Phytochemistry, Vol. 21, No. 7, pp. 1679–1691, 1982.
Printed in Great Britain.

0031-9422/82/071679-13$03.00/0

NEW SESQUITERPENE LACTONES, GERANYLLINALOL DERIVATIVES AND OTHER CONSTITUENTS FROM *GEIGERIA* SPECIES*

FERDINAND BOHLMANN, CHRISTA ZDERO and MANIRUDDIN AHMED

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

(*Received* 9 *September* 1981)

Key Word Index—*Geigeria aspera*; *G. brevifolia*; *G. burkei* subsp.; Compositae; Inuleae; sesquiterpene lactones; guaianolides; pseudoguaianolides; xanthanolides; geigeranolides; diterpenes; geranyllinalol derivatives; thiophene acetylenes; nerolidol derivative; new carbon skeleton.

Abstract—The investigation of three *Geigeria* species and five subspecies afforded, in addition to known compounds, the following 32 new compounds: two geigeranolides with a new carbon skeleton, two xanthanolides, five guaianolides, three pseudoguaianolides, a sesquiterpene related to ivaxillarin, a nerolidol derivative, 15 geranyllinalol derivatives, two thiophene acetylenes and a dimeric coniferyl isobutyrate. The structures and the stereochemistry of the new compounds were elucidated by spectroscopic methods and a few chemical transformations. Chemotaxonomic aspects and relationships of the compounds are discussed.

INTRODUCTION

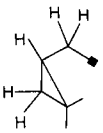
The genus *Geigera* (tribe Inuleae) with about 30 species is mainly distributed in the southern part of Africa, though a few species are known from North Africa and south Arabia. It has been placed in the subtribe Inulinae [1]. The three species investigated chemically, all contain sesquiterpene lactones [2–9]. In addition to the guaianolide geigerin [2], some modified guaianolides, griesenin and dihydrogriesenin [4, 8, 9] as well as gafrinin [5] and vermeerin [6] were isolated. From one species a pseudoguaianolide [3] was reported and from another a eudesmanolide [8]. We have now investigated eight further species, several being varieties, to see whether the chemistry of this genus is uniform and what kind of relationships to other genera can be recognized. In addition to known compounds, nine new sesquiterpene lactones were isolated, most of them closely related to those isolated before, while three of them were more unusual. Furthermore, 15 new geranyllinalol derivatives, a dihydroxy nerolidol and an ester with the carbon skeleton of ivaxillarin were present. The structure elucidation of these compounds will be discussed in this paper.

RESULTS AND DISCUSSION

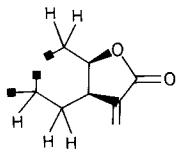
Geigeria aspera Harv., a bush responsible for a vomiting disease which kills many sheep [10], has been shown to contain several sesquiterpene lactones [5, 8]. We have now studied the constituents of the variety *G. aspera* Harv. var. *aspera*. The roots afforded bicyclogermacrene, kessane [11], the thiophene **1** and the corresponding dithio compound **3** [12], small amounts of the sesquiterpene lactones **5** [13], **6** [14], **8** [15], **12** [4], **14** [4], **19** [2] and **17** (a cyclopropane derivative) as well as a second acetylenic compound, the thiophene **4**. The structure of the latter followed from the spectroscopic data (see Experimental). Broad UV maxima at 338 and 318 nm were typical for a thiophene derivative with two conjugated acetylenic and one double bond [12]. The molecular formula was $C_{13}H_{10}OS$. The nature of the oxygen function followed from the ^1H NMR spectrum which displayed a pair of double doublets at δ 2.77 and 3.11, which were coupled with a proton (δ 3.94 *ddd*), which was further coupled with an olefinic proton, as could be shown by spin decoupling. The *cis*-configuration of the double bond and the relative position of the thiophene unit were deduced from the ^1H NMR data. As the methyl group showed a singlet at δ 2.08, it could not be placed directly at the thiophene, while the chemical shift of the methyl signal further indicated that only one triple bond was between the latter and the heterocyclic ring. This was further supported by the absence of allylic couplings of the thiophene protons. The structure of **17**, which could be separated from **5** only after transformation of the latter to the epoxide **7**, followed from the spectroscopic data. The molecular formula was $C_{15}H_{20}O_2$, while the ^1H NMR spectrum (Table 1) showed the presence of a methylene lactone. As the signals of the lactone moiety were nearly the same as those of isolantolactone, a similar situation for C-6–C-9 was assumed. Careful spin decoupling in different solvents allowed the assignment of all signals. Start-

*Part 422 in the series "Naturally Occurring Terpene Derivatives". For Part 421 see Bohlmann, F., Bapuji, M., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21** (in press).

ing with the highfield signal at δ 0.35, obviously that of a cyclopropane proton, the sequence **A** could be assigned, while starting with the signal of H-7 the sequence **B** could be determined:



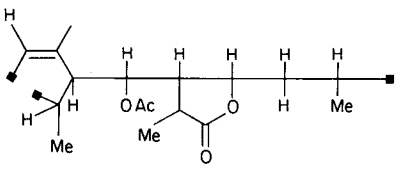
A



B

From these sequences and from the signals for the two additional methyl singlets the structure **17** was deduced. The stereochemistry at C-5–C-8 clearly followed from the couplings observed, while that at C-2 was deduced from the couplings of H-2. Inspection of models of the two possible structures, the cyclopropane ring α- or β-orientated, showed that only the angles in the former agreed with the couplings observed, while those with a β-cyclopropane ring would require nearly identical couplings of $J_{1\alpha,2}$ and $J_{1\beta,2}$. The ^{13}C NMR spectral data supported the structure (Table 1). The assignment of the signals required selective decouplings as the chemical shifts of some of the carbons were drastically different from those of β-cyclocostunolide, especially those of C-6 and C-10. Also the chemical shift of C-3 (δ 33.5) was somewhat unusual, its assignment, however, clearly followed from irradiations of H-3α and H-3β. The irradiation of H-3α enhanced the intensity of the C-5 signal which supported the proposed stereochemistry, as this surely was due to a NOE. The carbon skeleton of **17** seems to be new, we propose for it the name geigerane and for **17** geigeranolide.

The aerial parts afforded carophyllen-1,10-epoxide, bicyclogermacrene, germacrene D, the sesquiterpene lactones **12**, **14**, **19**, ivalin (**16**) [16] and the guaianolide **21** [17] as well as three further ones, the guaianolides **20**, **22** and **23**, the latter being isolated as its acetate **24**, as well as a derivative of dihydrogriesenin, the acetate **13**. The structure of **20** was easily deduced from the ^1H NMR spectrum (Table 3), as all signals were close to those of **19**. The considerable downfield shift of the signal of H-6 indicated that the acetate of **19** was present. The ^1H NMR spectral data of **22** (Table 3) were close to those of **21** [17]. However, the methylene signals of H-13 were replaced by a methyl doublet, indicating an 11, 13-dihydro derivative. In deuteriobenzene, spin decoupling allowed a clear assignment of the H-11 signal. The coupling $J_{7,11}$ being 12.5 Hz indicated an 11β-proton. The stereochemistry at C-8 in **21** and **22** obviously were the same. The chemical shifts of H-7 and H-8 indicated that both **21** and **22** were *cis*-8, 12-lactones (see below). The ^1H NMR spectrum of **24** (Table 3) displayed three methyl doublets and again no methylene signal was observed. Spin decoupling allowed the assignment of all signals. The downfield, narrowly split signal at δ 6.12 was that of H-2 as it was coupled with a broadened doublet at δ 3.44, which itself was coupled with a doublet quartet at δ 2.65 and by a very small coupling with the broadened doublet at δ 5.28. Further decouplings led to the sequence **C**:



C

Table 1. ^1H NMR spectral data of compounds **17** and **18** (400 MHz, TMS as int. standard) and ^{13}C NMR data of **17** and β-cyclocostunolide

	17 ($CDCl_3$)	**17** ($C_6D_6/CDCl_3$, 1:2)	**18** ($CDCl_3$)		**17** ($CDCl_3$)	β-Cyclocostunolide ($CDCl_3$)
H-1α	0.82 *dd* (*br*)	0.66 *dd* (*br*)	0.79 *dd* (*br*)	C-1	45.9 *dd*	42.2 *t*
H-1β	1.86 *dd*	1.70 *dd*	1.84 *dd*	C-2	26.2 *d*	27.5 *t*
H-2	1.17 *dddd*	1.03 *dddd*	1.15 *dddd*	C-3	33.5 *t*	36.8 *t*
H-3α	0.89 *dd*	0.79 *dd*	0.88 *dd*	C-4	26.5 *s*	149.0 *s*
H-3β	0.35 *dd*	0.24 *dd*	0.34 *dd*	C-5	52.8 *d*	40.5 *d*
H-5	1.00 *d*	0.78 *dd*	0.92 *dd*	C-6	27.9 *dd*	22.7 *t*
H-6α	1.98 *ddd*	1.71 *ddd*	1.88 *ddd*	C-7	41.5 *d*	46.2 *d*
H-6β	1.50 *ddd*	1.28 *ddd*	1.35 *ddd*	C-8	77.5 *d*	76.8 *d*
H-7	2.90 *ddddd*	2.56 *ddddd*	1.99 *ddd*	C-9	39.0 *dd*	41.4 *t*
H-8	4.46 *ddd*	4.17 *ddd*	4.64 *ddd*	C-10	49.8 *s*	34.3 *s*
H-9α	1.45 *dd*	1.22 *dd*	1.40 *dd*	C-11	141.8 *s*	142.4 *s*
H-9β	2.23 *dd*	2.04 *dd*	2.22 *d* (*br*)	C-12	170.5 *s*	170.5 *s*
H-11	—	—	2.45 *q*	C-13	120.2 *dd*	119.9 *t*
H-13	5.59 *d*	5.32 *d*	1.30 *d*	C-14	20.8 *q*	17.7 *q*
H-13'	6.15 *d*	6.00 *d*		C-15	18.5 *q*	106.6 *q*
H-14	1.03 *s* (*br*)	0.90 *s* (*br*)	1.03 *s* (*br*)			
H-15	1.09 *s*	0.95 *s*	1.10 *s*			

J (Hz): 1α, 1β = 13; 1α, 2 = 3; 1β, 2 = 7; 2, 3α = 8; 2, 3β = 4; 3α, 3β = 4; 5, 6α = 3; 5, 6β = 13; 6α, 6β = 13.5; 6α, 7 = 7.5; 6β, 7 = 10; 7, 8 = 5; 7, 13 = 1; 8, 9α = 5; 8, 9β = 1.5; 9α, 9β = 15 (compound **18**: 11, 13 = 7.5).

Table 2. ^{1}H NMR spectral data of compounds **12**, **13** and **15** (400 MHz, $CDCl_3$ TMS as int. standard)

	13	12	15 (C_6D_6)
H-2	5.42 *d* (*br*)	β2.55 *m* α2.17 *dd* (*br*)	2.14 *ddd* (*br*) 1.94 *m*
H-3α	2.08 *dd*	1.80 *m*	1.70 *m*
H-3β	2.01 *dd*		1.57 *m*
H-4	—	—	5.06 *ddq*
H-5	6.06 *dd*	5.58 *ddd*	5.15 *dd* (*br*)
H-6β	2.65 *ddd*	2.60 *ddd*	1.61 *ddd*
H-6α	2.18 *ddd*	2.10 *ddd*	1.85 *ddd*
H-7	3.24 *ddddd*	3.21 *ddddd*	2.76 *ddddd*
H-8	4.54 *ddd*	4.51 *ddd*	4.69 *ddd*
H-9β	2.67 *dd*	2.69 *dd*	1.80 *m*
H-9α	2.36 *dd*	2.31 *dd*	
H-13	6.32 *d*	6.30 *d*	6.23 *d*
H-13′	5.67 *d*	5.63 *d*	4.94 *d*
H-14β	4.22 *d*	3.99 *d*	1.00 *s*
H-14α	3.72 *d*	3.70 *d*	
H-15	1.49 *s*	1.49 *s*	1.18 *d*
OAc	2.05 *s*	—	1.76 *s*

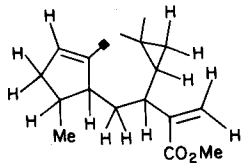
J (Hz): Compound **12**: 2α, 3α = 6; 2α, 2β = 15; 2β, 5 = 3; 5, 6α = 9; 5, 6β = 3; 6α, 7 = 3; 6β, 7 = 12; 6α, 6β = 15; 7, 8 = 8; 7, 13 = 2.5; 7, 13′ = 2; 8, 9α = 4; 8, 9β = 12; 9α, 9β = 13; 14α, 14β = 6.5; compound **13**: 2α, 3α = 6; 2β, 3α = 1.5; 5, 6α = 9; 5, 6β = 3; 6α, 7 = 3.5; 6β, 7 = 11; 6α, 6β = 16; 7, 13 = 2.5; 7, 13′ = 2; 7, 8 = 8; 8, 9α = 4; 8, 9β = 12; 9α, 9β = 13; 14α, 14β = 6.5; compound **15**: 2, 3 = 7; 2, 2′ = 15; 3, 4 = 4; 15 = 6.5; 6 = 9; 5, 6′ = 5; 6α, 7 = 3; 6β, 7 = 12; 7, 8 = 8.5; 7, 13 = 2.8; 7, 13′ = 2.5; 8, 9 = 9; 8, 9′ = 4.5 (in $CDCl_3$: H-7 3.34 *ddddd*, H-8 4.94 *ddd*).

As the IR spectrum indicated the presence of a conjugated keto group, the only possible structure therefore was **24**. The stereochemistry was deduced from inspection of a model. The observed angles agreed nicely with the couplings observed, that of H-5–H-6 being nearly 90°, while that of H-6–H-7 was about 70°. This required a β-orientation of the oxygen function at C-6. The same orientation of the C-10 methyl group was deduced from the width of the H-10 signal, which required a relatively large coupling $J_{9,10}$. A 10α-methyl group would have led to small couplings. The stereochemistry at C-4 and C-11 followed from the couplings of $J_{4,5}$ and $J_{7,11}$. **23** is an isomer of geigerin (**19**). We have, therefore, named the lactone isogeigerin.

The structure of **13** followed from the spectroscopic data. Though no molecular ion was observed, a strong fragment *m/z* 230 ($C_{15}H_{18}O_2$) was interpreted as the results of elimination of CH_2O and acetic acid. Chemical ionization showed a weak M + 1-peak, while *m/z* 261 (elimination of acetic acid) was the base peak. The ^{1}H NMR spectral data were in part close to those of **12** (Table 2), however, most signals were slightly shifted and an additional downfield signal at δ 5.42 (broadened doublet) was obviously that of the proton under the acetoxy group. One of the H-14 signals and the H-5 signal were clearly shifted downfield if compared with the shifts in the spectrum of **12**. Furthermore, the allylic coupling $J_{2,5}$ was missing. Therefore, the acetoxy group was at C-2. From a model the β-orientation was deduced as the angle H-2α–H-5 was nearly 0°, which explained the missing allylic coupling. Furthermore, one of the H-14 signals was shifted downfield. This required the β-orientation of C-14, which most likely should be the same in **12**, where the stereochemistry at C-10 so far has not been determined.

The aerial parts also contained the nerolidol derivatives **35** [18], **36** [19] and **37**. The structure of the latter followed from the ^{1}H NMR spectrum (see Experimental). In addition to three olefinic signals, one tertiary methyl signal was visible, while the position of the hydroxyl groups was deduced from the coupling of the signals of the olefinic protons at C-6 and C-10. The stereochemistry at C-3 and C-9 was not determined.

Finally a methyl ester, molecular formula $C_{16}H_{22}O_2$, was isolated. The structure was deduced from the ^{1}H NMR spectral data (Table 5). The position of the ester group followed from the chemical shift of the signals of the methylene protons. Careful spin decoupling in different solvents allowed the assignment of sequence **D**:

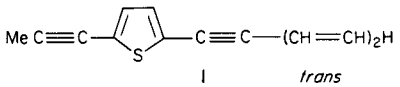


D

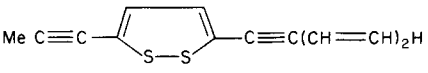
From this sequence and from the signal for the methyl singlet only structure **31** was in agreement with these results. The stereochemistry at C-4, C-5 and C-7 followed from the couplings observed. Inspection of models further showed, that an α-orientation of the cyclopropane ring was more likely, as the coupling $J_{7,8}$ was very small. In the 8-epimer, however, the angles observed would lead to a larger coupling. We have named **31** methyl asperageigerate. **31** is related to ivaxillarin [20], which has the same carbon skeleton and identical stereochemistry at C-7 and C-8 and where the coupling $J_{7,8}$ also is very small.

The roots of *G. brevifolia* (DC) Harv. afforded tridecapentaynene, lupeyl acetate, cadinol-T, **5**, **6**, **8**, **9** and **17**, while the aerial parts gave tridecapentaynene, germacrene D, bicyclogermacrene, squalene, phytol, lupeol and a complex mixture of unidentified aromatic compounds.

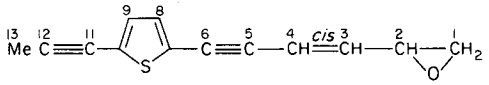
The roots of *G. burkei* Harv. subsp. *burkei* var. *burkei* afforded bisabolene, γ-humulene, kessane, **6**, **17** and the corresponding 11, 13-dihydro derivatives **18**. The ^{1}H NMR spectral data (Table 1) were in part very similar to those of **17**, the signals of the olefinic methylene protons, however, were replaced by a quartet at δ 2.45 and a doublet at δ 1.30. Spin decoupling allowed a clear assignment of all signals. Inspection of a model further showed that the methyl group at C-11 should be α-orientated as a nearly 90° angle between H-7 and H-11 would explain the missing coupling. **18**, therefore, was 11β, 13-dihydrogeigeranolide. Furthermore, in addition to **1** and **3**, the so far unknown *cis*-isomer **2** was isolated. The ^{1}H NMR spectrum clearly showed that the 3, 4-double bond was *cis* (see Experimental). Consequently, the



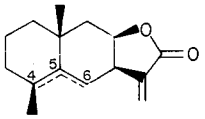
1
2 *trans*
cis



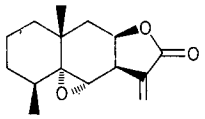
3



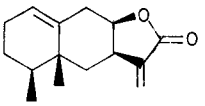
4



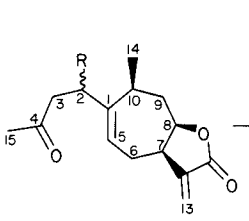
5 Δ5,6
6 Δ4,5



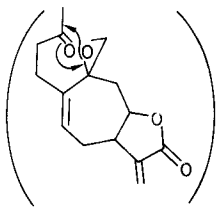
7

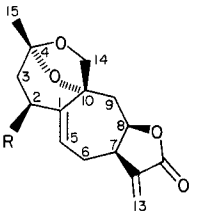


8

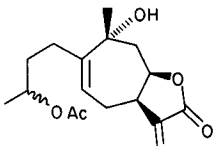


9 R = H
10 R = O Ac

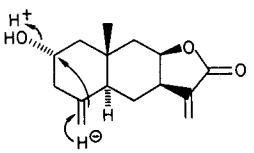




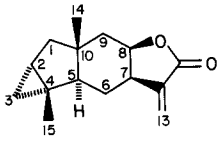
12 R = H
13 R = O Ac
14 Δ 2,3



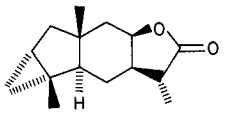
15



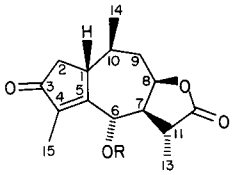
16



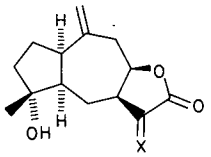
17



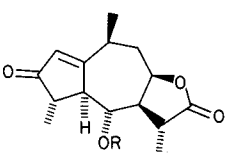
18



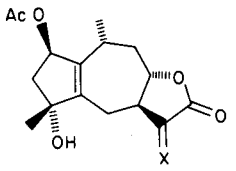
19 R = H
20 R = Ac



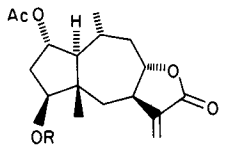
21 X = CH_2
22 X = α Me, H



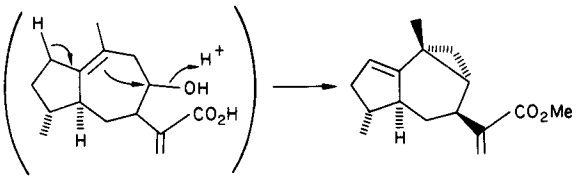
23 R = H
24 R = Ac



25 X = CH_2
26 X = α Me, H



27 R = H
28 R = Ac
29 R = Ac, 8αH



30 **31**

32 **33**

Table 3. ^{1}H NMR spectral data of compounds **20**, **22** and **24–26** (400 MHz, TMS as int. standard)

	20		**22**		**24**		**25**		**26**
	(C_6D_6)	($CDCl_3$)	(C_6D_6)	($CDCl_3$)	(C_6D_6)	($CDCl_3$)	($CDCl_3$)	(C_6D_6)	($CDCl_3$)
H-1	2.05 *dd* (*br*)	2.61 *m*	1.64 *dd* (*br*)	2.18 *m*	—	—	—	—	—
H-2	2.24 *dd*	2.70 *dd*	1.28 *m*	1.80 *m*	6.12 *dd*	5.90 *dd*	5.57 *ddd*	5.47 *ddd*	5.57 *ddd*
H-2′	1.73 *d* (*br*)	2.13 *d* (*br*)							
H-3α	—	—	1.58 *m*	1.73 *m*	—	—	2.38 *dd*	2.17 *dd*	2.38 *dd*
H-3β	—	—			—	—	1.91 *dd*	1.82 *dd*	1.89 *dd*
H-4	—	—	—	—	2.65 *dq*	2.16 *dq*	—	—	—
H-5	—	—	—	1.60 *ddd*	3.44 *d* (*br*)	2.44 *d* (*br*)	—	—	—
H-6α	4.97 *d* (*br*)	5.44 *d* (*br*)	1.75 *ddd*	2.14 *ddd*	5.28 *d* (*br*)	4.98 *d* (*br*)	2.86 *dd*	2.49 *dd*	2.61 *dd*
H-6β			0.47 *ddd*	1.12 *ddd*			1.85 *m*	1.44 *dddd*	1.95 *dddd*
H-7	2.14 *ddd*	2.81 *ddd*	1.28 *m*	1.75 *m*	2.74 *ddd*	2.18 *m*	2.64 *ddddd*	2.08 *ddddd*	1.68 *dddd*
H-8	3.69 *ddd*	4.45 *ddd*	3.61 *ddd*	4.26 *ddd*	4.63 *ddd**	3.90 *ddd*	4.02 *ddd*	3.37 *ddd*	4.03 *ddd*
H-9α	1.31 *ddd*	1.92 *m*	2.97 *dd* (*br*)	3.17 *dd* (*br*)	1.98 *m*	1.37 *m*	1.58 *ddd*	1.38 *ddd*	1.54 *ddd*
H-9β	1.12 *ddd*		2.31 *dd* (*br*)	2.51 *dd* (*br*)			2.31 *ddd*	1.93 *ddd*	2.21 *ddd*
H-10	0.43 *dddq*	1.29 *m*	—	—	2.85 *m*	2.11 *m*	2.50 *ddq*	1.84 *m*	2.49 *ddq*
H-11	1.95 *dq*	2.61 *dq*	1.75 *m*	2.30 *dq*	2.59 *dq*	1.84 *dq*	—	—	2.34 *dq*
H-13	1.19 *d*	1.43 *d*	1.03 *d*	1.25 *d*	1.40 *d*	1.17 *d*	6.23 *d*	6.11 *d*	1.28 *d*
H-13′							5.58 *d*	4.96 *d*	
H-14	0.55 *d*	1.18 *d*	4.92 *s* (*br*)	5.04 *s* (*br*)	1.38 *d*	1.09 *d*	1.21 *d*	0.92 *d*	1.20 *d*
			4.80 *s* (*br*)	4.95 *s* (*br*)					
H-15	1.75 *d*	1.84 *d*	0.91 *s*	1.20 *s*	1.07 *d*	0.81 *d*	1.33 *s*	1.07 *s*	1.30 *s*
OAc	1.56 *s*	2.16 *s*			2.00 *s*	1.49 *s*	2.06 *s*	1.66 *s*	2.04 *s*

*Not first order.

J (Hz): Compound **20**: 1, 2 = 6.5; 1, 2′ ~ 1; 1, 10 = 10; 2, 2′ = 18; 6, 7 = 11; 7, 8 = 9; 7, 11 = 10.5; 8, 9α = 2; 8, 9β = 11.5; 9, 9′ = 14; 9, 10 = 2; 9′, 10 = 11; 10, 14 = 7; 11, 13 = 7; compound **22**: 1, 2 = 9; 1, 5 = 9; 5, 6α = 3.5; 5, 6β = 12; 6α, 6β = 13; 6α, 7 = 3.5; 6β, 7 = 12; 7, 8 = 10; 7, 11 = 11.5; 8, 9α = 5; 8, 9β = 10; 9α, 9β = 15; 11, 13 = 7; compound **24**: 2, 5 = 2.10 = 1.7; 4, 5 = 6.5; 4, 15 = 10, 14 = 11, 13 = 7; 6, 7 = 3.3; 7, 8 = 7.5; 7, 11 = 13; 8, 9 = 11; 8, 9′ = 4; 9, 10 ~ 10; compound **25**: 2, 3α = 7; 2, 3β = 1.5; 6β = 1.5; 3α, 3β = 6α, 6β = 15; 6α, 7 = 2.5; 6β, 7 = 11; 7, 8 = 10; 7, 13 = 3; 8, 9α = 11; 8, 9β = 3; 9α, 9β = 12.5; 9α, 10 = 10; 9β, 10 = 3; compound **26**: 2, 3α = 7; 2, 3β = 2, 6β = 1.5; 3α, 3β = 6α, 6β = 15; 6α, 7 = 2.5; 6β, 7 = 11; 7, 8 = 11; 7, 11 = 11; 8, 9α = 11; 8, 9β = 3; 9α, 9β = 12.5; 9α, 10 = 12; 9β, 10 = 3; 10, 14 = 11.13 = 7.

Table 4. ^{1}H NMR spectral data of compounds **27–29** (400 MHz, TMS as int. standard)

	27		**28**		**29**
	($CDCl_3$)	($C_6D_6/CDCl_3/D_2O$)	($CDCl_3$)	(C_6D_6)	($CDCl_3$)
H-1	2.03 *m*		1.91 *dd*	1.46 *dd*	1.49 *dd*
H-2	4.94 *ddd*		4.97 *ddd*	4.86 *ddd*	4.87 *ddd*
H-3	1.86 *m*	1.96 *dd*	2.02 *m*	2.14 *ddd*	2.20 *dd*
H-3′		1.80 *dd*		1.99 *dd*	2.07 *m*
H-4	4.04 *ddd**	3.65 *dd*	4.99 *dd*	4.90 *ddd*	4.95 *dd*
H-6α	2.33 *dd*		2.25 *dd*	1.83 *dd*	1.78 *dd*
H-6β	1.37 *dd*		1.35 *dd*	0.92 *dd*	1.52 *dd*
H-7	2.84 *ddddd*	2.41 *ddddd*	2.84 *ddddd*	2.01 *ddddd*	3.23 *ddddd*
H-8	4.25 *ddd*	3.84 *ddd*	4.21 *ddd*	3.56 *ddd*	4.78 *ddd*
H-9α	1.41 *ddd*		1.42 *ddd*	0.93 *ddd*	1.81 *ddd*
H-9β	2.38 *ddd*	2.10 *ddd*	2.38 *ddd*	1.95 *ddd*	2.10 *ddd*
H-10	1.96 *m*	1.55 *m*	1.98 *dddq*	1.34 *dddq*	2.00 *m*
H-13	6.18 *d*	6.03 *d*	6.18 *d*	6.09 *d*	6.28 *d*
H-13′	5.46 *d*	5.16 *d*	5.43 *d*	4.86 *d*	5.60 *d*
H-14	0.98 *d*	0.77 *d*	0.99 *d*	0.75 *d*	1.05 *d*
H-15	0.93 *s*	0.60 *s*	1.00 *s*	0.58 *d*	0.95 *s*
OAc	2.03 *s*	1.83 *s*	2.10 *s*	1.72 *s*	2.10 *s*
			2.03 *s*	1.70 *s*	2.03 *s*
OH	1.59 *d*†				

*After addition of D_2O *dd*.

†Disappeared after addition of D_2O.

‡H-11, 1.76 *dq*.

J (Hz): Compounds **27**/**28**: 1, 2 = 8; 1, 10 = 10; 2, 3 = 9; 2, 3′ = 2; 3, 4 = 10; 3′, 4 = 8.5; 4, OH = 5; 6, 6′ = 15; 6, 7 = 5.5; 6′, 7 = 12; 7, 8 = 9.5; 7, 13 = 3.5; 7, 13′ = 3; 8, 9α = 11; 8, 9β = 3.5; 9α, 9β = 13; 9α, 10 = 11; 9β, 10 = 3.5; 10, 14 = 6.5; compound **29**: 1, 2 = 2, 3 = 9; 2, 3′ = 3; 3, 3′ = 15; 3, 4 = 3′, 4 = 9; 6α, 6β = 15; 6α, 7 = 4; 6β, 7 = 11; 7, 8 = 8; 7, 13 = 2.5; 7, 13′ = 2.3; 8, 9α = 3.5; 8, 9β = 11; 9α, 9β = 14; 9α, 10 = 1; 10, 14 = 7.

Table 5. ^{1}H NMR spectral data of compound **31** (400 MHz, TMS as int. standard)

	C_6D_6	$CDCl_3$
H-2	5.44 *s* (*br*)	5.35 *ddd*
H-3α	2.67 *dddd*	2.60 *dddd*
H-3β	1.97 *dddd*	1.89 *dddd*
H-4	2.36 *dddq*	2.42 *dddq*
H-5	2.25 *dddd*	2.35 *dddd*
H-6α	1.63 *ddd*	1.63 *ddd*
H-6β	1.25 *ddd*	1.08 *ddd*
H-7	2.93 *ddd*	2.76 *dd* (*br*)
H-8	0.88 *dd*	0.80 *m*
H-9	0.65 *dd*	0.63 *dd*
H-9′	0.78 *dd*	0.80 *m*
H-13	6.28 *d*	6.20 *d*
H-13′	5.44 *s* (*br*)	5.63 *dd*
H-14	1.27 *s*	1.25 *s*
H-15	0.88 *d*	0.85 *d*
OMe	3.47 *s*	3.78 *s*

J (Hz): 2, 3 = 2, 3′ = 2, 5 = 2; 3, 3′ = 16; 3α, 4 = 8; 3β, 4 = 3.5; 3α, 5 = 1.5; 4, 5 = 7; 4, 15 = 7; 5, 6α = 4; 5, 6β = 12; 6α, 6β = 12; 6α, 7 = 5; 6β, 7 = 12; 7, 8 ~ 1; 7, 13′ = 1; 8, 9 = 5; 8, 9′ = 8.5; 9, 9′ = 4; 13, 13′ = 1.

chemical shift of H-3 was influenced differently by the deshielding effect of the triple bond, but also the chemical shifts of the other signals were slightly different in the spectra of **1** and **2**. The polar fraction also gave a lignane, the dimer of coniferyl alcohol isobutyrate (**55**), as clearly followed from the ^{1}H NMR spectrum of **55** and of that of the diacetate **56**. The corresponding isovalerate had been isolated from a *Flaveria* species [21]. From the aerial parts, α-humulene, germacrene D, bisabolene, caryophyllene, bicyclogermacrene, stigmasterol and **1** were isolated. The polar fractions contained a complex mixture of diterpenes, from which finally, in addition to geranyllinalol (**38**), the following eight derivatives were isolated: the 13-hydroxy- and acetoxy compounds **39** and **40**, the diacetate **45**, the isomeric dihydroxy acetoxy derivatives **44** and **46**, the dehydro compound **52**, the glycol **49** and the precursor of **52**, the diol **51**. The structures were deduced from the ^{1}H NMR spectra (Tables 6 and 7), while the mass spectra in part gave no molecular ions. The positions of the oxygen functions in **39** and **40** followed from the results of careful spin decoupling. As one of the olefinic proton signals was a broadened doublet, the oxygen function had to be placed α- to this olefinic proton. Saturation of the signal of the latter caused a sharpening of two methyl signals. Consequently, the H-14 signal was irradiated and the oxygen function was at C-13. The other signals were close to those of

Table 6. ^{1}H NMR spectral data of compounds **39–46** (400 MHz, $CDCl_3$, TMS as int. standard)

	39 (C_6D_6–$CDCl_3$, 5:1)	**40**	**41**	**42**	**43**	**44** (C_6D_6)	**45**	**46** (C_6D_6)
H-1c	5.03 *dd*	5.07 *dd*	5.08 *dd*	5.06 *dd*	5.17 *dd*	5.16 *dd*	5.07 *dd*	5.20 *dd*
H-1t	5.25 *dd*	5.22 *dd*	5.23 *dd*	5.20 *dd*	5.38 *dd*	5.55 *dd*	5.25 *dd*	5.65 *dd*
H-2	5.83 *dd*	5.91 *dd*	5.91 *dd*	5.89 *dd*	5.93 *dd*	5.82 *dd*	5.87 *dd*	5.91 *dd*
H-4	1.6 *m*	1.6 *m*	1.63 *m*	1.55 *m*	1.84 *dd*	1.84 *dd*	2.0 *dd*	1.92 *dd*
H-4′					1.53 *dd*	1.41 *dd*	1.70 *dd*	1.47 *dd*
H-5	2.08 *dt* (*br*)	2.03 *m*	2.00 *m*	2.00 *dt* (*br*)	4.64 *ddd*	4.62 *ddd*	5.57 *ddd*	4.72 *ddd*
H-6	5.25 *t* (*br*)	5.08 *t* (*br*)	5.27 *t* (*br*)	5.18 *t* (*br*)	5.21 *d* (*br*)	5.31 *d* (*br*)	5.16 *d* (*br*)	5.29 *d* (*br*)
H-8	2.14 *m*	2.03 *m*	2.12 *m*	2.31 *dd* (*br*)	1.98 *t* (*br*)	2.40 *dd* (*br*)	2.32 *dd* (*br*)	1.98 *t* (*br*)
H-8′				2.10 *dd* (*br*)		2.16 *dd* (*br*)	2.15 *dd* (*br*)	
H-9	2.08 *dt* (*br*)		4.44 *ddd*	5.63 *ddd*	2.05 *dt* (*br*)	5.94 *ddd*	5.63 *ddd*	2.13 *dt* (*br*)
H-10	5.25 *t* (*br*)	5.14 *t* (*br*)	5.18 *d* (*br*)	5.09 *d* (*br*)	5.10 *t* (*br*)	5.33 *d* (*br*)	5.07 *d* (*br*)	5.27 *t* (*br*)
H-12	2.2 *m*	2.30 *m*	2.12 *t* (*br*)	2.05 *t* (*br*)	1.98 *t* (*br*)	2.06 *t* (*br*)	2.07 *m*	2.23 *dd* (*br*)
H-12′						2.15 *dt* (*br*)		1.98 *dd* (*br*)
H-13	4.47 *ddd*	5.62 *ddd*	2.00 *m*	2.00 *dt* (*br*)	2.05 *dt* (*br*)			6.00 *ddd*
H-14	5.30 *d* (*br*)	5.10 *d* (*br*)	5.10 *t* (*br*)	5.06 *t* (*br*)	5.09 *t* (*br*)	5.20 *t* (*br*)	5.07 *t* (*br*)	5.29 *d* (*br*)
H-16	1.70 *s* (*br*)	1.72 *d*	1.67 *s* (*br*)	1.67 *s* (*br*)	1.68 *s* (*br*)	1.72 *s* (*br*)	1.68 *s* (*br*)	1.61 *d*
H-17	1.65 *s* (*br*)	1.71 *d*	1.61 *s* (*br*)	1.59 *s* (*br*)	1.59 *s* (*br*)	1.58 *s* (*br*)	1.60 *s* (*br*)	1.53 *d*
H-18	1.62 *s* (*br*)	1.59 *s* (*br*)	1.69 *s* (*br*)	1.70 *d*	1.60 *s* (*br*)	1.65 *d*	1.70 *d*	1.71 *s* (*br*)
H-19	1.64 *s* (*br*)	1.62 *s* (*br*)	1.69 *s* (*br*)	1.62 *s* (*br*)	1.63 *d*	1.75 *d*	1.74 *d*	1.74 *d*
H-20	1.22 *s*	1.29 *s*	1.29 *s*	1.28 *s*	1.28 *s*	1.26 *s*	1.26 *s*	1.32 *s*
OAc	—	2.00 *s*	—	2.00 *s*	—	1.82 *s*	2.01 *s*	1.76 *s*
							2.00 *s*	

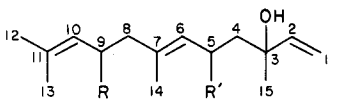
J (Hz): 1c, 1t = 1.5; 1c, 2 = 11; 1t, 2 = 17; 5, 6 = 9,10 = 13, 14 = 7; compounds **39/40**: 12, 13 = 5; 12′, 13 = 9; 13, 14 = 8; compounds **41/42**: 8, 9 = 7.5; 8′, 9 = 5.5; 8, 8′ = 13; 9, 10 = 9; 10, 18 = 1; compound **43**: 4, 4′ = 14; 4, 5 = 10.5; 4′, 5 = 2; 5, 6 = 8; 6, 19 = 1; compound **44**: 4, 4′ = 14; 4, 5 = 10.5; 4′, 5 = 2; 5, 6 = 8; compound **45**: 8, 9 = 7.5; 8′, 9 = 5.5; 8, 8′ = 13; 9, 10 = 9; compound **46**: 4, 4′ = 14; 4, 5 = 10.5; 4′, 5 = 2; 8, 9 = 7.5; 8′, 9 = 6; 9, 10 = 9; 12, 12′ = 14; 12, 13 = 4.5; 12′, 13 = 8.5; 14, 16 = 14, 17 = 1.

Table 7. ^{1}H NMR spectral data of compounds **47–54** (400 MHz, $CDCl_3$, TMS as int. standard)

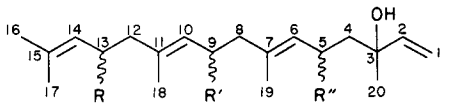
	47	**48**	**49**	**50**	**51**	**52**	**53**	**54**
H-1c	5.06 *dd*	5.16 *dd*	5.07 *dd*	5.07 *dd*	5.07 *dd*	5.06 *dd*	5.07 *dd*	5.06 *dd*
H-1t	5.21 *dd*	5.37 *dd*	5.25 *dd*	5.25 *dd*	5.22 *dd*	5.21 *dd*	5.22 *dd*	5.21 *dd*
H-2	5.90 *dd*	5.91 *dd*	5.89 *dd*	5.89 *dd*	5.91 *dd*	5.91 *dd*	5.91 *dd*	5.91 *dd*
H-4	1.60 *m*	1.82 *dd*	2.00 *m*	1.98 *m*	1.59 *m*	1.55 *m*	1.55 *m*	1.58 *m*
H-4′		1.50 *dd*						
H-5	2.00 *m*	4.62 *ddd*	2.09 *dt* (*br*)	2.07 *m*	2.00 *m*	2.01 *dt* (*br*)	2.03 *dt* (*br*)	2.02 *dt* (*br*)
H-6	5.15 *t* (*br*)	5.20 *d* (*br*)	5.14 *t* (*br*)	5.11 *t* (*br*)	5.14 *t* (*br*)	5.14 *t* (*br*)	5.15 *t* (*br*)	5.13 *t* (*br*)
H-8	2.10 *m*	2.07 *m*	2.05 *m*	2.08 *m*	2.00 *m*	2.02 *t* (*br*)	2.00 *t* (*br*)	2.02 *t* (*br*)
H-8′								
H-9			5.60 *ddd*	5.60 *ddd*	2.09 *dt* (*br*)	2.08 *dt* (*br*)	2.14 *dt* (*br*)	2.13 *dt* (*br*)
H-10	5.15 *t* (*br*)	5.13 *t* (*br*)	5.12 *d* (*br*)	5.11 *d* (*br*)	5.11 *t* (*br*)	5.14 *t* (*br*)	5.24 *t* (*br*)	5.30 *t* (*br*)
H-12	2.10 *m*	2.17 *t* (*br*)	2.00 *m*	1.98 *m*	2.67 *d* (*br*)	2.75 *d* (*br*)	3.04 *s* (*br*)	3.22 *d* (*br*)
H-12′								3.10 *d* (*br*)
H-13	1.44 *m*	1.60 *m*	1.60 *m*	1.66 *m*	5.57 *dt**	5.62 *dt*	—	—
	1.60 *m*							
H-14	3.33 *d* (*br*)	3.32 *d* (*br*)	3.33 *d* (*br*)	4.78 *dd*	5.63 *d**	6.17 *dt*	6.11 *qq*	3.48 *s*
H-16	1.20 *s*	1.15 *s*	1.16 *s*	1.19 *s*	1.32 *s*	1.84 *t*	1.88 *d*	1.23 *s*
H-17	1.15 *s*	1.17 *s*	1.20 *s*	1.20 *s*		4.88 *s* (*br*)	2.14 *d*	1.47 *s*
H-18	1.60 *s* (*br*)	1.60 *s* (*br*)	1.72 *d*	1.71 *d*	1.58 *s* (*br*)	1.59 *s* (*br*)	1.61 *s* (*br*)	1.59 *s* (*br*)
H-19	1.61 *s*(*br*)	1.58 *d*	1.61 *s* (*br*)	1.58 *s* (*br*)	1.60 *s* (*br*)	1.61 *s* (*br*)	1.62 *s* (*br*)	1.64 *s* (*br*)
H-20	1.27 *s*	1.28 *s*	1.29 *s*	1.28 *s*	1.29 *s*	1.28 *s*	1.28 *s*	1.28 *s*
OAc	—		2.02 *s*	2.01 *s*	—	—	—	—
				2.10 *s*				

*With $Eu(fod)_3$ 5.85 *d*, 5.79 *dt*.

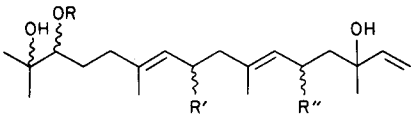
J (Hz): 1c, 1t = 1.5; 1c, 2 = 11; 1t, 2 = 17; 5, 6 = 9, 10 = 7; 13, 14 = 10; compound **48**: 4, 4′ = 14; 4, 5 = 10.5; 4′, 5 = 2; compound **49**: 8, 9 = 4.5; 8′, 9 = 8; 9, 10 = 8; compound **50**: 8, 9 = 4.5; 8, 9′ = 8; 9, 10 = 8; 13, 14 = 10; 13′, 14 = 3; compound **51**: 12, 13 = 6; 13, 14 = 15; compound **52**: 12, 13 = 7; 13, 14 = 15; 16, 17 = 1; compound **53**: 14, 16 = 14, 17 = 1; compound **54**: 12, 12′ = 15.



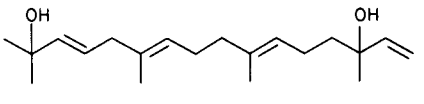
	34	35	36	37
R	H	OH	H	OH
R′	H	H	O Ac	OH



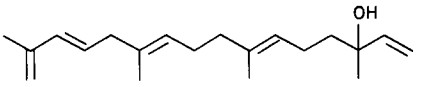
	38	39	40	41	42	43	44	45	46
R	H	OH	O Ac	H	H	H	H	H	O Ac
R′	H	H	H	OH	O Ac	H	O Ac	O Ac	H
R″	H	H	H	H	H	OH	OH	O Ac	OH



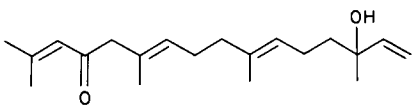
	47	48	49	50
R	H	H	H	Ac
R′	H	H	O Ac	O Ac
R″	H	OH	H	H



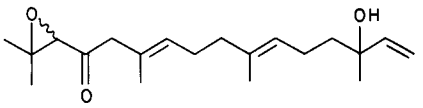
51



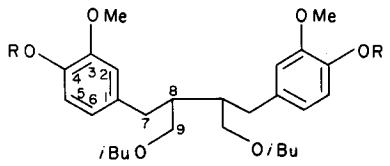
52



53



54



55 R = H
56 R = Ac

38, indicating identical stereochemistry of the double bonds. Acetylation of **39** afforded **40**, identical with the natural compound. The ^{1}H NMR spectra of the isomers **44** and **46** differed typically in the splitting of the signals of the protons under the oxygen functions, as the couplings $J_{4,5}$ were not identical with $J_{8,9}$ or $J_{12,13}$, this was obviously due to a hydrogen bond between the 3-hydroxyl and the oxygen function at C-5. Therefore, the position of the hydroxy groups could be assigned in both compounds, while the position of the acetoxy groups was determined by spin decoupling in part in different solvents, if the essential signals were overlapped. Irradiation of the broadened quartet of the allylic protons showed in the case of **46** coupling with one methyl signal, while the irradiation of the signal of the olefinic proton α-to the acetoxy group in the spectrum of **44** showed the coupling with one methyl group. Consequently, the positions of the acetoxy group could be determined. The spectrum of **45** showed that this compound was the corresponding acetate of **44**. While the position of one acetoxy group followed from the couplings of the corresponding downfield shifted signal, the second one caused the same behaviour as in the spectrum of **44**. The ^{1}H NMR spectrum of **52**, molecular formula $C_{20}H_{32}O$, clearly showed that we were dealing with a dehydro derivative of **38**. While in the ^{1}H NMR spectrum most signals were nearly the

same as in that of **38** those of H-11–H-17 differed markedly. The presence of a *trans*-double bond was indicated by the double triplets at δ 5.62 and 6.17, while its position followed from the chemical shifts and from the broadened two proton doublet at δ 2.75, which was coupled with the olefinic protons. Furthermore, as the olefinic methylene protons were coupled with those of an olefinic methyl group, the assigned position of the conjugated diene was the only possibility. The last diterpene, the acetate **49**, on acetylation afforded the diacetate **50**. Again the ^{1}H NMR spectra allowed a clear assignment of the relative positions of the oxygen functions which could be established in the same way as in the examples already discussed. The H-14 signal was a broadened doublet at δ 3.33 in the spectrum of **49**. The corresponding signal of **50** was shifted downfield and appeared as a double doublet at δ 4.78. As the signal of the other proton under the acetoxy group was coupled with allylic protons and with an olefinic one, this group could be placed only at C-9. The presence of a 13, 14-*trans*-double bond in the diol **51** was deduced from the couplings observed and from the results of spin decoupling. The signals of H-13 and H-14 were close together and only after addition of Eu(fod)$_3$ was a clear separation obtained. Irradiation of the H-12 signal clearly collapsed the doublet triplet of H-13 to a doublet. Further decouplings allowed the assignment of all signals, though some were overlapping multiplets.

The aerial parts of *G. burkei* Harv. subsp. *diffusa* (Harv.) Merxm. afforded sitosterol, stigmasterol, thymol, the sesquiterpene lactones **12**, **14**, **17** and **18**, the eremophilene derivative **32** [22] and the diterpenes **39**, **51**, **53** and **54**. The structures of **53** and **54** again followed from the ^{1}H NMR spectra (Table 7). The ^{1}H NMR signals of **53** showed that a 13-oxogeranyllinalol was present. Accordingly, the signals of H-16 and H-17 were downfield shifted doublets and the signal of H-14 was a quartet of quartets. Irradiation of the latter, therefore, collapsed the methyl doublets to singlets. The remaining signals were close to those of **38** indicating identical stereochemistry of the double bonds. Only the signals of H-12 and H-10 were shifted downfield. **54** obviously was the epoxide of **53**. Accordingly, the signals of H-16 and H-17 were upfield shifted singlets at δ 1.43 and 1.23, while H-14 was a sharp singlet at δ 3.48. Due to the new asymmetric centre, H-12 displayed a pair of broadened double doublets, while the remaining signals again were close to those of **38**.

The roots of *G. burkei* Harv. subsp. *fruticulosa* Merxm. afforded bisabolene, **1**, **3** and **55**, while the aerial parts gave α-humulene, **38** and **47**, the structure of the last compound followed from the ^{1}H NMR spectral data (Table 7). The presence of the 14, 15-diol group followed from the chemical shifts of H-14, H-16 and H-17, identical stereochemistry and substitution as in **38** was deduced from the similarity of the ^{1}H NMR spectra. Traces of sesquiterpene lactones were present, but they were not identified.

The roots of *G. burkei* Harv. subsp. *burkei* var. *zeyheri* (Harv.) Merxm. afforded bisabolene, **1**, **3** and **55**, while the aerial parts gave squalene, α-humulene, bisabolene, germacrene D, bicyclogermacrene, caryophyllenepoxide, **43**, **49** and **48**. The structure of the latter followed from the ^{1}H NMR spectral data (Table 7). As the signal of the proton under the secondary allylic hydroxy group was split as usual and the coupling partners were the typical double doublets, the position of this group was easily established, while the position of the other hydroxyls directly followed from the ^{1}H NMR spectrum. The structure of the diol **43** followed from the ^{1}H NMR spectrum as the signals of H-4–H-6 were the same as those of **44**, while the remaining signals were close to those of **38**. In addition to the above compounds, abienol (**33**) and minor quantities of sesquiterpene lactones were isolated. Careful ^{1}H NMR studies led to the structures **25**, **26** and **27**. The ^{1}H NMR spectrum of **27** (Table 4) was in part close to that of dihydroaromaticin [22] indicating the presence of a pseudoguaianolide with an 8,12-*trans*-lactone ring. Accordingly, the signals and the couplings of H-6 through H-10 were nearly the same in both lactones. The remaining downfield signals indicated the presence of a hydroxy and an acetoxy group. As the corresponding signals both were three-fold doublets, one being changed to a double doublet by deuterium exchange, only a 2, 4-substitution was possible. Inspection of a model showed that the couplings observed agreed best with a 2β- and a 4α-H. This was supported by comparing the corresponding signals with those of pulchellin [24], flexuosin A-acetate [25] and picrohelenin [26]. As in the spectrum of the latter the signals of H-2 and H-4 were a three-fold doublet and a double doublet respectively, while in the spectrum of flexuosin A-acetate with a 4α-hydroxyl group the H-4 signal is a broadened doublet. The 4β-orientation of the hydroxyl was further supported by the chemical shift of H-15, which obviously was influenced by the deshielding effect of the 4-hydroxyl group. The ^{1}H NMR spectral data of **25** and **26** (Table 3), which could not be separated completely, clearly showed that they differed only in the saturation of the 11, 13-bond. Accordingly, **26** was obtained pure after transformation of **25** to the corresponding pyrazoline. Extensive spin decoupling of the spectrum of **26** allowed the assignment of all signals. Starting with the proton under the lactone oxygen the signals of H-7 and H-9 were assigned. As the signals of H-7 and H-8 were at relatively high fields a *trans*-lactone was proposed. This was supported by the negative Cotton effect in the CD-spectrum of the pyrazoline of **25** [27]. As H-9α showed three large couplings both H-8 and H-10 must be β-orientated. Irradiation of the H-7 signal allowed the assignment of H-6 and H-11. The coupling of the latter being 11 Hz clearly indicated an α-orientated methyl group at C-11, thus establishing the whole sequence H-6–H-14. The remaining signals indicated the presence of an acetoxy group, a methylene group and a tertiary methyl carbinol, though the presence of the latter followed only indirectly from the chemical shift of the methyl singlet and the molecular formula. These observations, however, led to a guaianolide. The position of the acetoxy group followed from the homoallylic coupling between H-6β and the proton under the acetoxy group. The latter was further coupled with H-10 and the neighbouring methylene protons. The stereochemistry at C-2 and C-4 could not be determined with certainty. The one

proposed was based on the fact that the downfield shifted H-3 signal showed a larger coupling $J_{2,3}$. Models showed that the downfield shift required an α-orientated oxygen function. As the H-6α signal was shifted downfield a 4α-hydroxy group was very likely. Consequently, H-3α would also be deshielded. As this proton had the larger coupling with H-2 a 2β-acetoxy group was likely. The ^{1}H NMR data of **25** were close to those of **26**. Identical stereochemistry, therefore, had to be proposed. Guaianolides with a 1, 5-double bond seem to be unknown. We have named the corresponding lactone without oxygen functions at C-2 and C-4 burkeolide.

The roots of *G. burkei* Harv. subsp. *burkei* var. *elata* Merxm. afforded, in addition to bisabolene and squalene, **1** and **3**, while the aerial parts gave α-humulene, bicyclogermacrene, phytol, squalene, **43**, **44** and two further geranyllinalol derivatives, the diol **41** and the corresponding acetate **42**. The structures of **41** and **42** were deduced from the ^{1}H NMR spectral data (Table 6) as spin decoupling showed in both cases that the proton under the secondary oxygen function was coupled with one olefinic methyl group. Furthermore, the pseudoguaianolide **29** was present. The ^{1}H NMR spectrum showed (Table 4) that the compound was an isomer of **28** (see below). Accordingly, the signals of H-7 and H-8, which were assigned by spin decoupling, were at lower fields indicating a *cis*-8, 12-lactone in agreement with a negative Cotton effect in the CD spectrum [27]. This empirical rule, which has been discussed previously [14], seems to be valid for all sesquiterpenes, where a 8, 12-lactone is connected with a seven-membered ring (guaianolides, pseudoguaianolides and xanthanolides), as long as no special additional effect are encountered. Furthermore, $J_{7,13}$ seems to be larger in the *trans*-lactones.

The aerial parts of *G. burkei.* Harv. subsp. *burkei* var. *intermedia* (S. Moore) Merxm. Afforded germacrene D, bicyclogermacrene, bisabolene, **10**, **13**, **32**, **33** and **42–44** as well as two further sesquiterpene lactones, the pseudoguaianolide **28** and the xanthonolide **15**. The ^{1}H NMR spectral data of **28** (Table 4) were close to those of **27**, however, the H-4 signal was shifted downfield, indicating that the corresponding hydroxyl was acetylated. The signals of H-7 and H-8 differed typically from those of **29** as excepted for the 8β-H-epimer of the latter. The ^{1}H NMR spectrum of **15** (Table 2) was in part close to that of **9**, however, as shown by spin decoupling the H-8 signal was overlapped by a signal which was coupled with a methyl doublet, indicating that the keto group at C-4 was replaced by an acetoxy group. Furthermore, the H-14 signal was a singlet at δ 1.39 clearly showing that an additional hydroxy group was at C-10. This was in agreement with the molecular formula. While EI conditions only showed the M$-$H$_2$O-peak, chemical ionization led to the expected M+1-peak. In deuteriobenzene all signals could be assigned by spin decoupling, though some were overlapping multiplets. As the signal of H-9β was shifted downfield, if compared with the chemical shift of H-9β in the spectrum of **9**, the β-orientation of the 10-hydroxy group was likely. The stereochemistry at C-4 was not determined. The roots afforded bisabolene, bicyclogermacrene, kessane, **1** and **3**.

CONCLUSIONS

The chemistry of the genus *Geigeria* shows relationships to *Inula* and therefore its placement in the subtribe Inulinae is supported by the constituents. As in the genus *Inula* an unusual variation of different types of sesquiterpene lactones can be observed ranging from eudesmanolides, to guaianolides, pseudoguaianolides, xanthanolides, eremophilanolides and the new types, the geigeranolides, so far represented by two compounds. As the latter have been isolated from several species, they may be useful chemotaxonomic markers. The large variety of geranyllinalol derivatives is remarkable. They are present in all varieties of *G. burkei*, only two of which afforded the bicyclic diterpene abienol. Perhaps this is an indication that this genus has lost the ability to transform geranyllinalol to the widespread cyclic diterpenes. Most species contain thiophene acetylenes and the corresponding dithio compound **3**, which therefore also are good taxonomic markers. Concerning the biogenesis of the unusual sesquiterpene griesenin, the isolation of the xanthanolides **9**, **10** and **15** may be of interest. **15** could be the precursor of a diene, which after epoxidation could lead to **11**, a possible precursor of dihydrogriesenin (see Scheme). The isolation of the acetoxy derivative **13** may be an indication that griesenin is formed by elimination. The isolation of ivalin indicates a possible route for the biogenesis of geigeranolide (see Scheme), while the formation of **31** may be achieved starting with **30**, a probable precursor of the guaianolides (see Scheme). Further investigation should show whether the chemistry of the tribe Inuleae will help to establish a more clear subdivision into subtribes, as the taxonomic situation seems to be very complicated [1].

EXPERIMENTAL

The air-dried plant materials, collected in Transvaal, were extracted with Et$_2$O–petrol (1:2) and the resulting extracts were separated first by CC (Si gel) and further by repeated TLC (Si gel) using different solvent systems. Known compounds were identified by comparing the ^{1}H NMR spectra with those of authentic material. Voucher specimens were deposited in the Herbarium of the Botanic Research Institute, Pretoria.

G. aspera *var.* aspera (*voucher* 81/239). The roots (125 g) afforded 8 mg kessane, 3 mg bicyclogermacrene, 2 mg **1**, 0.3 mg **3**, 2 mg **4** (Et$_2$O–petrol, 1:20), 2 mg **5**, 1 mg **6**, 1 mg **8**, 5 mg **12**, 4 mg **14** and 8 mg **17** (Et$_2$O–petrol, 1:3, several developments) and 2 mg **19**, while the aerial parts (260 g) gave 2 mg caryophyllene epoxide, 2 mg bicyclogermacrene, 2 mg germacrene D, 200 mg **12**, 2 mg **13** (Et$_2$O–petrol, 3:1), 100 mg **14**, 3 mg **16**, 20 mg **19**, 15 mg **20** (Et$_2$O–petrol, 3:1), 2 mg **21**, 10 mg **22** (Et$_2$O–petrol, 3:1 and CH$_2$Cl$_2$–C$_6$H$_6$–Et$_2$O, 5:5:1), 5 mg **23**, isolated as its acetate **24** (Ac$_2$O, 1 hr, 70°, TLC Et$_2$O–petrol, 1:1, several developments), 5 mg **31** (Et$_2$O–petrol, 1:10), 50 mg **35**, 40 mg **36** and 1 mg **37** (Et$_2$O–C$_6$H$_6$–CH$_2$Cl$_2$, 1:1:1).

G. brevifolia (*voucher* 81/205). The roots (220 g) afforded 5 mg tridecapentaynene, 20 mg lupeyl acetate, 5 mg cadinol-T, 20 mg **5**, 2 mg **6**, 3 mg **8**, 2 mg **9** and 10 mg **17** (separated from **5** by addition of *m*-chloroperbenzoic acid in CHCl$_3$ in the presence of NaHCO$_3$ soln followed by TLC (Et$_2$O–petrol, 1:1) yielding **7**, which was easily separated from **17**). The aerial parts (100 g) gave 2 mg tridecapentaynene, 2 mg germacrene D, 2 mg bicyclogermacrene, 10 mg squalene,

10 mg phytol, 3 mg lupeol and a complex mixture of unidentified aromatic compounds.

G. burkei *subsp.* burkei *var.* burkei (*voucher* 81/64). The roots (120 g) afforded 100 mg bisabolene, 5 mg γ-humulene, 3 mg kessane, 2 mg **1**, 2 mg **2** (petrol), 1 mg **3**, 5 mg **6**, 10 mg **17**, 5 mg **18** (Et_2O–petrol, 1:3, several times, small amounts of **17** were separated by transforming the latter to the pyrazoline by addition of CH_2N_2) and 5 mg **55**. The aerial parts (660 g) gave 3 mg α-humulene, 2 mg bisabolene, 1 mg germacrene D, 1 mg caryophyllene, 1 mg bicyclogermacrene, 2 mg stigmasterol, 1 mg **1**, 100 mg **38**, 5 mg **39**, 10 mg **40**, 2 mg **44**, 2 mg **45**, 2 mg **46**, 5 mg **49**, 2 mg **51** and 2 mg **52**. The diterpenes were separated by TLC using petrol with different amounts of Et_2O and several developments. **43** could only be separated from **38** by $AgNO_3$-coated Si gel. The original amounts of the diterpenes must be higher, as the difficult separations caused considerable loss of material.

G. burkei *subsp.* diffusa (*voucher* 81/109). The aerial parts (220 g) afforded 3 mg sitosterol, 3 mg stigmasterol, 30 mg thymol, 5 mg **12**, 5 mg **14**, 2 mg **17**, 2 mg **18** [separated from **17** by addition of CH_2N_2 in Et_2O, evaporation after 30 min and separation by TLC (Et_2O–petrol, 1:1)], 6 mg **32**, 10 mg **39**, 4 mg **51** (Et_2O–petrol, 3:1), 5 mg **53** (same solvent), and 7 mg **54** (same solvent).

G. burkei *subsp.* fruticulosa (*voucher* 81/46). The roots (25 g) afforded 5 mg bisabolene, 2 mg **1**, 1 mg **3** and 2 mg **55**, while the aerial parts (150 g) gave 10 mg α-humulene, 50 mg **38** and 100 mg **47** (Et_2O–petrol, 3:1).

G. burkei *subsp.* burkei *var.* zeyheri (*voucher* 81/1). The roots (110 g) afforded 20 mg bisabolene, 4 mg **1**, 2 mg **3** and 4 mg **55**, while the aerial parts (500 g) gave 15 mg squalene, 5 mg caryophyllene-1, 10-epoxide, 5 mg α-humulene, 5 mg bisabolene, 1 mg bicyclogermacrene, 2 mg germacrene D, 2 mg **25**, 2 mg **26** (same solvent, not completely separated, after addition of CH_2N_2 pure **26** was obtained), 5 mg **27** (CH_2Cl_2–C_6H_6–MeOH, 20:20:1), 20 mg **33**, 40 mg **43**, 20 mg **48** (Et_2O, several developments) and 10 mg **49**.

G. burkei *subsp.* burkei *var.* elata (*voucher* 81/96). The roots (80 g) afforded 20 mg bisabolene, 20 mg squalene, 2 mg **1** and 0.5 mg **3**, while the aerial parts (210 g) gave 10 mg α-humulene, 20 mg bicyclogermacrene, 100 mg squalene, 80 mg phytol, 20 mg **29** (Et_2O–petrol, 3:1), 15 mg **41**, 50 mg **42**, 20 mg **43** and 15 mg **44** (**41**–**44** separated by TLC using Et_2O as solvent).

G. burkei *subsp.* burkei *var.* intermedia (*voucher* 81/229). The roots (50 g) afforded 30 mg bisabolene, 5 mg bicyclogermacrene, 20 mg kessane, 1 mg **1** and 0.3 mg **3**, while the aerial parts gave 2 mg germacrene D, 2 mg bicyclogermacrene, 3 mg bisabolene, 5 mg **10**, 10 mg **13**, 5 mg **15** (Et_2O–petrol, 3:1), 5 mg **28** (Et_2O–petrol, 1:1, several developments), 20 mg **32**, 10 mg **33**, 10 mg **42**, 5 mg **43** and 5 mg **44**.

2-*Prop*-1-*inyl*-5-(*hex*-3*c*, 5-*dien*-1-*inyl*)-*thiophene* (**2**). Yellow gum, UV $\lambda_{max}^{Et_2O}$ nm: 357, 334; MS *m/z* (rel. int.): 198.049 $[M]^+$ (100) ($C_{13}H_{10}S$), 197 $[M-H]^+$ (58), 165 $[197-S]^+$ (58); ^1H NMR ($CDCl_3$): δ 5.34 (*dd*, H-1c), 5.43 (*dd*, H-1t), 6.43 (*dd*, H-2), 6.45 (*dd*, H-3), 5.67 (*d*, H-4), 7.02 (*d*, H-8), 6.96 (*d*, H-9), 2.085 [*s*, H-13, *J* (Hz) 1c, 1t = 1.5; 1c, 2 = 11; 1t, 2 = 17; 2, 3 = 3, 4 = 10.5; 8, 9 = 3.7].

2-*Prop*-1-*inyl*-5-(5,6-*epoxyhex*-3*c*-*en*-1-*inyl*)-*thiophene* (**4**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 2190 (C≡C); UV $\lambda_{max}^{Et_2O}$ nm: 338, 318; MS *m/z* (rel. int.): 214.044 $[M]^+$ (100) ($C_{13}H_{10}OS$), 185 $[M-CHO]^+$ (58), 171 $[M-C_2H_3O]^+$ (19). ^1H NMR ($CDCl_3$): δ 2.77 (*dd*, H-1), 3.11 (*dd*, H-1'), 3.94 (*ddd*, H-2), 5.55 (*dd*, H-3), 5.98 (*d*, H-4), 7.03 (*d*, H-8), 6.96 (*d*, H-9), 2.08 [*s*, H-13, *J* (Hz) 1, 2 = 2.5; 1', 2 = 4; 1, 1' = 5.5; 2, 3 = 9; 3, 4 = 11; 8, 9 = 3.8].

2β-*Acetoxydihydrogriesenin* (**13**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1775 (γ-lactone), 1735, 1240 (OAc); MS *m/z* (rel. int.): 290 $[M-CH_2O]^+$ (0.5), 230.131 $[290-HOAc]^+$ (45) ($C_{15}H_{18}O_4$), 134 (100), 119 (48), 91 (67); CI (isobutane): 321 $[M+1]^+$ (2), 261 $[321-HOAc]^+$ (100), 231 $[261-CH_2O]^+$ (22).

10β-*Hydroxy*-10-*epi*-*tomentosin*-4-O-*acetate* (**15**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3590 (OH), 1775 (γ-lactone), 1730, 1250 (OAc); MS *m/z* (rel. int.): 290.152 $[M-H_2O]^+$ (5) ($C_{17}H_{22}O_4$), 230 $[290-HOAc]^+$ (10), 91 (86), 67 (100); CI (isobutane): 309 $[M+1]^+$ (20), 291 $[309-H_2O]^+$ (100), 231 $[291-HOAc]^+$ (41).

Geigeranolide (**17**). Colourless crystals, mp 92° (petrol), IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1775 (γ-lactone), 1265, 1130, 995, 980, 947; MS *m/z* (rel. int.): 232.146 $[M]^+$ (12) ($C_{15}H_{20}O_2$), 217 $[M-Me]^+$ (100), 191 (42), 171 (24), 145 (50), 131 (31), 121 (44), 119 (31), 107 (30), 105 (42), 95 (26), 93 (42), 91 (48), 81 (31), 79 (45), 77 (34), 68 (37), 67 (41), 55 (42), 53 (52);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+59 \quad +62 \quad +71 \quad +117} \quad (c = 3.0, CHCl_3).$$

11β, 13-*Dihydrogeigeranolide* (**18**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1780 (γ-lactone); MS *m/z* (rel. int.): 234.162 $[M]^+$ (12) ($C_{15}H_{22}O_2$), 219 $[M-Me]^+$ (88), 193 (30), 173 (18), 161 (30), 145 (100), 133 (28), 119 (79), 105 (70), 93 (58), 91 (51);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+10 \quad +10 \quad +10 \quad +20} \quad (c = 0.09, CHCl_3).$$

Geigerin acetate (**20**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1790 (γ-lactone), 1750, 1233 (OAc), 1710, 1650 (C=CC=O); MS *m/z* (rel. int.): 306.147 $[M]^+$ (11) ($C_{17}H_{22}O_5$), 264 $[M-ketene]^+$ (19), 246 $[M-HOAc]^+$ (100), 218 $[246-CO]^+$ (37), 204 $[246-C_2H_2O]^+$ (58).

11β, 13-*Dihydroinuviscolide* (**22**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 250.157 $[M]^+$ (10) ($C_{15}H_{22}O_3$), 232 $[M-H_2O]^+$ (59), 217 $[232-Me]^+$ (11), 71 (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+28 \quad +29 \quad +30 \quad +44} \quad (c = 0.13, CHCl_3).$$

Isogeigerin acetate (**24**). Obtained by acetylation (Ac_2O, 1 hr, 70°) of the natural compound, colourless crystals, mp 145° (Et_2O–petrol), IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1780 (γ-lactone), 1745, 1225 (OAc), 1710, 1610 (C=C–C=O); MS *m/z* (rel. int.): 306.147 $[M]^+$ (38) ($C_{17}H_{22}O_5$), 264 $[M-ketene]^+$ (45), 246 $[M-HOAc]^+$ (58), 123 (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+64 \quad +67 \quad +75 \quad +120} \quad (c = 0.27, CHCl_3).$$

2β-*Acetoxy*-4α-*hydroxyburkeolide* (**25**). Colourless gum, not free from **26**, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1775 (γ-lactone), 1740, 1240 (OAc); MS *m/z* (rel. int.): 306 $[M]^+$ (1), 288 $[M-H_2O]^+$ (1), 246.126 $[M-HOAc]^+$ (100) ($C_{15}H_{18}O_3$), 231 $[246-Me]^+$ (24), 228 $[246-H_2O]^+$ (6).

Addition of CH_2N_2 in Et_2O afforded the β-pyrazoline, ^1H NMR ($CDCl_3$): δ 5.18 (*ddd*, H-8, *J* = 11, 10, 3.5 Hz); CD (MeCN) $\Delta\epsilon_{326} = -2.4$.

2β-*Acetoxy*-4α-*hydroxy*-11β, 13-*dihydroburkeolide* (**26**). Colourless gum, which was separated from small amounts of **25** by addition of CH_2N_2 in Et_2O (30 min, RT) followed by TLC (CH_2Cl_2–C_6H_6–MeOH, 20:20:1), IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1740 (OAc); MS *m/z* (rel. int.): 290

$[M-H_2O]^+$ (2), 248.141 $[M-HOAc]^+$ (100) ($C_{15}H_{20}O_3$), 233 $[248-Me]^+$ (31), 230 $[248-H_2O]^+$ (4).

4-*Epipulchellin*-2-O-*acetate* (**27**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1775 (γ-lactone), 1740, 1240 (OAc); MS *m/z* (rel. int.): 290.152 $[M-H_2O]^+$ (4) ($C_{17}H_{22}O_4$), 248 $[M-AcOH]^+$ (72), 230 $[248-H_2O]^+$ (72), 215 $[230-Me]^+$ (24), 204 $[248-CO_2]^+$ (28), 159 (100).

4-*Epipulchellin*-2, 4-O-*diacetate* (**28**). Colourless crystals, mp 137° (Et_2O–petrol), IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1775 (γ-lactone), 1745, 1250 (OAc); MS *m/z* (rel. int.): 308 $[M-ketene]^+$ (1), 290.152 $[M-HOAc]^+$ (8) ($C_{17}H_{22}O_4$), 248 $[308-HOAc]^+$ (34), 230 $[290-HOAc]^+$ (100), 215 $[230-Me]^+$ (10);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+36.6 \quad +38.0 \quad +42.5 \quad +68.9} \quad (c = 0.71, CHCl_3).$$

4-*Epineopulchellin*-2, 4-O-*diacetate* (**29**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1770 (γ-lactone), 1740, 1240 (OAc); MS *m/z* (rel. int.): 350.173 $[M]^+$ (0.5) ($C_{19}H_{26}O_6$), 290 $[M-HOAc]^+$ (5), 248 $[290-ketene]^+$ (68), 230 $[290-HOAc]^+$ (93), 119 (100); CD (MeCN): $\Delta\epsilon_{260} = -0.1$.

Methyl asperageigerate (**31**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1720, 1630 ($C{=}CCO_2R$), 1460, 1440, 1370, 1280, 1250, 1200, 1165, 1130, 955; MS *m/z* (rel. int.): 246.162 $[M]^+$ (58) ($C_{16}H_{22}O_2$), 231 $[M-Me]^+$ (32), 214 $[M-MeOH]^+$ (10), 199 $[214-Me]^+$ (28), 186 $[214-CO]^+$ (38), 171 (70), 159 (39), 145 (71), 133 (48), 131 (48), 121 (64), 119 (100), 105 (95), 93 (84), 91 (93), 79 (54), 77 (61), 55 (64), 53 (41);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-43 \quad -46 \quad -53 \quad -102} \quad (c = 0.3, CHCl_3).$$

5, 9-*Dihydroxynerolidol* (**37**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3590, 3360 (OH), 920 ($CH{=}CH_2$); MS *m/z* (rel. int.): 236.177 $[M-H_2O]^+$ (0.1) ($C_{15}H_{24}O_2$), 85 $[C_5H_9O]^+$ (100); CI (isobutane): 237 $[M+1-H_2O]^+$ (4), 219 $[237-H_2O]^+$ (24), 201 $[219-H_2O]^+$ (10), 135 $[C_{10}H_{15}]^+$ (100); ^1H NMR ($CDCl_3$): δ 5.18 (*dd*, H-1c), 5.38 (*dd*, H-1t), 5.94 (*dd*, H-2), 1.85 (*dd*, H-4), 1.53 (*dd*, H-4'), 4.64 (*ddd*, H-5), 5.31 [*d* (*br*), H-6], 2.18 (*dd*, H-8), 2.11 [*dd* (*br*), H-8'], 4.47 (*ddd*, H-9), 5.16 (*dqq*, H-10), 1.69 [*s* (*br*), H-12, 13], 1.72 (*d*, H-14), 1.29 [*s*, H-15, *J* (Hz): 1c, 1t = 1.5; 1c, 2 = 10.5; 1t, 2 = 17; 4, 4' = 14.5; 4, 5 = 10.5; 4', 5 = 2.3; 5, 6 = 9; 8, 9 = 8; 8', 9 = 5; 8, 8' = 14; 9, 10 = 8; 6, 14 = 10, 12 = 10, 13 = 1]; $[\alpha]_D = +11°$ (c = 0.11, $CHCl_3$).

13-*Hydroxygeranyllinalol* (**39**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 3080, 930 ($CH{=}CH_2$); MS (CI, isobutane) *m/z* (rel. int.): 289 $[M+1-H_2O]^+$ (23), 271 $[289-H_2O]^+$ (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+8.2 \quad +8.6 \quad +9.4 \quad +17} \quad (c = 0.5, CHCl_3).$$

5 mg **39** on heating with 0.1 ml Ac_2O for 1 hr at 70° afforded after usual work-up 3 mg **40**, identical with the natural acetate.

13-*Acetoxygeranyllinalol* (**40**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 3080, 930 ($CH{=}CH_2$), 1740 (OAc); MS (CI, isobutane) *m/z* (rel. int.): 289 $[M+1-HOAc]^+$ (27), 271 $[289-H_2O]^+$ (100).

9-*Hydroxygeranyllinalol* (**41**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600, 3410 (OH), 3080, 935 ($CH{=}CH_2$); MS (CI, isobutane) *m/z* (rel. int.): 289 $[M+1-H_2O]^+$ (71), 271 $[289-H_2O]^+$ (100).

9-*Acetoxygeranyllinalol* (**42**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600, 3520 (OH), 1730, 1240 (OAc), 3080, 925 ($CH{=}CH_2$); MS (CI, isobutane) *m/z* (rel. int.): 289 $[M+1-HOAc]^+$ (47), 271 $[289-H_2O]^+$ (100), 71 $[C_4H_7O]^+$ (34); $[\alpha]_D = -7°$ (*c* = 0.3, $CHCl_3$).

5-*Hydroxygeranyllinalol* (**43**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3620, 3510 (OH); MS *m/z* (rel. int.): 270 $[M-2\times H_2O]^+$ (0.5), 69 $[C_5H_9]^+$ (100); CI (isobutane): 289 $[M+1-H_2O]^+$ (2), 271 $[289-H_2O]^+$ 219 $[287-C_4H_6O]^+$ (100).

9-*Acetoxy*-5-*hydroxygeranyllinalol* (**44**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1745, 1255 (OAc), 930 ($CH{=}CH_2$); MS *m/z* (rel. int.): 286.230 $[M-H_2O, HOAc]^+$ (1) ($C_{20}H_{30}O$), 70 $[C_4H_6O]^+$ (100).

5, 9-*Diacetoxygeranyllinalol* (**45**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3580 (OH), 3080, 930 ($CH{=}CH_2$), 1730, 1245 (OAc); MS *m/z* (rel. int.): 286.230 $[M-2\times HOAc]^+$ (1.5) ($C_{20}H_{30}O$), 135 $[C_{10}H_{15}]^+$ (78), 69 $[C_5H_9]^+$ (100); CI (isobutane): 347 $[M+1-HOAc]^+$ (2), 287 $[347-HOAc]^+$ (61), 269 $[287-H_2O]^+$ (100), 217 $[287-C_4H_6O]^+$ (88).

13-*Acetoxy*-5-*hydroxygeranyllinalol* (**46**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3590 (OH), 1730, 1250 (OAc), 3080, 930 ($CH{=}CH_2$); MS *m/z* (rel. int.): 304.240 $[M-HOAc]^+$ (1) ($C_{20}H_{32}O_2$), 135 $[C_{10}H_{15}]^+$ (47), 85 $[C_5H_9O]^+$ (100).

14, 15-*Dihydro*-14, 15-*dihydrogeranyllinalol* (**47**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3580, 3420 (OH), 3080, 930 ($CH{=}CH_2$); MS *m/z* (rel. int.): 306.256 $[M-H_2O]^+$ (0.5) ($C_{20}H_{34}O_2$), 288 $[306-H_2O]^+$ (0.2), 71 $[C_4H_7O]^+$ (100).

5, 14, 15-*Trihydroxy*-14, 15-*dihydrogeranyllinalol* (**48**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600, 3400 (OH); MS *m/z* (rel. int.): 322.251 $[M-H_2O]^+$ (0.1) ($C_{20}H_{24}O_3$), 304 $[322-H_2O]^+$ (0.1), 71 $[C_4H_7O]^+$ (100).

14, 15-*Dihydroxy*-9-*acetoxy*-14, 15-*dihydrogeranyllinalol* (**49**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3440 (OH), 1730, 1240 (OH), 1730, 1240 (OAc), 930 ($CH{=}CH_2$); MS *m/z* (rel. int.): 304.240 $[M-H_2O, HOAc]^+$ (0.3) ($C_{20}H_{32}O_2$), 246 $[304-Me_2CO]^+$ (3), 71 $[C_4H_7O]^+$ (100).

5 mg **49** were heated for 1 hr with 0.1 ml Ac_2O at 70°. TLC (Et_2O–petrol, 3:1) afforded 4 mg **50**, colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3580 (OH), 1735, 1240 (OAc), 930 ($CH{=}CH_2$); MS *m/z* (rel. int.): 424 $[M]^+$ (0.1), 346 $[424-HOAc, H_2O]^+$ (1), 71 $[C_4H_7O]^+$ (100); CI (isobutane): 425 $[M+1]^+$ (4), 407 $[425-H_2O]^+$ (5), 347 $[407-HOAc]^+$ (84), 287 $[347-HOAc]^+$ (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{7.1 \quad +8.2 \quad +8.6 \quad +14.3} \quad (c = 0.28, CHCl_3).$$

15-*Hydroxy*-13, 14-*dehydro*-14, 15-*dihydrogeranyllinalol* (**51**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3580 (OH), 970 (*tr* CH=CH), 925 ($CH{=}CH_2$); MS *m/z* (rel. int.): 288.245 $[M-H_2O]^+$ (0.3) ($C_{20}H_{32}O$), 270 $[288-H_2O]^+$ (0.5), 255 $[270-Me]^+$ (0.3), 135 $[C_{10}H_{15}]^+$ (27), 93 $[C_7H_9]^+$ (74), 55 $[C_4H_7]^+$ (100); CI (isobutane): 289 $[M+1-H_2O]^+$ (13), 271 $[289-H_2O]^+$ (100), 135 $[C_{10}H_{15}]^+$ (28).

14, 15-*Dihydro*-13, 14, 15, 16-*tetradehydrogeranyllinalol* (**52**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 930 ($CH{=}CH_2$), 890 ($C{=}CH_2$); MS *m/z* (rel. int.): 288 $[M]^+$ (0.3), 270 $[M-H_2O]^+$ (1), 255.211 $[270-Me]^+$ (2) ($C_{19}H_{27}$), 202 $[270-C_5H_8]^+$ (3), 134 $[C_{10}H_{14}]^+$ (40), 93 $[C_7H_9]^+$ (100); CI (isobutane): 289 $[M+1]^+$ (2), 271 $[289-H_2O]^+$ (49).

13-*Oxo-geranyllinalol* (**53**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1680, 1665 ($C{=}CC{=}O$); MS (CI, isobutane) *m/z* (rel. int.): 305 $[M+1]^+$ (6), 287 $[M+1-H_2O]^+$ (100), 189 $[287-C_6H_{10}O]^+$ (54), 83 $[C_4H_7CO]^+$ (52).

14, 15-*Epoxy*-13-*oxo*-14, 15-*dihydrogeranyllinalol* (**54**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600 (OH), 1715 (C=O), 930 ($CH{=}CH_2$); MS (CI, isobutane) *m/z* (rel. int.): 303 $[M+1-$

$H_2O]^+$ (100), 285 $[303-H_2O]^+$ (20);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-13.6 \quad -14.3 \quad -19.9 \quad -47.5} \quad (c = 0.28, CHCl_3).$$

Bis coniferylisobutyrate (**55**). Colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3550 (OH), 1730 (CO_2R), 1605, 1510 (aromatic); MS *m/z* (rel. int.): 502.257 $[M]^+$ (14) ($C_{28}H_{38}O_8$), 414 $[M-RCO_2H]^+$ (6), 326 $[414-RCO_2H]^+$ (12), 189 $[C_{10}H_{11}O_3]^+$ (41), 137 [hydroxymethoxytropylium ion]$^+$ (100); ^1H NMR ($CDCl_3$): δ 6.47 (*d*, H-5), 6.55 (*dd*, H-6), 2.66 (*dd*, H-7), 2.58 (*dd*, H-7′), 2.08 (*dddd*, H-8), 4.22 (*dd*, H-9), 4.00 (*dd*, H-9′), 3.80 (*s*, OMe), 2.56 (*qq*), 1.19 (*d*), 1.18 [*d*, OiBu, *J* (Hz): 2, 6 = 2; 5, 6 = 8; 7, 7′ = 14; 7, 8 = 7.5; 8, 9 = 6; 8, 9′ = 5.5; 9, 9′ = 11.5]. 3 mg **55** were heated for 1 hr with Ac_2O at 70°. TLC (Et_2O–petrol, 1:1) afforded 2 mg **56**, colourless gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 1780 (PhOAc), 1740 (CO_2R), 1610, 1520 (aromatic); ^1H NMR ($CDCl_3$): δ 6.66 (*d*, H-2), 6.91 (*d*, H-5), 6.62 (*dd*, H-6), 2.74 (*dd*, H-7), 2.64 (*dd*, H-7′), 2.05 (*m*, H-8), 4.27 (*dd*, H-9), 4.01 (*dd*, H-9′), 2.30 (*s*, OAc), 3.76 (*s*, OMe), 2.56 (*qq*), 1.19 (*d*), 1.18 [*d*, OiBu, *J* (Hz) see **55**].

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 material, 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, New York.
2. Barton, D. H. R. and Pinkey, J. T. (1960) *Proc. Chem. Soc.* 279.
3. de Villiers, D. P. and Pachler, K. G. R. (1963) *J. Chem. Soc.* 4989.
4. de Kock, W. T., Pachler, K. G. R. and Wessels, P. L. (1968) *Tetrahedron* **24**, 6045.
5. Anderson, L. A. P., de Kock, W. T., Aal, W., Pachler, K. G. R. and van Tonder, G. (1968) *Tetrahedron* **24**, 1687.
6. Anderson, L. A. P., de Kock, W. T. and Pachler, K. G. R. (1967) *Tetrahedron* **23**, 4153.
7. Herz, W., Aota, K., Holub, M. and Samek, Z. (1970) *J. Org. Chem.* **35**, 2611.
8. Vogelzang, M. E., Vermeulen, N. M. J., Potgieter, D. T. T. and Strauss, H. F. (1978) *Phytochemistry* **17**, 2030.
9. Vermeulen, N. M. J., Vogelzang, M. E., Potgieter, D. J. J. (1978) *Agrochemphysica* **10**, 1.
10. Grosskopf, J. F. W. (1965) Dept Agric. Techn. Serv. Rep. S. Afr. Techn. Commun. No. 21.
11. Hikino, H., Hikino, Y., Takeshita, Y., Shirata, K. and Takemoto, T. (1963) *Chem. Pharm. Bull., Tokyo* **11**, 547.
12. Bohlmann, F., Burkhardt, R. and Zdero, C. (1973) *Naturally Occurring Acetylenes.* Academic Press, New York.
13. Marshall, J. A. and Cohen, N. (1964) *J. Org. Chem.* **29**, 3727.
14. Bohlmann, F., Mahanta, P. K., Jakupovic, J., Rastogi, R. C. and Natu, A. A. (1978) *Phytochemistry* **17**, 1165.
15. Tanaka, N., Yazawa, T., Aoyama, K. and Muraki, T. (1976) *Chem. Pharm. Bull.* **24**, 1419.
16. Herz, W. and Högenauer, G. (1962) *J. Org. Chem.* **27**, 905.
17. Bohlmann, F., Czerson, H. and Schöneweiß, S. (1977) *Chem. Ber.* **110**, 1330.
18. Bohlmann, F. and Zdero, C. (1980) *Phytochemistry* **19**, 149.
19. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 1643.
20. Anderson, G. D. R., McEven, R. S. and Herz, W. (1972) *Tetrahedron Letters* 4423.
21. Bohlmann, F., Lonitz, M. and Knoll, K. H. (1978) *Phytochemistry* **17**, 330.
22. Bohlmann, F., Fritz, U. and Dutta, L. (1980) *Phytochemistry* **19**, 841.
23. Bohlmann, F. and Mahanta, P. K. (1979) *Phytochemistry* **18**, 887.
24. Aota, K., Coughlan, C. N., Emerson, M. T., Herz, W., Inayama, S. and Hague, M. (1970) *J. Org. Chem.* **35**, 1448.
25. Herz, W., Subramaniam, P. S. and Dennis, N. (1969) *J. Org. Chem.* **34**, 2915.
26. Kondo, Y., Tomimori, T., Hiraga, N. and Takemoto, T. (1979) *Heterocycles* **6**, 19.
27. Stöcklin, W., Waddell, T. G. and Geissman, T. A. (1970) *Tetrahedron* **26**, 2397.