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SESQUITERPENE LACTONES AND OTHER TERPENES FROM *GEIGERIA* SPECIES

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Key Word Index—*Geigeria* species; Compositae; sesquiterpene lactones; guaianolides; germacranolides; eudesmanolides; xanthanolides; dimeric sesquiterpene lactones; fulvene; nerolidol derivatives; geranyl linalol derivatives; ivaxillarane derivatives; eremophilane derivative.

Abstract—The investigation of seven further *Geigeria* species afforded, in addition to known compounds, 28 new sesquiterpene lactones, including two dimeric ones and a fulvene lactone, an eremophilane ketone, six nerolidol derivatives, including two glucosides, 5,13-dihydroxygeranyllinalol, a glucoside of a myrcene derivative and two ivaxillarane acids. The structures were elucidated by high field NMR techniques. The chemotaxonomic aspects are discussed.

INTRODUCTION

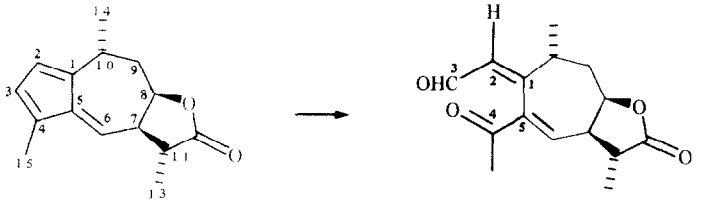
The mainly South African genus *Geigeria* is a well-defined genus which is placed in the tribe *Inuleae*, subtribe Inulinae [1]. As most species are toxic to sheep, causing vomiting disease, the first chemical investigations were performed some 28 years ago. So far six species and several subspecies have been studied [2–9]. In addition to more widespread sesquiterpene lactones, some very characteristic ones such as griesenin and its dihydro derivative [4] as well as geigeranolide and its dihydro derivative [9] were isolated. Furthermore, some species can be characterized by the occurrence of nerolidol and geranyllinalol derivatives [9] and from the roots typical thiophene acetylenes as well as the corresponding dithio derivatives are reported [9]. We have now studied seven further species, all from Namibia. The results are discussed in this paper.

RESULTS AND DISCUSSION

The extract of the aerial parts of *Geigeria ornativa* O. Hoffm. [=*G. africana* subsp. *ornativa* (O. Hoffm.) Merxm.], a very nice flowering species used by native people for preparing necklaces (hence the name of the plant), gave in addition to widespread compounds and the sesquiterpene lactones **2** and **3** [4] 11 new ones, the guaianolides **1**, **7–9**, the carabrone derivatives **20** and **21**, the pseudoguaianolide **22**, the hymenoxon derivatives **23** and **24** as well as the dimeric lactones **5** and **6**. Furthermore, in addition to nerolidol (**44**), the derivatives **48** [10], **49** [9], **53** [11], **56** [12] and **57** [12], **45**, **54** and **55** as well as the β-D-pyranoglucosides **42**, **50** and **51** were isolated. In addition to the known geranyllinalol derivatives **58–61** [9] a further one (**62**) and the valencene derivative **41** were present.

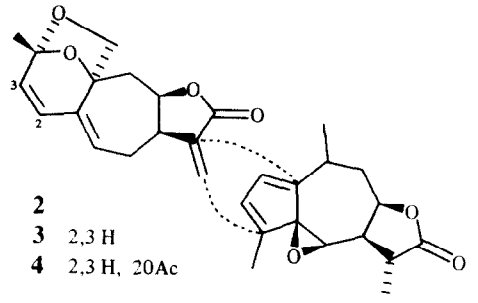
The easily crystallizing, orange coloured lactone **1**, molecular formula $C_{15}H_{18}O_2$, gave a ^{1}H NMR spectrum (Table 1) which indicated the presence of a 11,13-dihydrolactone. Spin decoupling allowed the assignment of all signals and their sequence. As irradiation at δ2.61 collapsed the methyl doublet at δ1.36 to a singlet and the three-fold doublet at δ3.28 to a double doublet, these signals must be due to H-11, H-13 and H-7. As the latter was further coupled with a three-fold doublet at δ4.97 and a narrowly split doublet at δ6.39, H-8 and H-6 could be assigned. Similarly, H-9, H-10 and H-14 were determined. As H-10 showed a small allylic coupling with the broadened quartet at δ6.07 and H-6 with the doublet quartet at δ6.00, H-2 and H-3 could be assigned. The ^{13}C NMR spectrum (Experimental) was also in agreement with the fulvene **1**. The stereochemistry was established by the observed NOE's [H-8 with H-7 (10%) and H-14 (4%), H-10 with H-11 (7%), H-2 (5%), H-9 (3%) and H-9′ (4%), H-15 with H-6 (15%) and H-3 (9%), H-13 with H-7 (6%), H-11 (9%) and H-6 (3%) as well as H-14 with H-2 (12%), H-8 (6%), H-10 (8%), H-9 (3%) and H-9′ (2%)]. The small coupling $J_{2,3}$ (*ca* 1.5 Hz) is remarkable. The only other known fulvene sesquiterpene lactones are the isomeric compound with a $\Delta^{1(10)}$ double bond reported from a *Stevia* species [13] and a pair of 11-epimers from a *Tanacetum* species with a 12,6-olide moiety [14]. Compound **1** was named geigeriafulvenolide. On standing in deuteriochloroform, it was transformed to **1a** as followed from its ^{1}H NMR spectrum (Experimental). A low field doublet at δ9.42 was coupled with a double doublet at δ6.15. The latter was further coupled with H-10, as followed from the decoupling of H-14 and H-9. Further decoupling gave the whole sequence. Furthermore, the IR bands at 1775, 1715 and 1685 cm^{-1} agreed with the nature of the proposed carbonyl groups. Most likely the ketoaldehyde is the result of an oxygen addition to the Δ^3 double bond followed by fragmentation of the oxetane. Crystals of the fulvene lactone remained unchanged at −10°.

Compound **5** was isolated in very small amounts. The ^{1}H NMR spectrum (Table 2) at a first glance looked like that of a mixture of two sesquiterpene lactones. However, the molecular formula, $C_{30}H_{34}O_7$, clearly indicated that a dimeric sesquiterpene lactone was present. One part of the signals was similar to those of **2**. However, the exomethylene protons (H-13) were missing. A pair of



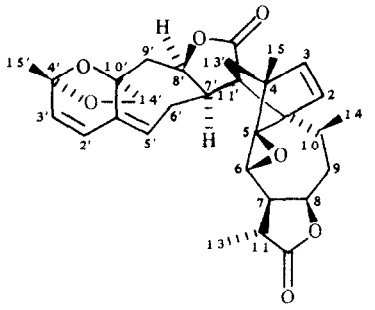
1

1a



2
3 2,3 H
4 2,3 H, 20Ac

1b

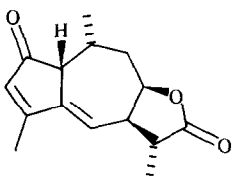


5
6 2',3'H

doublets at δ6.03 and 5.84 with a 6 Hz coupling led to the assumption that a cyclopentene moiety must be present. As the corresponding protons showed no additional vicinal coupling the double bond was flanked by quaternary carbons. Spin decoupling further showed that a 11,13-dihydroguaianolide part was present. Accordingly, a compound formed by a Diels–Alder addition of **2** and **1b** was likely. However, there are eight possible adducts. The direction of the addition as well as the stereochemistry at all 13 chiral centres could be deduced from the observed NOE's (Table 3). Thus the direction of the addition followed from the NOE of H-15 with H-13_1' and H-13_2', while NOE's with H-3 and H-6 established the assignment of H-15. Further important NOE's are those between H-10, H-7', H-8' and H-8 as well as between H-13, H-7 and H-11. A weak NOE between H-8' and the protons at C-14 allowed the assignment at this centre. As this stereochemistry should be identical with that of **3**, we have established the configuration of this lactone by the observed NOE's between H-8, H-7 (6%), H-14 (4%) and H-14' (5%). Thus the proposed configuration at C-10 of lactone **3** [9] has to be revised.

The ^{1}H NMR spectral data of **6** (Table 2) and its molecular formula clearly indicated that this compound was the corresponding dihydro derivative of **5**, obviously formed also by a Diels–Alder reaction of **3** with **1b**. Again the signals could be assigned by spin decoupling. For comparison the spectrum of **3** has been added in Table 2 as no clear data are reported in the literature. The similarity of the spectra indicated that the stereochemistry was the same in both compounds which we have named ornativolide (**5**) and dihydroornativolide (**6**). Surprisingly, the configuration at C-10 is different in these lactones and lactone **1** though lactone **1b**, the proposed precursor of **5** and **6**, should be formed by epoxidation of **1**. Therefore **5** and **6** may be formed by 2 + 4-addition of **2** and **3** respectively with **1**. Inspection of models indicated that this reaction would be sterically hindered by a 10α-methyl group. Accordingly, at this stage an isomerization of the allylic proton at C-10 may occur. After the addition, epoxidation could lead to the isolated compounds. Heating of **2** with the fulvene **1** for 4 hr at 140° did not result in the formation of an adduct. Accordingly, the dimeric lactones can not be artifacts.

The ^{1}H NMR spectrum of **8** (Table 1) indicated the presence of a senecioate of a 11,13-dihydroguaianolide. A broadened singlet at δ6.07 was coupled with a broadened methyl singlet at δ2.23. Thus the presence of a conjugated



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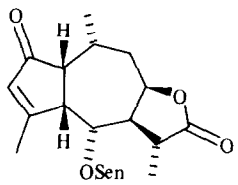

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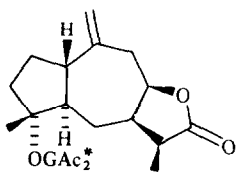

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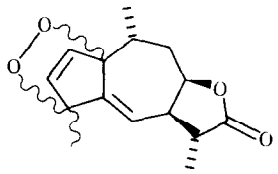
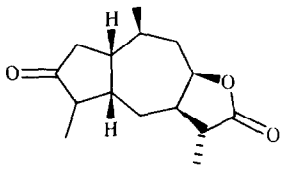
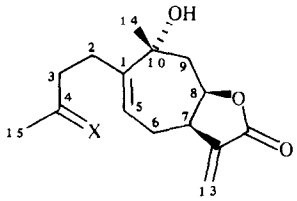


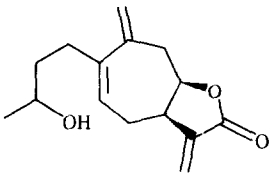
10 1α, 4α
11 1β, 4β



12 Δ^4
13 Δ^1, 4αH
14 Δ^1, 4βH



15 X = H,OH
16 X = O



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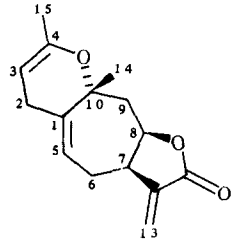

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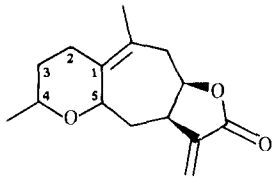


19

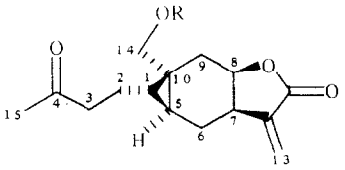
2-keto group was very likely. Spin decoupling allowed the assignment of all signals. The stereochemistry was determined by the observed NOE's between H-13, H-8 (3%) and H-7 (10%), H-14 and H-1 (10%), H-7 and H-8 (10%), H-5, H-1 (16%) and H-6 (5%), H-6, H-5 (10%) and H-11 (10%) as well as between H-10, H-6 (15%) and H-14 (10%). Accordingly, an unusual 1β,5β-guaianolide was present. The ^{13}C NMR spectrum (Experimental) also supported the structure.

The ^{1}H NMR spectrum of **7** (Table 1) indicated that the corresponding Δ^5-derivative was present. Again the signals were assigned by spin decoupling. The small coupling $J_{1,10}$ and those of H-8 and H-9 showed that the stereochemistry was that of **8**. Most likely lactone **7** is the precursor of the fulvene **1** which could be formed by reduction of **7** and elimination of water.

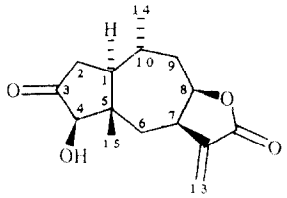
The structures of **20** and **21** could be easily deduced from the ^{1}H NMR spectra (Experimental) which were similar to that of the corresponding 14-*O*-acetate [15] though the esters could not be separated. The changed nature of the ester group followed from the typical signals of a senecioate and an angelate.

The structure of **9** also followed from its ^{1}H NMR spectrum (Experimental) which was in part close to that of the corresponding aglycone where the stereochemistry was established [16]. The nature of the glycoside part was determined by spin decoupling. The chemical shifts of H-2′ and H-6′ indicated that the acetate groups were at the corresponding carbons. The aglycone with a 13α-methyl is present in another *Geigeria* species [9].

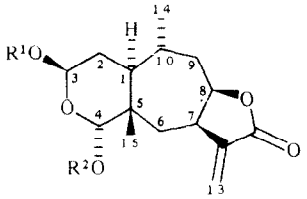
The ^{1}H NMR spectrum **22** (Table 4) indicated the presence of a pseudoguaianolide. Several signals were similar to those of related lactones. Spin decoupling allowed the assignment of all signals. The H-4 signal was a broadened doublet which showed a *W*-coupling with H-15 and a vicinal one with the hydroxy proton (δ3.87). Accordingly, a 4β-hydroxy derivative was present. The position of the keto group followed from the chemical shifts of H-2 (δ2.85 *dd* and 2.17 *dd*). Lactone **22** differed from peruvinin by the configuration at C-10 [17]. As



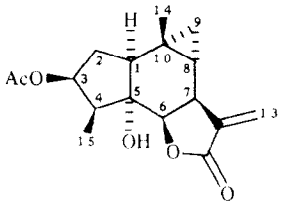
20 R = Sen
21 R = Ang



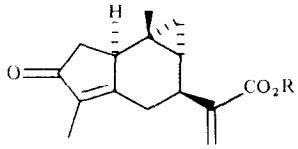
22



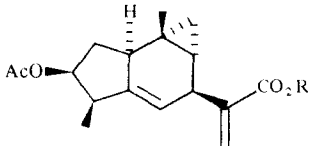
23 R^1 = Me, R^2 = H
24 R^1 = H, R^2 = Me



25



26 R = H
26a R = Me



27 R = H
27a R = Me

Table 1. ^{1}H NMR spectral data of compounds **1**, **1a**, **7** and **8** (400 MHz, $CDCl_3$, δ-values)

H	1	1a	7	8*
1	—	—	2.94 *br s*	2.62 *dd*
2	6.07 *ddd*	6.15 *dd*	—	—
3	6.00 *dq*	9.42 *d*	6.13 *br s*	6.07 *br s*
5	—	—	—	3.31 *br d*
6	6.39 *dd*	6.78 *d*	5.98 *dd*	5.41 *dd*
7	3.28 *ddd*	3.12 *ddd*	3.08 *br ddd*	2.26 *ddd*
8	4.97 *ddd*	4.64 *ddd*	4.74 *ddd*	4.61 *ddd*
9α	1.86 *ddd*	1.79 *ddd*	2.39 *dt*	1.94 *ddd*
9β	2.10 *ddd*	2.25 *ddd*	1.88 *ddd*	1.84 *ddd*
10	2.85 *br dq*	2.82 *m*	2.66 *dddq*	2.38 *m*
11	2.61 *dq*	2.62 *dq*	2.59 *dq*	2.55 *dq*
13	1.36 *d*	1.39 *d*	1.32 *d*	1.27 *d*
14	1.23 *d*	1.29 *d*	0.74 *d*	1.40 *d*
15	2.00 *br d*	2.42 *s*	2.20 *br s*	2.23 *br s*

*OSen: 5.70 *br s*, 2.23 *br s*, 1.97 *br s*.

J [Hz]: compound **1**: 2,3 = 2,10 = 2,6 = 3,15 ~ 1.5; 6,7 = 11,13 = 10,14 = 7; 7,8 = 8.5; 7,11 = 12; 8,9α = 3; 8,9β = 7; 9α,9β = 14; 9α,10 = 8.5; 9β,10 = 1.5; compound **1a**: 2,3 = 6.5; 2,10 = 2; 6,7 = 3.5; 7,8 = 8.5; 7,11 = 10; 8,9α = 1.5; 8,9β = 11; 9α,9β = 14; 9α,10 = 7; 9β,10 = 3; 10,14 = 11,13 = 7; compound **7**: 1,6 = 1.5; 6,7 = 8; 7,8 = 7; 7,11 = 13; 8,9α = 5.5; 8,9β = 12; 9α,9β = 14; 9α,10 = 5.5; 9β,10 = 2.5; 10,14 = 6.5; compound **8**: 1,5 = 7.5; 1,10 = 5,6 = 3; 6,7 = 11.5; 7,8 = 7,11 = 8,9 ~ 7; 8,9′ = 5; 9,9′ = 14; 9,10 = 6; 9′,10 = 9; 10,14 = 11,13 = 7.

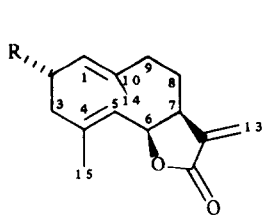
expected, some NMR signals have different chemical shifts.

The ^{1}H NMR spectra of **23** and **24** (Table 4) were close to that of hymenoxon its structure being established by X-ray analysis [18]. As followed from the chemical shifts and the presence of methoxy signals we were dealing with the isomeric *O*-methyl ethers. The stereochemistry of **23** was established by NOE difference spectroscopy. Thus effects were observed between H-15 and H-4, between H-8, H-14 and H-7, between OMe and H-3 as well as between H-7, H-8 and H-1. Probably lactone **22** is the precursor of hymenoxon as only a cleavage of the 3,4-bond would be necessary.

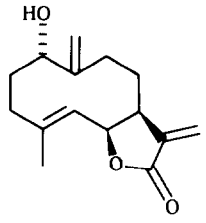
The structure of **41** followed from the ^{1}H NMR spectrum (Experimental), from the *W*-couplings of H-14 with H-6β and from H-1 with H-3, and from the observed NOE's between H-1 and H-9, between H-6 and H-8′, between H-15, H-14, H-3α and H-3β, between H-14, H-3α, H-6α and H-9α as well as between OH, H-3β and H-6β. A 11-hydroxy isomer of **41** has been reported from a *Teucrium* species [19] while valencene is present in *Cynara scolymus* [20].

The structure of **45** was easily deduced from its ^{1}H NMR spectrum (Experimental) as it was nearly identical with that of the acetate **46** [21] except for the signals of the ester residue.

Similarly the spectrum of **50** (Table 5) was in part close to that of **48**. Additional low field signals and an acetate singlet indicated the presence of a glycoside. Spin decoupling allowed the assignment of all signals and



28 R = H
29 R = OH



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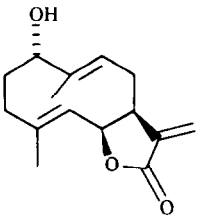

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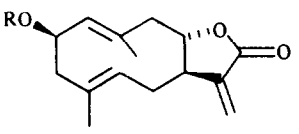
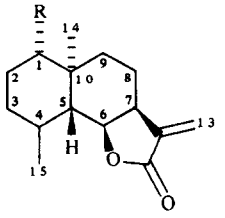
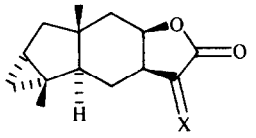


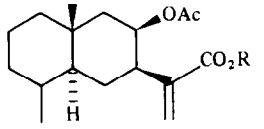
32 R = H
32Ac R = Ac



	33	**34**	**35**	**36**
	Δ^3	Δ^3	$\Delta^{4(15)}$	Δ^4
R	OH	H	OH	OH



37 X = CH_2
38 X = αMe,H

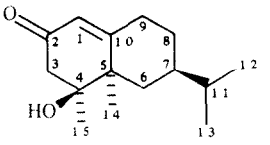


39 R = H, Δ^3
39a R = Me, Δ^3
40 R = H, $\Delta^{4(15)}$
40a R = Me, $\Delta^{4(15)}$

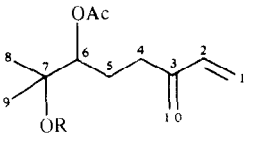
Table 2. ^{1}H NMR spectral data of compounds **3**, **5** and **6** (400 MHz, $CDCl_3$, δ-values)

H	5	6	H	5	6	3
2	6.14 *d*	6.16 *d*	2′	6.03 *d*	{ 2.58 *m* 2.17 *br dd*	{ 2.55 *m* 2.17 *br dd*
3	6.38 *d*	6.36 *d*	3′	5.84 *d*	1.75 *m*	1.80 *m*
6	2.97 *d*	2.95 *d*	5′	5.72 *br t*	5.60 *m*	5.58 *dt*
7	2.88 *ddd*	2.89 *ddd*	6′	2.40 *m*	2.34 *m*	{ 2.60 *dt* 2.10 *dt*
8	4.45 *ddd*	4.50 *ddd*	7′	2.95 *m*	2.96 *m*	3.21 *m*
9	1.72 *m*	1.72 *m*	8′	4.54 *ddd*	4.42 *m*	4.51 *ddd*
9′	1.65 *br d*	1.64 *br d*	$9'_1$	2.68 *dd*	2.63 *dd*	2.69 *t*
10	1.91 *m*	1.95 *m*	$9'_2$	2.47 *dd*	2.30 *dd*	—
11	2.40 *dq*	2.40 *dq*	$13'_1$	1.99 *d*	1.96 *d*	—
13	1.30 *d*	1.31 *d*	$13'_2$	1.74 *d*	1.78 *d*	{ 6.30 *d* 5.63 *d*
14	1.16 *d*	1.14 *d*	$14'_1$	3.90 *d*	4.01 *d*	3.99 *d*
15	1.59 *s*	1.49 *s*	$14'_2$	3.82 *d*	3.69 *d*	3.70 *d*
			15	1.02 *s*	1.03 *s*	1.42 *s*

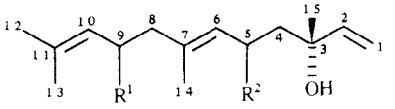
J [Hz]: compounds **5** and **6**: 2,3 = 6; 6,7 = 1.5; 7,8 = 7; 7,11 = 13; 8,9 = 10; 8,9′ = 3.5; 9,9′ = 15; 11,13 = 10,14′ = 7; 2′,3′ = 9; 5′,6′ = 6; 7′,8′ ~ 7; 8′,$9'_1$ = 11; 8′,$9'_2$ = 4; $9'_1$,$9'_2$ = 13; $14'_1$,$14'_2$ = 7.



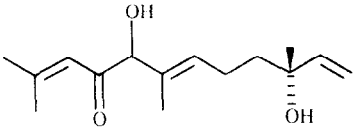
41



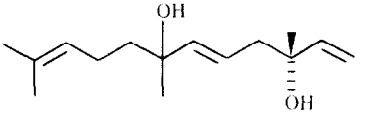
42 R = GAc*
43 R = H



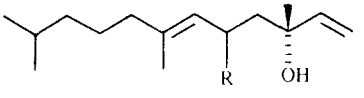
	44	45	46	47	48	49	50	51	52
R^1	H	H	H	H	OH	OH	OGAc*	$OGAc_2^*$	OG*
R^2	H	O*i*Val	OAc	OSen	H	OH	H	H	H



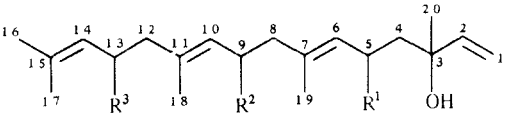
53



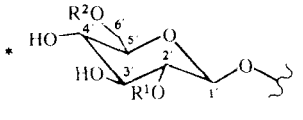
54



55 11 OH, Δ^{9E}, R = H
56 11 OH, Δ^{9E}, R = OH
57 10 OH, Δ^{11}, R = OH



	58	59	60	61	62
R^1	OH	OH	H	OH	OH
R^2	H	OAc	H	H	H
R^3	H	H	H	H	OH
	14,15 OH		14,15 OH		



OGAc: R^1 = Ac, R^2 = H; $OGAc_2$: R^1 = R^2 = Ac.
OG: R^1 = R^2 = H

the observed couplings indicated the presence of a β-glucopyranoside where the hydroxy group at C-2′ was acetylated. The position of the sugar moiety at C-9 was determined by the resulting sequences. Thus H-9 was coupled with H-10 which itself showed allylic couplings with two olefinic methyls (H-12 and H-13). The spectrum of **51** (Table 5) showed that this compound was the corresponding 2′,6′-*O*-diacetate. The configuration of the 6,7-double bond followed from the observed NOE between H-6 and H-8 while the position of the sugar part was established by the effect of H-9 with H-1′, H-13 and H-14. Saponification gave the glucopyranoside **52** and acetylation **52**Ac.*

The ^{1}H NMR spectrum of **54** (Experimental) indicated that an isomer of desacetyl **46** with a Δ^5 double bond was present. In deuteriobenzene all signals could be assigned by spin decoupling while in deuteriochloroform H-5 and H-6 gave a multiplet at δ5.62.

*The ^{1}H NMR data of **52**Ac differ from that of a tetraacetate obtained from a corresponding 6′-*O*-acetate from a *Gaillardia* species [Goa, F., Turner, B. L. and Mabry, T. (1988) *Phytochemistry* **27**, 2685]. Direct comparison of a sample indicated that the substitution was identical though several ^{1}H NMR signals were different. Clear NOE's further showed that the Δ^6 double bond had *E*-configuration. Accordingly, the two compounds can only differ in the configurations at C-3 or C-9. Perhaps this is relevant in hydrogen bridging of these glucosides.

Table 3. Observed NOE's with compound **5**

Irradiated	NOE's
H-15	13′$_1$(3%), 13′$_2$(3%), 3 (10%), 6 (18%)
H-14	9 (3%), 10 (3%), 2(10%), 8′ (3%)
H-13	7 (4%), 11 (5%)
H-10	7′ (6%), 8′ (3%), 8 (6%)
H-7	8 (5%), 13 (5%)
H-6	13 (10%), 15 (10%)
H-8	7 (6%), 10 (5%)
H-3	15 (4%)
H-2	14 (8%)
H-9′	8′ (5%), 14′$_2$(1%)
H-8′	14′$_1$(2%), 14′$_2$(1%)
H-7′	8 (4%), 10 (6%), 14′$_2$(1%)

The spectral data of **55** (Experimental) showed that the corresponding 9*E*-isomer derived from **48** was present. Accordingly, two additional methyl singlets and the signals of a *trans*-double bond (δ5.55 *dt* and 5.63 *d*) were visible. Most likely, both **55** and **56** [12] are formed by an ene-reaction of **44** with oxygen followed by reduction of the hydroperoxides formed. In the ^{1}H NMR spectrum of **62** (Experimental) in deuteriobenzene the relative position of the hydroxy group could be assigned by spin decoupling. As in the case of **58**, the three-fold doublet at δ4.72 was coupled with a broadened doublet of an olefinic proton and with two doublets at δ1.97 and 1.47 (H-4). Furthermore, the signal at δ4.47 was coupled with a broadened doublet at δ5.26 which itself showed allylic couplings with two olefinic methyls. Thus a 9-hydroxy isomer could be excluded.

The structure of **42** followed from the ^{1}H NMR spectrum (Experimental) which showed that again a 2-*O*-acetyl glucopyranoside was present. The remaining signals were in part identical with those of a myrcene obtained by acetylation of the corresponding diol [22].

The extract of the aerial parts of *G. plumosa* Muschler gave geranylisobutyrate, caryophyllene and its epoxide, large amounts of **2** and **3**, the acetate **4** [9] (as its stereochemistry is the same as that of **3** (s.a.) its structure has to be revised), the acetate **46** [21], the ivaxillarin derivative **26**, the tomentosin derivatives **15**, **16** and **17** as well as traces of the epimeric *endo* peroxides **10** and **11**.

The structure of **15** could be deduced from the ^{1}H NMR spectrum (Table 6) which was very similar to that of the corresponding 4-*O*-acetate which has been isolated in traces from another *Geigeria* species [9]. We have now studied again the configuration at C-10. Clear NOE's between H-8 and H-7 (6%) as well as between H-14, H-2 (5%), H-9α (5%) and H-9β (5%) but not with H-8 required a 10α-hydroxy group. While acetylation gave the expected 4-*O*-acetate, which was identical with the previously isolated one, oxidation with pyridine chlorochromate led to the cyclic ether **19** as followed from the molecular formula ($C_{15}H_{20}O_3$) and its ^{1}H NMR spectrum (Table 6). All signals could be assigned by spin decoupling. The presence of an ether ring followed from the couplings of H-2 and H-3 while the position of the double bond was deduced from the observed homoallylic couplings between H-14 and H-2 as well as from the chemical shifts of H-2 and H-9. Most likely **19** was formed by protonation of the 10-hydroxy group and attack of the 4-hydroxy group at the allylic cation at C-10.

Compound **16** was in equilibrium with the cyclic hemiacetal which was easily transformed to the enol ether **18** on standing in deuteriochloroform as followed from

Table 4. ^{1}H NMR spectral data of compounds **10**, **11** and **22**–**24** (400 MHz, $CDCl_3$, δ-values)

H	**10***		**11***	**22**†	**23**‡	**24**§
1	—		—	1.56 *ddd*	1.72 *m*	1.67 *m*
2	6.00		6.08 *d*	2.85 *dd*	1.89 *dt*	1.97 *dt*
2′				2.17 *dd*	1.32 *ddd*	1.28 *ddd*
3	6.08		6.21 *d*	—	4.92 *dd*	5.07 *dd*
4	—		—	4.13 *br d*	4.76 *br s*	4.16 *s*
6	4.92		4.91 *d*	1.36 *dd*	1.72 *m*	1.67 *m*
6′				1.93 *dd*	1.62 *m*	
7	2.91		2.90 *ddd*	3.19 *ddddd*	3.53 *m*	3.44 *m*
8	4.64		4.66 *ddd*	4.78 *ddd*	4.76 *ddd*	4.73 *ddd*
9		2.28 *m*		2.16 *ddd*	1.85 *br dd*	1.84 *br dd*
9′		1.75 m		1.91 *br dd*	2.07 *ddd*	2.06 *ddd*
10		2.28 *m*		1.74 *m*	1.72 *m*	1.67 *m*
13	1.31		1.25 *d*	6.32 *d*	6.24 *d*	6.23 *d*
13′				5.60 *d*	5.57 *d*	5.52 *d*
14	1.29		1.28 *d*	1.09 *d*	1.09 *d*	1.08 *d*
15	1.61		1.64 *s*	1.08 *s*	1.03 *s*	1.04 *s*

†OH: 3.87 *S*; ‡OMe: 3.47 *s*; §OMe: 3.45 *s*; *H-11 2.49 and 2.35 *dq*.

J [Hz]: compounds **10** and **11**: 2,3 = 6; 6,7 = 7; 7,8 = 8; 7,11 = 12; 8,9 = 7; 8,9′ = 10; 10,14 = 11,13 = 7; compound **22**: 1,2 = 6; 1,2′ = 12; 1,10 = 12; 2,2′ = 19; 4,OH = 11; 6,6′ = 15; 6,7 = 12; 6′,7 = 3; 7,8 = 8; 7,13 = 3; 7,13′ = 2.5; 8,9 = 12; 8,9′ = 3; 9,9′ = 15; 9,10 = 12; 10,14 = 7; compounds **23** and **24**: 1,2 = 2.5; 1,2′ = 10; 2,2′ = 13; 2,3 = 3; 2′,3 = 10.5; 7,8 = 8; 7,13 = 2.5; 7,13′ = 2; 8,9 = 3.5; 8,9′ = 9,9′ = 12; 9,10 = 5.

Table 5. ^{1}H NMR spectral data of compounds **50**–**52** and **52**Ac (400 MHz, $CDCl_3$, δ-values)

H	**50**	**51**	**52**	**52**Ac
1c	5.09 *dd*	5.04 *dd*	5.07 *dd*	5.05 *dd*
1t	5.21 *dd*	5.19 *dd*	5.20 *dd*	5.19 *dd*
2	5.85 *dd*	5.89 *dd*	5.86 *dd*	5.89 *dd*
5	2.10 *m* 1.99 *dt*	2.10 *m* 1.99 *dt*	2.21 *m* 2.16 *m*	2.05 *m*
6	5.15 *br t*	5.15 *br t*	5.29 *br t*	5.15 *br t*
8	2.14 *m* 2.00 *m*	2.31 *dd* 2.00 *m*	2.05 *m*	2.32 *dd* 2.05 *m*
9	4.50 *dt*	4.60 *dt*	4.64 *dt*	4.60 *ddd*
10	4.86 *dqq*	4.86 *dqq*	4.99 *br d*	4.83 *br d*
12	1.73 *d*	1.76 *d*	1.74 *d*	1.77 *br s*
13	1.63 *d*	1.65 *d*	1.64 *d*	1.65 *br s*
14	1.59 *br s*	1.56 *br s*	1.63 *br s*	1.57 *br s*
15	1.21 *s*	1.26 *s*	1.23 *s*	1.27 *s*
1′	4.33 *d*	4.39 *d*	4.26 *d*	4.48 *d*
2′	4.69 *dd*	4.74 *dd*	3.33 *t*	4.97 *dd*
3′	3.62 *t*	3.56 *t*	3.59 *t*	5.17 *t*
4′	3.52 *t*	3.44 *t*	3.49 *t*	5.04 *t*
5′	3.15 *dt*	3.36 *ddd*	3.19 *dt*	3.60 *ddd*
$6'_1$	3.79 *d*	4.37 *dd*	3.81 *br s*	4.21 *dd*
$6'_2$		4.33 *dd*		4.13 *dd*
OAc	2.08 *s*	2.10 *s*	—	2.07 *s*
		2.09 *s*	—	2.01 *s*
				2.00 *s*
				1.99 *s*

J [Hz]: 1c,1t = 1.5; 1c,2 = 11; 1t,2 = 17; 5,5′ = 14; 5,6 = 7; 8,8′ = 13; 8,9 = 6; 8′,9 = 9,10 = 9; 10,12 = 10,13 = 1; 1′,2′ = 7.5; 2′,3′ = 3′,4′ = 4′,5′ = 9; 5′,6′ = 2; (compound **51**: 5′,$6'_1$ = 5; 5′,$6'_2$ = 2.5; $6'_1$,$6'_1$, = 12).

the ^{1}H NMR data (Table 6). While the data of **16** were close to those of tomentosin the presence of **18** followed from the observed allylic and homoallylic couplings and from the downfield shift of H-2.

The structure of **26** followed from the ^{1}H NMR spectrum in C_6D_6 and from that of the methyl ester **26a** (Table 7) where all signals could be assigned by spin decoupling. Starting with the high field signals at δ0.24, 0.33 and 0.45, which obviously were due to cyclopropane protons, the whole sequence could be determined as a homoallylic coupling was present between H-15 and H-6. The chemical shifts of the remaining part (H-1 and H-2) indicated a 3-keto group. Thus the rare carbon skeleton of ivaxallarin [23] was present. The stereochemistry followed from the observed NOE's between H-7, H-1 (4%) and H-9α (3%), between H-1, H-7 (6%) and H-9α (4%) as well as between H-14 and H-2 (5%). The resulting configurations are the same as those of ivaxillarin. The acid **26** therefore we have named 3-oxoivaxillar-4,11(13)-dien-12-oic acid which is closely related to anhydroivaxillarin [23]. The ^{1}H NMR spectrum of the corresponding methyl ester also supported the structure.

The structures of the epimeric endoperoxides **10** and **11** followed from the ^{1}H NMR data (Table 4) which indicated the presence of compounds with a 2,3-double bond in a cyclopentane ring. The remaining signals were similar to those of **1** which surely is the precursor of the endoperoxides. A separation was not possible as the compounds were extremely sensitive and destroyed during HPLC in a methanol–water mixture.

The aerial parts of *G. rigida* O. Hoffm. gave bisabolene, thymol, geigeranolide (**37**) [9], its dihydro derivative **38** [9], the steiractinolide **34** [24, 25], the germacranolides **28**–**32**, the steiractinolides **33**, **35** and **36**, lactone **25** which turned out to be identical with axivalin [23], the eudesmane derivatives **39** and **40** as well as the acetate **27**.

As no sample for comparison was available the structure of **25** was deduced from its ^{1}H NMR spectrum (Table 7) which was in part similar to that of **26**. The presence of a trisubstituted cyclopropane followed from the signals at δ0.40 (*dd*), 0.54 (*dd*) and 1.08 (*dd*). Furthermore, spin decoupling indicated that one of the cyclopropane protons (δ0.54) showed a very small coupling with H-7 (δ3.40 *br d*) which itself was assigned by irradiation at δ4.12 (*dd*, H-6) which also sharpened the signal of H-1. The latter further coupled with the three-fold doublets at δ2.48 and 1.67 (H-2). The low field signal at δ5.24 was due to the proton under the acetoxy group. The latter was coupled with the signal at δ2.24 (*dq*) which was due to H-4 as its irradiation collapsed the methyl doublet at δ1.08 to a singlet. Accordingly, all data clearly indicated that an ivaxillarin derivative was present. The stereochemistry was deduced from the observed NOE's. Clear effects between H-14, H-8, H-9β, H-2α, H-2β and H-1, between H-9α, H-6, H-7 and OH, between H-7, H-6 and H-8, between OH, H-6, H-4 and H-1 as well as between H-3, H-2 and H-4 required the proposed configuration which also was supported by a *W*-coupling of H-6 with H-1. The ^{13}C NMR data (Experimental) and all other data agreed with the presence of axivalin [23] where the absolute and relative configuration was determined by X-ray analysis [26].

The ^{1}H NMR spectrum of the main constituent **28** (Table 8) indicated that an isomer of costunolide was present. In particular the couplings of H-1 and H-6 indicated a changed configuration of the lactone ring. The observed values agreed with those of other 6,7-*cis*-lactones [24]. While the spectrum at room temperature was very clear on heating at 70°, all signals were heavily broadened due to the presence of a complex mixture of conformers. At room temperature in the preferred conformation the methyls at C-4 and C-10 were both below the plane as followed from the NOE's.

The ^{1}H NMR spectra of **29**, **30** and **31** (Table 8) indicated that these lactones were derived from **28** by allylic oxidation, most likely, via an ene reaction with oxygen followed by reduction of the hydroperoxide formed. Inspection of models indicated that the proposed attack would lead to α-hydroxy derivatives if the preferred conformation of **28** was proposed. In all cases the signals were assigned by spin decoupling which led to sequences which allowed the placement of the hydroxy group.

The spectrum of **32** and of its acetate **32**Ac obtained by mild acetylation (Table 8) showed that a 7,8-*trans*-germacranolide was present. At room temperature one main conformer was present. Some additional small signals [δ4.04 (H-8), 5.15 (H-5), 1.69 (H-15), 1.61 (H-14), 2.08 (OAc), intensity *ca* 15% of those of the main conformer] indicated that a second conformer was present. Again, at elevated temperature, a complex mixture of conformers led to highly broadened signals.

The ^{1}H NMR spectra of **33**, **35** and **36** (Table 8) were in part close to those of the corresponding lactones with an

Table 6. ^{1}H NMR spectral data of compounds **15–19** (400 MHz, $CDCl_3$, δ-values)

H	**15**	C_6D_6	**16**	**17**	**18**	**19**
2	2.2–2.4 *m*	2.39 *ddd*	2.35 *m*	2.38 *dt*	2.91 *dddq*	2.69 *ddd*
2′		2.03 *m*		2.21 *dt*	2.42 *br dd*	1.91 *br dd*
3	1.62 *m*	1.62 *m*	2.82 *ddd*	1.56 *m*	4.43 *ddq*	1.74 *ddt*
			2.70 *ddd*			1.26 *m*
4	3.83 *m*	3.87 *m*	—	3.77 *tq*	—	3.69 *m*
5	5.58 *ddd*	5.27 *ddd*	5.54 *ddd*	5.67 *br t*	5.68 *ddd*	3.97 *br t*
6	2.2–2.4 *m*	1.93 *m*	2.35 *m*	2.87 *ddd*	2.34 *ddd*	2.12 *m*
6′		1.69 *m*		2.27 *ddd*	2.23 *m*	
7	3.33 *m*	2.87 *m*	3.26 *m*	3.29 *ddddd*	3.40 *m*	3.54 *m*
8	4.94 *ddd*	4.89 *ddd*	4.95 *ddd*	4.67 *ddd*	4.94 *ddd*	4.73 *ddd*
9	2.15 *dd*	2.09 *dd*	2.35 *m*	3.08 *br dd*	2.23 *m*	2.63 *br d*
9′	2.27 *dd*	1.95 *dd*		3.00 *br dd*		2.25 *m*
13	6.25 *d*	6.23 *d*	6.26 *d*	6.24 *d*	6.28 *d*	6.29 *d*
13′	5.55 *d*	5.04 *d*	5.54 *d*	5.54 *d*	5.54 *d*	5.63 *d*
14	1.37 *s*	1.26 *s*	1.37 *s*	5.16 *br s*	1.38 *s*	1.77 *br s*
				5.11 *br s*		
15	1.18 *d*	1.29 *d*	2.16 *s*	1.20 *d*	1.72 *br s*	1.16 *d*

J [Hz]: Compound **15**: 2,2′ = 15; 2,3 = 7; 2,3′ = 9; 2,6′ = 1.5; 4,15 = 6; 5,6 = 5; 5,6′ = 10; 7,8 = 8.5; 7,13 = 3.5; 7,13′ = 3; 8,9 = 2.5; 8,9′ = 12; 9,9′ = 14; compound **16**: 2,3 = 6; 2′,3 = 8; 2,3′ = 2′,3′ = 6; 3,3′ = 18; 2,5 = 1.5; 5,6 = 5; 5,6′ = 9; 7,8 = 8; 7,13 = 3.5; 7,13′ = 3; 8,9 = 2; 8,9′ = 12; compound **17**: 2,2′ = 14; 2,3 = 2′,3 = 3,4 = 7; 4,15 = 5,6 = 6; 6,6′ = 17; 6,7 = 10; 6′,7 = 7,13 ~ 3; 7,8 = 9; 8,9α = 5; 8,9β = 10; 9α,9β = 13; compound **18**: 2,2′ = 18; 2,3 = 2,5 = 2,15 ~ 2; 2,3 = 4; 3,15 ~ 1.5; 5,6 = 5; 5,6′ = 8; 6,6′ = 13; 6,7 = 4; 7,8 = 8.5; 7,13 = 3.5; 7,13′ = 3; 8,9 = 3; 8,9′ = 10; compound **19**: 2,2′ = 13.5; 2,3 = 3; 2,3′ = 4; 2′,3 = 4; 2′,3′ = 12; 2′,9 = 2′,14 ~ 2; 3,3′ = 13; 5,6 = 3; 4,15 = 6; 7,8 = 8.5; 8,9 = 3; 8,9′ = 12; 9,9′ = 14.

Table 7. ^{1}H NMR spectral data of compounds **25**, **26** and **26a** (400 MHz, $CDCl_3$, δ-values)

H	**25***	**26** (C_6D_6)	**26a**
1	2.17 *dd*	1.95 *br s*	2.61 *br s*
2	2.48 *ddd*	2.28 *d*	2.52 *dd*
2′	1.67 *ddd*		2.42 *dd*
3	5.24 *ddd*	—	—
4	2.24 *dq*	—	—
6	4.12 *dd*	2.22 *br dd*	2.55 *m*
		2.12 *br dd*	
7	3.40 *br d*	2.69 *br ddd*	2.90 *ddd*
8	0.54 *dd*	0.33 *ddd*	0.66 *ddd*
9α	1.08 *dd*†	0.24 *dd*	0.57 *dd*
9β	0.40 *dd*	0.45 *dd*	0.75 *dd*
13	6.21 *d*	6.35 *br s*	6.25 *br s*
13′	5.75 *d*	5.28 *br s*	5.58 *br s*
14	0.99 *s*	0.59 *s*	0.95 *s*
15	1.08 *d*	1.63 *br s*	1.60 *br s*

*OAc: 2.09 *s*. †Overlapped from NOE assigned.

J [Hz]: Compound **25**: 1,2 = 8.5; 1,2′ = 13; 1,6 = 0.7; 2,2′ = 13.5; 2,3 = 8.5; 2′,3 = 6; 3,4 = 9.5; 4,15 = 7; 6,7 = 6; 7,8 ~ 0.5; 7,13 = 1.5; 7,13′ = 1; 8,9α = 9; 8,9β = 5; 9α,9β = 4; compounds **26** and **26a**: 1,2 = 5; 1,15 = 6′,15 = 1.5; 6,6′ = 17; 6,7 = 9; 6′,7 = 5; 7,8 = 6; 8,9α = 4.5; 8,9β = 8; 9α,9β = 4.5 (compound **26a**: 1,2 = 6; 1,2′ = 3; 2,2′ = 18).

additional oxygen function at C-8 [24]. The characteristic couplings of H-6 and H-7 and the chemical shifts indicated the presence of steiractinolides (eudesmanolides with a changed configuration at C-5 and C-10 [24]). The configuration at C-1 followed from the couplings and the position of the double bonds from the signals of H-3 and H-15. Surely the precursor of the lactones **33**, **35** and **36** is the germacranolide **28**. The preferred conformation of this lactone (s.a.) would lead to an α-epoxide which by proton attack would give the steiractinolides **33**, **35** and **36**. As in the case of the lactones from a *Pegolettia* species [23], the Cotton-effect of lactone **36** was positive while those of **33** and **35** were negative. Obviously, this is due to the changed conformation of the lactone **36**.

The structure of **27**, which was isolated as its methyl ester **27a**, followed from its ^{1}H NMR spectrum (Table 9) which was in part close to that of **25**. Spin decoupling allowed the assignment of all signals. As the narrowly split signal at δ5.05 was coupled with H-7 (δ3.52) a Δ^5 bond was present. Most likely **27** is the precursor of **25** which may be formed by opening of the corresponding 5α,6α-epoxide by the carboxyl group.

The ^{1}H NMR spectra of **39a** and **40a** (Table 9) clearly showed that we were dealing with derivatives of costic acid and its Δ^3-isomer. An additional low field signal at δ5.24 in both spectra was due to a proton under an acetoxy group. Spin decoupling indicated that it had to be placed at C-8. The stereochemistry followed from the coupling and the observed NOE's by clear effects between

Table 8. ^{1}H NMR spectral data of compounds **28–33**, **35**, **36** and **32Ac** (400 MHz, $CDCl_3$, δ-values)

H	28	29	30	31	32	32Ac*	33	35	36
1	4.98 *dtq*	5.04 *br d*	3.99 *dd*	4.46 *br d*	5.06	5.02 *br d*	3.48 *dd*	3.35 *dd*	3.48 *dd*
2	2.16 *m*	4.60 *dt*	1.93 *m*	2.04 *m*	4.71	5.63 *ddd*	2.33 *br d*	1.77 *m*	1.75 *m*
2′				1.66 *m*			1.95 *br dd*	1.53 *m*	
3	2.27 *dt*	2.20 *m*	2.22 *m*	2.26 *m*	2.62	2.61 *br dd*	5.38 *br s*	2.34 *ddd*	2.25 *m*
3′	1.97 *ddd*	2.02 *m*	2.12 *m*		2.09	2.18 *br t*		2.02 *br dd*	2.16 *m*
5	4.88 *br d*	5.08 *br d*	5.26 *br d*	5.04 *br d*	5.20	5.23 *br t*	1.87 *br d*	1.57 *br d*	
6	5.21 *dd*	5.19 *dd*	5.18 *dd*	5.22 *dd*	2.32	2.31 *m*	4.66 *dd*	4.86 *dd*	5.31 *br d*
					1.97	1.98 *ddd*			
7	3.10 *dtt*	3.07 *br t*	3.07 *dddd*	3.17 *dddd*	2.70	2.71 *ddddd*	3.29 *dddt*	3.28 *ddddd*	3.30 *ddddd*
8	2.20 *m*	2.19 *m*	2.07 *m*	2.53 *ddd*	4.54	4.54 *ddd*	2.00 *m*	2.03 *m*	2.16 *m*
8′	1.57 *br d*	1.56 *br d*	1.64 *br d*	2.24 *m*					1.80 *m*
9	2.55 *br dt*	2.55 *br dd*	2.45 *m*	5.12 *br d*	3.01	3.03 *br dd*	1.77 *dt*	1.81 *ddd*	1.62 *dt*
9′	1.91 *br dt*	1.88 *br dt*	2.05 *m*		1.67	1.70 *br dd*	1.23 *m*	1.24 *dt*	1.41 *dt*
13	6.26 *d*	6.27 *d*	6.28 *d*	6.33 *d*	6.32	6.33 *d*	6.29 *d*	6.30 *d*	6.21 *d*
13′	5.63 *d*	5.64 *d*	5.60 *d*	5.88 *d*	5.66	5.67 *d*	5.55 *d*	5.54 *d*	5.57 *d*
14	1.66 *d*	1.52 *d*	5.09 *br s*	1.72 *dd*	1.60	1.64 *br s*	0.83 *s*	0.75 *s*	0.99 *s*
			4.88 *br s*						
15	1.71 *d*	1.75 *d*	1.62 *d*	1.57 *br s*	1.72	1.81 *br s*	1.83 *br s*	5.00 *br s*	1.76 *br s*
								4.86 *br s*	

*OAc: 2.06 *s*

J [Hz]: Compounds **28** and **29**: 1,14 = 1.5; 5,6 = 11; 5,15 = 1.5; 6,7 = 7; 7,8 = 9; 7,8′ = 7,13 = 7,13′ ~ 2; 8,9 = 8′,9 = 3.5; 8,9′ = 13; 8′,9′ = 4.5; 9,9′ = 13; (compound **28**: 1,2 = 8; 2,3 = 2′,3 = 3; 2,3′ = 2′,3′ ~ 9; 3,3′ = 12); compound **30**: 1,2 = 4; 1,2′ = 6; 5,6 = 11; 5,15 = 1.5; 6,7 = 7.5; 7,8 = 7; 7,8′ = 7,13 = 2.5; 8,8′ = 13; compound **31**: 1,2 = 10; 5,6 = 11; 6,7 = 9; 7,8 = 11; 7,8′ = 7,13 = 3; 8,8′ = 14; 8,9 = 11; 8′,9 ~ 2; 8,14 = 9,14 ~ 1.5; compounds **32** and **32Ac**: 1,2 = 11; 2,3 = 5; 2,3′ = 11; 3,3′ = 12; 5,6 = 7; 5,6′ = 11; 6,6′ = 12; 6,7 = 7,13 = 7,8 ~ 3; 6′,7 = 6; 8,9 = 6; 8,9′ = 11; 9,9′ = 13; compound **33**: 1,2 = 7; 1,2′ = 10; 2,2′ = 17; 5,6 = 10.5; 6,7 = 7; 7,8 ~ 5; 7,13 = 3.5; 7,13′ = 3; 8,9 = 8′,9 = 4.5; 9,9′ = 13; compound **35**: 1,2 = 4; 1,2′ = 11; 2,3 = 2.5; 2′,3 = 4.5; 2′,3′ = 11; 3,3′ = 14; 5,6 = 10; 6,7 = 6; 7,8 = 6; 7,13 = 3.5; 7,13′ = 3; 8′,9 = 4.5; 8,9 = 3.5; 8,9′ = 5; 8′,9′ = 13; 9,9′ = 13; compound **36**: 1,2 = 7; 1,2′ = 10; 6,7 = 7; 7,8 ~ 3; 7,13 = 2.5; 7,13′ = 2.7; 7,8′ = 9; 8,9 = 3; 8′,9 = 6; 8,9′ = 5; 8′,9′ = 9,9′ = 13.

H-7, H-8 and H-5 as well as between H-14, H-6β and H-2β. Thus **39** and **40** were the acetates of the precursors of the corresponding alantolactone isomers.

The aerial parts of *G. alata* (DC) Benth. et Hook. f. ex Oliver et Hiern. afforded bisabola-2,10-dien-1-one [27], dihydrogeigeranolide (**38**) [9], the myrcene derivative **43**, which was identical with the acetylation product of the known diol [22], and the guaianolides **12–14**.

The structure of **12** followed from its ^{1}H (Table 10) and ^{13}C NMR spectrum (Experimental). Spin decoupling allowed the assignment of all signals and the resulting sequence indicated the presence of a 12,8β-guaianolide with a keto group at C-3 and a 4,5-double bond. A methyl doublet at δ 1.34 and a doublet quartet at δ 2.42 required a 11,13-dihydrolactone. The stereochemistry followed from the NOE's of H-8 with H-7 (6%) and H-10 (4%), of H-1 with H-14 (5%) and H-9β (4%), of H-10 with H-8 (6%), H-2α (5%) and H-9α (4%), of H-13 with H-7 (4%) and of H-14 with H-1 (4%) and H-2β (6%), the chemical shift of H-10 is remarkable (δ 1.27). Inspection of a model indicated that this proton is shielded by the enone. Most signals are close to those of geigerin, the 6α-hydroxy derivative of **12**, where the stereochemistry is established by X-ray [28]. The ^{1}H NMR spectra of the corresponding 1-*epi*-isomer [29] and the 8-*epi* derivative [30, 31] differ clearly from that of **12**.

The ^{1}H NMR spectra of **13** and **14** (Table 10) indicated that those lactones were the Δ^1 isomers of **12**. Accordingly, a third methyl doublet was visible in both spectra. Again spin decoupling allowed the assignment of all signals. The data of **13** and **14** mainly differed in the chemical shift of H-4, H-5 and H-15 indicating that they were epimeric at C-4 or C-5. The stereochemistry was settled by NOE difference spectroscopy. Lactone **13** showed effects between H-8, H-10 (3%) and H-7 (6%), between H-10, H-8 (3%) and H-9α (6%), between H-5, H-11 (5%) and H-15 (4%), between H-14, H-10 (5%), H-6β (3%) and H-9β (3%) as well as between H-13 and H-7 (4%).

The isomer **14** showed NOE's between H-8, H-10 (4%) and H-7 (6%), between H-5, H-4 (6%) and H-11 (4%) as well as between H-13 and H-7 (4%). This isomer was slowly converted to **13** on standing in chloroform in the presence of traces of acid.

The aerial parts of *G. schinzii* O. Hoffm. subsp. *schinzii* gave no sesquiterpene lactones, but in addition to widespread compounds again gave the geranyl linalol derivatives **58** and **59** as well as the nerolidol acetate **46** together with the corresponding senecioate **47**. The structure of the latter followed from the ^{1}H NMR spectrum (Experimental) which was very similar to that of **45**. The changed nature of the ester residue clearly followed from the typical signals of a senecioate. The position of the oxygen function was determined by spin decoupling which showed that the senecioyloxy group was at C-5 as irradiation of the corresponding proton collapsed the double doublet of H-4 to doublets and the broadened doublet of H-6 to a singlet. As the latter was coupled only with one olefinic methyl a C-9 position of the ester group could be excluded.

Table 9. ^{1}H NMR spectral data of compounds **27a**, **39a** and **40a** (400 MHz, $CDCl_3$, δ-values)

H	**27a**	**39a**	**40a**
1	2.38 *m*	1.38 *m*	1.63 *m* 1.25 *dt*
2	2.47 *ddd*	1.33 *m*	1.63 *m*
2′	1.35 *ddd*	2.09 *m*	1.46 *m*
3	5.26 *ddd*	1.99 *m*	2.32 *br d* 2.03 *br ddd*
4	2.57 *m*	—	—
5	—	2.09 *m*	1.96 *m*
6	5.05 *br ddd*	1.65 *m*	1.83 *ddd*
6′			1.46 *m*
7	3.52 *br ddd*	2.89 *br ddd*	2.92 *br dt*
8	0.58 *ddd*	5.24 *ddd*	5.24 *ddd*
9	0.74 *dd*	1.81 *dd*	1.84 *dd*
9′	0.24 *dd*	1.47 *dd*	1.54 *dd*
13	6.22 *d*	6.27 *br s*	6.28 *br s*
13′	5.61 *t*	5.59 *t*	5.63 *t*
14	1.04 *s*	0.95 *s*	0.87 *s*
15	0.97 *d*	1.65 *br s*	4.76 *q* 4.53 *q*
OAc	2.02 *s*	1.95 *s*	1.94 *s*
OMe	3.80 *s*	3.75 *s*	3.75 *s*

J [Hz]: Compound **27a**: 1,2 = 7; 1,2′ = 2,2′ = 12; 2,3 = 7; 2′,3 = 5.5; 3,4 = 4,15 ~ 7; 4,7 = 7,8 = 7,13 ~ 1; 6,7 = 3; 8,9 = 8.5; 8,9′ = 4; 9,9′ = 5; 13,13′ = 1; compound **39a**: 6,7 ~ 7; 6′,7 ~ 8; 7,8 = 3; 7,13 = 13,13′ = 1; 8,9 = 2.5; 8,9′ = 3.5; 9,9′ = 14.5; compound **40a**: 1,1′ = 1′,2 = 13; 1′,2′ = 6; 2,3′ = 7; 2′,3′ = 3,3′ = 13; 5,6 = 6,6′ = 6,7 = 12.5; 6′,7 = 7,8 = 2.5; 7,13 = 13,13′ = 1; 8,9 = 2.5; 8,9′ = 3; 9,9′ = 15.

The aerial parts of *G. odontoptera* O. Hoffm. gave caryophyllene and the sesquiterpene lactones **2**, **3**, **4** and **15** while those of *G. acaulis* Benth. et Hook. f. ex Oliver et Hiern., only gave widespread compounds (Experimental).

CONCLUSIONS

The additional results on the chemistry of the genus *Geigeria* indicated again that its placement in the subtribe Inulinae is strongly supported by the chemistry. In Table 11 the results are summarized. In particular the wide range of different sesquiterpene lactones resembles that of the main genus *Inula*. The accumulation of 11,13-dihydrolactones seems to be typical for *Geigeria*. Several more special lactones may indicate a more close relationships to special genera. Thus the occurrence of 6,7-*cis*-lactones may indicate that *Geigeria* is close to *Pegolettia*, especially, as these two genera also share further common types of constituents [24, 32]. But the South African genera *Calostephane* [33], *Ondetia* [34], *Anisopappus* and *Antiphiona* [35] show in part similar types of constituents. These genera are also taxonomically closely related to *Geigeria* [1]. The proposed subdivision of the genus into the sections Angolensis (1), Pectideae (2) and Africanae (3) [36] is only supported in part by the chemistry. Characteristic for section 3 seems to be the occurrence of griesenin and its dihydro derivative. However, these lactones are in part also present in species placed in section 2 while they are absent in representatives of section 1. Geranyllinalol derivatives are reported only from representatives of section 3 and guaianolides only in section 3 while the remaining sesquiterpene lactone types are not restricted to members of a distinct

Table 10. ^{1}H NMR spectral data of compounds **12**–**14** (400 MHz, $CDCl_3$, δ-values)

H	**12**	(C_6D_6)	**13**	(C_6D_6)	**14**
1	2.32 *br ddd*	—	—	—	—
2	2.63 *dd*	2.27 *dd*	5.94 *t*	5.68 *t*	5.98 *t*
2′	2.06 *dd*	1.75 *dd*			
4	—	—	2.06 *m*	1.63 *dq*	2.60 *dq*
5	—	—	2.70 *br ddd*	1.96 *m*	3.23 *br ddd*
6	3.04 *dd*	2.31 *dd*	2.10 *m*	1.17 *ddd*	2.03 *ddd*
6′	2.24 *dd*	1.36 *dd*	1.84 *m*	0.94 *ddd*	1.71 *ddd*
7	2.40 *m*	1.68 *dddd*	2.34 *dddd*	1.49 *dddd*	2.32 *dddd*
8	4.42 *ddd*	3.80 *ddd*	4.54 *ddd*	3.78 *ddd*	4.54 *ddd*
9α	1.90 *br d*	1.42 *dt*	2.10 *ddd*	1.41 *ddd*	2.05 *ddd*
9β	1.95 *dddd*	1.29 *ddd*	1.84 *m*	1.09 *br ddd*	1.90 *ddd*
10	1.27 *m*	0.54 *dddq*	2.92 *ddq*	1.98 *m*	2.87 *ddq*
11	2.42 *dq*	1.83 *dq*	2.44 *dq*	1.79 *dq*	2.49 *dq*
13	1.34 *d*	1.05 *d*	1.27 *d*	0.94 *d*	1.26 *d*
14	1.14 *d*	0.67 *d*	1.28 *d*	0.72 *d*	1.30 *d*
15	1.71 *d*	1.55 *br s*	1.20 *d*	1.04 *d*	1.12 *d*

J [Hz]: Compound **12**: 1,2 = 6; 1,2′ = 1.5; 1,10 = 10; 1,15 = 1; 2,2′ = 18; 6,6′ = 6′,7 = 12; 6,7 = 5.5; 7,8 = 8; 7,11 = 10; 8,9α = 2; 8,9β = 11; 9α,9β = 14; 9α,10 = 2; 9β,10 = 10; 10,14 = 11,13 = 6.5; compound **13**: 2,5 = 2,10 ~ 1.5; 4,5 = 7.5; 4,15 = 7.5; 5,6 = 4.5; 5,6′ = 7; 6,7 = 4; 6′,7 = 8.5; 6,6′ = 15; 7,8 = 7.5; 7,11 = 11; 8,9α = 4; 8,9β = 11; 9α,9β = 14; 9α,10 = 4; 9β,10 = 11; 10,14 = 11,13 = 7; compound **14**: 2,5 = 2,10 = 1.3; 4,5 = 3.5; 4,15 = 7; 5,6 = 4; 5,6′ = 7; 6,7 = 3.5; 6′,7 = 7; 6,6′ = 15; 7,8 = 7.5; 7,11 = 11; 8,9α = 3.5; 8,9β = 10; 9α,9β = 14; 9α,10 = 4; 9β,10 = 8; 10,14 = 7; 11,13 = 7.

Table 11. Typical constituents of *Geigeria* species

Species	Sect.	Griesenin +dihydro	Xanthano-lides	Guaiano-lides	Pseudo guainolides +seco	Germacra-nolides	Eudesma-nolides	Geigerano-lides	Nerolidols	Geranyl linalols	Mono-terpenes	Ivaxillarone
G. africana	3	+	+	+	+							
G. aspera	3	+		+	+		+					
G. aspera var. *aspera*	3	+		+			+	+	+			+
G. brevifolia	1		+				+	+				
G. burkei subsp. *burkei* var. *burkei*	3						+	+		+		
var. *alata*	3				+					+		
var. *intermedia*	3	+	+		+					+		
var. *zeyheri*	3			+	+					+		
subsp. *diffusa*	3	+						+		+		
subsp. *fruticulosa*	3									+		
G. filifolia	3	+										
G. acaulis	3										+	
G. alata	2			+				+			+	
G. odontoptera	2	+			+							
G. ornativa	3	+	+	+	+	+			+	+	+	
G. plumosa	2	+	+						+		+	+
G. rigida	2	+	+			+	+	+			+	+
G. schinzii subsp. *schinzii*	3								+	+		

section. The investigation of more species from the section Angolensis may show whether a clear chemical separation is possible.

EXPERIMENTAL

The air-dried acrial parts (collected in March 1988 in Namibia, vouchers deposited in the South West African Herbarium of Windhoek) were extracted with MeOH–Et_2O–petrol (1:1:1) at room temp. The extracts were worked-up and separated as reported previously [37].

The extract of the aerial parts (1.6 kg) of *Geigeria ornativa* (voucher 88/27, collected at the Uis Pass, W of Windhoek) was defatted with MeOH and the soluble part was first separated by CC into six fractons [1 petrol; 2 Et_2O–petrol (1:3); 3 Et_2O–petrol (1:1); 4 Et_2O–petrol (3:1); 5 Et_2O; 6 Et_2O–MeOH (9:1)]. TLC of fraction 1 gave 100 mg squalene, of fraction 2 (Et_2O–petrol, 3:1) 5 mg **44** and 5 mg **45** (R_f 0.60) and of fraction 3 (Et_2O–petrol, 1:3) 50 mg **45** and 150 mg **1** (R_f 0.42). TLC of fraction 4 (Et_2O–petrol, 1:1) gave 280 mg **58** and 6 mg **59**. HPLC (MeOH–H_2O, 4:1) of fraction 5 gave 10 mg **60** and seven fractions (5/1–5/7). TLC of 5/1 ($CHCl_3$–C_6H_6–Et_2O, 1:1:1) gave 15 mg **3**, 5 mg **2** and two further bands (5/1/3 and 5/1/4). HPLC of 5/1/3 (MeOH–H_2O, 3:2) afforded 2 mg **7** (R_t 5.6 min) and HPLC of 5/1/4 (MeOH–H_2O, 3:2) 2 mg **24** (R_t 9.4 min) and 8 mg **23** (R_t 11.2 min). TLC of 5/2 (Et_2O–petrol, 3:1) gave 5 mg **59**, 3 mg **53**, 2 mg **5** which were purified by HPLC (MeOH–H_2O, 4:1, R_t 4.6 min) and a mixture which gave by HPLC (MeOH–H_2O, 13:7) 1 mg **56**, 2 mg **57** and 3 mg of a mixture of **20** and **21** (R_t 9.2 min, *ca* 1:2). TLC of 5/3 (Et_2O–petrol, 3:1) gave 3 mg caryophyllenepoxide, 2 mg **59** and a crude fraction (R_f 0.35) which gave by HPLC 5 mg **8**. TLC of 5/4 (Et_2O–petrol, 3:1) gave 30 mg **60**, 4 mg **48**, 6 mg **61**, 2 mg **49** and after purification by HPLC (MeOH–H_2O, 4:1) 2 mg **5** (R_t 5.7 min). TLC of 5/5 (Et_2O–petrol, 3:1) gave 2 mg **59**, 5 mg **55** (R_f 0.56) and after HPLC (MeOH–H_2O, 4:1) 5 mg **41** (R_t 5.2 min). HPLC of 5/6 (MeOH–H_2O, 4:1) gave 10 mg **54** (R_t 6.5 min). TLC of 5/7 (Et_2O–petrol, 1:1) gave 10 mg **62** (R_f 0.48). CC fraction 6 was again separated by medium pressure CC (silica gel, Φ 30–60 μ, Et_2O–petrol, 1:1, Et_2O and Et_2O–MeOH, 4:1) affording in addition to 1 g **51** and 200 mg **50** a mixture which was further separated by HPLC (MeOH–H_2O, 4:1) into four crude fractions (6/1–6/4). TLC of 6/1 ($CHCl_3$–C_6H_6–Et_2O, 1:1:1 + 3% MeOH) followed by HPLC (MeOH–H_2O, 3:2) gave 5 mg **22** (R_t 3.7 min). HPLC of 6/2 (MeOH–H_2O, 3:2) gave 10 mg **9** (R_t 5.7 min) and HPLC of 6/3 (MeOH–H_2O, 3:2) 8 mg **16** (R_t 5.8 min) and 20 mg **50** (R_t 11.0 min). Fraction 6/4 contained 100 mg **51** (R_t 4.1 min).

The extract of the aerial parts (400 g) of *Geigeria plumosa* (voucher 88/25, collected near Regenstein, S of Windhoek) was separated first by CC into four fractions [1: petrol; 2: Et_2O–petrol (1:3 and 1:1); 3: Et_2O; 4: Et_2O–MeOH (9:1)]. Fraction 1 gave 30 mg caryophyllene, fraction 2 30 mg geranylisobutyrate, 15 mg caryophyllenepoxide and 50 mg **46**. Fraction 3 gave 1 g **2** and 2.5 g **3**. Fraction 4 was separated again by medium pressure CC affording 2 mg **10** and **11** (TLC: Et_2O–petrol, 1:1, R_f 0.50), 10 mg **2**, 20 mg **3**, 100 mg **4**, 5 mg **17** (TLC: Et_2O, R_f 0.42), 10 mg **16** (TLC: $CHCl_3$–C_6H_6–Et_2O, 1:1:1, R_f 0.8) and 70 mg **15** (TLC: Et_2O–MeOH, 99:1, R_f 0.65).

The extract of the aerial parts of *Geigeria rigida* (210 g, voucher 88/118, collected near the Spitzkoppe, Namibia) gave by CC five fractions [(1: petrol; 2: Et_2O–petrol (1:3); 3: Et_2O–petrol (3:1); 4: Et_2O and 5: Et_2O–MeOH (9:1)]. Fraction 1 gave 30 mg bisabolene, fraction 2 20 mg thymol and fraction 3 by TLC (Et_2O–petrol, 1:1) 100 mg **28** (R_f 0.53) and a mixture (R_f 0.65). The mixture gave by repeated TLC 30 mg **34** and 5 mg **38**. MPCC of fraction 4 (Et_2O–petrol, 1:3 to Et_2O and Et_2O–MeOH, 9:1) gave 20 mg **37**, 100 mg **25**, 600 mg **28** and a mixture of the acids **27**, **39** and **40**. Esterification with CH_2N_2 gave **27a**, **39a** and **40a** which were separated by HPLC (MeOH–H_2O, 17:3) affording 2 mg **27a** (R_t 4.3 min) and a mixture of **39a** and **40a** (R_t 6.0 min). The mixtures were separated by TLC ($AgNO_3$ coated silica gel, Et_2O–petrol, 1:1) affording 25 mg **39a** (R_f 0.70) and 35 mg **40a** (R_f 0.62). HPLC of fraction 5 (MeOH–H_2O, 11:9) gave 8 mg **29** (R_t 4.3 min), 10 mg **30** (R_t 5.3 min), 10 mg **32** (R_t 6.4 min), 3 mg **36** (R_t 7.4 min), 6 mg **33** (R_t 8.9 min), 60 mg **25** (R_t 10.1 min) and a mixture (R_t 5.7 min) which gave by TLC ($CHCl_3$–C_6H_6–Et_2O–MeOH, 40:40:20:1) 5 mg **35** (R_f 0.60) and 6 mg **31** (R_f 0.52).

The extract of the aerial parts (190 g) of *Geigeria alata* (voucher 88/114, collected near the Brandberg, Namibia) gave by CC, TLC and HPLC 130 mg bisabola-2,10-dien-1-one, 20 mg **43**, 50 mg **38** and by HPLC (MeOH–H_2O, 1:1) 1 g **12** (R_t 10.3 min), 100 mg **14** (R_t 7.8 min) and 200 mg **13** (R_t 7.0 min).

The extract of 270 g aerial parts of *Geigeria acaulis* (voucher 88/110, collected near Omaruru, Namibia) afforded 15 mg neryl-isobutyrate, 5 mg thymol and 7 mg 8,9-epoxy-10-isobutyryloxy thymolisobutyrate and no sesquiterpene lactones.

The extract of the aerial parts (190 g) of *Geigeria schinzii* subsp. *schinzii* (voucher 88/88, collected near the road Grootfontain-Tsumeb, Namibia) afforded by CC and TLC 5 mg caryophyllene and its epoxide 20 mg **58**, 30 mg **59**, 30 mg **46** and 20 mg **47** (TLC: Et_2O–petrol, 1:1, R_f 0.78).

The extract of 190 g aerial parts of *Geigeria odontoptera* (voucher 88/93, collected N of Tsumeb) gave by CC and HPLC 5 mg caryophyllene, 200 mg **2**, 1 g **3**, 80 mg **4** and 60 mg **15**.

Known compounds were identified by comparing the ^1H NMR 400 MHz spectra with those of authentic material.

Geigeriafulvenolide (**1**). Orange-red coloured crystals, mp 103°; UV $\lambda_{max}^{Et_2O}$ 407, 255 nm; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone); MS *m/z* (rel. int.): 230.131 $[M]^+$ (91) (calc. for $C_{15}H_{18}O_2$: 230.131), 215 (10), 212 (7), 174 (36), 159 (92), 157 (100), 156 (71), 145 (44), 143 (44), 115 (32), 91 (35), 71 (32), 69 (48); ^{13}C NMR ($CDCl_3$, C-1–C-15): 146.2, 127.2, 128.2, 139.3, 132.6, 130.6, 42.8, 78.6, 38.4, 28.6, 47.1, 177.9, 14.7, 21.4, 12.2; $[\alpha]_D^{24°}$ +200 ($CHCl_3$; *c* 0.72).

After 24 hr, 10 mg **1** in 0.5 ml $CDCl_3$ became colourless; HPLC (MeOH–H_2O, 7:3) gave 5 mg **1a** (R_t 1.5 min), colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775 (γ-lactone), 2740, 1715 (C=CCHO), 1685 (C=CC=O); MS *m/z* (rel. int.): 262.131 $[M]^+$ (24) (calc. for $C_{15}H_{18}O_4$: 262.131), 233 $[M-CHO]^+$ (54), 219 $[M-COMe]^+$ (100), 191 $[219-CO]^+$ (32), 149 (90), 91 (81); ^1H NMR ($CDCl_3$): δ6.15 (*dd*, H-2), 9.42 (*d*, H-3), 6.78 (*d*, H-6), 3.12 (*ddd*, H-7), 4.64 (*ddd*, H-8), 2.25 (*ddd*, H-9), 1.79 (*ddd*, H-9′), 2.82 (*m*, H-10), 2.62 (*dq*, H-11), 1.29 (*d*, H-13), 1.39 (*d*, H-14), 2.42 (*s*, H-15) (*J* [Hz]: 2,3 = 7; 2,10 = 2; 6,7 = 4; 7,8 = 8; 7,11 = 10; 8,9 = 8.5; 8,9′ = 1.5; 9,9′ = 14; 9,10 = 11; 9′,10 = 3; 10,14 = 11,13 = 7).

Ornativolide (**5**). Colourless crystals, decomp ~ 220°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770 (γ-lactone); MS *m/z* (rel. int.): 506.231 $[M]^+$ (0.2) (calc. for $C_{30}H_{34}O_7$: 506.230), 476 $[M-CH_2O]^+$ (0.5), 246 $[476-C_{14}H_{14}O_3]^+$ (12), 230 $[476-C_{15}H_{18}O_2]^+$ (22), 218 (5), 159 (20), 134 (100), 133 (56), 91 (36), $[\alpha]_D^{24°}$ +129 ($CHCl_3$; *c* 0.14).

Dihydroornativolide (**6**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770 (γ-lactone); MS *m/z* (rel. int.): 508.246 $[M]^+$ (0.4) (calc. for $C_{30}H_{36}O_7$: 508.246), 246 $[C_{15}H_{18}O_3]^+$ (42), 230 $[C_{14}H_{14}O_3]^+$ (100), 159 (45), 136 (61), 91 (75).

1-*Oxo*-1β,10β,11β*H*-*guaia*-3,5-*dien*-12,8β-*olide* (**7**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1790 (γ-lactone), 1715, 1600 (C=CC=O); MS *m/z* (rel. int.): 246.126 $[M]^+$ (26) (calc. for $C_{15}H_{18}O_3$: 246.126), 231 (3), 228 (4), 173 (33), 172 (26), 136 (100), 91 (38).

1-*Oxo*-6α-*senecioyloxy*-1β,5β,10β,11β*H*-*guaia*-3-*en*-12,8β-*olide* (**8**). Colourless crystals, mp 89°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1790 (γ-lactone), 1725, 1655 (C=CCO$_2$R), 1715, 1630 (C=CC=O); MS *m/z* (rel. int.): 346.178 $[M]^+$ (1) (calc. for $C_{20}H_{26}O_5$: 346.178), 264

(3), 246 (8), 218 (18), 148 (21), 83 (100); $[\alpha]_D^{24}$ −86 ($CHCl_3$; *c* 0.15); ^{13}C NMR ($CDCl_3$, C-1–C-15): δ50.9, 209.1, 134.4, 165.1, 50.2, 75.1, 48.5, 71.5, 34.6, 27.2, 39.7, 177.9, 19.7, 27.7, 20.5; OSen: 175.8, 114.6, 160.7, 15.3, 22.0.

4α-Hydroxy-1β,5α,11αH-guaian-10(14)-ene-12,8β-olide-[2,6-O-diacetyl-β-D-glucopyranoside] (**9**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590, 3470 (OH), 1765 (γ-lactone), 1740, 1245 (OAc); MS *m/z* (rel. int.): 418 $[M-H_2O, HOAc]^+$ (0.1), 358 $[418-HOAc]^+$ (0.3), 247.081 $[M-C_{15}H_{21}O_3]^+$ (29) (calc. for $C_{10}H_{15}O_7$: 247.081), 233 $[C_{15}H_{21}O_2]^+$ (68), 229 $[247-H_2O]^+$ (32), 187 $[247-HOAc]^+$ (60), 159 (100), 127 $[187-HOAc]^+$ (76); ^1H NMR ($CDCl_3$): δ2.53 (*dddd*, H-7), 4.54 (*dd*, H-8), 2.20 and 2.91 (*dd*, H-9), 2.84 (*dq*, H-11), 1.22 (*d*, H-13), 4.93 and 4.89 (*br s*, H-14), 1.20 (*s*, H-15), 4.52 (*d*, H-1′), 4.72 (*dd*, H-2′), 3.60 (*m*, H-3′), 3.43 (*m*, H-4′, 5′), 4.43 and 4.28 (*dd*, H-6′), 2.12 and 2.10 (*s*, OAc) (*J* [Hz]: 6,7 = 3; 6′,7 = 12; 7,8 = 7,11 = 7; 8,9 = 2; 8,9′ = 11; 9,9′ = 13; 11,13 = 7; 1′,2′ = 8; 2′,3′ = 9; 5′,6′ = 3.5 + 1.5; $6'_1,6'_2$ = 12); $[\alpha]_D^{24}$ −23 ($CHCl_3$; *c* 0.8).

Guaia-2,5-dien-12,8β-olide-1,4-endoperoxide (**10** and **11**). Colourless gum, which could not be separated; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone); MS *m/z* (rel. int.): 230.130 $[M-O_2]^+$ (22) (calc. for $C_{15}H_{18}O_3$: 230.130), 215 (17), 55 (100).

Desoxygeigerin (**12**). Colourless crystals, mp 133°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775 (γ-lactone), 1705, 1660 (C=CCO); MS *m/z* (rel. int.): 248.141 $[M]^+$ (calc. for $C_{15}H_{20}O_3$: 248.141), 233 (8), 206 (22), 175 (39), 133 (100); ^{13}C NMR ($CDCl_3$, C-1–C-15): δ49.9, 41.8, 207.8, 137.1, 170.7, 30.8, 42.5, 80.7, 36.7, 39.3, 40.4, 178.0, 14.1, 22.6, 7.6 (determined by 2D-techniques); $[\alpha]_D^{24}$ −17 ($CHCl_3$; *c* 0.67).

Desoxy-5-epi-isogeigerin (**13**). Colourless crystals, mp 106°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775 (γ-lactone), 1705, 1615 (C=CC=O); MS *m/z* (rel. int.): 248.141 $[M]^+$ (42) (calc. for $C_{15}H_{20}O_3$: 248.141), 233 (23), 220 (6), 206 (10), 175 (100), 133 (38), 55 (58); $[\alpha]_D^{24}$ +163 ($CHCl_3$; *c* 0.17).

Desoxy-4,5-bisepi-isogeigerin (**14**). Colourless crystals, mp. 104°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775 (γ-lactone); 1700, 1610 (C=CC=O); MS *m/z* (rel. int.): 248.141 $[M]^+$ (43) (calc. for $C_{15}H_{20}O_3$: 248.141), 233 (26), 220 (6), 206 (12), 175 (100), 133 (42), 55 (52); $[\alpha]_D^{24}$ +113 ($CHCl_3$; *c* 0.32).

10α-Hydroxy-4H-tomentosin (**15**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1765 (γ-lactone); MS *m/z* (rel. int.): 248.141 $[M-H_2O]^+$ (48) (calc. for $C_{15}H_{20}O_3$: 248.141), 233 (82), 212 (31), 161 (56), 91 (100), 71 (96), 55 (91). Acetylation (Ac_2O, 1 hr, 70°) gave the monoacetate **15**Ac, colourless oil; ^{13}C NMR ($CDCl_3$, C-1–C-15): δ144.9, 27.8, 36.3, 70.5, 121.8, 28.0, 41.6, 76.6, 43.7, 73.7, 139.3, 171.2, 122.4, 30.4, 21.4; OAc: 20.0, 170.2; $[\alpha]_D^{24}$ +62 ($CHCl_3$; *c* 2.55). Oxidation (PCC, $CHCl_3$, NaOAc) gave the cyclic ether **19**, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone); MS *m/z* (rel. int.): 248.141 $[M]^+$ (15) (calc. for $C_{15}H_{20}O_3$: 248.141), 233 $[M-Me]^+$ (100), 215 (8), 203 (11), 161 (23), 91 (44).

10α-Hydroxytomentosin (**16**). Colourless oil, which was converted to **18** during HPLC, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone); MS *m/z* (rel. int.): 246.126 $[M]^+$ (26) (calc. for $C_{15}H_{18}O_3$: 246.126), 231 (21), 203 (42), 185 (36), 157 (56), 131 (62), 91 (100).

10(14)-Dehydro-4H-tomentosin (**17**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH), 1780 (γ-lactone); MS *m/z* (rel. int.): 248 $[M]^+$ (3), 233.118 $[M-Me]^+$ (44) (calc. for $C_{14}H_{17}O_3$: 233.118), 230 $[M-H_2O]^+$ (12), 190 $[M-C_3H_6O]^+$ (44), 175 (35), 159 (58), 145 (81), 119 (100), 105 (86), 91 (90); $[\alpha]_D^{24}$ +68 ($CHCl_3$; *c* 0.38).

14-Senecioyloxy and angeloyloxy-carabrone (**20** and **21**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760 (γ-lactone), 1710, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 346.178 $[M]^+$ (0.2) (calc. for $C_{20}H_{26}O_5$: 346.178), 289 $[M-CH_2COMe]^+$ (1), 247 $[M-OCOR]^+$ (3), 246 $[M-RCO_2H]^+$ (3.5), 83 $[RCO]^+$ (100), 55 $[83-CO]^+$ (41); ^1H NMR ($CDCl_3$): δ0.71 (*m*, H-1), 2.56 and 2.54 (*t*, H-3), 0.77 (*m*, H-5), 2.33 (*dt*) and 0.97 (*m*, H-6), 3.09 (*m*, H-7), 4.83 (*ddd*, H-8), 2.63 and 2.62 (*dd*, H-9), 0.97 (*m*, H-9′), 6.25 and 6.26 (*d*, H-13), 5.58 and 5.59 (*d*, H-13′), 4.12 and 4.19 (*d*, H-14), 3.95 and 3.99 (*d*, H-14′), 2.15 (*s*, H-15), (*J* [Hz]: 2,3 = 5,6 = 6,7 = 8,9 = 7; 5,6′ = 9; 6,6′ = 9,9′ = 14; 7,8 = 8.5; 7,13 = 2.5; 7,13′ = 2; 8,9′ = 11; 14,14′ = 12); OSen: 5.67 *qq*, 2.18 *d*, 1.92 *d*; OAng: 6.11 *qq*, 2.01 *dq*, 1.91 *dq*.

4β-Hydroxy-3-oxo-1α,10βH-pseudoguaia-11(13)-en-12,8β-olide (**22**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1760 (γ-lactone), 1720 (C=O); MS *m/z* (rel. int.): 264.136 $[M]^+$ (5) (calc. for $C_{15}H_{20}O_4$: 264.136), 246 $[M-H_2O]^+$ (100), 202 $[246-CO_2]^+$ (27).

3-O-Methylhymenoxon (**23**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (γ-lactone); MS *m/z* (rel. int.): 264.136 $[M-MeOH]^+$ (5) (calc. for $C_{15}H_{20}O_4$: 264.136), 246 $[264-H_2O]^+$ (17), 193 (62), 147 (70), 146 (73), 107 (100).

4-O-Methylhymenoxon (**24**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1765 (γ-lactone); MS *m/z* (rel. int.): 278.152 $[M-H_2O]^+$ (3) (calc. for $C_{16}H_{24}O_5$: 278.152), 246 $[278-MeOH]^+$ (9), 232 (32), 193 (100), 107 (62).

Axivalin (**25**). Colourless crystals, mp 141° (lit. [20] 139–140°); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone), 1725 (OAc); MS *m/z* (rel. int.): 306.147 $[M]^+$ (3) (calc. for $C_{17}H_{22}O_5$: 306.147), 246 $[M-HOAc]^+$ (24), 231 $[246-Me]^+$ (12), 228 $[246-H_2O]^+$ (30), 213 $[228-Me]^+$ (18), 123 (100); ^{13}C NMR ($CDCl_3$, C-1–C-15): δ50.2, 36.5, 70.9, 39.1, 78.1, 75.5, 44.3, 23.1, 17.9, 18.2, 142.4, 171.6, 121.6, 7.0, 24.8; OAc: 21.1, 169.9; $[\alpha]_D^{24}$ −142 ($CHCl_3$; *c* 0.77) (lit. [20] 132.4).

3-Oxo-ivaxallar-4,11(13)-dien-12-oic acid (**26**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520–2600, 1700 (CO_2H, C=CC=O); MS *m/z* (rel. int.): 246.126 $[M]^+$ (23) (calc. for $C_{15}H_{18}O_3$: 246.126), 231 $[M-Me]^+$ (12), 228 $[M-H_2O]^+$ (8), 204 (37), 185 (26), 173 (34), 91 (50), 73 (56), 61 (100). Addition of CH_2N_2 gave the methyl ester **26a**, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (C=CCO_2R); 1710, 1660 (C=CC=O); MS *m/z* (rel. int.): 260.141 $[M]^+$ (54) (calc. for $C_{16}H_{20}O_3$: 260.141), 245 (18), 228 (44), 201 (66), 185 (66), 91 (100); $[\alpha]_D^{24}$ +118 ($CHCl_3$; *c* 1.45).

3β-Acetoxyivaxallar-5,11(13)-dien-12-oic acid (**27**). Isolated as its methyl ester **37a**, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (OAc), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 244.146 $[M-HOAc]^+$ (18) (calc. for $C_{16}H_{20}O_2$: 244.146), 229 (11), 197 (12), 169 (43), 145 (61), 91 (58), 55 (100).

6-epi-Costunolide (**28**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1660 (C=C); MS *m/z* (rel. int.): 232.146 $[M]^+$ (19) (calc. for $C_{15}H_{20}O_2$: 232.146), 217 (29), 204 (10), 199 (10), 176 (23), 171 (23), 145 (28), 121 (53), 105 (52), 91 (51), 81 (100), 79 (52); $[\alpha]_D^{24}$ −164 ($CHCl_3$; *c* 0.91).

2α-Hydroxy-6-epi-costunolide (**29**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 248.141 $[M]^+$ (3.5) (calc. for $C_{15}H_{20}O_3$: 248.141), 233 (25), 215 (10), 204 (13), 71 (100).

1α-Hydroxygermacra-4E,10(14),11(13)-trien-12,6β-olide (**30**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1765 (γ-lactone); MS *m/z* (rel. int.): 248.141 $[M]^+$ (3) (calc. for $C_{15}H_{20}O_3$: 248.141), 233 (8), 230 (22), 215 (28), 159 (41), 145 (56), 133 (61), 119 (86), 105 (94), 91 (100; $[\alpha]_D^{24}$ −86 ($CHCl_3$; *c* 0.68).

1α-Hydroxygermacra-4E,9E,11(13)-trien-12,6β-olide (**31**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone); MS *m/z* (rel. int.): 248.141 $[M]^+$ (2) (calc. for $C_{15}H_{20}O_3$: 248.141), 230 (39), 215 (24), 202 (12), 159 (36), 119 (76), 105 (80), 91 (100).

2β-Hydroxygermacra-1(10)E,4E,11(13)-trien-12,8α-olide (**32**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 248 $[M]^+$ (2), 230.131 $[M-H_2O]^+$ (18) (calc. for $C_{15}H_{18}O_2$: 230.131), 215 (12), 204 (11), 164 (42), 135 (45), 95 (50), 91 (48), 84 (100), 68 (54). Acetylation (Ac_2O, 1 hr, 70°) gave **32**Ac, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1740 (OAc); MS

m/z (rel. int.): 290.152 $[M]^+$ (3) (calc. for $C_{17}H_{22}O_4$: 290.152), 230 $[M-HOAc]^+$ (100), 215 (40), 202 (18), 187 (21), 164 (62), 119 (46), 95 (60), 84 (100); $[\alpha]_D^{24°} -14$ ($CHCl_3$; *c* 0.45).

1α-*Hydroxysteiractin*-3,11(13)-*dien*-12,6β-*olide* (**33**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 248.141 $[M]^+$ (40) (calc. for $C_{15}H_{20}O_3$: 248.141), 230 (45), 215 (37), 165 (56), 119 (62), 107 (100), 91 (72); CD (MeCN): $\Delta\varepsilon_{260}$ −0.35.

1α-*Hydroxysteiractin*-4(15),11(13)-*dien*-12,6β-*olide* (**35**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3605 (OH), 1765 (γ-lactone); MS *m/z* (rel. int.): 248 $[M]^+$ (0.2), 230.131 $[M-H_2O]^+$ (100) (calc. for $C_{15}H_{18}O_2$: 230.131), 215 (34), 202 (18), 159 (48), 133 (53), 91 (56); CD (MeCN): $\Delta\varepsilon_{259}$ −0.51.

1α-*Hydroxysteiractin*-4,11(13)-*dien*-12,6β-*olide* (**36**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3605 (OH), 1760 (γ-lactone); MS *m/z* (rel. int.): 248.141 $[M]^+$ (9) (calc. for $C_{15}H_{20}O_3$: 248.141), 230 (11), 215 (20), 159 (67), 145 (74), 117 (78), 91 (100); CD (MeCN): $\Delta\varepsilon_{256}$ +1.17.

8β-*Acetoxycostic acid* (**39**). Isolated as its methyl ester **39a**, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1250 (OAc), 1725 (C=CCO_2R); MS *m/z* (rel. int.): 306.183 $[M]^+$ (4.3) (calc. for $C_{18}H_{26}O_4$: 306.183), 246 $[M-HOAc]^+$ (59), 231 $[246-Me]^+$ (100), 187 (44), 171 (44), 91 (61); $[\alpha]_D^{24°} -18$ ($CHCl_3$; *c* 2.13).

8β-*Acetoxyisocostic acid* (**40**). Isolated as its methyl ester **40a**, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1250 (OAc), 1725, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 306.183 $[M]^+$ (5.3) (calc. for $C_{18}H_{26}O_4$: 306.183), 246 (80), 231 (100), 171 (66), 91 (54); $[\alpha]_D^{24°}$ −21 ($CHCl_3$; *c* 2.23).

2-*Oxo*-4β-*hydroxyvalencene* (**41**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3420 (OH), 1675 (C=CC=O); MS *m/z* (rel. int.): 236.178 $[M]^+$ (7) (calc. for $C_{15}H_{24}O_2$: 236.178), 218 $[M-H_2O]^+$ (6), 178 $[M-C_3H_6O]^+$ (100), 175 $[218-C_3H_7]^+$ (21); ^1H NMR (C_6D_6): δ 5.90 (*br s*, H-1), 2.50 (*dd*, H-3, *J* = 17, 1 Hz), 2.37 (*dd*, H-3′, *J* = 17, 1), 1.75 (*t*, H-6, *J* = 12.5), 1.34 (*m*, H-6′, H-11), 1.16 (*m*, H-7), 1.45 (*br d*, H-8, *J* = 13), 0.85 (*m*, H-8′), 1.98 (*m*, H-9), 0.86 (*d*, H-12, *J* = 7), 0.84 (*d*, H-13, *J* = 7), 0.78 (*s*, H-14), 0.85 (*s*, H-15); $[\alpha]_D^{24°}$ +46 ($CHCl_3$; *c* 0.41).

6-*Acetoxy*-7-*hydroxymyrcene*-7-O-β-D-*glucopyranoside*-2′-O-*acetate* (**42**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1745 (OAc); MS *m/z* (rel. int.): 275 [M−HOAc, $CH_2C(=CH_2)-CH=CH_2$]$^+$ (2), 247.082 $[C_{10}H_{15}O_7]^+$ (61) (calc. for $C_{10}H_{15}O_7$: 247.082), 235 $[275-ketene]^+$ (47), 229 $[247-H_2O]^+$ (51), 187 $[247-HOAc]^+$ (68), 127 $[187-HOAc]^+$ (100), 81 $[H_2C=CH-C(=CH_2)CH_2]^+$ (72); ^1H NMR ($CDCl_3$): δ 5.18 (*d*, H-1t), 5.05 (*d*, H-1c), 6.34 (*dd*, H-2), 2.17 (*m*, H-4), 1.72 (*m*, H-5), 4.95 (*dd*, H-6), 1.22 (*s*, H-8), 1.19 (*s*, H-9), 5.02 and 4.99 (*br s*, H-10), 4.63 (*d*, H-1′), 4.72 (*m*, H-2′), 3.58 (*m*, H-3′, H-4′), 3.33 (*m*, H-5′), 3.86 and 3.78 (*dd*, H-6′), 2.11 and 2.10 (*s*, OAc) (*J* [Hz]: 1c, 2 = 11; 1t, 2 = 17; 5, 6 = 10; 5′, 6 = 2.5; 1′, 2′ = 8; 5′, $6'_1$ = 2.5; 5′, $6'_2$ = 4; $6'_1$, $6'_2$ = 12).

5-*Isovaleryloxynerolidol* (**45**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3560 (OH), 1740 (CO_2R); MS *m/z* (rel. int.): 322.251 $[M]^+$ (0.1) (calc. for $C_{20}H_{34}O_3$: 322.251), 220 $[M-RCO_2H]^+$ (1), 202 $[220-H_2O]^+$ (9), 187 $[202-Me]^+$ (5), 69 $[C_5H_9]^+$ (100); ^1H NMR ($CDCl_3$): δ 5.26 (*dd*, H-1t), 5.07 (*dd*, H-1c), 5.88 (*dd*, H-2), 2.01 and 1.73 (*dd*, H-4), 5.59 (*ddd*, H-5), 5.08 (*br d*, H-6), 5.03 (*br t*, H-10), 1.66 (*br s*, H-12), 1.58 (*br s*, H-13), 1.71 (*d*, H-14), 1.26 (*s*, H-15); *Oi*Val: 2.13 *dd*, 2.06 *m*, 0.92 *d* (6H) (*J* [Hz]: 1c, 1t = 1; 1t, 2 = 17; 1c, 2 = 11; 4, 4′ = 15; 4, 5 = 4.5; 4′, 5 = 5, 6 = 9; 5, 14 = 1; 9, 10 = 7).

5-*Senecioylnerolidol* (**47**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1730, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 320.235 $[M]^+$ (0.7) (calc. for $C_{20}H_{32}O_3$: 320.235), 249 $[M-C_4H_7O]^+$ (0.8), 220 $[M-RCO_2H]^+$ (1.5), 202 $[220-H_2O]^+$ (9), 151 $[220-C_5H_9]^+$ (15), 83 $[RCO]^+$ (100), 71 $[C_4H_7O]^+$ (73), 69 $[C_5H_9]^+$ (96); ^1H NMR ($CDCl_3$): δ 5.26 (*dd*, H-1t), 5.07 (*dd*, H-1c), 5.89 (*dd*, H-2), 2.00 and 1.74 (*dd*, H-4), 5.61 (*ddd*, H-5), 5.12 (*br d*, H-6), 2.05 and 1.99 (*m*, H-8, H-9), 5.05 (*br t*, H-10), 1.67 (*br s*, H-12), 1.59 (*br s*, H-13), 1.72 (*d*, H-14), 1.27 (*s*, H-15); OSen: 5.63 (*br s*), 2.15 and 1.88 (*d*) (*J* [Hz]: s. **45**).

9-*Hydroxynerolidol*-9-O-β-D-*glucopyranoside*-2′-O-*acetate* (**50**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1750 (OAc); MS *m/z* (rel. int.): 289 $[M-C_{10}H_{17}O]^+$ (2), 205.071 $[C_8H_{13}O_6]^+$ (100), 187 $[205-H_2O]^+$ (22), 127 $[187-HOAc]^+$ (73), 85 $[C_5H_9O]^+$ (48).

9-*Hydroxynerolidol*-9-O-β-D-*glucopyranoside*-2′,6′-O-*diacetate* (**51**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1750 (OAc); MS *m/z* (rel. int.): 331 $[M-C_{10}H_{17}O]^+$ (0.5), 247.081 $[C_{10}H_{15}O_7]^+$ (100), 229 $[289-HOAc]^+$ (58), 187 $[247-HOAc]^+$ (30), 127 $[187-HOAc]^+$ (58); $[\alpha]_D^{24°}$ −23 ($CHCl_3$; *c* 1.76). Saponification (KOH/MeOH, 30 min, 70°) gave **52**, colourless gum; MS *m/z* (rel. int.): 247 $[M-C_{10}H_{17}O]^+$ (3), 221.191 $[C_{15}H_{25}O]^+$ (1), 85 $[C_5H_9O]^+$ (100). Acetylation (Ac_2O, 2 hr, 70°) gave the tetraacetate **52**Ac.

7-*Hydroxy*-6,7-*dihydro*-5,6*E*-*dehydronerolidol* (**54**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3070, 1640, 990 (CH=CH_2); MS *m/z* (rel. int.): 220.183 $[M-H_2O]^+$ (1) (calc. for $C_{15}H_{24}O$: 220.183), 205 (1), 202 (2.3), 135 (22), 107 (34), 85 (30), 71 $[C_4H_7O]^+$ (100), 69 $[C_5H_9]^+$ (95); ^1H NMR (C_6D_6): δ 5.28 (*dd*, H-1t), 5.02 (*dd*, H-1c), 5.86 (*dd*, H-2), 2.22 and 2.18 (*dd*, H-4), 5.73 (*dt*, H-5), 5.50 (*dt*, H-6), 5.26 (*br t*, H-10), 1.72 (*br s*, H-12), 1.62 (*br s*, H-13), 1.22 (*s*, H-14), 1.20 (*s*, H-15), (*J* [Hz]: 1t, 2 = 17; 1c, 2 = 11; 1t, 1c = 1.5; 4, 4′ = 14; 4, 5 = 7; 4, 6 = 1; 5, 6 = 15; 9, 10 = 6.5); $[\alpha]_D^{24°}$ +18 ($CHCl_3$; *c* 0.84).

11-*Hydroxy*-10,11-*dihydro*-9,10*E*-*dehydronerolidol* (**55**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 220.182 $[M-H_2O]^+$ (1) (calc. for $C_{15}H_{24}O$: 220.183), 202 $[220-H_2O]^+$ (3), 138 (62), 93 (100), 71 (97); ^1H NMR ($CDCl_3$): δ 5.22 (*dd*, H-1t), 5.07 (*dd*, H-1c), 5.91 (*dd*, H-2), 5.16 (*br t*, H-6), 2.66 (*br d*, H-8), 5.55 (*dd*, H-9), 5.63 (*d*, H-10), 1.28 (3H) and 1.31 (6H) (*s*, H-12, H-13, H-15), 1.56 (*br s*, H-14) (*J* [Hz]: 1t, 2 = 17; 1c, 2 = 11; 1t, 1c = 1.5; 5, 6 = 7; 8, 9 = 6; 9, 10 = 15.5).

5,13-*Dihydroxygeranyllinalol* (**62**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600, 3540, 3480 (OH); MS *m/z* (rel. int.): 85 $[C_5H_9O]^+$ (100), 71 $[C_4H_7O]^+$ (62); ^1H NMR ($CDCl_3$): δ 5.38 (*dd*, H-1t), 5.15 (*dd*, H-1c), 5.93 (*dd*, H-2), 1.81 (*dd*, H-4), 1.51 (*dd*, H-4′), 4.61 (*ddd*, H-5), 5.16 (*br d*, H-6), 2.05 (*m*, H-8, H-9), 5.14 (*br t*, H-10), 2.19 (*m*, H-12), 4.37 (*dd*, H-13), 5.15 (*br d*, H-14), 1.72 (*br s*, H-16), 1.66 (*br s*, H-17), 1.62 (*br s*, H-18), 1.68 (*br s*, H-19), 1.26 (*s*, H-20) (*J* [Hz]: 1t, 1c = 1.5; 1t, 2 = 17; 1c, 2 = 11; 4, 5 = 8; 4′, 5 = 2; 4, 4′ = 10; 5, 6 = 8; 9, 10 = 7; 12, 13 = 3.5; 12′, 13 = 12, 12′ = 9).

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