Phytochemistry, Vol. 22, No. 7, pp. 1637–1644, 1983.
Printed in Great Britain.

0031-9422/83 $3.00 + 0.00
Pergamon Press Ltd.

8-HYDROXYPEGOLETTIOLIDE, A SESQUITERPENE LACTONE WITH A NEW CARBON SKELETON AND FURTHER CONSTITUENTS FROM *PEGOLETTIA SENEGALENSIS**

FERDINAND BOHLMANN, JASMIN JAKUPOVIC and ANGELICA SCHUSTER

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany

(*Received* 11 *October* 1982)

Key Word Index—*Pegolettia senegalensis*; Compositae; sesquiterpene lactones; 6,12-*cis*-germacranolides, 8,12-*trans*-germacranolide; 8-hydroxypegolettiolide; 6,12-*cis*-eudesmanolides; elemanolides; germacrenoic acids; geranyl nerol derivative; fatty acid derivatives.

Abstract—The investigation of *Pegolettia senegalensis* afforded several new sesquiterpene lactones, eight *cis*-6,12-germacra-*trans*,*trans*-1(10),4,11-trienolides, five *cis*-6,12-eudesmanolides, two elemanolides, 8,14-cyclogermacra-1(10),4,7(11)-trien-6,12-olide with a new carbon skeleton, three germacra-1(10),4,11(13)-trien-12-oic acids with ester residues of 2-, 3-hydroxygeranyl nerol, 3,4-dihydroxydihydrocinnamate and a mixture of esters of 3,4-dihydroxy-dihydrocinnamyl alcohol. The structures were elucidated by high field ^{1}H NMR spectroscopy and some chemical transformations. The C-10 configuration of 6,12-*cis*-eudesmanolides from *Cladostephane divaricata* and *Inula crithmoides* most likely has to be corrected. The chemotaxonomic situation of the genus *Pegolettia* and biogenetic considerations are discussed briefly.

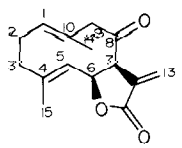
INTRODUCTION

So far nothing is known of the chemistry of the small South African genus *Pegolettia* (Compositae, tribe Inuleae) which is placed in the subtribe *Inulinae sensu amplo* [1]. As the subtribal classification of the whole tribe still causes difficulties [1], it may be of interest to study the chemistry of as many genera as possible. We have now investigated *Pegolettia senegalensis* Cass. which belongs to the Inulinae group [1].

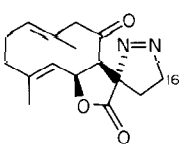
RESULTS AND DISCUSSION

The aerial parts of *Pegolettia senegalensis* afforded taraxasterol and its acetate and a very complex mixture of polar compounds. Finally, after CC and TLC and in part by HPLC, nine *cis*-6,12-germacranolides (**1**, **5** [2], **7**, **9**–**12**, **14** and **15**), one *trans*-6,12 (**4**) and one 8,12-germacranolide (**8**), a sesquiterpene lactone with a new carbon skeleton (**16**), five eudesmanolides (**17**–**21**), two elemanolides (**23** and **24**), three germacra-1(10),4,11(13)-trienoic acids (**26**–**28**), 18-hydroxygeranyl nerol (**32**), the C_{18}-diol, **34**, and a mixture of esters of 3,4-dihydroxy-dihydrocinnamyl alcohol (**37**) were obtained. The keto lactone, **1**, molecular formula $C_{15}H_{18}O_3$, was a methylene lactone

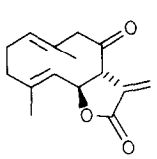
*Part 477 in the series "Naturally Occurring Terpene Derivatives". For Part 476 see Bohlmann, F., Tsankova, E. and Jakupovic, J. (1983) *Phytochemistry* **22**, (in press).



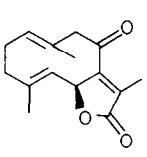
1 6α-H
2 6β-H



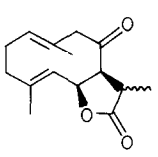
3



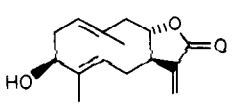
4



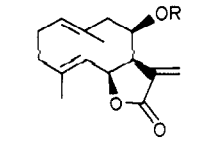
5

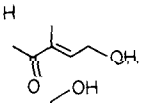
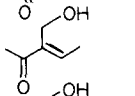
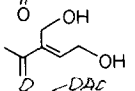
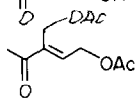
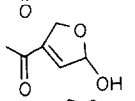
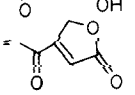
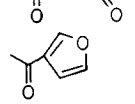


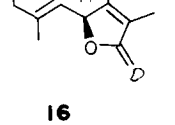
6 11α-H
7 11β-H



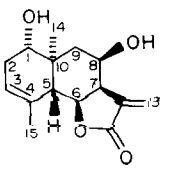
8



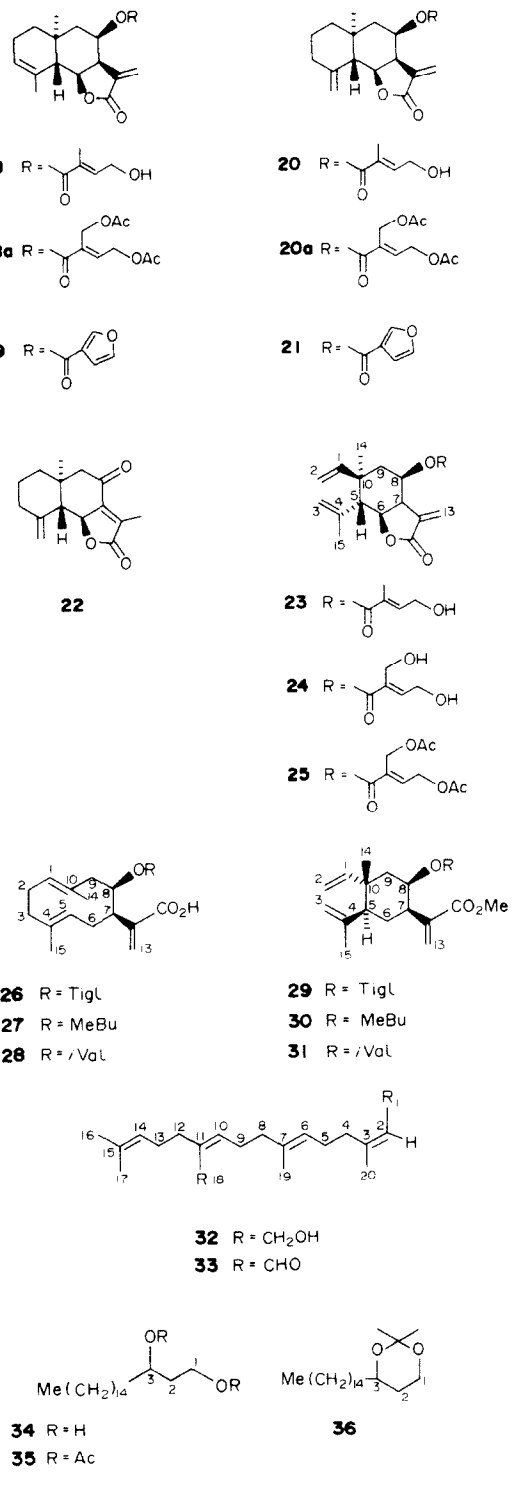
9 R = H
10 R = 
11 R = 
12 R = 
13 R = 
14 R = 
14a R = 
15 R = 



16



17



with an unconjugated keto group as shown by the ^{1}H NMR spectrum (Table 1) and the IR bands at 1780 and 1720 cm^{-1}. Spin decoupling allowed the assignment of all signals though a few were overlapping multiplets. The magnitude of the couplings $J_{7,13}$ and $J_{6,7}$ indicated a *cis*-6,7-lactone if the data were compared with those of other *cis*-6,12-germacranolides [2–6]. The position of the keto group followed from the downfield shift of the H-7 signal and those of H-9, which could be assigned because one of them was coupled with H-1 and H-2. Inspection of a model showed that **1** most likely had a conformation with both methyls below the plane. This was supported by the coupling $J_{5,6}$ and the chemical shifts of H-14 and H-15. The keto group most likely was above the plane. This assumption was established by NOE difference spectra. Irradiation of H-14 showed a clear NOE with H-7 and H-9α, that of H-9 with H-7 and H-14 (weak with H-15), that of H-7 with H-9α and H-14 (H-15 weak), that of H-1 with H-9β, that of H-5 no effect with H-14 and H-15 and that of H-15 a NOE with H-6. As the signal of H-14 and H-15 were too close, a NOE could not be determined between these two. However, the effects observed agreed with the proposed conformation.

Sodium borohydride reduction of **1** afforded **9**, identical with an alcohol also isolated from the plant, and a mixture of **1** and **6**. Compound **6** could only be obtained pure after removal of **1** by transformation to the pyrazoline, **3**. Compound **6** was the 11-epimer of **7** as revealed by the coupling $J_{7,11}$ (Table 1). Accordingly, **1** was attacked by boranate as well as by diazomethane from the α-face only. This supported the proposed conformation of the ketone, **1**. The ^{1}H NMR spectra of **3** and **6** (Table 1) further supported the proposed structures. The downfield shift of the H-6 signal in the spectrum of **3** allowed the assignment of the stereochemistry, while the coupling $J_{7,11}$ in the spectrum of **6** showed the 11β-methyl configuration.

In addition to **1**, a small amount of the isomer **4** was present. As shown by the ^{1}H NMR spectrum (Table 1) this ketone was a *trans*-6,12-lactone and the enantiomer of **2** which has been prepared by oxidation of eupatolide [7]. Accordingly, the ^{1}H NMR spectral data were identical, but the optical rotation was opposite, perhaps **4** was an artefact formed by isomerization of **1**. The second isomer, the conjugated ketone, **5**, was previously isolated from a *Wunderlichia* species [2]. The ^{1}H NMR spectral data agreed with those reported [2]. Compound **5** was probably not an artefact as acid treatment of **1** at 80° in benzene gave **22** (see below), still mixed with unchanged **1**, while **4** and **5** were absent. The formation of **22** indicated that probably first a proton-catalysed transformation to an eudesmanolide was achieved followed by double bond migration. No trace of the corresponding $\Delta^{11(13)}$-isomer of **22** was detected while a small amount of the Δ^3-isomer was visible in the ^{1}H NMR spectrum of crude **22**.

The spectral data of **7** were close to those of **6** (Table 1). However, the coupling $J_{7,11}$ showed that **7** had a 11α-methyl group. This was further supported by the chemical shift of H-13. Identical couplings of H-5–H-7 indicated again a *cis*-6,12-lactone. Spin decoupling allowed the assignment of all signals.

The ^{1}H NMR spectra of **9**–**15** (Table 2), which could be separated only by HPLC, showed that again *cis*-6,12-lactones were present. As **9** was obtained by boranate reduction of **1** its structure was established. A clear ^{1}H NMR spectrum was obtained at elevated temperature which allowed the assignment of all signals by spin decoupling. A considerable downfield shift of the H-8 signal in the spectra of **10**–**15** showed that these lactones were esters of **9**. The other signals were close to those of **9** and the nature of the ester residues followed from the additional ^{1}H NMR spectral data. While **10**–**12** were usual esters, those of **14** and **15** were rare ones. Compound **12** was very insoluble and, therefore, was transformed to

Table 1. ^{1}H NMR spectral data of compounds **1**, **3**, **4**, **6** and **7** (400 MHz, $CDCl_3$, TMS as internal standard)

	1	**3***	**4**	**6**	**7**
H-1	5.09 *br dd*	5.11 *br dd*	5.16 *br d*	5.06 *br d*	5.06 *br dd*
H-2	2.31 *m*†	2.33 *m*†	2.44 *m*†	2.32 *m*†	2.30 *m*†
H-2′	2.17 *m*†	2.22 *m*†	2.30—	2.14 *m*†	2.16 *m*†
H-3	2.25 *m*†	2.31 *m*†	2.20 *m*	2.24 *m*†	2.22 *m*†
H-3′	2.04 *m*†	2.17 *ddd*		2.13 *m*†	2.05 *m*†
H-5	4.87 *br d*	4.94 *br d*	5.07 *br dq*	4.89 *br d*	4.77 *br d*
H-6	5.20 *dd*	6.02 *dd*	4.83 *dd*	5.11 *dd*	5.31 *dd*
H-7	4.03 *br d*	3.56 *d*	4.03 *ddd*	3.47 *br dd*	3.10 *br d*
H-9α	2.95 *d*	2.75 *d*	2.98 *br d*	2.74 *d*	2.87 *d*
H-9β	3.26 *br d*	3.29 *br d*	3.44 *br d*	3.23 *br d*	3.25 *br d*
H-11	—	—	—	2.85 *dq*	2.80 *dq*
H-13	6.30 *d*	2.35 *ddd*	6.34 *d*	1.17 *d*	1.36 *q*
H-13′	5.60 *d*	1.29 *ddd*	5.46 *d*		
H-14	1.76 *br s*	1.78 *br s*	1.54 *br s*	1.80 *br s*	1.73 *br s*
H-15	1.68 *d*	1.80 *br s*	1.56 *d*	1.68 *br d*	1.69 *d*

*H-10 4.86 *ddd* and H-16′ 4.64 *ddd*.

†Not first order.

J (Hz): Compound **1**: 1, 2 = 11.5; 1, 2′ = 4; 1, 9β = 2, 9β ~ 1; 5, 6 = 10.5; 5, 15 = 1; 6, 7 = 7; 7, 13 = 1.5; 7, 13′ = 1.3; 9, 9′ = 13; compound **3**: 1, 2 = 11; 1, 2′ = 4; 2, 3′ = 3, 3′ = 11.5; 2′, 3′ = 4.5; 5, 6 = 9.5; 6, 7 = 5.5; 7, 13 = 1.5; 17, 13 = 1; 9, 9′ = 12.5; 13, 13′ = 18; 13, 16 = 4; 13, 16′ = 9; 13, 16′ = 10; 13′, 16′ = 8; 16, 16′ = 13.5; compound **4**: 1, 2 = 11.5; 5, 6 = 10.5; 5, 15 = 1.7; 6, 7 = 9.5; 7, 13 = 7, 13′ = 3.2; 9, 9′ = 10.5; compound **6**: 1, 2 = 11.5; 5, 6 = 9.5; 5, 15 = 1.5; 6, 7 = 5.5; 7, 11 = 11, 13 = 7; 9, 9′ = 13; compound **7**: 1, 2 = 11.5; 1, 2′ = 4; 5, 6 = 10; 5, 15 = 1.5; 6, 7 = 6.5; 7, 11 = 1.5; 9, 9′ = 13.5; 11, 13 = 8.

Table 2. ^{1}H NMR spectral data of compounds **9**–**16** (440 MHz, $CDCl_3$, TMS as internal standard)

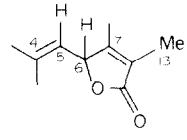
	9 (60°)	**10** (60°)	**11** (60°)	**12**	**13**	**14**	**15**	**16**
H-1	5.18 *br dd*	4.92 *br dd*	4.92 *br dd*	5.01 *br dd*	5.01 *br s*	4.99 *br s*	4.97 *br d*	5.04 *m*
H-2	2.17 *dddd*	2.05 *dddd*	2.05 *dd*	2.5 *dddd*	2.14 *m*	2.14 *dddd*	2.14 *dddd*	2.20 *m*
H-2′	2.22 *m*	2.10 *m*	2.10 *m*	2.21 *m*	2.20 *m*	2.22 *m*	2.20 *m*	1.70 *m*
H-3	2.26 *ddd*	2.19 *ddd*	2.19 *ddd*	2.30 *ddd*	2.29 *ddd*	2.31 *ddd*	2.31 *ddd*	2.20 *m*
H-3′	1.98 *ddd*	1.86 *ddd*	1.86 *ddd*	1.96 *ddd*	1.95 *ddd*	1.93 *ddd*	1.92 *ddd*	1.70 *m*
H-5	5.54 *br d*	5.29 *br s*	5.29 *br s*	5.36—	5.32 *m*	5.33*m*	5.40 *br s*	4.45 *br dq*
H-6	5.27 *dd*	5.16 *dd*	5.16 *dd*	5.25 *m*			5.33 *dd*	5.51 *dq*
H-7	3.22 *br d*	3.22*br d*	3.22 *br d*	3.41 *br s*	3.39 *br s*	3.39 *m*	3.41 *br s*	—
H-8	4.26 *br dd*	5.29 *br s*	5.29 *br s*	5.36 *br s*	5.38 *br s*	5.33 *m*	5.36 *br s*	—
H-9	2.67 *br dd*	2.74 *dd*	2.78 *dd*	2.83 *br dd*	2.76 *br d*	2.77 *br d*	2.87 *dd*	3.30 *ddd*
H-9′	2.39 *dd*	2.30 *dd*	2.31 *dd*	2.43 *dd*	2.40 *br dd*	2.44 *br dd*	2.44 *dd*	2.87 *dddd*
H-13	6.38 *d*	6.28 *d*	6.28 *d*	6.36 *d*	6.35 *d*	6.37 *d*	6.37 *d*	2.01 *d*
H-13′	5.68 *d*	5.58 *br s*	5.58 *br s*	5.76 *d*	5.78 *br s*	5.77 *d*	5.79 *br s*	2.69 *br d*
H-14	1.45 *br s*	1.32 *br s*	1.32 *br s*	1.44 *br s*	1.45 *br s*	1.42 *br s*	1.44 *br s*	2.60 *dddd*
H-15	2.74 *d*	2.63 *br s*	2.63 *br s*	2.75 *br s*	2.76 *br s*	2.74 *br s*	2.75 *br s*	2.58 *d*
		6.74 *tq*	6.89 *q*	6.93 *t*	6.95 *t*	6.65 *ddd*	7.98 *dd*	
		4.16 *br d*	4.27 *br s*	4.45 *d*	4.92 *dd*	4.89 *ddd*	7.41 *dd*	
		1.74 *dt*	1.77 *d*	4.39 *m*	4.87 *dd*	4.69 *ddd*	6.67 *dd*	
					4.82 *d*	2.87 *d*		
					4.79 *d*			
					2.09 *s*			
					2.06 *s*			

J (Hz): Compounds **9**–**15**: 1, 2 = 11; 1, 2′ = 6; 2, 2′ = 12 = 2, 3′ = 12; 2, 3 = 4; 2′, 3 = 3; 2′, 3′ = 5; 3, 3′ = 12; 5, 6 = 11; 5, 15′ = 1.5; 6, 7 = 7; 7, 13 = 7, 13′ = 2; 8, 9 = 2.5; 8, 9′ = 5; 9, 9′ = 14.5; compound **16**: 1, 9 ≈ 1, 9′ ≈ 1, 14 ≈ 1, 14′ ≈ 1; 5, 6 = 11; 5, 15 = 1.5; 6, 13 = 2; 9, 9′ = 14, 14′ = 14; 9′, 14′ = 6.

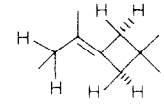
the diacetate, **13**. In all cases again, broad signals were observed at room temperature indicating flexible conformations. Surprisingly, **14** was not a mixture of epimers. Usually such hemiacetals are obtained as epimeric mixtures. Oxidation afforded **14a** and its ^{1}H NMR spectrum further supported the nature of the ester group. Obviously the ester residues of **10**–**15** are closely related.

The lactone, **8**, molecular formula $C_{15}H_{20}O_3$, again showed very broad ^{1}H NMR signals at room temperature. At $-50°$ two conformers (*ca* 2:1) were visible which allowed the assignment of the signals by spin decoupling (Table 3). The couplings $J_{7,13}$ indicated an 8,12-*trans*-lactone and those of H-3 favoured a β-orientated hydroxyl, though the flexibility of the system did not allow an unambigious assignment of the stereochemistry. As a mixture of conformers was present, the Cotton effect was not conclusive for a decision concerning the lactone configuration. Compound **8** was the only 8,12-lactone isolated from this species.

The molecular formula of **16** ($C_{15}H_{18}O_3$) together with the IR spectrum, which indicated the presence of a hydroxy lactone (3620, 1775, 1745 cm^{-1}), required a tricyclic compound with three double bonds. The ^{1}H NMR spectrum (Table 2) displayed two doublets of olefinic methyls, one of them being coupled with an olefinic broadened quartet at δ 4.45 and the other coupled with a double quartet at 5.51, which itself was coupled with the proton which gave rise to the doublet at 4.45. These results indicated that the sequence **A** was present



A



B

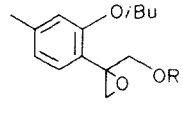
A further low field broad signal at δ 5.04 was probably due to H-1 in a modified germacranolide. Spin decoupling showed that this proton was vicinally coupled with allylic multiplets at δ 2.20 and 1.70 and was allylic with two pairs of geminal coupling signals at 3.30 and 2.87 and at 2.69 and 2.60. The signals at δ 2.87 and 2.60 showed a 6 Hz *W*-coupling characteristic for a cyclobutane ring. In agreement with a model only the 9α- and 14α-cyclobutane protons showed these couplings. All data, therefore, agree with sequence **B** and structure **16**. Irradiation of H-15 showed a NOE of H-6 indicating a H-6α configuration. Furthermore, a biogenetic consideration supported this proposal. Protonation of the isomer, **41**, derived from **1** by shifts of two double bonds, would lead to **16** as shown in Scheme 1. We have given the name pegolettiolide to this new type of sesquiterpene lactone without a hydroxy group at C-8.

The ^{1}H NMR spectra of **18**–**21** (Table 4) showed that we were dealing with two pairs of isomers which differed in the nature of the ester groups and in the position of the double bonds (Δ^3 and $\Delta^{4(15)}$, respectively). Most probably **18**–**21** were closely related to **10** and **15**. As shown in Scheme 1 proton addition to **10** would explain the formation of **18** and **20** via the ion **42**. Spin decoupling allowed the assignment of all signals in the spectra of **18**–**21**. Inspection of models of **10**, **18** and **20** showed that the proposed stereochemistry at C-5 and C-10 was most likely. As already discussed in the case of **1** the preferred conformation of *cis*-6,12-germacra-1(10),4,13-trien-olides probably has both methyls below the plane. The acid catalysed cyclization of **10** would then lead to eudesmanolides with a 10α-methyl and a 5β-proton. In agreement with this stereochemistry, $J_{5,6}$ was 10.5 Hz in all cases while $J_{6,7}$ was 7 Hz and 7.5 Hz, respectively.

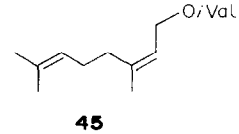
Table 3. ^{1}H NMR spectral data of compounds **8a** and **8b** (400 MHz, $CDCl_3$, TMS as internal standard)

	Conformer **8a**	**8b**
H-1	5.15 *br dd*	4.87 *br dd*
H-2	2.77 *ddd*	2.35 *m*
H-2′	1.96 *ddd*	
H-3	4.40 *dd*	4.30 *dd*
H-5	5.10 *dd*	5.20 *dd*
H-6	2.66 *m*	2.52 *ddd*
H-6′	1.91 *ddd*	2.26 *ddd*
H-7	2.70	2.70 *m*
H-8	4.25 *ddd*	4.46 *ddd*
H-9	2.61 *dd*	2.93 *dd*
H-9′	2.07 *dd*	1.60 *dd*
H-13	6.35 *d*	6.34 *d*
H-13′	5.69 *d*	5.71 *d*
H-14	1.60 *br s*	1.64 *br s*
H-15	1.56 *br s*	1.57 *br s*

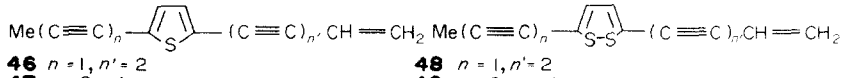
J (Hz): Conformer **8a**: 1, 2 = 1, 2′ = 2, 3 = 2, 3′ = 9; 2, 2′ = 14; 5, 6 = 6.5; 5, 6′ = 10; 6, 6′ = 6′, 7 = 12; 7, 8 = 5; 7, 13 = 7, 13′ = 3; 8, 9 = 3; 8, 9′ = 12; conformer **8b**: 1, 2 = 4.5; 1, 2′ = 11.5; 2′, 3 = 7; 2′, 3 = 11; 5, 6 = 8; 5, 6′ = 9; 6, 7 = 5; 6′, 7 = 6; 6, 6′ = 15; 7, 8 = 3.5; 7, 13 = 7, 13′ = 2.5; 8, 9 = 6; 8, 9′ = 12.5; 9, 9′ = 14.



43 R = H
44 R = *i*Bu

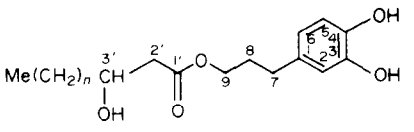


45

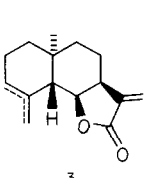


46 *n* = 1, *n*′ = 2
47 *n* = 2, *n*′ = 1
48 *n* = 1, *n*′ = 2
49 *n* = 2, *n*′ = 1

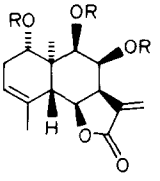
Scheme 1.



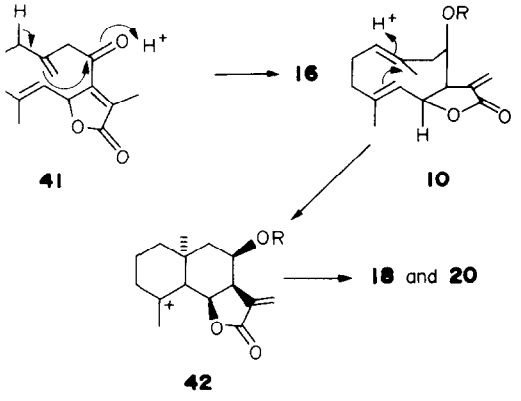
37 (n = 14,16,18)



38 Δ^3
39 $\Delta^{4(15)}$



40 R = Ang, Epang, H



Compounds **20** and **21** most probably had a normal chair–chair conformation, as followed from the couplings of H-7 and H-8. Surprisingly, these couplings were different in the spectra of **18** and **19** and required a pseudo axial orientation of the C-8 ester groups. While absorption of **13** on acidic Si gel gave no change, heating in benzene in the presence of a trace of *p*-toluenesulfonic acid afforded a mixture of **18a** and **20a**. The ^{1}H NMR spectra were nearly identical with those of **18** and **20**. This result supported the proposed stereochemistry of **18–21**.

Compounds **18a** and **20a** had the same stereochemistry at C-10 as the chemical shifts of H-14 were nearly identical in both isomers. Furthermore, in the acid catalysed cyclization *trans*-decalin formation should be favoured, especially as only two isomers, which differed in the position of the double bond (Δ^3 or $\Delta^{4(15)}$), were obtained.

The ^{1}H NMR spectrum of **17** (Table 4) showed that this diol again was a eudesmanolide closely related to **20**. All signals could be assigned by spin decoupling. The couplings observed indicated the same stereochemistry as that of **20**. The presence of an equatorial 1α-hydroxyl also followed from the couplings.

As mentioned before, **1** was cyclized to **22** and its structure was similar to **17** and **20**. The ^{1}H NMR spectrum (Table 4) showed that the Δ^{11} double bond had shifted to $\Delta^{7(11)}$. A clear *W*-coupling between H-14 and H-1 and between H-14 and to H-9 supported the presence of a *trans*-decalin system.

The ^{1}H NMR spectra of **17–21** were, in part, close to the spectra of a group of similar *cis*-6,12-lactones isolated from *Calostephane divaricata* [8]. Therefore, the stereochemistry of these compounds probably has to be cor-

Table 4. ^{1}H NMR spectral data of compounds **17–23** and **25** (400 MHz, $CDCl_3$, TMS as internal standard)

	17	**18**	**19**	**20**	**21**	**22**	**23**	**25**
H-1	3.63 *dd*	1.46 *m*	1.46 *m*	1.35 *ddd*	1.36 *m*	1.65—	5.69 *dd*	5.71 *dd*
H-1′				1.62 *ddd*	1.63 *ddd*	1.50 *m*		
H-2*c*	2.33 *br d*	2.05 *m*	2.05 *m*	1.55 *m*	1.5—	1.74 *m*	4.97 *d*	4.99 *d*
H-2*t*	1.94 *br d*				1.6 *m*		4.92 *d*	4.93 *d*
H-3	5.40 *br s*	5.46 *br s*	5.46 *m*	1.97 *m*	1.99 *m*	2.45 *br d*	5.09 *br s*	5.10 *br s*
H-3′				2.38 *br d*	2.38 *br d*	2.04 *m*	4.77 *br s*	4.78 *br s*
H-5	2.59 *br d*	2.41 *br d*	2.43 *br d*	1.94 *br d*	1.95 *br d*	2.24 *br d*	1.91 *br d*	1.93 *br d*
H-6	4.61 *br dd*	4.60 *dd*	4.63 *dd*	4.83 *dd*	4.86 *dd*	5.15 *dq*	4.82 *dd*	4.83 *dd*
H-7	3.41 *dddd*	3.61 *dddd*	3.66 *dddd*	3.73 *dddd*	3.80 *ddd*	—	3.77 *dddd*	3.78 *dddd*
H-8	4.33 *ddd*	5.44 *ddd*	5.51 *ddd*	5.45 *ddd*	5.56 *ddd*	—	5.47 *ddd*	5.50 *ddd*
H-9	2.01 *dd*	1.90 *dd*	1.93 *dd*	1.76 *dd*	1.82 *dd*	2.56 *d*	1.89 *dd*	1.91 *dd*
H-9′	1.78 *dd*	1.65 *dd*	1.74 *dd*	1.70 *dd*	1.76 *dd*	2.34 *dq*	1.67 *dd*	1.69 *dd*
H-13	6.38 *d*	6.29 *d*	6.30 *d*	6.32 *d*	6.33 *d*	2.04 *d*	6.34 *d*	6.35 *d*
H-13′	5.94 *d*	5.81 *d*	5.84 *d*	5.95 *d*	5.97 *d*		5.96 *d*	5.96 *d*
H-14	0.90 *s*	0.95 *s*	0.96 *s*	0.87 *s*	0.89 *s*	0.97 *br s*	1.09 *s*	1.11 *s*
H-15	1.86 *dddd*	1.87 *br s*	1.86 *br s*	4.99 *br s*	5.00 *br s*	5.11 *br s*	1.77 *br s*	1.77 *br s*
H-15′				4.82 *br s*	4.83 *br s*	5.05 *br s*		
OR	—	6.76 *tq*	7.97 *dd*	6.82 *tq*	8.02 *dd*	—	6.84 *tq*	6.98 *t*
		4.35 *m*	7.43 *dd*	4.39 *m*	7.46 *dd*		4.38 *m*	4.92 *d*
		1.81 *dt*	6.69 *d*	1.86 *dt*	6.73 *dd*		1.86 *dt*	4.90 *d*
								4.84 *d*

(Hz): Compound **17**: 1,2 = 6, 1,2′ = 10; 2,2′ = 17; 2,15 = 2′,15 = 3, 15 = 5, 15 = 1; 5,6 = 10; 6,7 = 7; 7,8 = 4.5; 7,13 = 7, 13′ = 2.5; 8, 9 = 5.5; 8, 9′ = 4.5; compounds **18** and **19**: 5, 6 = 10.5; 6, 7 = 7; 7, 8 = 5; 7, 13 = 7, 13′ = 2.5; 8, 9 = 8, 9′ = 5.5; compounds **20** and **21**: 1, 1′ = 1,2′ = 13; 1, 2 = 6; 1′, 2 = 1′, 2′ = 3.5; 3, 3′ = 14; 5, 6 = 10.5; 6, 7 = 7.5; 7, 8 = 8, 9 = 5; 7, 13 = 7, 13′ = 3; 8, 9′ = 10; 9, 9′ = 13.5; compound **22**: 3, 3′ = 14; 5, 6 = 11; 6, 13 = 2; 9, 9′ = 15.5; 9, 14 = 1; compounds **23** and **25**: 1, 2*c* = 10.5; 1, 2*t* = 17.5; 5, 6 = 11; 6, 7 = 7; 7, 13 = 7, 13′ = 3; 7, 8 = 6; 8, 9 = 11.5; 8, 9′ = 4.5; 9, 9′ = 13.

rected to **40**, while the *cis*-6,12-eudesmanolides from a *Critonia* species [9], which showed a positive Cotton effect, may be better written as their mirror images, **38** and **39**. Also, the C-10 configuration of a eudesmanolide from *Inula crithmoides* [10] may have to be changed to 10α-methyl (**40a**), as the ^{1}H NMR spectrum is very similar to that of **17**. However, for final confirmation a reisolation is necessary. The ^{1}H NMR spectral data of these lactones are close to those of **17**.

The ^{1}H NMR spectra of **23** and **25**, the latter obtained by acetylation of the naturally occurring diol **24** (Table 4), showed that we were dealing with elemanolides closely related to **10** and **12**. Spin decoupling allowed the assignment of all signals. The coupling observed required a chair conformation especially as $J_{8,9\beta}$ was 11.5 Hz and as a *W*-coupling $J_{9,14}$ was visible. Therefore, a somewhat distorted boat conformation had to be assumed only in the cases of **18** and **19** though no clear argument is apparent to explain these differences.

The acids **26–28** were converted to the corresponding methyl esters which could not be separated. Heating at 200° afforded the elemane derivatives, **29–31**, but their separation again was difficult and only **29** could be enriched by TLC. The ^{1}H NMR spectral signals (see Experimental), were assigned by spin decoupling. The small couplings of H-8 required an axial orientation of the ester groups. Perhaps **26** may be a precursor of **10–15**, as their formation would require only allylic oxidation.

The ^{1}H NMR spectra of **32** and **33** (Table 5) in conjunction with the results of spin decoupling showed that the hydroxyl groups were at C-1 and C-18 while the stereochemistry followed from the chemical shifts in the spectrum of **33**. The aldehyde group at C-1 caused a downfield shift of H-4 while that at C-18 shifted the signal of H-9 to lower fields.

The structure of the diol, **34**, which on acetylation afforded the diacetate **35** and which was also converted to the acetonide, **36**, followed from the ^{1}H NMR and mass spectra (see Experimental). The nature of the end groups was deduced from the ^{1}H NMR signals of the diacetate, **35**, while the spectrum of the diol only showed overlapping multiplets in the low field part. The chain length and also the position of the oxygen functions was deduced from the fragmentation patterns in the mass spectra of **34–36**. The presence of a mixture of 3,4-dihydroxydihydrocinnamyl alcohol esters, which could not be separated, was revealed by the ^{1}H NMR spectrum (see Experimental). Also, the general nature of the ester groups could be deduced from the characteristic signals for H-2_1 and H-3_1, while the chain length followed from the molecular formula.

Table 5. ^{1}H NMR spectral data of compounds **32** and **33** (400 MHz, $CDCl_3$, TMS as internal standard)

	32	**33**
H-1	4.09 *br d*	9.89 *d*
H-2	5.44 *br t*	5.87 *br d*
H-4	2.09 *m*	2.59 *br t*
H-5	2.09 *m*	2.25 *br dt*
H-6	5.10 *m*	5.15 *br t*
H-8	2.00 *br t*	2.13 *br t*
H-9	2.16 *dt*	2.69 *dt*
H-10	5.24 *t*	6.40 *br t*
H-12	2.09 *m*	2.16 *m*
H-13	2.09 *m*	2.04 *dt*
H-14	5.10 *m*	5.06 *br t*
H-16	1.66 *br s*	1.65 *d*
H-17	1.58 *br s*	1.55 *br s*
H-18	4.10 *br s*	10.07 *s*
H-19	1.58 *br s*	1.60 *br s*
H-20	1.72 *br s*	1.97 *d*

J (Hz): Compound **32**: 1, 2 = 8, 9 = 9, 10 = 7; compound **33**: 1, 2 = 4, 5 = 5, 6 = 8, 9 = 9, 10 = 12, 13 = 13, 14 = 7; 14, 16 = 2, 20 = 1.

The roots afforded the thiophenes and dithio compounds, **46–49** [11], the thymol derivatives, **43** and **44** [12], and nerolisovalerate (**45**).

The chemistry of the genus *Pegolettia* supports the proposed close relationship to *Calostephane* [1] by the co-occurrence of *cis*-6,12-eudesmanolides [8]. A relationship to *Geigeria* is indicated by the isolation of a geranyl nerol derivative which is present also in *Geigeria* [13]. However, the nature of the *Geigeria* sesquiterpene lactones is different. The acetylenes of types **46–49** were reported from a *Geigeria* species [13] while the proposed relationship of *Pegolettia* to *Pulicaria* [1] is only supported by the co-occurrence of thymol derivatives [14] which are widespread in the tribe.

More species from genera placed in the subtribe *Inulinae* have to be investigated to obtain a clearer picture of the chemotaxonomy in this group.

EXPERIMENTAL

The air-dried plant material, collected in February 1981 in Transvaal (voucher 81/48, deposited in the Botanic Research Institute, Pretoria), was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by CC (Si gel) and further by repeated TLC (Si gel) and, in part, by HPLC (reversed phase, MeOH–H_2O). Known compounds were identified by high field ^{1}H NMR spectroscopy. The aerial parts (200 g) afforded 5 mg germacrene D, 30 mg taraxasterol, 100 mg taraxasteryl acetate, 150 mg **1** (Et_2O–petrol, 3:1), 10 mg **4** (Et_2O–petrol, 1:1), 15 mg **5** (Et_2O–petrol, 3:1), 10 mg **7** (Et_2O–petrol, 3:1), 4 mg **8** (Et_2O–CH_2Cl_2, 1:1), 5 mg **9** (Et_2O–petrol, 3:1), 20 mg **10**, 10 mg **11**, 50 mg **12**, 10 mg **14** (Et_2O and HPLC, MeOH–H_2O, 13:7), 10 mg **15** (Et_2O–CH_2Cl_2, 1:1), 3 mg **16** (Et_2O–CH_2Cl_2, 1:1), 30 mg **17** (Et_2O), 5 mg **18** and 6 mg **20** (Et_2O and HPLC, MeOH–H_2O, 13:7), 3 mg **19** and 4 mg **21** (Et_2O–CH_2Cl_2, 1:1 and HPLC, MeOH–H_2O, 7:3), 5 mg **23** (Et_2O), 15 mg **24** (Et_2O), 4 mg **26**, **27** and **28** (*ca* 1:1:1, Et_2O–petrol, 3:1) and 35 mg **32**, 50 mg **34** and 30 mg **37** (Et_2O–petrol, 3:1). Due to the small amounts several lactones could not be included to crystallize. The roots (20 g) gave 10 mg **43**, 10 mg **44**, 3 mg **45** and *ca* 1 mg each of **46–49**.

8-*Oxo-germacra*-trans,trans-1(10),4,11-*trien*-cis-6,12-*olide* (**1**). Colourless crystals, mp 98° (Et_2O–petrol); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1720 (C=O); *m/z* (rel. int.): 246.126 $[M]^+$ (8) ($C_{15}H_{18}O_3$), 228 $[M-H_2O]^+$ (11), 218 $[M-CO]^+$ (10), 107 (84), 67 (100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-314 \quad -327 \quad -382 \quad -753}$$ ($CHCl_3$; *c* 0.5).

To 20 mg **1** in 1 ml MeOH, 8 mg $NaBH_4$ and, after 5 min, dilute H_2SO_4 were added. TLC (Et_2O–petrol, 3:1) afforded 4 mg **9**, identical with the natural lactone, and 10 mg of a mixture of **1** and

6. After addition of CH_2N_2 in Et_2O HPLC (MeOH H_2O, 7:3) afforded 4 mg **1** and 3 mg **6** (^{1}H NMR spectra, Table 1). Compound **1** (10 mg) was heated for 2 hr in C_6D_6 with a trace of *p*-toluenesulfonic acid. TLC (Et_2O–petrol, 1:1) gave 4 mg **22** (containing a trace of the Δ^3-isomer) and starting material.

8-*Oxo*-7*β*H-*germacra*-trans,trans-1(10),4,11-*trien*-trans-6,12-*olide* (**4**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1720 (C=O); MS *m/z* (rel. int.): 246.126 [M]$^+$ (7) ($C_{15}H_{18}O_3$), 228 [M − H_2O]$^+$ (4), 218 [M − CO]$^+$ (3), 107 (51), 67 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+149 \quad +173 \quad +217 \quad +476} \text{ (CHCl}_3\text{; } c \text{ 0.14).}$$

Oxidation of eupatolide with pyridine dichromate in CH_2Cl_2 afforded **2** [7] which is laevorotatory; ^{1}H NMR spectrum identical with that of **4**.

8-*Oxo*-11*β*-H-*germacra*-trans,trans-1(10),4-*dien*-cis-6,12-*olide* (**7**). Colourless crystals, mp 137–138°, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1710 (C=O); MS *m/z* (rel. int.): 248.141 [M]$^+$ (7) ($C_{15}H_{20}O_3$), 230 [M − H_2O]$^+$ (2), 220 [M − CO]$^+$ (6), 107 (20), 69 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-190 \quad -196 \quad -213 \quad -491} \text{ (CHCl}_3\text{; } c \text{ 0.07).}$$

3*β*-*Hydroxygermacra*-trans,trans-1(10),4-*dien*-trans-8,12-*olide* (**8**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 248.141 [M]$^+$ (6) ($C_{15}H_{20}O_3$), 230 [M − H_2O] (6), 204 [M − CO_2]$^+$ (6), 189 [204 − Me]$^+$ (3), 84 (100), 81 (85).

8*β*-*Hydroxygermacra*-trans, trans-1(10),4,11-*trien*-cis-6,12-*olide* (**9**). Colourless crystals, mp 130°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1765 (γ-lactone); MS *m/z* (rel. int.): 248.141 [M]$^+$ (5) ($C_{15}H_{20}O_3$), 230 [M − H_2O]$^+$ (42), 215 [230 − Me]$^+$ (42), 67 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-90 \quad -95 \quad -111 \quad -206} \text{ (CHCl}_3\text{; } c \text{ 0.4).}$$

8*β*-(4′-*Hydroxy- and 5′-hydroxytigloyloxy*)-*germacra*-trans, trans-1(10),4,11-*trien*-cis-6,12-*olide* (**10** *and* **11**). Colourless gum, which could not be separated, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 346.178 [M]$^+$ (0.3) ($C_{20}H_{26}O_5$), 230 [M − RCO_2H]$^+$ (53), 215 [230 − Me]$^+$ (25), 99 [C_4H_6(OH)CO]$^+$ (100), 81 [99 − H_2O]$^+$ (30), 71 [99 − CO]$^+$ (44).

8*β*-(4′,5′-*Dihydroxytigloyloxy*)-*germacra*-trans,trans-1(10),4,11-*trien*-cis-6,12-*olide* (**12**). Colourless crystals, mp 106°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1765 (γ-lactone), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 230.131 [M − RCO_2H]$^+$ (100), 215 [230 − Me]$^+$ (22), 157 (68), 115 (70). 20 mg **12** were heated for 2 hr in 0.1 ml Ac_2O at 80°. TLC (Et_2O–petrol, 3:1) gave 20 mg **13**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1760 (OAc), 1725 (C=CCO_2R) (^{1}H NMR spectrum see Table 2).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-113 \quad -116 \quad -134 \quad -187} \text{ (CHCl}_3\text{; } c \text{ 0.64).}$$

Compound **13** (5 mg) in 0.5 ml C_6D_6 was heated 30 min with 5 mg *p*-toluenesulfonic acid. TLC (Et_2O–petrol, 3:1) gave 1.5 mg **18a** and 1.5 mg **20a**. ^{1}H NMR spectral data identical with those of **18** and **20**, respectively, except for the signals of the ester group.

8*β*-*Hydroxygermacra*-trans,trans-1(10),4,11-*trien*-cis-6,12-*olide*-(2′-*hydroxy*-2.5H-*furan*-4′-*oate*) (**14**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1765 (γ-lactone), 1720 (C=CCO); MS *m/z* (rel. int.): 360.157 [M]$^+$ (0.1) ($C_{20}H_{24}O_6$), 342 [M − H_2O]$^+$ (0.3), 230 [M − RCO_2H]$^+$ (37), 215 [230 − Me]$^+$ (18), 95[furoyl ion]$^+$ (100). Compound **14** (5 mg) in 2 ml Et_2O was stirred for 1 hr with 50 mg MnO_2. TLC afforded 3 mg **14a**, ^{1}H NMR ($CDCl_3$): *δ* 6.71 (H-3′, *t*, *J* = 2.2 Hz), 4.97 (H-5′, *d*, *J* = 2.2 Hz); other signals see **14** (Table 2).

8*β*-(*β*-*Furoyloxy*)-*germacra*-trans,trans-1(10),4,11-*trien*-cis-6,12-*olide* (**15**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (γ-lactone), 1730 (C=CCO_2R); MS *m/z* (rel. int.): 342.147 [M]$^+$ (0.2) ($C_{20}H_{22}O_5$), 230 [M − RCO_2H]$^+$ (8), 215 [230 − Me]$^+$ (5), 95 [furoyl ion]$^+$ (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-124 \quad -132 \quad -146 \quad -267} \text{ (CHCl}_3\text{; } c \text{ 0.3).}$$

8-*Hydroxypegolettiolide* (**16**). Colourless crystals, mp 155°, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1775, 1745 (γ-lactone); MS *m/z* (rel. int.): 246.126 [M]$^+$ (7) ($C_{15}H_{18}O_3$), 231 [M − Me]$^+$ (4), 203 [231 − CO]$^+$ (6), 107 (63), 91 (64), 55 (100); CIMS (*iso*-butane): 247 [M + 1]$^+$ (100), 229 [247 − H_2O]$^+$ (6). $[\alpha]_D \sim 0°$ ($CHCl_3$; *c* 0.3).

1*α*,8*β*-*Dihydroxy*-5*β*-H,10*α*-*methyleudesma*-3,11-*dien*-cis-6,12-*olide* (**17**). Colourless crystals, mp 211°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620, 3420 (OH), 1770 (γ-lactone); MS *m/z* (rel. int.): 264 [M]$^+$ (0.3), 246.126 [M − H_2O]$^+$ (6), 228 [246 − H_2O]$^+$ (9), 202 [246 − CO_2]$^+$ (8), 83 (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546\,nm}{-101 \quad -110 \quad -116} \text{ (CHCl}_3\text{; } c \text{ 0.17).}$$

8*β*-(4′-*Hydroxytigloyloxy*)-5*β*-H,10*α*-*methyleudesma*-3,11-*dien*-cis-6,12-*olide* (**18**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OH), 1770 (γ-lactone), 1710 (C=CCO_2R); MS *m/z* (rel. int.): 328.167 [M − H_2O]$^+$ (0.3) ($C_{20}H_{24}O_4$), 230 [M − RCO_2H]$^+$ (100), 215 [230 − Me]$^+$ (12), 99 [RCO]$^+$ (26), 71 (99 − CO]$^+$ (23).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-65 \quad -70 \quad -82 \quad -145} \text{ (CHCl}_3\text{; } c \text{ 0.06).}$$

8*β*-(*β*-*Furoyloxy*)-5*β*-H,10*α*-*methyleudesma*-3,11-*dien*-cis-6,12-olide (**19**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (γ-lactone), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 230.130 [M − RCO_2H]$^+$ (82) ($C_{15}H_{28}O_2$), 215 [230 − Me]$^+$ (10), 95 [RCO]$^+$ (100); CD (MeCN): $\Delta\varepsilon_{263} + 0.3$, $\Delta\varepsilon_{305} - 0.4$.

8*β*-(4′-*Hydroxytigloyloxy*)-5*β*-H,10*α*-*methyleudesma*-4(15),11-*dien*-cis-6,12-*olide* (**20**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OH), 1780 (γ-lactone), 1710 (C=CCO_2R); MS *m/z* (rel. int.): 328.167 [M − H_2O]$^+$ (3) ($C_{20}H_{24}O_4$), 230 [M − RCO_2H]$^+$ (100), 99 [RCO]$^+$ (46).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-107 \quad -117 \quad -139 \quad -247} \text{ (CHCl}_3\text{; } c \text{ 0.07).}$$

8*β*-(*β*-*Furoyloxy*)-5*β*-H,10*α*-*methyleudesma*-4(15),11-*dien*-cis-6,12-*olide* (**21**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1730 (C=CCO_2R); MS *m/z* (rel. int.): 230.131 [M − RCO_2H]$^+$ (57) ($C_{15}H_{18}O_2$), 215 [230 − Me]$^+$ (6), 95 [RCO]$^+$ (100); CD (MeCN): $\Delta\varepsilon_{262} + 0.6$.

8*β*-(4′-*Hydroxytigloyloxy*)-5*β*-H,10*α*-*methylelema*-1,3,11-*trien*-cis-6,12-*olide* (**23**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OH), 1780 (γ-lactone), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 230.131 [M − RCO_2H]$^+$ (42), ($C_{15}H_{18}O_2$), 215 [230 − Me]$^+$ (21), 99 [RCO]$^+$ (100).

8*β*-(4′,5′-*Dihydroxytigloyloxy*)-5*β*-H,10*α*-*methylelema*-1,3,11-*trien*-cis-6,12-*olide* (**24**). Colourless gum which was purified as its diacetate, **25** (2 hr Ac_2O, 80°), colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1750, 1230 (OAc), 1725 (C=CCO_2R); MS *m/z* (rel. int.): 344 [M − ketene, HOAc]$^+$ (4), 326 [M − 2 × HOAc]$^+$ (3), 230.131 [M − RCO_2H]$^+$ (72) ($C_{15}H_{18}O_2$), 215 [230 − Me]$^+$ (24), 157 [RCO − ketene]$^+$ (100), 115 [157 − ketene]$^+$ (94).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-7 \quad -11 \quad -12 \quad -19} \text{ (CHCl}_3\text{; } c \text{ 0.27).}$$

8β-(Tigloyloxy, 2-methylbutyryloxy and isovaleryloxy)-germacra-trans,trans-1(10),4,11-*trien*-12-*oic acid* (**26–28**). Colourless gum which, by addition of CH_2N_2 in Et_2O, afforded the corresponding esters, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2700, 1690 (C=CCO_2H), 1730 (CO_2R); MS *m/z* (rel. int.): 334.214 $[M]^+$ (0.3) ($C_{20}H_{30}O_4$), 232 $[M-RCO_2H]^+$ (18), 85 $[RCO]^+$ (31), 83 $[RCO]^+$ (28). These esters could not be separated. Heating of the mixture in C_6H_6 for 2 hr at 200° afforded, after TLC (Et_2O–petrol, 3:1), 2.5 mg **29–31** which again could not be separated completely, only **29** was enriched. ^{1}H NMR ($CDCl_3$): δ 5.80 (*dd*, H-1), 4.92 (*d*, H-2*c*), 4.89 (*d*, H-2*t*), 4.88 (*br s*, H-3), 4.68 (*br s*, H-3′), 2.18 (*br d*, H-5), 2.10 (*ddd*, H-6), 1.43 (*br d*, H-6′), 2.92 (*br d*, H-7), 5.30 (*br s*, H-8), 1.77 (*m*, H-9), 6.27 (*br s*, H-13), 5.60 (*br s*, H-13′), 1.10 (*s*, H-14), 1.77 (*br s*, H-15), 6.78 (*br q*), 1.78 (*br d*), 1.80 (*br s*) (OTigl), 2.30 (*tq*), 1.08 (*d*), 0.86 (*t*) (OMeBu), 2.18 (*d*), 0.90 (*d*) (O*i*Val) [*J* (Hz): 1*c*,2 = 10; 1*t*,2 = 17; 5,6 ~ 10; 6,6′ = 13; 6,7 ~ 10; 6′,7 ~ 3; 7,8 = 8,9 ~ 3].

18-*Hydroxygeranyl nerol* (**32**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH); MS *m/z* (rel. int.): 302.225 $[M]^+$ (0.1) ($C_{20}H_{30}O_2$), 284 $[M-H_2O]^+$ (1), 256 $[284-CO]^+$ (6), 109 (62), 81 (75), 69 (100). Compound **32** (15 mg) in 2 ml Et_2O was stirred for 2 hr with 150 mg MnO_2. TLC (Et_2O–petrol, 1:3) gave 10 mg **33**, colourless gum; ^{1}H NMR spectrum see Table 5.

1,3-*Dihydroxyoctadecane* (**34**). Colourless crystals, mp 64° (Et_2O–petrol), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH); ^{1}H NMR ($CDCl_3$): δ 3.85 (*m*, H-1, H-3), 0.85 (*t*, H-18, *J* = 7 Hz); MS *m/z* (rel. int.): 268 $[M-H_2O]^+$ (0.5), 250 $[268-H_2O]^+$ (3), 239 $[268-CHO]^+$ (11), 75 $[HOCH_2CH_2CH(OH)]^+$ (100). Acetylation (Ac_2O, 1 hr, 80°) afforded **35**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1245 (OAc); MS *m/z* (rel. int.): 310 $[M-HOAc]^+$ (6), 250 $[310-HOAc]^+$ (41), 159 $[AcOCH_2CH(OAc)]^+$ (38), 55 (100); ^{1}H NMR ($CDCl_3$): δ 4.08 (*t*, H-1, *J* = 6.5 Hz), 1.86 (*m*, H-2), 4.97 (*tt*, H-3, *J* = 7, 7 Hz), 1.55 (*m*, H-4), 1.28 (*m*, H-5–H-17), 0.85 (*t*, H-18, *J* = 7 Hz). Compound **34** (10 mg) in 2 ml Me_2CO containing a drop of H_2SO_4 and 20 mg dry Cu_2SO_4 was stirred for 15 min. Usual work-up and TLC (Et_2O–petrol, 1:10) gave 10 mg **36**, colourless gum; MS *m/z* (rel. int.): 326.318 $[M]^+$ (1) ($C_{21}H_{46}O_2$), 311.295 $[M-Me]^+$ (100) ($C_{20}H_{39}O_2$), 115 (2,2-dimethyl-1,3-dioxane)$^+$ (33); ^{1}H NMR ($CDCl_3$): δ 3.82 (*m*, H-1), 1.54 (*m*, H-2), 3.95 (*ddd*, H-3, *J* = 12, 12, 3 Hz), 1.43 (*s*) and 1.37 (*s*, acetonide Me), 0.86 (*t*, H-18, *J* = 7 Hz).

3,4-*Dihydroxydihydrocinnamyl alcohol esters* **37**. Colourless gum which could not be separated. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610, 3550 (OH), 1740 (CO_2R); MS *m/z* (rel. int.): 506.397 (3), 478.366 (3) and 450.335 $[M]^+$ (2) ($C_{31}H_{54}O_5$, $C_{29}H_{50}O_5$, $C_{27}H_{46}O_5$), 150 $[M-RCO_2H]^+$ (38), 55 (100); ^{1}H NMR ($CDCl_3$): δ 6.68 (*d*, H-2), 6.61 (*dd*, H-5), 6.78 (*d*, H-6), 2.59 (*t*, H-7), 1.92 (*tt*, H-8), 4.16 (*dt*, H-9), 4.08 (*dt*, H-9′), 2.49 (*dd*, H-2_1), 2.35 (*dd*, H-$2'_1$), 4.00 (*ddt*, H-3_1), 0.86 (*t*, Me, *J* = 7 Hz) [*J* (Hz): 2, 5 = 2; 5, 6 = 8; 7, 8 = 8, 9 = 7; 9, 9′ = 11; 2_1, $2'_1$ = 17; 2_1, 3_1 = 2.5; $2'_1$, 3_1 = 9; 3_1, 4_1 = 7].

Acknowledgements—We thank Dr. B. de Winter and Miss M. Welman, Botanic Research Institute, Pretoria, for their help during plant collection and identification of the species and the Deutsche Forschungsgemeinschaft for financial support.

REFERENCES

1. Merxmüller, H., Leins, P. and Roessler, H. (1977) in *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.) p. 577. Academic Press, London.
2. Vichnewski, W., Herz, W. and Kumar, N. (1979) *J. Org. Chem.* **44**, 2575.
3. Samek, Z., Holub, M., Rychlewska, V., Grabarczyk, H. and Drozdz, B. (1979) *Tetrahedron Letters* 2691.
4. Herz, W., Govindan, S. V. and Blount, F. (1980) *J. Org. Chem.* **45**, 1113.
5. Bohlmann, F. and Le Van, N. (1978) *Phytochemistry* **17**, 1957.
6. Bohlmann, F. and Zdero, C. (1980) *Phytochemistry* **19**, 587.
7. Doskotch, R. W. and El-Feraly, F. S. (1970) *J. Org. Chem.* **35**, 1928.
8. Bohlmann, F., Jakupovic, J. and Ahmed, M. (1982) *Phytochemistry* **21**, 2027.
9. Bohlmann, F., Jakupovic, J. and Lonitz, M. (1977) *Chem. Ber.* **110**, 301.
10. Mahmoud, Z. F., Salam, N. A., Sarg, T. M. and Bohlmann, F. (1981) *Phytochemistry* **20**, 735.
11. Bohlmann, F., Burkhardt, T., Zdero, C. (1973) *Naturally Occurring Acetylenes* p. 62. Academic Press, London.
12. Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16**, 1243.
13. Bohlmann, F., Zdero, C. and Ahmed, M. (1982) *Phytochemistry* **21**, 1679.
14. Schulte, K. E., Reisch, J. and Hopmann, J. (1963) *Arch. Pharm.* **296**, 353.