*	1.96 *dd*	2.05 *dd*	2.12 *dd*
H-13	4.55 *d*	5.12 *d*	4.41 *d*	4.40 *d*	4.54 *d*	4.47 *d*	4.58 *d*
H-13′	4.47 *d*	4.79 *d*	4.23 *d*	4.21 *d*	4.26 *d*	4.23 *d*	4.27 *d*
H-14	1.71 *s*	1.70 *s*	1.70 *s*	1.70 *s*	1.58 *s*	1.70 *s*	1.71 *s*
H-15	1.40 *s*	1.77 *s*	1.40 *s*	1.77 *s br*	2.05 *s br*	1.41 *s*	1.77 *s*
OAc	2.21 *s*	2.21 *s*	2.21 *s*	2.20 *s*	1.98 *s*	2.21 *s*	2.15 *s*
	1.98 *s*	2.07 *s*	1.97 *s*	2.06 *s*	1.96 *s*	1.96 *s*	1.92 *s*
	2.06 *s*	2.04 *s*	2.03 *s*	1.93 *s*	1.69 *s*	—	1.89 *s*
		1.94 *s*	—	1.91 *s*	1.67 *s*	—	—
	—	1.92 *s*	—	—	—	—	—
OMe	—	—	3.34 *s*	3.33 *s*	3.15 *s*	3.34 *s*	3.34 *s*
OR	—	—	—	—	—	2.54 *qq*	5.99 *dq*
						1.17 *d*	5.62 *dq*
						1.08 *d*	1.95 *s br*

J (Hz): 2, 2′ = 15; 2, 3 = 4.5; 2, 3′ = 3; 2′, 3 = 15; 2′, 3′ = 5; 3, 3′ = 14; 8′, 9 = 2; 8′, 9′ = 4; 13, 13′ = 11.5; 9, 9′ = 15.

observed with **12b** between H-15 (assigned by a W-coupling with H-3) and H-2β and between H-3α and H-5. The *cis*-annealation of the cyclohexane rings was deduced from the NOEs between H-14 and both H-9 protons and a NOE with H-2α. The axial orientation of the ester group at C-8 followed from the small couplings $J_{8,9}$. The ^{13}C NMR spectra of **12b** and its acetate (see Experimental) further supported the proposed structures. The structures of **12a**, **12c** and **12d**, which also were transformed to their 4-*O*-acetates, were deduced from the ^{1}H NMR spectra which were close to that of **12b** and its acetate respectively (Table 5). The changed nature of the oxygen functions followed from the typical ^{1}H NMR signals.

A reinvestigation of *Vernonia cotoneaster* Less. gave **1**, vernonallenolide (**9c**) [19, 20] as well as two further allenes, the diol **9a** and the monoacetate **9b**. The structures of **9a** and **9b** followed from their ^{1}H NMR spectral data (Table 6) which were close to those of **9c** [19, 20]. As expected the signals of H-8 and H-13 in **9a** were shifted to higher field, and in the spectrum of **9b** the position of the acetoxy group also could be deduced from the chemical shifts of these signals. The previously unknown configurations at C-2 and C-10 could be assigned on the basis of NOEs between H-14 and H-9α, between H-8 and H-15 and between H-5 and H-3α, and the Δ^4 double bond has the *E*-configuration (NOE between H-6 and H-15). The ^{1}H NMR spectrum of **1** (Table 6) showed that this lactone was the 8,13-*bis*-desacetyl derivative of a triacetate isolated previously from the same species [5] whose C-3 stereochemistry originally assumed to be α, was subsequently corrected to β by NOE difference spectroscopy [6]. The position of the acetoxy group in the lactone **1** followed from the chemical shift of H-2.

Some additional *Vernonia* species gave only known lactones. *Vernonia acuminata* Less., *V. arctioides* Less. and

Table 6. ^{1}H NMR spectral data of sesquiterpene lactones **1**, **9a**, **9b** and **13** (400 MHz, $CDCl_3$, TMS as int. standard)

	1	**9a**	**9b**	**13**
H-1	5.16 *d br*	—	—	
H-2	5.73 *ddd br*	5.32 *dddq*	5.38 *dddq*	2.18 *m**, 3.36 *m**
H-3	2.23 *dd*	2.28 *dd*	2.30 *dd*	2.34 *m**
H-3′	2.78 *dd*	2.87 *dd*	2.89 *dd*	1.80 *m**
H-5	4.49 *dq*	4.60 *d br*	4.66 *d br*	3.41 *d*
H-6	5.67 *d br*	5.71 *ddd*	5.89 *d br*	4.80 *d*
H-8	4.14 *m*	4.14 *ddd*	4.95 *dd*	5.23 *dd*
H-9	2.44 *dd*	2.24 *dd*	2.24 *dd*	2.18 *dd*
H-9′	2.94 *dd br*	2.94 *ddd*	2.90 *ddd*	3.17 *dd*
H-13 }	4.71 *s br*	4.66 *d br*	4.55 *d br*	6.65 *s*
H-13′ }		4.72 *d br*	4.52 *dd*	5.99 *s*
H-14	1.55 *s*	1.66 *d*	1.69 *d*	1.46 *s*
H-15	1.81 *d*	1.95 *d*	2.01 *d*	1.35 *s*
OAc	2.11 *s*	—	2.08 *s*	—
OH	—	3.84 *d*	2.74 *t br*	—
OCOR	—	—	—	6.07 *dq*
				5.62 *dq*
				1.88 *dd*

*Not first order.

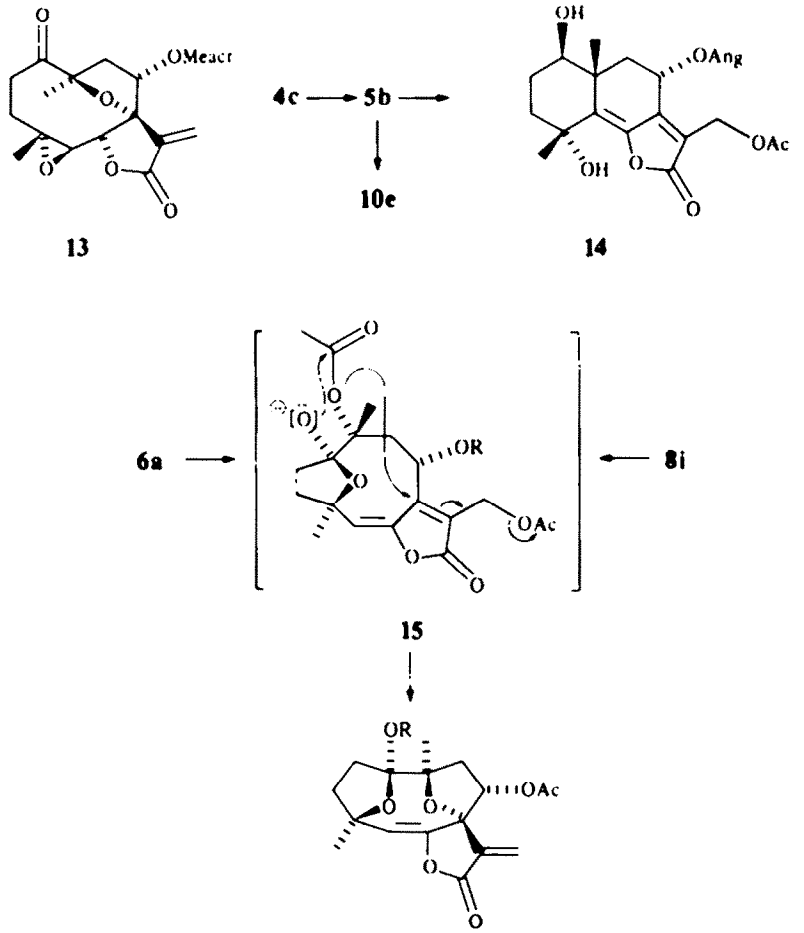
J (Hz): **1**: 1, 2 = 2, 3′ = 8; 2, 3 = 2.5; 3, 3′ = 13; 5, 6 = 10; 5, 15 = 1; 8, 9 = 10.5; 8, 9′ = 5; 9, 9′ = 12.5; compounds **9a** and **9b**: 2, 3 = 7; 2, 3′ = 2.5; 2, 9′ = 2, 14 = 3; 3, 3′ = 13.5; 5, 6 = 9; 5, 15 = 1; 8, 9 = 11; 8, 9′ = 5; 9, 9′ = 13; 13, 13′ = 13; (**9a**: 6, 13 = 6, 13′ = 1; 8, OH = 8); compound **13**: 5, 6 = 9.5; 8, 9 = 7.5; 8, 9′ = 7.5; 9, 9′ = 13.5.

V. brachiata Benth. ex Oerst. afforded **6a** [8], while *V. aurea* Mart ex DC. contained **6a**, **8i** [9] and **8k** [15]; a reinvestigation of *V. mariana* Mart. [12] gave **4d** [6], **5a** and 11β,13-dihydroxy-11,13-dihydroeremanthin [21] and *V. greggii* A. Gray **6b** as previously [22], and **8l** [18].

Pseudoelephantopus spicatus (B. Juss.) Rohr. gave **2a**, **6a** and **13**. The structure of **13** followed from the ^{1}H NMR spectral data (Table 6) which were in part similar to that of **16b** (see below). The absence of couplings from the signal of H-13 required substitution at C-7. Spin decoupling allowed the assignment of most signals though those of H-2 and H-3 were not first order multiplets. Obviously **13** was formed via the 10-*O*-desacetyl derivative of **6b** by an addition–elimination process starting with an alcoholate ion of the 10-hydroxy group.

As mentioned above the 4,5-epoxyglaucolide **3** was converted easily to **7a** by mild treatment with potassium carbonate. Similarly **4c** was transformed probably via **5b** to **14** and **10e**. The structure of **14** was deduced from the ^{1}H NMR spectral data (Table 7). All signals could be assigned by spin decoupling and the stereochemistry followed from the couplings observed and from comparison of the spectra with those of closely related lactones. The lactones **14** and **10e** most likely were formed by reaction of the 5,6-double bond of **5b** with the epoxide carbons C-1 and C-2 respectively. While the corresponding decalin ion then is transformed by loss of a proton to **14**, the formation of **10e** required a hydride migration from C-5 to C-6 followed by addition of the 4-hydroxy oxygen at C-5.

Compounds **6a** and **8i** reacted readily with base, both giving **16b**, while **6a** most likely was first transformed to an intermediate **15** by opening of the epoxide and hemiacetal formation. Transesterification and addition–elimination at the $\Delta^{7(11)}$-double bond then presumably led to **16a** which was hydrolysed to **16b** (see Scheme 1). The structure of **16b** was deduced from the ^{1}H NMR spectrum (Table 7) and by NOE difference spectroscopy. Clear NOEs between H-8β and H-3β, between H-14 and H-9 and between H-15 and H-5 required the proposed configurations. The absence of a keto band in the IR spectrum and the molecular formula further supported the structure. The high reactivity of the 4,5-epoxides also could be observed in the case of **2b** and **20** [20]. Base treatment of **20** gave the allene carbinol **21** [20] and the isomeric 1,2-dehydro bourbonenolides **22b** and **23** as well as the corresponding desacetyl derivative **22a**. The structures of these products followed from their



Scheme 1.

Table 7. ^{1}H NMR spectral data of sesquiterpene lactones **14**, **16b**, **17** **19**, **22a**, **22b** and **23** (400 MHz, $CDCl_3$, TMS as int. standard)

			17a (C_6D_6)*		**17b**†						
	14	**16b**	Conf. I	Conf. II	Conf. I	Conf. II	**18**	**19**	**22a**	**22b**	**23**
H-1	3.40 *dd*		4.55 *d br*	4.53 *d br*	4.83 *d br*	4.86 *d br*	2.38 *d br*	2.24 *ddd*		—	
H-2	2.04 *m*	2.11 *m*	2.64 *dddd*	‡	2.76 *dddd*	2.29 *dddd*	‡	‡	5.56 *ddd*	5.56 *ddd*	5.88 *ddd*
H-2′	1.58 *m*		‡	‡	‡	‡	‡	‡	—	—	—
H-3	1.90 *m*	2.29 *m*	‡	‡	‡	‡	‡	‡	2.82 *dd br*	2.82 *ddd br*	2.75 *d br*
H-3′		2.01	‡	‡	‡	‡	‡	‡	2.44 *ddd*	2.47 *ddd*	2.35 *ddd*
H-5	—	5.42 *s*	5.81 *s*	4.63 *s*	5.69 *s*	5.01 *s*	2.69 *d*	2.42 *d*	3.91 *ddd*	3.93 *ddd*	3.52 *dd br*
H-8	6.11 *dd*	5.52 *dd*	6.34 *dd*	5.51 *dd*	6.34 *dd*	5.52 *dd*	6.35 *dd br*	6.14 *dd br*	4.81 *ddd*	5.95 *ddd br*	6.29 *dd br*
H-9	2.28 *dd*	2.78 *dd*	2.59 *dd br*	2.16 *dd*	2.83 *dd*	2.36 *dd*	2.59 *dd*	2.43 *dd*	2.58 *dd*	2.52 *dd*	2.66 *dd*
H-9′	2.21 *dd*	2.01 *dd*	2.04 *d br*	2.39 *d br*	2.23 *d br*	2.63 *d br*	1.94 *dd*	1.85 *dd*	2.39 *dd*	2.43 *dd*	2.08 *dd*
H-13	4.98 *d*	6.41 *s*	4.94 *d*	5.21 *d*	4.62 *d br*	4.69 *s br*	4.89 *d br*	4.86 *dd*	5.15 *d br*	4.98 *dd*	4.93 *dd*
H-13′	4.78 *d*	5.85 *s*	4.91 *d*	5.00 *d*	4.56 *d br*		4.75 *d br*	4.75 *d br*	4.94 *d br*	4.75 *d br*	4.81 *dd*
H-14	1.16 *s*	1.57 *s*	1.86 *dd*	1.81 *dd*	1.92 *dd*	1.81 *dd*	1.09 *s*	1.26 *s*	1.44 *s*	1.44 *s*	1.51 *s*
H-15	1.49 *s*	1.55 *s*	1.42 *s*	1.16 *s*	1.71 *s*	1.48 *s*	1.22 *s*	1.38 *s*	1.13 *s*	1.16 *s*	1.61 *s*
OAc	1.98 *s*	2.00 *s*	1.68 *s*	1.65 *s*	–	—	2.05 *s*	2.01 *s*	2.07 *s*	2.15 *s*	2.07 *s*
							—	-	–	1.98 *s*	2.08 *s*
OH			‡	‡	‡	‡	2.95 *s*	‡	4.89 *d*	2.03 *s*	2.02 *s*
OR	6.13 *qq*	—	6.95 *qq*		6.92 *qq*	7.01 *qq*	6.91 *qq*	6.89 *qq*		-	
	1.94 *qq*		1.76 *dq*		1.88 *dq*	1.93 *dq*	1.86 *s br*	1.84 *dq*			
	1.83 *dq*		1.33 *dq*		1.87 *dq*	1.91 *dq*	1.83 *d br*	1.82 *d*			

*Ca 9:1.

†Ca 3:2.

‡Unassigned multiplets.

J (Hz): Compound **14**: 1, 2 = 7.5; 1, 2′ = 11.5; 8, 9 = 9; 8, 9′ = 4.5; 9, 9′ = 14.5; 13, 13′ = 13; compound **16b**: 8, 9 = 7.5; 8, 9′ = 4.5, 9, 9′ = 14; compounds **17a** and **17b**: 1, 2 = 2, 2′ = 2, 3′ ≈ 13; 1, 14 = 1; 2, 3 = 2; 13, 13′ = 13; Conf. I: 8, 9 = 5.5; 8, 9′ = 2.5; 9, 9′ = 14; Conf. II: 8, 9 = 2; 8, 9′ = 11; 9, 9′ = 12; compound **18**: 1, 2 = 1, 5 = 7; 8, 9 = 9; 8, 9′ = 7; 13, 13′ = 12.5; compound **19**: 1, 2 = 2, 1, 2′ = 4; 1, 5 = 6; 8, 9 = 9; 8, 9′ = 4; 8, 13 = 1; 9, 9′ = 15.5; 13, 13′ = 13; compounds **22a** and **22b**: 2, 3 = 2, 3′ = 3, 5 = 3′, 5 = 3; 2, 5 = 2; 3, 3′ = 16.5; 8, 9 = 11; 8, 9′ = 7.5; 8, 13 = 1.5; 9, 9′ = 14.5; 13, 13′ = 12.5; (compound **22b**: 8, OH = 6.5); compound **23**: 2, 3 = 1.5; 2, 3′ = 3.5; 2, 5 = 3; 3, 3′ = 16.5; 3, 5 = 2.5; 3′, 5 = 0.5; 8, 9 = 8.5; 8, 9′ = 8; 8, 13 = 1.5; 9, 9′ = 14.5; 13, 13′ = 13.

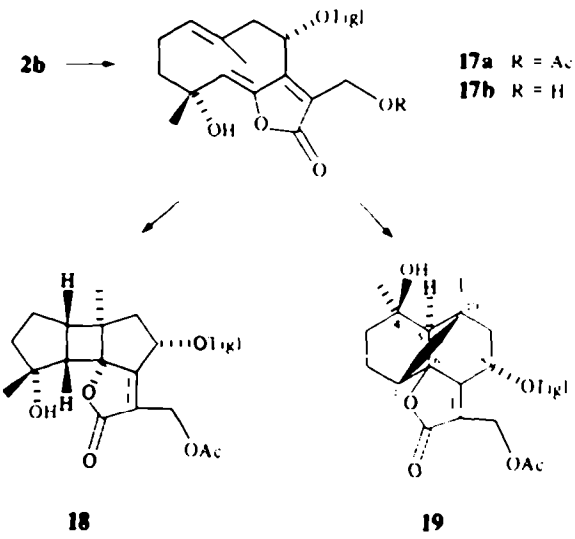
Table 8. NOE data for sesquiterpene lactones (intensities in parentheses)

irr. of	3	4c	5b	7a	8a	9c	10a	12b	16b	17a(I)	17a(II)	18	19	21	22b	23
H-5		H-3 (7)		H-10 (6) H-15				H-3α (6)			H-8 (15)	H-1 (8) H-8 (12) H-15		H-3α (6) OH		
H-6						H-8 (5) H-15 (8)	H-8 (10)									
H-8					H-2β H-3β	H-6 (5) H-15 (5)			H-3β (10)		H-5 (12)	H-1 (6) H-5 (12)		H-15	H-15	
H-10	H-8 (10)			H-5 (8) H-8 (6)												
H-14		H-8 (12) H-9 (5)	H-8 (6) H-9 (7)		H-1 (7) H-8 (8)	H-9α (6)	H-6 (8) H-8 (8)	H-2α (6) H-9 (5) H-9′ (5)	H-9 (8)	H-5 (8)		H-9α (8)	H-5 (2) H-1 (2)	H-9α (7)	H-2 (8) H-9α (8)	H-2 (10) H-9β (10)
H-15	H-6 (10) H-8 (6)	H-6 (12) H-8 (7)	H-8 (19)	H-5 (8)		H-6 (6) H-8 (8)	H-6 (12)	H-2β (12)	H-5 (15)		H-5 (10)	H-5 (10)	H-5 (12)	H-8 (12)	H-3β (10) H-8 (12)	H-3β (6)
OH														H-5 (10) H-15	H-5 (8)	H-5 (5)

^{1}H NMR spectra (Table 7). As in the case of **9a–9c** the configuration of the allenic bond in **20** and **21** could be assigned as shown. The configuration of the Δ^5-double bond in **21** previously not written clearly [20] also is *E*. The structures of the cyclobutane derivatives **22b** and **23** were deduced by spin decoupling which allowed the assignment of all signals. The presence of an allylic coupling between H-5 and H-2 as well as of homoallylic couplings between H-5 and H-3 and H-8 and H-13 allowed combination of the obtained sequences. The stereochemistry was established by NOE difference spectroscopy. A clear NOE between H-15 and H-8 in the case of **22b** required a *syn*-configuration. The corresponding *anti*-stereochemistry of **23** could be deduced from the NOEs between H-14, H-2 and H-9β and between H-15 and H-2β. In both cases a NOE between the hydroxyl proton and H-5 indicated a 4β-methyl group.

Reaction of **2b** with base gave first **17a** and by hydrolysis **17b**. The structures followed from the ^{1}H NMR spectra (Table 7). On standing in solution in daylight **17a** was transformed to a mixture of the isomeric cyclobutane derivatives **18** and **19**. All data of **18** were identical with those of a naturally occurring bourbonenolide (**13** of ref. [10]). Additional NOE difference spectroscopy results showed that the proposed stereochemistry of this substance as well as its congeners numbered **12–14** in lit. [10] have to be revised (see Table 9). Thus clear NOEs were observed between H-5, H-8 and H-15 and between H-14 and H-9α (The configuration proposed for compounds numbered **18a** and **18b** in lit. [20] could be established by clear NOEs between H-14 and H-1 (7%), H-5 (2%) and H-9β (6%), between H-15 and H-5 (8%) as well as between H-1 and H-5 (10%)). The isomer **19** showed NOEs between H-5, H-14 and H-15. Furthermore a typical 6 Hz W-coupling between H-1 and H-5 indicated a cyclobutane derivative.

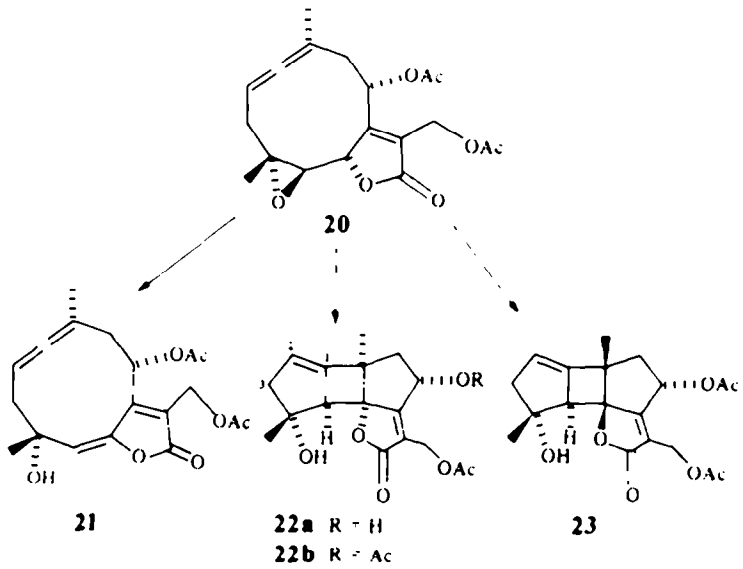
Compounds **18** and **19** obviously are formed by a photochemically induced [2 + 2]-cyclo addition. The ^{1}H NMR spectrum of **17a** showed that this lactone was present in two conformations with different proportions



Scheme 2.

in chloroform and benzene. NOE difference spectroscopy allowed the assignment of the nature of the conformers. In the preferred one the C-10 methyl is below and the lactone ring above the plane while in the second conformer both are below the plane. As the relative amounts of the isomers obtained is influenced by the solvent most likely the two conformers are transformed to the different isomers. This assumption nicely agree with inspection of models.

The observed base catalysed transformations of several sesquiterpene lactones from *Vernonia* species also may be of interest in connection with their biogenesis. Most likely nearly all types of sesquiterpene lactones reported from *Vernonia* species are biogenetically closely related. Accordingly, it is very likely that the stereochemistry of the lactones is always the same at C-4 (4β-methyl), C-8



Scheme 3.

Table 9. Summary of sesquiterpene lactone formulae which have had to be amended

New overall structure (this paper)	Formulae numbers in previous papers (lit. references in brackets)*
3	1–4 (1α-OR) [2], 5/6 [2]
5	4 [5]
8a	36† [4], 7/8 [5], 14† [12], 7† [14]
8b	10/11 [2], 21–23 [4], 29–31 [4]
8h	8–13 [9], 13a–13c [12], 3/4 [14], 3–7 [15] 1/2 [16], 1g/1h [17], 1a–1f [18]
18	12–14 [10]
20	4‡ [19], 15‡ [20], 16 [20]
21	13 [5], 17 [20]

*Other authors have also pointed out in print that these structures were in error, see refs [17, 26].

†Δ^1.

‡4,5-Desoxy.

(8α-OR), C-10 (10α-methyl,* but 10β-methyl with oxygen function at C-10), C-6 (6β-H if present) and *E*-configuration of the Δ^5-double bond.

The isolation of **6a** from *Vernonia arctioides* may be of interest as this species is placed in the section *Leiboldia* [23] which together with *Lepidonia* are proposed to be ancient relictual elements within the New World Vernonias. From *V. jonesii*, however, which belongs to the same group of more primitive species, a *bis*-epoxide, which lacks the 7(11)-double bond, was isolated [24]. A detailed discussion of biogenetic relationships of the sesquiterpene lactones in the tribe Vernonieae will be published elsewhere.

EXPERIMENTAL

The air dried plant material was extracted with MeOH–Et_2O–petrol (1:1:1) and the extracts obtained after treatment with MeOH to remove long chain hydrocarbons were separated in the usual way [25] first by CC (SiO_2) followed by TLC (SiO_2, PF 254) and in part by HPLC (RP 8, flow rate, 3 ml/min, *ca* 100 bar).

The extract of the aerial parts of *Vernonia patens* (200 g), collected in Peru, voucher RMK 9148, gave a polar CC fraction (Et_2O, Et_2O–MeOH, 9:1), which was separated again by CC affording three fractions: 1 (Et_2O–petrol, 1:1), 2 (Et_2O) and 3 (Et_2O–MeOH, 19:1). TLC of 1 (Et_2O–petrol, 3:1) gave 150 mg **4c** (R_f 0.61) and a mixture, which by repeated TLC ($CHCl_3$, five developments) afforded 40 mg **3** (R_f 0.45), 20 mg **4c** (R_f 0.48) and 6 mg **4d** (R_f 0.38). TLC of fraction 2 (Et_2O) gave 30 mg **8b** (R_f 0.66) and a mixture, which by repeated TLC ($CHCl_3$–Et_2O, 3:1) gave 10 mg **5b** (R_f 0.33) and 2 mg **5a** (R_f 0.28). TLC of fraction 3 ($CHCl_3$–Et_2O, 3:1, three developments) afforded 5 mg **8a** (R_f 0.45), 3 mg **10c** (R_f 0.4), 2 mg **10e** (R_f 0.38) 2 mg **10a** (R_f 0.35) and 3 mg **7a** (R_f 0.21).

The extract of the aerial parts of *Vernonia jalcana* (500 g, collected in Peru, voucher RMK 9250) gave a crude polar CC fraction (Et_2O and Et_2O–MeOH, 9:1) which after repeated CC afforded three fractions: 1 (Et_2O), 2 (Et_2O–MeOH, 9:1) and 3 (Et_2O–MeOH, 3:1). HPLC (MeOH–H_2O, 3:2) of fraction 1 gave 10 mg **8d** (R_t 4.3 min), 4 mg **8f** (R_t 6.0 min), 5 mg **8e** (R_t 7.8 min), 3.5 mg **8g** (R_t 11.2 min) and 2 mg apigenin 7-methyl ether. HPLC (MeOH–H_2O, 1:1) of fraction 2 gave 2 mg **8c** (R_t 4.5 min), 10 mg **12b** (R_t 5.9 min), 52 mg **4a** (R_t 6.2 min), 51 mg **8d** (R_t 6.9 min), 21 mg **8h** (R_t 7.8 min), 30 mg **6a** (R_t 10.5 min), 6 mg **8f** (R_t 10.9 min), 15 mg **4d** (R_t 14.0 min), 3 mg **2a** (R_t 14.9 min), 5 mg **4b** (R_t 16.2 min), 4.7 mg **8e** (R_t 17.7 min), 1.5 mg **11** (R_t 20.4 min), 13 mg **6b** (R_t 27.0 min) and a mixture (R_t 4.9 min), which by TLC (CH_2Cl_2–C_6H_6–Et_2O, 2:2:1, five developments) gave 1.5 mg **10d** (R_f 0.85) and 3 mg **10b** (R_f 0.60). HPLC (MeOH–H_2O, 3:2) of 40 mg of fraction 3 gave 2 mg **12a** (R_t 3.2 min) 6 mg **12b** (R_t 4.0 min) and an unresolved mixture. The remaining part of fraction 3 was acetylated (AcCl, $C_6H_5NMe_2$, 72 hr, 20°). HPLC (MeOH–H_2O, 1:1) gave 8 mg **12b**-acetate (R_t 8.0 min), 3 mg **12a** (R_t 5.0 min), 15 mg **12a**-acetate (R_t 8.5 min), 4 mg **12c** (R_t 21.0 min) and 3 mg **12d**-acetate (R_t 22.0 min).

The aerial parts of *Vernonia cotoneaster* (130 g, collected in the Province Bahia, Brazil, voucher RMK 8783) gave by CC a polar fraction (Et_2O, Et_2O–MeOH, 9:1), which by TLC (Et_2O–petrol, 3:1) afforded 15 mg **9c** (R_f 0.4), 3 mg **9a** (R_f 0.2), 12 mg **9b** (R_f 0.27) and 0.5 mg **1** (R_f 0.3).

The extract of the aerial parts of *Pseudoelephantopus spicatus* (170 g, collected in Jamaica, voucher Jam 9) afforded a polar CC fraction (Et_2O and Et_2O–MeOH, 9:1) which gave after TLC (Et_2O) a mixture and 180 mg **6a**. HPLC of the mixture (MeOH–H_2O, 7:3) gave 2 mg **13** (R_t 2.0 min), 10 mg **6a** (R_t 2.2 min) and 2 mg **2a** (R_t 3.7 min).

Similarly the extract of the aerial part of *Vernonia acuminata* (170 g, collected in Jamaica, voucher Jam 19) gave 100 mg **6a**, that of the aerial parts of *V. arctioides* (230 g, collected in Mexico, voucher TEX 15527) gave 20 mg **6a**, that of the aerial parts of *V. aurea* (450 g, collected in the province Bahia, Brazil, voucher RMK 8793) gave 25 mg **6a**, 100 mg **8i** and 40 mg **8k**, that of the aerial parts of *V. brachiata* (500 g, collected in Costa Rica) 15 mg **6a**, that of the roots of *V. mariana* (100 g, collected in the province Bahia, Brazil, voucher RMK 8558) 3 mg **4d**, 1 mg **5a** and 1 mg 11β,13-dihydroxy-11,13-dihydroeremanthin and that of the aerial parts of *V. greggii* (120 g, collected near Monterrey, Mexico, voucher 1643/84) 10 mg **6b** and 10 mg **8i**.

2β-Acetoxy-8α,13-dihydroxygermacra-1(10),4,7(11)-trien-6α,12-olide (**1**). Colourless oil; CIMS *m/z* (rel. int.): 323 $[M+1]^+$ (100), 305 $[323-H_2O]^+$ (21), 263 $[323-HOAc]^+$ (28), 245 $[263-H_2O]^+$ (49).

8-Desacylmarginatin 8-O-acetate (**2a**). Colourless crystals, mp 112–114°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770 (γ-lactone), 1750, 1230 (OAc); MS *m/z* (rel. int.): 364.152 $[M]^+$ (1) (calc. for $C_{19}H_{24}O_7$: 364.152), 304 $[M-HOAc]^+$ (3), 244 $[304-HOAc]^+$ (20), 216

*So far the only exceptions are compound **1** in ref. [3] and **1–6** in ref. [13].

[244 – CO]$^+$ (60), 68 (100).

$$[\alpha]_{24}^{\lambda} = \frac{589}{-35}\ \frac{578}{-35}\ \frac{546}{-41}\ \frac{436\,nm}{-72}\ (CHCl_3;\ c\ 0.3).$$

Stilpnotomentolide 8-O-*angelate* (3). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1745, 1230 (OAc), 1725 (OCOR), 1710 (C=O); MS *m/z* (rel. int.): 420.178 [M]$^+$ (3) (calc. for $C_{22}H_{28}O_6$: 420.178), 360 [M – HOAc]$^+$ (5), 321 [M – OCOR]$^+$ (3), 261 [321 – HOAc]$^+$ (4), 260 [360 – RCOOH]$^+$ (5), 83 [C_4H_7CO]$^+$ (100), 55 [83 – CO]$^+$ (95).

$$[\alpha]_{24}^{\lambda} = \frac{589}{-77}\ \frac{578}{-80}\ \frac{546}{-92}\ \frac{436\,nm}{-161}\ (CHCl_3;\ c\ 0.76).$$

8-*Desacylvernonataloide* 8-O-*acetate* (4a). Colourless crystals, mp 169–171°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1760, 1240 (OAc); MS *m/z* (rel. int.): 320.126 [M – AcOH]$^+$ (4) (calc. for $C_{17}H_{20}O_6$: 320.126), 278 [320 – ketene]$^+$ (14), 260 [320 – AcOH]$^+$ (10), 69 (90), 57 (100).

$$[\alpha]_{24}^{\lambda} = \frac{589}{+106}\ \frac{578}{+110}\ \frac{546}{+124}\ \frac{436\,nm}{+207}\ (CHCl_3;\ c\ 1.25).$$

8-*Desacylvernonataloide* 8-O-*isobutyrate* (4b). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770 (γ-lactone), 1740, 1240 (OCOR, OAc); MS *m/z* (rel. int.): 348.157 [M – AcOH]$^+$ (1.5) (calc. for $C_{19}H_{24}O_6$: 348.157), 320 [M – RCO_2H]$^+$ (1), 278 [348 – $Me_2C{=}C{=}O$]$^+$ (3), 260 [348 – RCO_2H]$^+$ (6), 71 [C_3H^7CO]$^+$ (100).

8-*Desacylvernonataloide* 8-O-*angelate* (4c). Colourless crystals, mp 126.5°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1750, 1230 (OAc), 1725 (OCOR); MS *m/z* (rel. int.): 420.178 [M]$^+$ (1) (calc. for $C_{22}H_{28}O_6$: 420.178), 360 [M – HOAc]$^+$ (2), 321 [M – OCOR]$^+$ (2), 320 [M – RCOOH]$^+$ (17), 261 [321 – HOAc]$^+$ (3), 260 [320 – HOAc]$^+$ (4), 83 [C_4H_7CO]$^+$ (90), 55 [83 – CO]$^+$ (100).

8α-(2-*Methylacryloyloxy*)-*compactifloride* (5a). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1750 (OAc), 1720 (C=CCO_2R); CIMS *m/z* (rel. int.): 407 [M + 1]$^+$ (4), 389 [407 – H_2O]$^+$ (3), 321 [407 – RCO_2H]$^+$ (7), 261 [321 – HOAc]$^+$ (21), 243 [261 – H_2O]$^+$ (21).

8α-*Angeloyloxycompactifloride* (5b). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (γ-lactone), 1750, 1235 (OAc), 1725 (OCOR); MS *m/z* (rel. int.): 360.157 [M – HOAc]$^+$ (2) (calc. for $C_{20}H_{24}O_6$: 360.157), 260 [360 – RCOOH]$^+$ (2), 83 [C_4H_7CO]$^+$ (90), 55 [83 – CO]$^+$ (100).

$$[\alpha]_{24}^{\lambda} = \frac{589}{-99}\ \frac{578}{-105}\ \frac{546}{-120}\ \frac{436\,nm}{-232}\ (CHCl_3;\ c\ 0.58).$$

Vernopatensolide 8-O-*angelate* (7a). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1805, 1790 (γ-lactone), 1750, 1230 (OAc), 1725 (OCOR), 1710 (C=O); MS *m/z* (rel. int.): 420.178 [M]$^+$ (0.5) (calc. for $C_{22}H_{28}O_6$: 420.178), 403 [M – OH]$^+$ (0.5), 360 [M – HOAc]$^+$ (1), 320 [M – RCOOH]$^+$ (4), 260 [320 – HOAc]$^+$ (4), 83 [C_4H_7CO]$^+$ (100), 55 [83 – CO]$^+$ (90).

$$[\alpha]_{24}^{\lambda} = \frac{589}{+37}\ \frac{578}{+40}\ \frac{546}{+46}\ \frac{436\,nm}{+101}\ (CHCl_3;\ c\ 0.2).$$

15 mg 3 were stirred for 2 hr at 60° in 0.5 ml dioxane and 0.1 ml 1 N K_2CO_3. Usual work-up and TLC (Et_2O) gave 10 mg 7a, identical with the natural product, and 3 mg 7b. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1725 (OCOR), 1710 (C=O); MS *m/z* (rel. int.): 378 [M]$^+$ (0.5), 360 [M – H_2O]$^+$ (0.5), 278 [M – RCOOH]$^+$ (2) (calc. for $C_{15}H_{18}O_5$: 278.115), 260 [278 – H_2O]$^+$ (4), 83 [C_4H_7CO]$^+$ (100), 55 [83 – CO]$^+$ (86).

8α-*Angeloyloxy*-10α-*hydroxy*-1-*desoxyhirsutinolide* 13-O-*acetate* (8a). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1745, 1230 (OAc), 1720 (OCOR); MS *m/z* (rel. int.): 420.178 [M]$^+$ (3) (calc. for $C_{22}H_{28}O_6$: 420.178), 360 [M – HOAc]$^+$ (8), 260 [360 – RCOOH]$^+$ (40), 218 [260 – C_2H_2O]$^+$ (75), 83 [C_4H_7CO]$^+$ (100), 55 [83 – CO]$^+$ (100).

$$[\alpha]_{24}^{\lambda} = \frac{589}{+24}\ \frac{578}{+26}\ \frac{546}{+33}\ \frac{436\,nm}{+83}\ (CHCl_3;\ c\ 0.33).$$

8α-*Angeloyloxyhirsutinolide* 13-O-*acetate* (8b). Colourless crystals, mp 125°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (γ-lactone), 1750, 1230 (OAc), 1715 (OCOR); MS *m/z* (rel. int.): 420.178 [M]$^+$ (3) (calc. for $C_{22}H_{28}O_6$: 420.178), 360 [M – HOAc]$^+$ (1), 260 [360 – RCOOH]$^+$ (8), 83 [C_4H_7CO]$^+$ (100), 55 [83 – CO]$^+$ (76).

$$[\alpha]_{24}^{\lambda} = \frac{589}{+88}\ \frac{578}{+95}\ \frac{546}{+112}\ \frac{436\,nm}{+232}\ (CHCl_3;\ c\ 0.4).$$

8α-*Acetoxy*-10α-*hydroxyhirsutinolide* (8c). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3521 (OH), 1765 (γ-lactone), 1750, 1230 (OAc); MS *m/z* (rel. int.): 354.1315 [M]$^+$ (6) (calc. for $C_{17}H_{22}O_6$: 354.1315), 336 [M – H_2O]$^+$ (1), 318 [336 – H_2O]$^+$ (1), 59 (100).

8α-*Acetoxy*-10α-*hydroxy*-13-O-*methyl hirsutinolide* (8d). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OH), 1770 (γ-lactone), 1750 (OAc); MS *m/z* (rel. int.): 368.147 [M]$^+$ (8) (calc. for $C_{18}H_{24}O_6$: 368.147), 353 [M – Me]$^+$ (6), 336 [M – MeOH]$^+$ (2), 309 [M – OAc]$^+$ (4), 308 [M – AcOH]$^+$ (3.5), 276 [308 – MeOH]$^+$ (16), 55 (100).

8α-*Methacryloyloxy*-10α-*hydroxy*-13-O-*methyl hirsutinolide* (8e). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OH), 1770 (γ-lactone), 1730 (OCOR); MS *m/z* (rel. int.): 394.163 [M]$^+$ (0.2) (calc. for $C_{20}H_{26}O_6$: 394.163), 377 [M – OH]$^+$ (0.3), 309 [M – OCOR]$^+$ (0.8), 308 [M – RCO_2H]$^+$ (0.6), 276 [308 – MeOH]$^+$ (5), 234 (20), 69 [C_3H_5CO]$^+$ (100).

8α-*Acetoxy*-10α-*hydroxy*-1,13-bis-O-*methyl hirsutinolide* (8f). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OH), 1770 (γ-lactone), 1750, 1230 (OAc); MS *m/z* (rel. int.): 382.163 [M]$^+$ (2.5) (calc. for $C_{19}H_{26}O_6$: 382.163), 351 [M – OMe]$^+$ (6), 350 [M – MeOH]$^+$ (2.5), 290 [350 – AcOH]$^+$ (10), 248 [290 – C_2H_2O]$^+$ (40), 232 (85), 55 (100).

8α-*Methacryloyloxy*-10α-*hydroxy*-1,13-bis-O-*methyl hirsutinolide* (8g). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1780 (γ-lactone), 1740 (OCOR); MS *m/z* (rel. int.): 408.178 [M]$^+$ (1) (calc. for $C_{21}H_{28}O_6$: 408.178), 376 [M – MeOH]$^+$ (0.5), 345 [377 – MeOH]$^+$ (0.2), 290 [376 – RCO_2H]$^+$ (6), 248 (20), 232 (40), 69 [C_3H_5CO]$^+$ (100).

Bis-*desacetyl vernoallenolide* (9a). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600, 3400 (OH), 1945 (allene), 1760 (γ-lactone); MS *m/z* (rel. int.): 262.121 [M]$^+$ (0.5) (calc. for $C_{15}H_{18}O_4$: 262.121), 244 [M – H_2O]$^+$ (9), 211 [226 – Me]$^+$ (6), 105 (100).

13-*Desacetyl vernoallenolide* (9b). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3450 (OH), 1750 (γ-lactone, OAc); MS *m/z* (rel. int.): 244.110 [M – HOAc]$^+$ (41) (calc. for $C_{15}H_{16}O_3$: 244.110), 226 [244 – H_2O]$^+$ (24), 211 [226 – Me]$^+$ (25), 183 [211 – CO]$^+$ (21), 105 (100).

8α-*Angeloyloxy*-4α,5α-*epoxyjalcaguaianolide* (10a). Colourless oil which was purified by acetylation (AcCl, $C_6H_5NMe_2$, 24 hr, 20°). TLC (Et_2O) gave 10a-diacetate; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1750 (OAc), 1730 (OCOR); MS *m/z* (rel. int.): 462.189 [M]$^+$ (6) (calc. for $C_{24}H_{30}O_9$: 462.189), 403 [M – OAc]$^+$ (1), 402 [M – HOAc]$^+$ (0.5), 360 [402 – ketene]$^+$ (1), 342 [402 – HOAc]$^+$ (0.5), 260 [360 – RCOOH]$^+$ (3), 242 [342 – RCOOH]$^+$ (4), 83 [C_4H_7CO]$^+$ (100), 55 [83 – CO]$^+$ (56).

8α-*Acetoxy*-4α,5α-*epoxy*-13-O-*methyl jalcaguaianolide* (10b). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1770 (γ-lactone), 1750, 1220 (OAc); MS (CI, isobutane) *m/z* (rel. int.): 353 [M + 1]$^+$ (20) (calc. for $C_{17}H_{24}O_7$ + 1), 335 [M + 1 – H_2O]$^+$ (100), 293 [M + 1 – AcOH]$^+$ (25), 261 [293 – MeOH]$^+$ (16), 243 [261 – H_2O]$^+$ (50).

8α-Angeloyloxy-4α,5α-epoxy-13-O-methyl jalcaguaianolide (**10c**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1735 (OCOR); MS *m/z* (rel. int.): 392 [M]$^+$ (0.5), 360.155 [M − MeOH]$^+$ (3) (calc. for $C_{20}H_{24}O_6$: 360.155), 260 [360 − RCOOH]$^+$ (4), 83 [C_4H_7CO]$^+$ (100), 55 [83 − CO]$^+$ (50).

8α-Acetoxy-4α,5α-epoxyjalcaguaianolide 13-O-acetate (**10d**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1775 (γ-lactone), 1755, 1230 (OAc); MS (CI, isobutane) *m/z* (rel. int.): 381 ($C_{19}H_{25}O_8$) [M + 1]$^+$ (10), 363 [M + 1 − H_2O]$^+$ (20), 321 [363 − ketene]$^+$ (40), 303 [363 − AcOH]$^+$ (10), 243 [303 − AcOH]$^+$ (100).

8α-Angeloyloxy-4α,5α-epoxyjalcaguaianolide 13-O-acetate (**10e**). Colourless oil, which was purified as its acetate (**10a**-diacetate) which was identical with the acetylation product of **10a** (see above).

4α-Hydroxy-8α-isobutyroyloxy-4,5-dihydro-5,6-dehydro-10,13-bis-O-methyljalcaguaianolide (**11**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1770 (γ-lactone), 1740 (OCOR); CIMS *m/z* (rel. int.): 395 [M + 1]$^+$ (25), 377 [M + 1 − H_2O]$^+$ (20), 363 [M + 1 − MeOH]$^+$ (50), 275 [363 − RCO_2H]$^+$ (50), 243 [275 − MeOH]$^+$ (55), 73 (100).

Vernojalcanolide 8-O-acetate (**12a**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3520, 3400 (OH), 1770 (γ-lactone); 1745, 1240 (OAc); MS *m/z* (rel. int.): 378.131 [M − HOAc, H_2O]$^+$ (8) (calc. for $C_{19}H_{22}O_8$: 378.131), 336 [M − ketene]$^+$ (8), 318 [M − AcOH]$^+$ (22), 276 [318 − ketene]$^+$ (55), 258 [318 − AcOH]$^+$ (30), 99 [$C_5H_7O_2$]$^+$ (90), 55 (100).

12a-*acetate*. Colourless oil; (^{1}H NMR data see Table 5); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3560, 3321 (OH), 1770 (γ-lactone), 1740-1760, 1210–1260 (OAc); MS *m/z* (rel. int.): 480.163 [M − AcOH]$^+$ (3) (calc. for $C_{23}H_{28}O_{11}$: 480.163), 420 [480 − AcOH]$^+$ (40), 378 [420 − ketene]$^+$ (20), 318 [378 − AcOH]$^+$ (40), 276 [318 − ketene]$^+$ (100), 258 [318 − AcOH]$^+$ (75), 99.045 [$C_5H_7O_2$]$^+$ (75) (calc. for $C_5H_7O_2$: 99.045); CIMS: 541 [M + 1]$^+$ (15) ($C_{25}H_{33}O_{13}$), 481 [M + 1 − AcOH]$^+$ (100), 421 [481 − AcOH]$^+$ (75).

13-O-*Methylvernojalcanolide 8-O-acetate* (**12b**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580, 3460 (OH), 1785 (γ-lactone), 1760, 1260 (OAc); MS *m/z* (rel. int.): 438.1526 [M − MeOH]$^+$ (2) (calc. for $C_{21}H_{26}O_{10}$: 438.1526), 378 [438 − AcOH]$^+$ (20), 318 [378 − AcOH]$^+$ (40), 276 [318 − ketene]$^+$ (95), 258 [318 − AcOH]$^+$ (60), 99 (100); ^{13}C NMR ($CDCl_3$): (C-1–C-15): 89.2 *s*, 30.6 *t*, 35.9 *t*, 73.3 *s*, 76.1 *d*, 76.9 *s*, 157.1 *s*, 64.9 *d*, 34.1 *t*, 84.4 *s*, 129.7 *s*, 168.9 *s*, 63.1 *t*, 19.1 *q*, 23.4 *q*, OMe: 58.5 *q*, OAc: 22.9 *q*, 21.1 *q*, 20.4 *q*, 171.3 *s*, 171.1 *s*, 170.4 *s*.

12b-*acetate*. Colourless oil; (^{1}H NMR see Table 5). ^{13}C NMR ($CDCl_3$) (C-1–C-15): 88.9 *s*, 29.9 *t*, 32.5 *t*, 84.1 *s*, 73.1 *d*, 75.9 *s*, 156.8 *s*, 64.6 *d*, 33.9 *t*, 84.4 *s*, 130.6 *s*, 168.6 *s*, 63.0 *t*, 19.6 *q*, 18.7 *q*, OMe: 58.5 *q*, OAc: 22.4 *q*, 22.1 *q*, 21.1 *q*, 20.1 *q*, 170.7 *s*, 170.6 *s*, 169.4 *s*, 168.9 *s*.

13-O-*Methylvernojalcanolide 8-O-isobutyrate* (**12c**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1770 (γ-lactone), 1755-1740, 1250–1210 (OCOR, OAc); MS *m/z* (rel. int.): 378.131 [M − MeOH, RCO_2H]$^+$ (5) (calc. for $C_{19}H_{22}O_8$: 378.131), 318 [378 − AcOH]$^+$ (15), 276 [318 − ketene]$^+$ (50), 258 [318 − AcOH]$^+$ (40), 99 (60), 71 [C_3H_7CO]$^+$ (100).

12d-*acetate*. Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3460 (OH), 1770 (γ-lactone), 1750, 1260 (OCOR, OAc); CIMS *m/z* (rel. int.): 539 [M + 1]$^+$ ($C_{26}H_{35}O_{12}$) (8), 507 [M + 1 − MeOH]$^+$ (6), 479 [M + 1 − AcOH]$^+$ (25), 421 [507 − RCO_2H]$^+$ (100), 419 [479 − AcOH]$^+$ (35).

Pseudoelephantopide 8-O-methacrylate (**13**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1740 (OCOR), 1720 (C=O); MS *m/z* (rel. int.): 333 [M − CHO]$^+$ (5), 276.100 [M − RCOOH]$^+$ (3) (calc. for $C_{15}H_{16}O_5$: 276.100), 69 [C_3H_5CO]$^+$ (100).

Reaction with K_2CO_3. (1) 15 mg **4c** were stirred in 3 ml dioxane for 1 hr at 60° with 0.5 ml 0.1 N K_2CO_3 soln. TLC (Et_2O, three developments) gave 3 mg **10e**, identical with the natural compound, and 2.5 mg **14** (R_f 0.31) (^{1}H NMR see Table 7). Similarly 3 mg **5b** gave 2 mg **10e** (R_f 0.42).

(2) 30 mg **6a** in 3 ml dioxane were stirred for 2 hr at 60° with 0.5 ml 1 N K_2CO_3 soln. TLC (Et_2O) gave 20 mg **16b** (R_f 0.48), colourless crystals, mp 137°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1750 (OAc); MS *m/z* (rel. int.): 336.121 [M]$^+$ (2) (calc. for $C_{17}H_{20}O_7$: 336.121), 318 (2) [M − H_2O]$^+$, 276 (12) [M − HOAc]$^+$, 218 (70), 163 (100), 99 (90).

(3) Similarly 50 mg **8i** gave after stirring for 90 min by TLC (Et_2O) 30 mg **16b** and 10 mg starting material.

(4) 50 mg **20** were stirred in 5 ml dioxane 90 min at 60° with 1 ml 0.1 N K_2CO_3. TLC (Et_2O) gave 30 mg **21** (R_f 0.52), 10 mg of a mixture (R_f 0.34) and 1.5 mg **22a** (R_f 0.28). Repeated TLC ($CHCl_3$–Et_2O, 2:1) of the mixture gave 7 mg **22b** (R_f 0.30) and 2.5 mg **23** (R_f 0.37). **22b**: Colourless oil; MS *m/z* (rel. int.): 362 [M]$^+$ (0.5), 302.115 [M − HOAc]$^+$ (14) (calc. for $C_{17}H_{18}O_5$: 302.165), 259 [302 − COMe]$^+$ (45), 243 [302 − OAc]$^+$ (50), 242 [302 − HOAc]$^+$ (50), 199 (100). **23**: Colourless oil; MS *m/z* (rel. int.): 362.137 [M]$^+$ (4) (calc. for $C_{19}H_{22}O_7$: 362.137), 302 [M − HOAc]$^+$ (40), 259 [302 − COMe]$^+$ (70), 243 [302 − OAc]$^+$ (66), 242 [302 − HOAc]$^+$ (62), 199 (100).

(5) 25 mg **2b** in 2 ml dioxane were stirred for 15 min with 0.6 ml 0.1 N K_2CO_3 soln at 70°. TLC ($CHCl_3$–Et_2O, 1:1) gave 15 mg **17a** and 5 mg **17b** (^{1}H NMR see Table 7). Acetate **17a** on standing in C_6H_6 at room temp. in daylight gave after TLC ($CHCl_3$–Et_2O, 1:1) 1 mg **18** (R_f 0.65), identical with natural material and 10 mg **19** (R_f 0.61), colourless oil; MS *m/z* (rel. int.): 344.162 [M]$^+$ (1) (calc. for $C_{20}H_{24}O_5$: 344.162), 262 [M − O=C=C(Me)CH=CH_2]$^+$ (4), 244 [M − RCO_2H]$^+$ (6), 218 [244 − CO]$^+$ (6), 186 (18), 83 [C_4H_7CO]$^+$ (100), 55 [83 − CO]$^+$ (70).

X-Ray analysis of **8b**. Crystals were orthorhombic, space group $P2_12_12_1$, unit cell parameters a = 20.978 Å, b = 12.175 Å, c = 12.75 Å (α, β, γ = 19°). Data were collected by aid of a four-circle diffractometer Syntex P2 using MoKα radiation. Details will be published elsewhere.

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