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SESQUITERPENE LACTONES FROM *GNEPHOSIS* SPECIES

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Key Word Index—*Gnephosis arachnoidea*, *G. brevifolia*, *G. exilis*; Compositae; Inuleae; sesquiterpene lactones; eudesmanolides; germacranolide; guaianolides; seco-eudesmanolides; aromadendrane derivative.

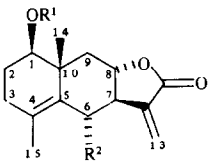
Abstract—From two *Gnephosis* species, in addition to known compounds, six eudesmanolides, desmethyl ivangulin, the germacranolide 2α-hydroxylaurenobiolide, a guaianolide and an aromadendrane derivative were isolated. The structures were elucidated by high field NMR techniques. Chemotaxonomic aspects are discussed briefly.

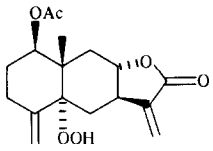
INTRODUCTION

The Australian genus *Gnephosis* with 12 species is traditionally placed in the tribe Inuleae, subtribe Angianthinae. Recently, members of this subtribe have been transferred to the Gnaphaliinae in the *Angianthus* group [1]. As the chemistry of this group is heterogeneous, we were interested in the constituents of further genera of this group. We have, therefore, studied the chemistry of three *Gnephosis* species about which nothing had been reported. The results are discussed in this paper.

RESULTS AND DISCUSSION

The extract of the aerial parts of *Gnephosis arachnoidea* Turcz. afforded longifolene, the eudesmanolides **1** [2] and **2**–**8**, the germacranolide **9** and the ivangulin derivatives **10** and **11**. The extract of *G. brevifolia* (A. Gray) Benth. gave in addition to desacetoxylaurenobiolide (**12**) [3], its 4α,5β-epoxide (**13**) [4, 5], tomentosin (**14**) [6], pseudoivalin (**15**) [7], inuviscolide (**16**) [9], the 11α,13-dihydro derivative of the latter (**17**) and the aromadendrane derivative **18**. From the extract of *G. exilis* W. Fitzg. no





	1	2	3	4	5
R^1	H	Ac	H	H	Ac
R^2	H	H	OH	OAc	OAc

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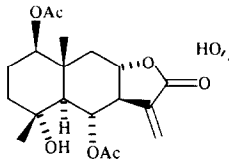
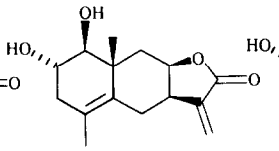
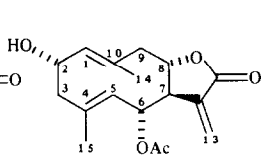
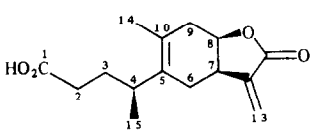
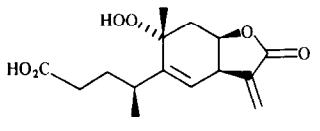




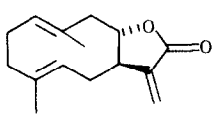


7 8 9



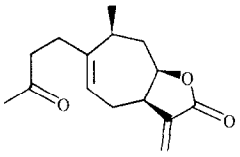


10 11



12

13 4α,5β epoxide



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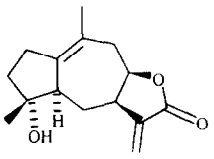

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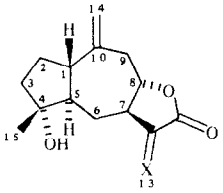
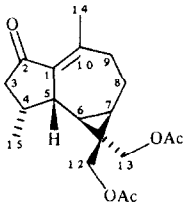


16 X = H_2

17 X = βMe,H



18

characteristic compounds were isolated.

The structure of **2** directly followed from the ^{1}H NMR spectrum (Table 1) which was of course very close to that of **1** [1]. As expected the H-1 signal was shifted downfield (δ 4.84 *dd*) and an acetate methyl singlet was visible (δ 2.08 *s*). Acetylation of **1** gave an acetate which was identical with the natural product. The ^{1}H NMR spectrum of **3** (Table 1) was in part also similar to that of **1**. However, the H-6 signals were replaced by a broadened doublet at δ 4.71 and the H-13′ signal was shifted downfield. In agreement with the molecular formula ($C_{15}H_{20}O_4$) therefore a 6-hydroxy derivative of 8-epiivangustin (**1**) was present. The configuration at C-6 followed from the large coupling of H-6.

The ^{1}H NMR spectra of **4** (Table 1) indicated that the acetate of the lactone **3** was present and similarly, the diacetate **5** showed ^{1}H NMR data which only agreed with the acetate of **4** (Table 1). All signals in the spectra of **2**–**5** could be assigned by spin decoupling, only a few being multiplets.

The ^{1}H NMR spectrum of lactone **6** (Table 1) indicated the presence of a hydroperoxide (δ 7.37 *s*). Again all signals could be assigned by spin decoupling. The obtained sequences only agreed with those expected for the acetate **6**. Most likely this compound was an artifact formed by attack of oxygen on acetate **2**.

The ^{1}H NMR spectrum of **7** (Table 1) was in part similar to that of **5** indicating the presence of a further eudesma-8α,12-olide. However, the olefinic methyl signal was replaced by a sharp singlet at δ 1.31. Furthermore, spin decoupling indicated the presence of H-5. In agreement with the mass spectrum therefore the presence of a 4-hydroxy-5H-derivative of **5** was very likely. The stereochemistry followed from the observed NOEs. Clear effects were obtained between H-14, H-6 and H-8, between H-15 and H-6 as well as between H-7 and H-5.

The ^{1}H NMR spectral data of **8** (Table 1) differed more markedly from those of **2**–**7**. Spin decoupling allowed the assignment of all signals leading to a sequence which

Table 1. ^{1}H NMR spectral data of compounds

H	2	3	4	5	6*
1	4.84 *dd*	3.63 *dd*	3.59 *dd*	4.80 *dd*	5.26 *dd*
2	1.80 *m*	1.78 *m*	1.65 *m*	1.77 *m*	2.01 *m*
2′					1.63 *m*
3	2.30 *m*	2.28 *m*	2.21 *m*	2.25 *m*	2.59 *br ddd*
3′	2.08 *m*	2.09 *m*	2.05 *m*	2.07 *m*	2.30 *ddd*
6	3.01 *dd*	4.71 *br d*	5.78 *br d*	5.78 *br d*	2.68 *dd*
	1.95 *br dd*				1.71 *dd*
7	2.30 *m*	2.55 *dddd*	2.78 *dddd*	2.79 *dddd*	3.12 *ddddd*
8	4.05 *ddd*	4.09 *ddd*	4.16 *ddd*	4.13 *ddd*	4.00 *ddd*
9	2.30 *dd*	2.51 *dd*	2.59 *dd*	2.32 *dd*	2.02 *dd*
9′	1.47 *br dd*	1.50 *br dd*	1.49 *br dd*	1.50 *br dd*	1.91 *br dd*
13	6.12 *d*	6.19 *d*	6.15 *d*	6.16 *d*	6.11 *d*
13′	5.45 *d*	6.03 *d*	5.53 *d*	5.54 *d*	5.45 *d*
14	1.17 *s*	1.06 *s*	1.16 *s*	1.24 *s*	1.01 *s*
15	1.68 *br s*	1.97 *br s*	1.72 *br s*	1.73 *br s*	5.19 *d*
					4.93 *br s*
OAc	2.08 *s*	—	2.17 *s*	2.18 *s*	2.04 *s*
				2.09 *s*	

*OOH 7.37 *s*; †H-5 1.88 *d*; ‡H-5 4.83 *br d*; §H-4 2.71 *ddq*; ‖H-4 2.48 *m*.

[*J*] {Hz}: compounds **2**–**7**: 1,2 = 5; 1,2′ = 11; 6,7 = 7,8 = 11.5; 7,13 = 3.2; 7,13′ = 3; 2,3 = 6; 2,3′ = 1.5; 2′,3 = 3,3′ = 14; 2′,3′ = 5.5; compound **8**: 1,2 = 10; 2,3 = 7; 2,3′ = 9; 8,9 = 4.5; 8,9′ = 11; 9,9′ = 14; compound **7**: 5,6 = 10.5; compound **9**: 1,2 = 2,3′ = 5,6 = compound **10**: 2,2′ = 16.5; 2,3 = 7; 2,3′ = 2′,3 = 7,8 = 9; 2′,3′ = 5.5; 3,3′ = 14; 3,4 = 6′,7 = 2.2; compound **11**: 4,15 = 6.5; 6,7 = 8,9 = 4.5; 7,8 = 8,9′ = 6.5; 7,13 =

required again an eudesmanolide. At first glance the couplings of H-8 looked like those of a 8α,12-olide. However, the NOEs showed that a *cis*-lactone was present. Thus effects were observed between H-14 and H-2 as well as between H-8, H-7 and H-1. Accordingly, a 1β,2α-hydroxy derivative of the Δ^4 isomer of alantolactone was present. Obviously, the conformation was slightly changed due to the quasi-exocyclic double bond as in similar cases [10].

The ^{1}H NMR spectrum of **9** (Table 1) indicated the presence of a laurenobiolide derivative as followed from the sequences obtained by spin decoupling. An additional threefold doublet at δ4.74 was coupled with the signal of the olefinic proton (H-1). Accordingly, a 2-hydroxy derivative was present. In contrast to the spectrum of laurenobiolide that of lactone **9** was not very much broadened, obviously due to the additional function which favoured one of the possible conformations. The stereochemistry followed from the observed couplings and the NOE's between H-6 and H-8, between H-7 and H-5 as well as between H-2 and H-14. In the favoured conformation therefore the methyls at C-4 and C-10 are both above the plane as in costunolide.

The ^{1}H NMR spectrum of **10** (Table 1) was very close to that of ivangulin [11]. However, the methoxy singlet was missing. In agreement with the molecular formula ($C_{15}H_{20}O_4$) therefore the corresponding free acid was present. The stereochemistry was identical with that of ivangulin [11] as followed from the NOEs between H-7 and H-8. The spectral data of **11** (Table 1) indicated that this lactone again was a hydroperoxide most likely formed by an ene reaction of **10** with oxygen. Therefore this compound may be an artifact. The position of the double bond and of the hydroperoxide group followed from the ^{1}H NMR data while the configuration at C-10 was not established. Inspection of a model of **10** shows that the proposed configuration is most likely as a β-attack of oxygen is hindered by the lactone moiety.

The ^{1}H NMR spectrum of **17** (Experimental) was close to that of **16** [9], however, the signals of the exomethylene protons were replaced by signals at δ2.71 *dq* and 1.21 *d* (3H). Therefore a 11,13-dihydro derivative was very likely. The stereochemistry again followed from the observed NOEs. Clear effects were obtained between H-7, H-5 and H-11, between H-8 and H-1 as well as between H-15 and H-1. Thus lactone **17** is the 11-*epi* isomer of the known dihydro derivative with an 11α-methyl group [12]. The latter also was obtained as the only product on boranate reduction of **16.**

The molecular formula of **18** was $C_{19}H_{26}O_5$. As the ^{1}H NMR spectrum (Table 2) indicated the presence of a diacetate (δ2.09 and 2.06 *s*) a sesquiterpene with three oxygen functions was very likely. In the ^{1}H NMR spectrum two pairs of doublets around δ4.0 were attributed to acetoxy methylene groups. A methyl doublet at δ2.13 required an olefinic methyl group which was deshielded by a conjugated keto group. The splitting of the signals at δ1.35 and 1.07 could be an indication of a cyclopropane ring. Spin decoupling allowed the assignment of all signals which led to a sequence which required an aromadendrane derivative. This was strongly supported by the ^{13}C NMR data (Table 2). The *cis* orientation of H-5, H-4 and H-12, of H-12, H-5 and H-8β, of H-13, H-6 and H-7 as well as of H-15 and H-6 could be deduced from the observed NOEs. Accordingly, the stereochemistry was also settled.

Gnephosis exilis, which gave no characteristic compounds, is considered by Short (pers. commun.) to war-

2–11 ($CDCl_3$, 400 MHz, δ-values)

7†	8	9‡	10§	11‖
4.69 *m*	3.34 *d*	5.00 *br d*	—	—
1.6 – 1.85 *m*	3.90 *ddd* 2.51 *br ddd* 2.05 *br dd*	4.74 *ddd* 2.63 *dd* 2.05 *dd*	2.13 *ddd* 2.03 *ddd* 1.61 *dddd* 1.43 *dddd*	1.6 – 2.1 *m*
5.67 *br dd*	2.86 *dd* 1.97 *br dd*	5.34 *dd*	2.19 *br dd* 2.03 *br dd*	5.52 *d*
2.81 *dddd*	3.09 *m*	3.11 *dddd*	3.23 *ddddd*	3.63 *dddd*
3.99 *ddd*	4.49 *ddd*	3.99 *br dd*	4.88 *ddd*	4.97 *ddd*
2.21 *dd*	2.27 *dd*	2.69 *br d*	2.40 *dd*	2.56 *dd*
1.50 *br dd*	1.53 *br dd*	2.49 *dd*	2.33 *br dd*	1.94 *dd*
6.12 *d*	6.30 *d*	6.39 *d*	6.28 *d*	6.24 *d*
5.36 *d*	5.63 *d*	5.94 *d*	5.66 *d*	5.65 *d*
1.12 *s*	1.09 *s*	1.72 *br s*	1.72 *br s*	1.34 *s*
1.31 *s*	1.68 *br s*	1.70 *br s*	0.96 *d*	1.14 *d*
2.13 *s* 2.08 *s*		2.08 *s*		

8,9 = 4; 8,9′ = 9,9′ = 12; compounds **2** and **6**: 6,6′ = 14; 6,7 = 3.5; compound **6**: 3,3′ = 18; 3,6′ = 2; 6,6′ = 13.5; 6,7 = 7.5; 6′,7 = 10.5; 7,8 = 8; 7,13 = 3; 7,13′ = 2.5; 6,7 = 10; 2,3 = 6; 3,3′ = 11.5; 7,8 = 6.5; 7,13 = 3; 7,13′ = 2.5; 8,9′ = 9.5; 9,9′ = 13; = 8,9 = 8,9′ = 4.5; 3′,4 = 10.5; 4,15 = 7; 6,6′ = 9,9′ = 15; 6,7 = 6.5; 7,13 = 3; 7,13′ 2.5; 7,13′ = 2.2; 9,9′ = 14.

Table 2. NMR spectral data of compound **18** ($CDCl_3$, δ-values)

H	^{1}H 400 MHz (J[Hz])	C	^{13}C (100.6 MHz)
3	2.39 *dd* (7, 16)	1	133.0 *s*
3′	2.10 *dd* (7, 16)	2	206.6 *s*
4	2.30 *dddq* (7, 7, 7, 7)	3	47.5 *t*
5	3.04 *br dd* (7, 11)	4	38.4 *d*
6	1.35 *dd* (9.5, 11)	5	29.7 *d*
7	1.07 *ddd* (5.5, 9.5, 11)	6	27.3 *d*
8	1.86 *m*	7	23.0 *d*
8′	1.75 *m*	8	20.6 *t*
9	2.48 *m*	9	38.6 *t*
12	4.39 *d* (12)	10	151.6 *s*
12′	4.34 *d* (12)	11	61.8 *t*
13	4.01 *d* (11.5)	12	61.8 *t*
13′	3.87 *d* (11.5)	13	69.6 *t*
14	2.13 *d* (1.6)	14	21.4 *q*
15	1.03 *d* (7)	15	16.5 *q*
OAc	2.09, 2.06 *s*	OAc	171.1, 171.0 *s*
			20.9, 20.6 *q*

rant a new genus of its own. The chemistry of two other *Gnephosis* species is relatively uniform as in both cases desacetoxylaurenobiolide [12] or its 8-*epi* isomer are the likely precursors of most lactones. However, in one case the transformation to eudesmanolides dominated while in the other guaianolides are formed. The seco compounds **10** and **14** are also biogenetic derivatives of the corresponding eudesmanolide and guaianolide respectively. Similar sesquiterpene lactones are reported from several *Inula* species [13], a genus placed in the subtribe Inulinae. However, from an *Angianthus* species a xanthanolide [14] and from a *Calocephalus* species the guaianolide pseudoivalin [8] have been isolated. Both genera are also currently placed in the *Angianthus* group [1]. From two other genera of this group no lactones are reported. Thus from *Myrriocephalus* only diterpenes [15] and from *Actinobole* [16] a eudesmane aldehyde have been isolated. From all the other groups of the subtribe Gnaphaliinae no sesquiterpene lactones are reported. These observations lend further weight to the argument provided by Short [18] that the *Angianthus* group is an artificial assemblage of genera. In particular, they would seem to indicate that the position of those genera currently included in the subtribe Gnaphaliinae [1] and previously placed in the separate subtribe Angianthinae [17] deserves further investigation, especially as the classification of the Inuleae is still unclear [19]. Further taxonomic revision within this group is required before the relationships of the many genera involved can be resolved.

EXPERIMENTAL

The air-dried aerial parts were collected in August 1986 in W. Australia, vouchers are deposited in the US National Herbarium, Washington, and in the West Australian Herbarium, Perth. The chopped material was extracted with a mixture of Et_2O–MeOH–petrol (1:1:1) at room temp. The extracts obtained were treated with MeOH to remove long chain saturated hydrocarbons and the soluble parts were first separated by CC (silica gel) and further by TLC (silica gel, PF 254). In part HPLC (always RP 8, LiChromosorb Merck AG, columns 8 × 250 mm, *ca* 100 bar, flow rate 3 ml/min) was used for further separations as reported previously [20]. The extract of 53 g of *G. arachnoidia* (voucher RMK 9561) was separated into three crude CC fractions. TLC of fraction 1 gave 5 mg longifolene and TLC of fraction 2 (CH_2Cl_2, × 3) 2 mg **2** (R_f 0.61) and 20 mg **5** (R_f 0.43). TLC of fraction 3 (Et_2O) afforded 15 mg **5** and three mixtures (3/1–3/3). TLC of fraction 3/1 (CH_2Cl_2–Et_2O, 2:1, × 3) gave 20 mg **1** and 50 mg **4** (R_f 0.62). TLC of fraction 3/2 (CH_2Cl_2–Et_2O, 1:1, × 3) afforded 5 mg **4**, 5 mg **9** (R_f 0.43) and a mixture, which gave by HPLC (MeOH–H_2O, 3:2) 2 mg **3** (R_t 1.8 min), 4 mg **6** (R_t 1.5 min) and 5 mg **11** (R_t 1.1 min). TLC of fraction 3/3 (CH_2Cl_2–Et_2O, 1:1) gave 2 mg **9**, 5 mg **7** (R_f 0.37) and a mixture which yielded by HPLC (MeOH–H_2O, 3:2) 3 mg **8** (R_t 2.5 min) and 25 mg **10** (R_t 4.8 min). The extract of 162 g *G. brevifolia* (voucher RMK 9577) was separated into four crude CC fractions. The first one gave by TLC (Et_2O–petrol, 1:3) 10 mg **12** and the second one (Et_2O–petrol, 1:1) 20 mg **18** (R_f 0.34), 160 mg **13** and 20 mg **14**. Fraction 3 afforded by TLC (Et_2O–petrol, 3:1) 30 mg **13**, 40 mg **14** and 70 mg **16**. The last fraction gave by TLC (CH_2Cl_2–Et_2O, 2:1) 150 mg **16** and a mixture which gave by HPLC (MeOH–H_2O, 3:2) 2 mg **17** (R_t 4.7 min) and 10 mg **15**. The extract of 100 g *G. exilis* (voucher RMK 9583) gave no characteristic compounds. Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

8-epi-*Ivangustin acetate* (**2**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770 (γ-lactone), 1735 (OAc); MS *m/z* (rel. int.): 290 $[M]^+$ (1) 230.131 $[M-HOAc]^+$ (58) (calc. for $C_{15}H_{18}O_2$: 230.131), 215 (46), 120 (100), 119 (70), 94 (72), 81 (66). Acetylation of **1** (Ac_2O, 1 hr, 70°) gave **2**, identical with the natural product (^{1}H NMR, TLC).

6α-*Hydroxy*-8-epi-*ivangustin* (**3**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1765 (γ-lactone); MS *m/z* (rel. int.): 264.136 $[M]^+$ (8) (calc. for $C_{15}H_{20}O_4$: 264.136), 246 (15), 228 (8), 123 (36), 69 (100).

6α-*Acetoxy*-8-epi-*ivangustin* (**4**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1750 (OAc); MS *m/z* (rel. int.): 306.147 $[M]^+$ (10) (calc. for $C_{17}H_{22}O_5$: 306.147), 246 (100), 228 (85), 213 (51), 202 (71); $[\alpha]_D^{24}$ −25 ($CHCl_3$; *c* 0.58).

6α-*Acetoxy*-8-epi-*ivangustin acetate* (**5**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1785 (γ-lactone), 1745 (OAc); MS *m/z* (rel. int.): 348 $[M]^+$ (0.2), 288.136 $[M-HOAc]^+$ (4.5) (calc. for $C_{17}H_{20}O_4$:

288.136), 246 [288 − ketene]$^+$ (28), 228 (100), 213 (24); $[\alpha]_D^{24°}$ −20 ($CHCl_3$; *c* 0.58).

5α-Hydroperoxy-α-cyclopyrethrosin acetate (**6**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OOH), 1770 (γ-lactone), 1720 (OAc); MS *m/Z* (rel. int.): 306 [M − H_2O]$^+$ (9), 289 [M − OOH]$^+$ (47), 246 [306 − HOAc]$^+$ (54), 229 [289 − HOAc]$^+$ (50), 57 (100).

1β,6α-Diacetoxy-4α-hydroxyeudesm-11-en-8α,12-olide (**7**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1765 (γ-lactone), 1740 (OAc); MS *m/z* (rel. int.): 351 [M − Me]$^+$ (0.3), 246.126 [M − 2 × HOAc]$^+$ (7.5) (calc. for $C_{15}H_{18}O_3$: 246.126), 228 [246 − H_2O]$^+$ (10), 188 (41), 164 (52), 83 (100); $[\alpha]_D^{24°}$ −7 ($CHCl_3$; *c* 0.25).

2α-Hydroxyivangustin (**8**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1765 (γ-lactone); MS *m/z* (rel. int.): 264.136 [M]$^+$ (92) (calc. for $C_{15}H_{20}O_4$: 264.136), 246 (17), 231 (32), 228 (8), 205 (100), 204 (64), 159 (56), 93 (72); $[\alpha]_D^{24°}$ +39 ($CHCl_3$; *c* 1.09).

2α-Hydroxylaurenobiolide (**9**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone), 1750 (OAc); MS *m/z* (rel. int.): 306 [M]$^+$ (0.3), 246.126 [M − HOAc]$^+$ (14) (calc. for $C_{15}H_{18}O_3$: 246.126); $[\alpha]_D^{24°}$ +49 ($CHCl_3$; *c* 0.21).

Ivangulinic acid (**10**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500–2700, 1720 (CO_2H), 1755 (γ-lactone); MS *m/z* (rel. int.): 264.136 [M]$^+$ (31) (calc. for $C_{15}H_{20}O_4$: 264.136), 246 (30), 228 818), 191 [M − $CH_2CH_2CO_2H$]$^+$ (100).

Hydroperoxide **11**. Colourless gum; CIMS *m/z* (rel. int.): 297 [M + 1]$^+$ (1).

11α,13-Dihydroinuviscolide (**17**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (γ-lactone); ^{1}H NMR ($CDCl_3$): 2.13 (*m*, H-1), 1.92 and 1.78 (*m*, H-2), 1.81 and 1.72 (*m*, H-3), 1.60 (*ddd*, H-5), 1.96 (*ddd*, H-6α), 1.17 (*ddd*, H-6β), 2.23 (*dddd*, H-7), 4.40 (*ddd*, H-8), 3.17 (*br dd*, H-9α), 2.54 (*br dd*, H-9β), 2.71 (*dq*, H-11), 1.21 (*d*, H-13), 5.02 and 4.95 (*br s*, H-14), 1.20 (*s*, H-15) (*J* [Hz]: 1,5 = 5,6β = 12; 5,6α = 3; 6α,6β = 6β,7 = 12.5; 6α,7 = 3; 7,8 = 8,9β = 10.5; 7,11 = 11,13 = 8; 8,9α = 5; 9α,9β = 15.5).

12,13-Diacetoxy-2-oxo-aromadendr-1(10)-ene (**18**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745 (OAc), 1710, 1620 (C=CCO); MS *m/z* (rel. int.): 334.178 [M]$^+$ (44) (calc. for $C_{19}H_{26}O_5$: 334.178), 274 (18), 215 [274 − OAc]$^+$ (62), 214 (100), 199 (76), 171 [199 − CO]$^+$ (71).

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. 596. Academic Press, London.
2. Bohlmann, F., Mahanta, P. K., Jakupovic, J., Rastogi, R. C. and Natu, A. A. (1978) *Phytochemistry* **17**, 1165.
3. Bohlmann, F., Umemoto, K., Jakupovic, J., King, R. M. and Robinson, H. (1984) *Phytochemistry* **23**, 1669.
4. Bohlmann, F., Jakupovic, J. and Schuster, A. (1981) *Phytochemistry* **20**, 1891.
5. Bohlmann, F., Jakupovic, J., Ahmed, M. and Schuster, A. (1983) *Phytochemistry* **22**, 1623.
6. Ito, K. and Lida, T. (1981) *Phytochemistry* **20**, 271.
7. Herz, W., Romo de Vivar, A. and Lakshmikanthara, M. V. (1965) *J. Org. Chem.* **30**, 118.
8. Batterham, T. J., Hart, N. K. and Lamberton, J. A. (1966) *Aust. J. Chem.* **19**, 143.
9. Zdero, C., Bohlmann, F., King, R. M. and Robinson, H. (1987) *Phytochemistry* **26**, 1207.
10. Zdero, C., Bohlmann, F. and Müller, M. (1987) *Phytochemistry* **26**, 2763.
11. Herz, W., Sumi, Y., Sudarsanam, V. and Raulais, P. (1967) *J. Org. Chem.* **32**, 3658.
12. Bohlmann, F., Zdero, C. and Ahmed, M. (1982) *Phytochemistry* **21**, 1679.
13. Seaman, F. C. (1982) *Botl. Rev.* **48**, 195.
14. Bohlmann, F., Czerson, H. and Schöneweiβ, S. (1977) *Chem. Ber.* **110**, 1330.
15. Zdero, C., Bohlmann, F., Haegi, L. and King, R. M. (1987) *Liebigs Ann. Chem.* 665.
16. Jakupovic, J., Lehmann, L., Bohlmann, F., King, R. M. and Robinson, H. (1988) *Phytochemistry* **27**, (in press).
17. Hoffmann, O. (1984) in *Die natürlichen Pflanzenfamilien* (Engler, A. and Prantl, K. eds) vol. 4, p. 192.
18. Short, P. S. (1983) *Muelleria* **5**, 143.
19. Bremer, K. (1987) *Cladistics* **3**, 210.
20. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1984) *Phytochemistry* **23**, 1979.