Phytochemistry, 1981, Vol. 20, pp. 251–256. © Pergamon Press Ltd. Printed in England. 0031-9422/81/0201 0251 $02.00/0

SESQUITERPENES FROM *KLEINIA* SPECIES*

FERDINAND BOHLMANN,† MANIRUDDIN AHMED,† JASMIN JAKUPOVIC† and CHARLES JEFFREY‡

† Institute for Organic Chemistry, Technical University of Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, West Germany; ‡ Royal Botanic Gardens, Kew, Richmond, U.K.

(*Received* 30 *May* 1980)

Key Word Index—*Kleinia fulgens*; *Senecio implexus*, *K. articulata*, *K. mandraliscae*; Compositae; sesquiterpenes; germacranes; oplopanes.

Abstract—The investigation of four *Kleinia* species afforded, in addition to known compounds, seven new germacrane and three oplopane derivatives, all highly oxygenated. This kind of sesquiterpene seems to be characteristic of the genus *Kleinia* and related succulent species, and its tentative grouping is discussed.

INTRODUCTION

From the South African *Kleinia* group (Compositae, tribe Senecioneae) several species have been investigated already [1–3]. So far no eremophilane derivatives, widespread in the tribe, have been isolated; they are replaced by other highly oxygenated sesquiterpenes. Furthermore triterpenes, mainly lupane derivatives, seem to be widespread in this group. To establish the differences to other groups of the tribe Senecioneae we now have investigated four further succulent species. Again they all contain highly oxygenated sesquiterpenes, mainly of the germacrane type.

RESULTS AND DISCUSSION

The roots of *Kleinia fulgens* afforded a complex mixture of highly oxygenated germacrane derivatives. ^{1}H NMR studies showed that these compounds are most probably **2**–**6** and **8**. The structure of **2** easily followed from the NMR spectral data as the isomer **1** has previously been obtained by acetylation of the corresponding 8-hydroxy derivative, which was isolated from *Senecio rhomboideus* [4]. Comparing the chemical shifts of 8-H and 9-H clearly indicated that an angelate residue at C-9 caused shifts which were very useful in determining the relative positions of the ester groups at C-8 and C-9 in the other compounds. As the chemical shift of 3-H was nearly identical in the spectra of **1** and **2**, the structure of **2** was established. The ^{1}H NMR data of **3** showed that the acetate groups were replaced by 2-methylbutyrate and that the 4,5-epoxide was transformed to a diol which was established by spin decoupling. The observed couplings for 5-H (J = 2.5 and 2.5 Hz) required an α-orientation of the hydroxyl group. This assumption was supported by the downfield shifts of the 7-H and 8-H signals. Inspection of models showed that the observed couplings, especially $J_{6\beta,7\alpha}$ and $J_{7\alpha,8\alpha}$, would agree with a conformation where the methyls at C-4 and C-10 as well as the isopropenyl group were orientated above the plane. The structure of **4** was established by partial saponification, which led to **3**. Therefore the additional acetate group could be placed only at the 5-hydroxy group. The next two esters **5** and **6** had identical molecular formula and their ^{1}H NMR data (Table 1) showed that they were isomers. Comparing the ^{1}H NMR data with those of **4** clearly showed that a new oxygen function had to be placed at C-2. Consequently the epoxide proton at C-1 now was a doublet. Inspection of a model showed that the observed coupling $J_{1,2}$ required a β-orientation of the oxygen function at C-2. Partial saponification of both **5** and **6** led to the same diol **7**, indicating that the relative positions of the ester groups in **5** and **6** were the same. The chemical shifts again supported the same relative position as in **1** and **3**, though, due to the additional oxygen functions small differences in the shifts could be observed. The last compound was obviously the epoxide of **8**. In the ^{1}H NMR spectrum (Table 1) the signals of the vinyl protons were replaced by two doublets with the typical chemical shifts of epoxide protons. The olefinic methyl signal was missing and replaced by an additional methyl singlet. In C_6D_6 all signals could be assigned. Spin decoupling established the assignments. Though the relative positions of the ester groups were in part not really established, it was very likely, also from biogenetical considerations, that they were the same in all cases. We have named the compound without oxygen functions at C-4 and C-5 kleinifulgin and compound **2** is isorhomboidol acetate. The aerial parts of the plant also contained **3**, **4** and **6** and friedelin.

The aerial parts of *Senecio implexus*, so far not placed in the genus *Kleinia*, afforded germacrene D, unidentified triterpenes and two sesquiterpene esters, the tetraester **11** and the corresponding triester **9**. The ^{1}H NMR data (Table 2) of the tetraester were very similar to those of the oplopane derivative abrotanifolone [5]. An additional ester residue must be placed at C-1. The coupling $J_{1,9}$ indicated an α-orientation, if the corresponding angles in a model were considered. The ^{1}H NMR data showed that in addition to an acetate, two 2-methylbutyrate and a 4-methylsenecioate group were present. As shown in the case of abrotanifolone [5] in the MS of **11** the loss of a 2-methylbutyryloxy radical established the 7-position of

* Part 311 in the series "Naturally Occurring Terpene Derivatives". For Part 310 see Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1981) *Phytochemistry* (in press).

Table 1. ^{1}H NMR spectral data of compounds **1**–**8** ($CDCl_3$)

				4					**8**	
	1	**2**	**3**	$CDCl_3$	C_6D_6	**5**	**6**	**7**	$CDCl_3$	C_6D_6
1-H	2.76 *dd*	2.75 *dd*	2.75 *dd*	2.73 *dd*	2.54 *dd*	2.79 *d*	2.90 *d*	2.85 *d*	2.83 *d*	2.82 *d*
2α-H	2.00 *m*	2.15 *m*	2.10 *ddd*	2.0 *m*	2.0 *m*	3.79 *dd*	5.08 *dd*	3.76 *dd*	3.54 *dd*	3.63 *dd*
2β-H	1.81 *m*	1.83 *m*	1.70 *m*			—	—	—	—	—
3α-H	5.37 *dd*	5.39 *dd*	5.53 *dd*	5.52 *dd*	5.71 *dd*	5.36 *d*	5.62 *d*	5.44 *d*	5.32 *d*	5.52 *d*
5α-H	3.21 *d* (*br*)	3.20 *d* (*br*)	—	—	—	—	—	—	—	—
5β-H	—	—	3.90 *dd* (*br*)	5.07 *dd*	5.38 *dd*	5.05 *dd*	3.91 *dd* (*br*)	3.91 *dd*	5.06 *dd*	5.41 *dd*
6α-H	2.00 *m*	2.13 *m*	2.42 *ddd*	2.38 *ddd*	2.37 *ddd*	2.41 *dd* (*br*)	2.42 *dd* (*br*)	2.42 *dd*	2.05 *m*	2.19 *ddd*
6β-H			2.00 *m*	2.31 *dd*		2.0 *m*	2.00 *m*	2.0 *m*		2.05 *m*
7α-H	2.49 *dd* (*br*)	2.49 *dd* (*br*)	3.09 *d* (*br*)	2.90 *d* (*br*)	3.13 *d* (*br*)	3.08 *d* (*br*)	3.20 *d* (*br*)	3.19 *d* (*br*)	2.90 *dd* (*br*)	3.24 *dd* (*br*)
8α-H	5.40 *d* (*br*)	5.35 *m*	5.58 *dd* (*br*)	5.61 *dd* (*br*)	5.99 *dd* (*br*)	5.63 *dd* (*br*)	5.58 *dd* (*br*)	5.60 *dd* (*br*)	5.83 *dd* (*br*)	6.26 *dd* (*br*)
9α-H	5.28 *d*		5.23 *d*	5.16 *d*	5.45 *d*	5.16 *d*	5.24 *d*	5.22 *d*	5.06 *d*	5.36 *d*
12-H	5.25 *s*	5.27 *s*	5.31 *s*	5.32 *s*	5.31 *s*	5.31 *s*	5.29 *s*	5.32 *s*	2.94 *d*	2.85 *d*
12'-H	5.05 *s*	5.08 *s*	5.08 *s*	5.07 *s*	4.89 *s*	5.10 *s*	5.14 *s*	5.18 *s*	2.77 *d*	2.67 *d*
13-H	1.33 *s*	1.32 *s*	1.29 *s*	1.27 *s*	1.32 *s*	1.36 *s*	1.42 *s*	1.37 *s*	1.15 *s*	1.11 *s*
14-H	1.30 *s*	1.29 *s*	1.29 *s*	1.27 *s*	1.07 *s*	1.29 *s*	1.27 *s*	1.29 *s*	1.26 *s*	1.21 *s*
15-H	1.30 *s*	1.26 *s*	1.27 *s*	1.16 *s*	1.07 *s*	1.17 *s*	1.26 *s*	1.27 *s*	1.30 *s*	1.32 *s*
OAc	2.06 *s*	2.02 *s*	-	2.10 *s*	1.67 *s*	2.10 *s*	2.10 *s*	-	2.07 *s*	1.70 *s*
OAng	6.12, 6.05 *qq*	6.11 *qq*	6.10, 6.06 *qq*	6.11 *qq*	5.78, 5.70 *qq*	6.15, 6.10 *qq*	6.18, 6.05 *qq*	6.14, 6.06 *qq*	6.20, 6.13 *qq*	5.81, 5.75 *qq*
	2.00 *dq*	1.99 *dq*	2.01, 1.99 *dq*	2.00 *dq*	2.03, 1.97 *dq*	2.01, 1.99 *dq*	2.03, 1.97 *dq*	2.02, 1.98 *dq*	2.04, 2.01 *dq*	2.03 *dq*
	1.94, 1.93 *dq*	1.93, 1.88 *dq*	1.95, 1.87 *dq*	1.93, 1.87 *dq*	2.04, 1.85 *dq*	1.95, 1.86 *dq*	1.98, 1.86 *dq*	1.97, 1.87 *dq*	1.95, 1.88 *dq*	1.95, 1.90 *dq*
OMebu	-		2.34 *tq*	2.34 *tq*	2.0 *m*	2.35 *tq*	2.34 *tq*	2.36 *tq*	2.37 *tq*	2.0 *m*
			1.67 *ddq*	1.65 *ddq*	1.60 *ddq*	1.67 *ddq*	1.65 *m*	1.67 *ddq*	1.71 *ddq*	1.67 *ddq*
			1.42 *ddq*	1.40 *m*	1.20 *ddq*	1.42 *ddq*	1.40 *m*	1.42 *ddq*	1.44 *ddq*	1.31 *ddq*
			1.14 *d*	1.14 *d*	0.99 *d*	1.15 *d*	1.13 *d*	1.15 *d*	1.17 *d*	1.02 *d*
			0.88 *t*	0.86 *t*	0.75 *t*	0.87 *t*	0.87 *t*	0.87 *t*	0.92 *t*	0.82 *t*
OH	-	-	3.27 *s*	3.36 *s*	3.33 *s*	3.35 *s*	3.18 *s*	3.28 *s*	3.17 *s*	2.32 *s*

J(Hz): Compound **2**: 1,2 = 6; 1,2′ = 5; 2,3 = 8; 2′,3 = 6; 5,6 = 4.5; 6,7 = 12; 6′,7 = 6.5; Compound **3**: 1,2 = 6.5; 1,2′ = 5; 2,3 = 7; 2′,3 = 7; 2,2′ = 15; 5,6 = 5,6′ = 2.5; 6,7 = 14; 6′,7 = 7,8 = 3; 6,6′ = 14; 8,9 = 3; Compound **4**: 1,2 = 7; 1,2′ = 4; 2,3 = 7; 2′,3 = 7; 5,6 = 5,6′ = 2.5; 6,7 = 12; 6′,7 = 7,8 = 3; 6,6′ = 14; 8,9 = 3; Compounds **5** and **7**: 1,2 = 2,3 = 7; 5,6 = 5,6′ = 3; 6,7 = 12; 6′,7 = 2.5; 7,8 = 3; 8,9 = 3; Compound **6**: 1,2 = 8; 2,3 = 7; 5,6 = 5,6′ = 3; 6,7 = 13; 6,6′ = 14; 7,8 = 8,9 = 3; Compound **8**: 1,2 = 7; 2,3 = 8; 5,6 = 5,6′ = 2.5; 6,7 = 12; 6′,7 = 5; 7,8 = 8,9 = 3.

one 2-methylbutyrate residue. The chemical shifts of 6-H and 14-H and biogenetical considerations indicated the same positions for the acetate and the 4-methylsenecioate group, which, however, could not be confirmed, while the configurations at all centres were the same as in abrotanifolone. The structure of **9** also followed from the ^{1}H NMR data. While the signal for an acetate group was missing, a typical olefinic methyl doublet indicated the presence of a conjugated ketone, obviously formed by elimination of acetic acid. The chemical shift of the methyl signal also indicated the stereochemistry of the double bond. A very similar compound was isolated from the roots in addition to germacrene D and **11**. This ketone was the isomer **10** of the ketone **9**. The signal of the olefinic methyl was now shifted downfield. However, there were pronounced differences in the chemical shifts and also in the couplings observed. Inspection of models showed that in **11** most probably a boat conformation of the 6-ring is preferred to avoid the strong interactions of the 14-methyl with the substituent at C-5. Consequently the coupling $J_{5,6}$ was reduced and several chemical shifts were altered. Though again the relative position of the ester residues could not really be established, most probably they were the same as in **9**. The absence of the acetate group in **9** and **10** indirectly supported the proposed structure of **11**. We have named **9** and **10** as 3,14*Z*- and 3,14*E*-implexin respectively and **11** as 14-acetoxy-3, 14-dihydroimplexin. The compounds isolated indicated that this species also may be better placed in *Kleinia*.

The aerial parts of *K. articulata* afforded lupenone, lupeol, its acetate, 28-hydroxylupeol, the diols **17** and **18** (already prepared by reduction of the corresponding methyl esters [2]), α-zingiberene, α-curcumene, bicyclogermacrene, and a germacrane derivative, the angelate **15**. The structure of **15** followed from the ^{1}H NMR data (Table 2) and from the results of a partial saponification, which afforded the hydroxyangelate **16**. By spin decoupling all signals could be assigned. Inspection of models showed that the diepoxide had a preferred conformation, where the angles 1,2α, 6,7α and 7α,8α were about 90°. Consequently the corresponding couplings were very small. In the spectrum of the hydroxyangelate the signal of 6-H was shifted upfield. A 9 Hz H,OH coupling indicated a hydrogen bond between the 6-hydroxyl and the epoxide oxygen, which led to a small variation of the conformation as shown by the differences in the couplings $J_{5,6}$ and $J_{6,7}$ (Table 3).

The roots of *K. mandraliscae* afforded the known germacrane derivatives **12** and **13** [2] as well as the eudesmane hydroxyangelate **14**, while the aerial parts gave germacrene D, lupenone, lupeol acetate, and $\Delta^{9(11)}$- and Δ^{12}-dihydrolupeol acetates (**12** and **13**).

The chemical data now available on *Kleinia* and related species show that they support the proposed tentative grouping from the botanical point of view.

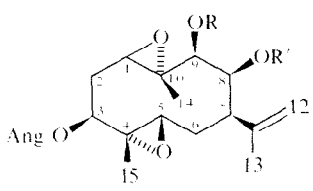
The species of the genus *Kleinia* mostly contain no typical sesquiterpenes (Table 4, group 4). They are replaced by high concentrations of triterpenes [2]. Since

Table 2. ^{1}H NMR spectral data of compounds **9**–**11** ($CDCl_3$)

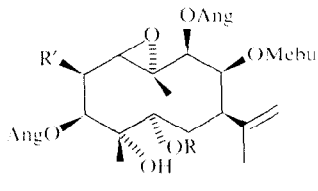
	9	**10**	**11*** (C_6D_6, 80°)
1-H	5.56 *d*	5.67 *d*	5.53 *d*
6-H	5.15 *dd*	5.21 *dd*	5.35 *dd*
7-H	5.63 *d*	5.59 *d*	6.13 *d*
10-H	5.24 *s* (*br*)	5.28 *s* (*br*)	5.26 *d* (*br*)
10′-H	4.96 *s* (*br*)	5.05 *s* (*br*)	4.99 *d* (*br*)
12-H	2.83 *d*	2.95 *d*	2.77 *d*
12′-H	2.66 *d*	2.79 *d*	2.62 *d*
13-H	1.53 *s*	1.68 *s*	1.23 *s*
14-H	6.44 *dq*	6.84 *dq*	5.27 *dq*
15-H	2.22 *dd*	2.03 *dd*	1.04 *d*
MeSen	5.66 *s* (*br*)	5.67 *s* (*br*)	5.87 *tq*
	2.18 *q* (*br*)	2.20 *q* (*br*)	1.93 *dq*
	1.09 *t*	1.10 *t*	0.98 *t*
	2.15 *s* (*br*)	2.19 *s* (*br*)	2.19 *d*
Mebu	2.37, 2.38 *tq*	2.37 *m*	2.42, 2.27 *m*
	1.68 *m*	1.65 *m*	1.60 *m*
	1.47 *m*	1.45 *m*	0.87, 0.83 *t*
	0.92, 0.88 *t*	0.90, 0.88 *t*	1.34 *d*, 1.04 *d*
	1.16, 1.12 *d*	1.15, 1.10 *d*	
OAc	—	—	1.85 *s*

* At room temp. several signals very broad.

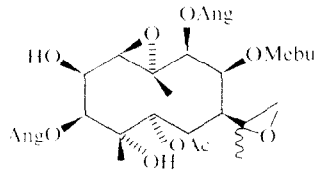
J (Hz): Compounds **9**/**10**: 1, 9 = 4.5; 4, 14 = 2; 5, 6 = 7; 6, 7 = 2.5; 12, 12′ = 4.5; 14, 15 = 7, 5; compound **11**: 1, 9 = 5; 3, 14 = 3.5; 5, 6 = 10; 6, 7 = 3.5; 9, 10 = 2; 12, 12′ = 4.5; 14, 15 = 7; (2.42 *dd*, *J* = 10, 3.5 Hz, 3-H; 2.47 *dddd*, *J* = 10, 4, 2, 2 Hz, 9-H); OMeSen: 2′, 4′ = 2′, 5′ ~ 1; 4′, 5′ = 7; OMebu: 2′, 3′ = 2′, 5′ = 3′, 4′ = 7, $2'_1$, $2'_2$ = 14.



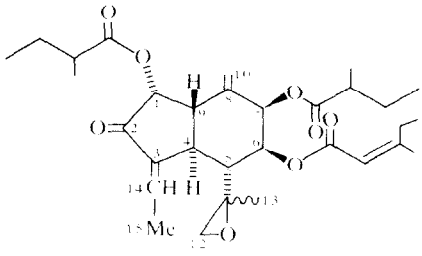
1 2
R Ang Ac
R' Ac Ang



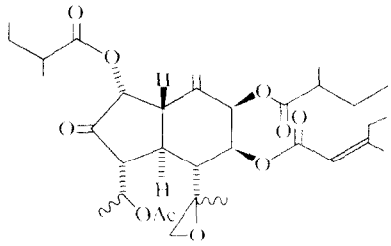
3 4 5 6 7
R H Ac Ac H H
R' H H OH OAc OH



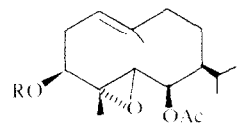
8



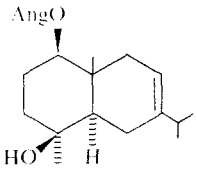
9 3,14Z 10 3,14E



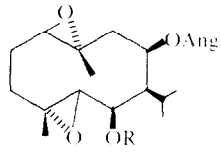
11



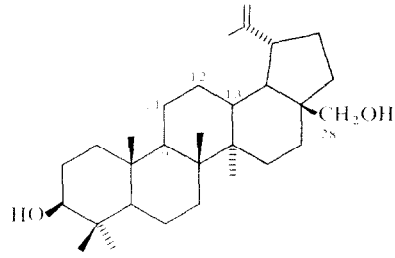
12 R = Ang 13 R = Tigl



14



15 R = Ac 16 R = H



17 18

Table 3. ^{1}H NMR spectral data of compounds **15** and **16** (270 MHz, $CDCl_3$)

	15	**16**
1-H	3.14 *d* (*br*)	3.04 *d* (*br*)
2α-H	1.50 *dddd*	1.38 *dddd*
2β-H	2.12 *ddd*	2.11 *ddd*
3-H	2.22 *ddd*	2.24 *ddd*
3'-H	1.33 *ddd*	1.3 *m*
5-H	3.18 *d*	3.14 *d*
6-H	4.97 *dd*	3.57 *ddd*
7-H	1.67 *d* (*br*)	1.60 *d* (*br*)
8-H	5.68 *dd* (*br*)	5.43 *dd* (*br*)
9β-H	2.27 *dd*	2.48 *dd*
9α-H 11-H	1.97 *m*	1.86 *m*
12-H	1.20 *d*	1.16 *d*
13-H	1.01 *d*	1.00 *d*
14-H	1.32 *s*	1.27 *s*
15-H	1.50 *s*	1.51 *s*
OAc	1.97 *s*	–
OAng	6.10 *qq*	6.19 *qq*
	2.02 *dq*	2.02 *dq*
	1.90 *dq*	1.89 *dq*
OH	–	3.31 *d*

J (Hz): 1, 2β = 10; 2α, 2β = 15; 2α, 3α = 3.5; 2α, 3β = 13; 3α, 3β = 14; 5, 6 = 6.5; 6, 7 = 1.3; 7, 11 = 10; 8, 9α = 5.5; 8, 9β = 12.5; 11, 12 = 11, 13 = 6.5; compound **16**: 5, 6 = 7.5; 6, OH = 9; 6, 7 = 2.

from two species acylpyrroles were isolated [2, 6], which are closely related to the pyrrolizidine alkaloids, these alkaloids may be typical for many species of the whole tribe. Two further groups (2 and 3) of succulent species, which are also placed in the *Kleinia* group (Table 4) again afforded no eremophilanes but most of them contain in addition to triterpenes highly oxygenated germacrane derivatives [1, 2]. Another group (group 1) contains highly oxygenated oplopane derivatives [3], which are also present in some *Senecio* species, which belong to the Eusenecioids [1, 2]. This supports the proposed taxonomic relationship of these *Kleinia* groups (1–3) to the latter. However, the chemistry of *Gynura* [7], which is related botanically to *Kleinia*, shows no similarity and further investigations are necessary for a final grouping of this complex tribe.

EXPERIMENTAL

Optical rotation: $CHCl_3$; MS: 70 eV, direct inlet; ^{1}H NMR: 270 MHz, TMS as int. standard.

The fresh plant material (Kew Gardens) was extracted with Et_2O–petrol (1:2) and the resulting extracts were first separated by CC (Si gel, act grade II) and further by repeated TLC (Si gel, GF 254).

Kleinia fulgens *Hook.* The roots (30 g) afforded 3 mg **2** (Et_2O–petrol, 3:1), 12 mg **3** (Et_2O), 3 mg **4** (Et_2O), 10 mg **5** (Et_2O), 11 mg **6** (Et_2O) and 7 mg **8** (Et_2O), while the aerial parts (100 g) yielded 10 mg friedelin, 6 mg **3**, 1 mg **4** and 8 mg **6**.

Senecio implexus *Bally.* The roots (10 g) afforded 5 mg germacrene D, 2 mg **9** (Et_2O–petrol, 2:1) and 6 mg **11** (Et_2O–petrol, 2:1), while the aerial parts (150 g) yielded 8 mg germacrene D, 6 mg $C_{31}H_{52}O$, not identified, 4 mg **10** (Et_2O–petrol, 1:1) and 10 mg **11**.

Table 4. Distribution of the main terpene types in the proposed *Kleinia* groups

	Germacranes	Oplopanes	Triterpenes
Senecio implexus	–	+	+
Group 1			
Kleinia tomentosa	–	+	+
Group 2			
K. acaulis	+	–	+
K. archeri	+	–	+
K. articulatus	+	–	+
K. crassifolius	+	–	+
K. cylindricus	+	–	+
K. ficoides	+	–	+
K. mandraliscae	+	–	+
K. serpens	*		+
K. vitalis	+	–	+
Group 3			
K. barbertonicus	–	–	+†
K. phonolithicus	*	–	+
K. viminalis	–	–	+
Group 4			
K. anteuphorbium	–	–	+
K. coccineiflorus	–	–	+
K. coccinea	–	–	+
K. fulgens	+	–	+
K. kleinioides	–	–	+†
K. longiflora	–	–	+†
K. neriifolia	–	–	+
K. petraeus	+	–	+

* Highly oxygenated eudesmanes.
† Acylpyrroles.

Kleinia articulata (*Linn.f.*) *Haw.* The roots (50 g) afforded 4 mg lupenone and the aerial parts (100 g) gave 40 mg lupenone, 25 mg lupeol, 5 mg lupeol acetate, 5 mg 28-hydroxylupeol, 1 mg **17**, 1 mg **18**, 3 mg α-zingiberene, 3 mg α-curcumene, 3 mg bicyclogermacrene and 15 mg **15** (Et_2O–petrol, 1:3).

Kleinia mandraliscae *Fin. ex Lojac.* The roots (10 g) afforded 14 mg **12**, 6 mg **13** and 8 mg **14**, while the aerial parts (100 g) yielded 10 mg germacrene D, 15 mg **12**, 13 mg **13**, 9 mg lupenone, 4 mg lupeol acetate and 6 mg of the $\Delta^{9(11)}$- and Δ^{12}-isomers of lupeol.

Isorhombiodol acetate (**2**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750, 1250 (OAc), 1720, 1650 (C=CCO_2R); MS *m/e* (rel. int.): 490.257 (M^+, 0.2) ($C_{27}H_{38}O_8$), 391 (M – OAng, 1), 331 (391 – HOAc, 0.5), 231 (331 – AngOH, 1), 83 ($C_4H_7CO^+$, 100).

4α,5α-*Dihydroxykleinifulgin* (**3**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3560 (OH), 1740 (CO_2R), 1720, 1650 (C=CCO_2R); MS *m/e* (rel. int.): 550.314 (M$^+$, 1) ($C_{30}H_{46}O_9$), 532 (M – H_2O, 0.5), 451 (M – OAng, 2), 450 (M – AngOH, 1), 432 (532 – AngOH, 1), 348 (450 – $C_4H_9CO_2H$), 85 ($C_4H_9CO^+$, 16), 83 ($C_4H_7CO^+$, 100), 57 (85 – CO, 55), 55 (83 – CO, 53).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-31.9 \quad -31.9 \quad -36.2 \quad -62.2} (c = 0.91).$$

5α-*Acetoxy*-4α-*hydroxykleinifulgin* (**4**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1750, 1230 (OAc), 1730 (CO_2R), 1730, 1650 (C=CCO_2R); MS *m/e* (rel. int.): 592.325 (M$^+$, 1) ($C_{32}H_{48}O_{10}$), 575 (M – OH, 0.5), 493 (M – OAng, 2), 492 (M – AngOH, 2), 390 (492 – $C_4H_9CO_2H$, 1), 330 (390 – HOAc, 1), 231 (330 – OAng, 3), 213 (231 – H_2O, 3), 85 ($C_4H_9CO^+$, 18), 83 ($C_4H_7CO^+$, 100), 57 (85 – CO, 52), 55 (83 – CO, 68).

5α-*Acetoxy*-2β,4α-*dihydroxykleinifulgin* (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3585 (OH), 1750, 1230 (OAc), 1730 (CO_2R), 1730, 1650 (C=CCO_2R); MS *m/e* (rel. int.): 608.320 (M$^+$, 0.3) ($C_{32}H_{48}O_{11}$), 508 (M – AngOH, 0.3), 408 (508 – AngOH, 1), 348 (408 – HOAc, 0.2), 306 (408 – $C_4H_9CO_2H$, 0.5), 246 (348 – $C_4H_9CO_2H$, 1), 85 ($C_4H_9CO^+$, 8), 83 ($C_4H_7CO^+$, 100), 57 (85 – CO, 25), 55 (83 – CO, 41).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-45.3 \quad -47.3 \quad -54.1 \quad -94.1} (c = 1.1).$$

2β-*Acetoxy*-4α,5α-*dihydroxykleinifulgin* (**6**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1750, 1235 (OAc), 1730 (CO_2R), 1730, 1650 (C=CCO_2R); MS *m/e* (rel. int.): 608.320 (M$^+$, 0.5) ($C_{32}H_{48}O_{11}$), 590 (M – H_2O, 0.5), 548 (M – HOAc, 0.5), 509 (M – OAng, 1), 448 (548 – AngOH, 0.5), 85 ($C_4H_9CO^+$, 18), 83 ($C_4H_7CO^+$, 100), 57 (85 – CO, 68), 55 (83 – CO, 45).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-68.5 \quad -72.0 \quad -82.2 \quad -143.4} (c = 1.15).$$

5α-Acetoxy-2β,4α-dihydroxy-11,12-epoxy-11,12-dihydrokleinifulgin (**8**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1750, 1235 (OAc), 1730 (CO_2R), 1730, 1650 (C=CCO_2R); MS *m/e* (rel. int.): 624.316 (M^+, 0.5) ($C_{32}H_{48}O_{12}$), 606 (M − H_2O, 0.1), 523 (M − $C_4H_9CO_2$, 0.2), 423 (523 − AngOH, 0.3), 422 (M − AngOH, $C_4H_9CO_2H$, 0.2), 363 (423 − HOAc, 0.2), 322 (422 − AngOH, 0.5), 305 (322 − OH, 0.3), 85 ($C_4H_9CO^+$, 10), 83 ($C_4H_7CO^+$, 100), 57 (85 − CO, 26), 55 (83 − CO, 28).

Partial saponification. To 3 mg **4**, 10 mg **5** or 10 mg **6** in 2 ml MeOH 20 mg K_2CO_3 in 0.3 ml H_2O were added at room temp. After 45 min dil. H_2SO_4 was added. TLC afforded **3** (from **4**) and **8** (from **5** and **6**). Yields were 50–60%.

3,14Z-Implexin (**9**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745 (CO_2R), 1725 (C=CCO); MS *m/e* (rel. int.): 544.304 (M^+, 7) ($C_{31}H_{48}O_8$), 443 (M − $O_2CC_4H_9$, 1), 430 (M − $HO_2CC_5H_9$, 1), 97 ($C_5H_9CO^+$, 100), 85 ($C_4H_9CO^+$, 12), 57 (85 − CO, 49).

3,14E-Implexin (**10**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R), 1725 (C=CCO); MS *m/e* (rel. int.): 544.304 (M^+, 1), 443 (M − $O_2CC_4H_9$, 2), 97 ($C_5H_9CO^+$, 100), 85 ($C_4H_9CO^+$, 14), 57 (85 − CO, 47).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-58.9 \quad -63.0 \quad -77.0 \quad -217.3} \quad (c = 0.37).$$

14-Acetyoxy-3,14-dihydroimplexin (**11**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735 (CO, CO_2R), 1725, 1650 (C=CCO_2R); MS *m/e* (rel. int.): 604 (M^+, 0.2), 544.307 (M − HOAc, 3), 503 (M − $O_2CC_4H_9$, 8), 502 (M − $HO_2CC_4H_9$, 1), 388 (502 − $C_5H_9CO_2H$, 3), 328 (388 − HOAc, 3), 226 (328 − $C_4H_9CO_2H$, 12), 97 ($C_5H_9CO^+$, 100), 85 ($C_4H_9CO^+$, 27), 55 (85 − CO, 57).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-15.6 \quad -16.4 \quad -20.3 \quad -58.6} \quad (c = 0.43).$$

6β-Acetoxy-8β-angeloyloxy-1β,10α,4α,5β-diepoxygermacrane (**15**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750, 1240 (OAc), 1725, 1650 (C=CCO_2R); MS *m/e* (rel. int.): 394.236 (M^+, 1) ($C_{22}H_{34}O_6$), 334 (M − HOAc, 0.5), 295 (M − OAng, 1), 235 (295 − HOAc, 2), 83 ($C_4H_7CO^+$, 100), 55 (93 − CO, 71).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{365\,\text{nm}}{-10.5} \quad (c = 0.59).$$

To 5 mg **15** in 1 ml MeOH 20 mg K_2CO_3 in 0.2 ml H_2O were added at room temp. After 1 hr dil. H_2SO_4 were added and the reaction products isolated with Et_2O. TLC (Et_2O petrol. 1:1) afforded 1 mg **16**, colourless oil, MS *m/e* (rel. int.): 352 (M^+, 1) ($C_{20}H_{32}O_5$), 83 ($C_4H_7CO^+$, 100).

Acknowledgement—We thank the Deutsche Forschungsgemeinschaft for finanical support.

REFERENCES

1. Bohlmann, F., Zdero, C., Berger, D., Suwita, A., Mahanta, P. and Jeffrey, C. (1979) *Phytochemistry* **18**, 79.
2. Bohlmann, F., Knoll, K.-H., Zdero, C., Mahanta, P. K., Grenz, M., Suwita, A., Ehlers, D., LeVan, N., Abraham, W.-R. and Natu, A. A. (1977) *Phytochemistry* **16**, 965.
3. Bohlmann, F. and Suding, H. (1980) *Phytochemistry* **19**, 687.
4. Bohlmann, F. and Zdero, C. (1978) *Phytochemistry* **17**, 1337.
5. Bohlmann, F. and Suwita, A. (1976) *Chem. Ber.* **109**, 2014.
6. Bohlmann, F. and Knoll, K.-H. (1978) *Phytochemistry* **17**, 599.
7. Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16**, 494.