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# SESQUITERPENE LACTONES AND OTHER CONSTITUENTS FROM *CASSINIA, ACTINOBOLE* AND *ANAXETON* SPECIES

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**Key Word Index**—*Cassinia laevis, C. subtropica, C. uncata; Actinobole uliginosum; Anaxeton arborescens*; Compositae; Inuleae; sesquiterpene lactones; germacranolides; eudesmanolides; elemanolide; sesquiterpenes; eudesmane derivatives; germacrene derivative.

**Abstract**—The investigation of five representatives of Australian Gnaphaliinae species afforded in addition to several known compounds 17 new sesquiterpene lactones, 13 eudesmane derivatives derived from costic acid, ten further various sesquiterpenes and an unusual ester. The structures were elucidated by high field NMR techniques. The chemotaxonomic situation is discussed briefly.

## INTRODUCTION

The genus *Cassinia* (Compositae, tribe Inuleae) with *ca* 20 species has been placed in the large subtribe Gnaphaliinae [1]. Comparison of the morphology in this group led to the conclusion that this genus could still be included technically in the Helichrysum group due to the truncate stylar arms [1]. However, a clear decision can not be made. We have continued therefore our studies of Australian *Inuleae* by investigation of three further *Cassinia*, an *Actinobole* and an *Anaxeton* species as so far little is known on the chemistry of these genera. The presence of polyacetylenes is reported from a few *Cassinia* species [2] while some sesquiterpenes were isolated from *C. longifolia* [3].

## RESULTS AND DISCUSSION

The aerial parts of *C. laevis* R. Br. afforded several known sesquiterpenes and triterpenes (see Experimental), the flavonols mikanin [4], kaempferol-3-*O*-[glucopyranoside] (=astragalin) [5] and the corresponding 3-*O*-[rhamnopyranoside] (=afzelin) [6]. Furthermore the eudesmane derivatives **6d–6q** and **6m**, all closely related to costic acid, were isolated.

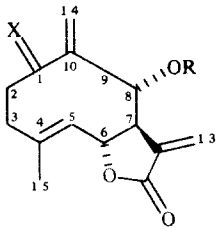
The aerial parts of *C. subtropica* F. Muell. afforded several widespread compounds, a few well known sesquiterpenes (see Experimental) and a large variety of sesquiterpene lactones. These included costunolide and its 8α-acetoxy, 8β-hydroxy [7] and 8α-hydroxy-4α,5β-epoxy derivatives [8], laurenobiolide [9] and its desacetyl derivative [10] and the 4α,5β-epoxide of the latter [11], tatridin A [12], tanachin (**2a**) [13], and the related lactones **2b** [14], **2c** [13], **2d** [14] and **2e** [15]. Also obtained were the germacranolides **1a** [16] and **1b–1d**, the eudesmanolides **3a–3f**, **3j–3p**, **3g** [17], **3h** [16] and **3i** [13], the elemanolide **4a**, the isomer **8** of ledol, the methyl esters **6a** and **6b**, the acids **6c** and **7**, and the eudesmanes **9a** and **9b**.

The roots of *C. uncata* Cunn. ex DC afforded obliquin **12a** [18] and its derivatives **12b** [19], **12c** [19] and **12d** [20], the precursor prenyletin (**12e**) [21] and its methyl ether **12f** [22], the eudesmane derivative **9f** and **9g**, the dialdehyde **10** and ferulyl aldehyde. The aerial parts gave several widespread sesquiterpenes and the keto ester **11**, the sesquiterpene lactones desacetoxylaurenobiolide [10], **4b** [23], **4c** [24] and **5** [25], pectolinarigenin, betulin and the eudesmane derivatives **6e**, **6g–6l**, **9c** and **9d**.

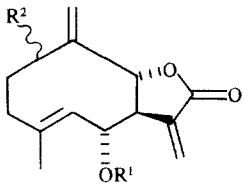
The aerial parts of *Actinobole uliginosum* (A. Gray) H. Eichler gave several common compounds (see Experimental), the sesquiterpene aldehyde **9e**, **12a–12c** and **12e**. The aerial parts of *Anaxeton arborescens* (L.) Less placed in the subtribe Athrixiinae [1] also gave **12a** and **12e**.

The structures of **1c** and **1d** followed from their $^1$H NMR spectra (Table 1) which were similar to those of the corresponding lactone where the 8α-oxygen function was missing [26]. The broadened singlet at δ7.70 in the spectrum of **1d** indicated a hydroperoxide. Triphenylphosphine reduction gave **1c**. The configuration at C-8 followed from the large couplings of H-8. In the spectrum of **1b** the H-14 signals were shifted down field and the H-1 signal was missing. Accordingly, 8α-hydroxyanhydroverlotorin was present.

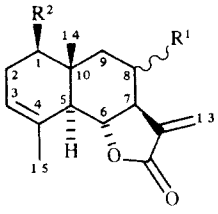
The $^1$H NMR spectrum of **3a** (Table 2) differed from that of α-cyclocostunolide by the additional low field threefold doublet at δ4.61. Spin decoupling and the couplings indicated an 8β-hydroxy-group. Similarly, the spectrum of **3b** (Table 2) differed from that of santamarin by the H-8 signal at δ4.56. Again the couplings required a 8β-hydroxy group while in the spectrum of **3c** (Table 2) the corresponding signal (δ4.01) showed large vicinal coupling typical for a 8α-oxygen function. The $^1$H NMR spectrum of **3d** (Table 2) indicated that a trihydroxy derivative of arbusculin B was present. Spin decoupling and the observed couplings required a 1β,3α,8β-trihydroxyarbusculin B. The $^1$H NMR spectrum of **3e** (Table 2) showed that it was a derivative of armexifolin [27]. The couplings of the additional low field signal at

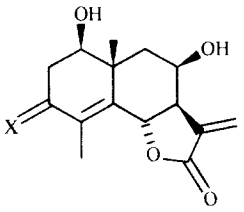


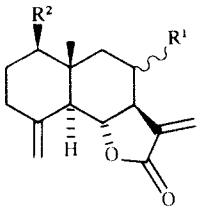
| | 1a | 1b | 1c | 1d |
|---|---|---|---|---|
| R | H | H | Ac | Ac |
| X | βOH,H | =O | βOH,H | βOOH,H |



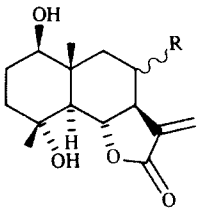
| | 2a | 2b | 2c | 2d | 2e |
|---|---|---|---|---|---|
| $R^1$ | H | H | H | H | Ac |
| $R^2$ | αOH | αOOH | βOH | βOOH | αOH |

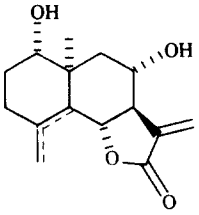


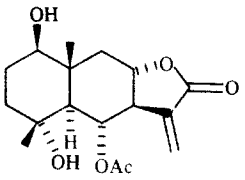




| | 3a | 3b | 3c | 3d | 3e | 3f | 3g | 3h | 3i |
|---|---|---|---|---|---|---|---|---|---|
| $R^1$ | βOH | βOH | αOH | αOH,H | =O | βOH | βOH | αOH | αOAc |
| $R^2$ | H | OH | OH | | | H | OH | OH | OH |







| | 3j | 3k | 3l | 3m | 3n | 3o | 3p |
|---|---|---|---|---|---|---|---|
| R | βOH | αOH | αOAc | αOAc | $\Delta^4$ | $\Delta^{4,15}$ | |
| | | | | 4*epi* | | 5αH | |

δ4.59 required again an 8β-hydroxy group. The presence of 8β-hydroxy-β-cyclocostunolide (**3f**) followed from comparison of the $^1$H NMR spectrum (Table 2) with that of the parent compound. Again the couplings of H-8 led to the proposed configuration.

The $^1$H NMR spectra of **3j** and **3k** (Table 3) were close to that of arbusculin A [28]. Spin decoupling showed that additional hydroxy groups were at C-1 and C-8. Again the stereochemistry followed from the couplings and that at C-4 from the observed NOE's between H-14, H-15 and H-6. In the case of **3l** also an NOE was visible between H-14 and H-8.

The spectrum of **3l** (Table 3) clearly indicated that the 8-*O*-acetate of **3k** was present while that of **3m** showed some typical shift differences which obviously were due to the changed configuration at C-4. The 4β-position of the hydroxy group led to the expected upfield shift of the H-5 and a downfield shift of the H-6 signal. The $^1$H NMR spectrum of **3p** (Table 3) was in part very similar as that of **3l**, notably the splitting of the signal was identical. The chemical shifts of H-6 and H-8 did not agree with that of **3l**. Accordingly, a 6α-acetoxy-12,8α-olide must be proposed. The stereochemistry followed from the couplings and also from the observed NOE's. Thus clear effects were obtained by saturation of H-14 with H-15, H-6 and H-8.

The $^1$H NMR spectra of **3n** and **3o** (Table 2) were in part similar to those of arbusculin B and β-cyclocostunolide. Two additional low field signals required hydroxy groups at C-1 and C-8, both being equatorial as followed from the couplings. However, the chemical shifts differed from those of similar eudesmanolides. Accordingly, a changed stereochemistry was very likely. Thus in the case of **3n** clear effects were present between H-14, H-9α and H-7 as well as between H-6, H-8 and H-15. Similarly, the lactone **3o** showed NOE's between H-14, H-9α and H-5 as well as between H-8 and H-1.

The $^1$H NMR spectrum of **4a** (Table 2) showed that an elemanolide was present. The substitution pattern and the stereochemistry followed from the observed data.

The $^1$H NMR spectra of **6a** and **6b** (Table 3) indicated that these methyl esters were derived from the eudesmanolides **3l** and **3h**, respectively, by methanolysis. Accordingly, as in similar compounds the H-13 signals differed

Table 1. $^1$H NMR spectral data of compounds **1b–1d** (400 MHz, $CDCl_3$, $\delta$-values)

| H | 1b | 1c | 1d |
|---|---|---|---|
| 1 | — | 3.89 *br dd* | 4.15 *br dd* |
| 5 | 5.08 *br d* | 5.23 *br d* | 5.32 *br d* |
| 6 | 4.17 *dd* | 4.41 *dd* | 4.43 *dd* |
| 7 | 2.74 *dddd* | 3.28 *dddd* | 3.21 *dddd* |
| 8 | 3.96 *m* | 5.15 *ddd* | 5.15 *ddd* |
| 9 | 3.41 *dddd* | 2.35 *br d* | 2.62 *br d* |
| 9′ | 2.15 *dd* | 2.46 *br dd* | 2.42 *br dd* |
| 13 | 6.38 *dd* | 6.15 *d* | 6.24 *d* |
| 13′ | 6.17 *dd* | 5.55 *d* | 5.67 *d* |
| 14 | 5.84 *d* | 5.21 *br s* | 5.46 *br s* |
| 14′ | 5.80 *d* | 5.18 *br s* | 5.28 *br s* |
| 15 | 1.67 *br s* | 1.71 *br s* | 1.72 *br s* |
| OAc | — | 2.07 *s* | 2.14 *s* |
| | | | 7.70 *br s* (OOH) |

*In $CDCl_3$–$CD_3OD$, 4:1, 60°.

*J* [Hz]: Compound **1b**: 5,6 = 6,7 = 9.5; 7,8 = 7,13 = 7,13′ = 8,9 = 3; 8,9′ = 11; 9,9′ = 13; 9,14 = 1.5; 9,14′ = 2; compounds **1c** and **1d**: 5,6 = 6,7 = 7,8 = 10; 7,13 = 3.5; 7,13′ = 3; 8,9 = 6.5; 8,9′ = 2.5; 9,9′ = 17; compound **1c**: 1,2 = 9; 1,2′ = 4; compound **1d**: 1,2 = 12; 1,2′ = 3.

significantly from those of the lactones. Furthermore, a slight shift difference was observed. Possibly these esters were artifacts formed during the extraction with methanol. The $^1$H NMR spectrum of the methyl ester of **6c** (Table 4) indicated that a 3$\beta$-acetoxy derivative of the methyl ester of isocostic acid was present. The structure of **6d** followed from the $^1$H NMR spectrum of the corresponding methyl ester (Table 4). All signals could be assigned by spin decoupling. The configuration at C-3 in the esters **6c** and **6d** was deduced from the observed couplings of H-3.

The $^1$H NMR spectra of the methyl esters of **6e–6l** (Table 4) were similar. Spin decoupling indicated that all esters were derived from costic acid where an oxygen function at C-15 was introduced most likely by an ene-reaction. In the spectrum of **6e** the chemical shift of the H-15 signals indicated a free hydroxy group while in the other spectra the corresponding signals were shifted downfield. The nature of the ester groups at this carbon was deduced from the typical $^1$H NMR signals. In addition to the *E*- and *Z*-coumarates and *E*- and *Z*-cinnamates also present were the *n*-propionate, *n*-butyrate and tiglate.

The $^1$H NMR spectrum of the methyl ester of **6m** (Table 4) showed that now the oxygen function at C-15 was an aldehyde group as followed from the singlet at $\delta$9.42 and the down field shift of the H-3 signal ($\delta$6.71 *dd*). The structure was also supported by the $^{13}$C NMR spectrum of this ester [(C-1–C-15, $CDCl_3$): $\delta$36.4, 27.3, 153.0, 142.2, 39.7, 24.5, 43.5, 26.9, 36.4, 32.1, 145.5, 167.8, 123.0, 15.8, 194.8; OMe 51.7].

The $^1$H NMR spectrum of the methyl ester of **7** showed some similarities with that of $\beta$-vetivone. However, the signals at $\delta$3.77 *s* (3H), 6.17 *d*, 5.61 *dd* and 2.98 *br dddd* indicated the presence of a 7-[2-prop-2-enoic] side chain. Nearly all signals could be assigned by spin decoupling [5.77 (*q*, H-1), 2.43 (*dd*, H-3), and 2.24 (*dd*, H-3′), 2.14 (*ddq*, H-4), 2.18 (*ddd*, H-6), 1.44 (*dd*, H-6′), 2.98 (*dddd*, H-7), 2.06 and 1.69 (*m*, H-8), 1.90 (*m*, H-9), 6.17 (*d*, H-13), 5.61 (*dd*, H-13′), 1.99 (*d*, H-14), 1.10 (*d*, H-15); *J* [Hz]: 1,14 = 1; 3,3′ = 16; 3,4 = 4; 3′,4 = 10; 4,15 = 7; 6,6′ = 12; 6,7 = 6; 6,8 = 1; 6′,7 = 7,8′ = 11.5; 7,8 = 6; 7,13 = 13,13′ = 1]. The configuration at C-4 was supported by the observed NOE between H-15 and H-7. Also a NOE was obtained between H-14 and H-13′. Both effects together indicated the relative stereochemistry at C-4 and C-5.

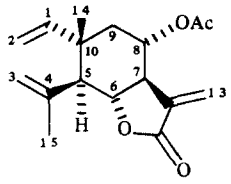
The $^1$H NMR data of the alcohol **8** (Table 5) were similar to those of alloaromadendrene and not so close to that of aromadendrene. Spin decoupling supported the

Table 2. $^1$H NMR spectral data of compounds **3a–3f**, **3n**, **3o** and **4a** (400 MHz, $CDCl_3$, $\delta$-values)

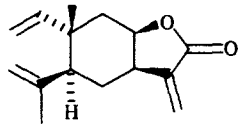
| H | 3a | 3b($CD_3OD$) | 3c | 3d($CD_3OD$) | 3e($CD_3OD$) | 3 | 3n | 3o | 4a† |
|---|---|---|---|---|---|---|---|---|---|
| 1 | * | 3.58 *dd* | 3.63 *dd* | 3.72 *dd* | 3.78 *dd* | * | 3.58 *dd* | 3.78 *dd* | 5.32 *dd* |
| 3 | 5.37 *br s* | 5.35 *br s* | 5.30 *br s* | 3.92 *br s* | — | 2.34 *m*<br>2.03 *m* | * | * | 5.10 *br s*<br>4.76 *br s* |
| 5 | 2.43 *br d* | 2.44 *br d* | 2.04 *br d* | — | — | 2.31 *br d* | — | 2.03 *br d* | 2.40 *br d* |
| 6 | 4.43 *dd* | 4.44 *dd* | 3.94 *dd* | 5.18 *br d* | 5.45 *dq* | 4.54 *dd* | 4.70 *br d* | 3.86 *dd* | 4.16 *dd* |
| 7 | 2.70 *dddd* | 2.75 *dddd* | 2.46 *dddd* | 2.86 *dddd* | 3.10 *dddd* | 2.74 *dddd* | 3.05 *dddd* | 2.54 *m* | 2.83 *dddd* |
| 8 | 4.61 *ddd* | 4.56 *ddd* | 4.01 *ddd* | 4.54 *ddd* | 4.59 *ddd* | 4.61 *ddd* | 3.61 *ddd* | 4.10 *ddd* | 5.20 *ddd* |
| 9 | 1.89 *dd* | 2.20 *dd* | 2.42 *dd* | 2.30 *dd* | 2.37 *dd* | 1.91 *dd* | 2.42 *dd* | 2.78 *dd* | 2.01 *dd* |
| 9′ | * | 1.45 *dd* | 1.39 *dd* | 1.52 *dd* | 1.69 *dd* | * | 1.83 *dd* | 1.40 *dd* | 1.64 *br dd* |
| 13 | 6.23 *d* | 6.12 *d* | 6.09 *d* | 6.22 *d* | 6.27 *d* | 6.24 *d* | 6.22 *d* | 6.18 *d* | 6.14 *d* |
| 13′ | 5.50 *d* | 5.58 *d* | 5.94 *d* | 5.63 *d* | 5.69 *d* | 5.49 *d* | 5.87 *d* | 5.98 *d* | 5.55 *d* |
| 14 | 1.17 *s* | 1.13 *s* | 0.82 *s* | 1.25 *s* | 1.45 *s* | 1.11 *s* | 1.36 *s* | 1.06 *s* | 1.16 *s* |
| 15 | 1.88 *br s* | 1.84 *br s* | 1.88 *br s* | 1.99 *d* | 2.01 *d* | 4.96 *br ddd*<br>4.87 *br ddd* | 1.83 *br s* | 5.09 *br s*<br>4.93 *br s* | 1.82 *br s* |

*Obscured; †H-2c 5.05 *d*, H-2*t* 5.01 *d*, OAc 2.11 *s*.

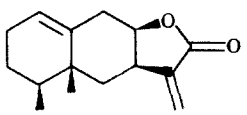
*J* [Hz]: Compounds **3a**, **3b** and **3f**: 5,6 = 6,7 = 11; 7,8 = 7,13 = 7,13′ = 8,9 = 8,9′ ~ 3; 9,9′ = 14.5; compound **3b**: 1,2 = 10; 1,2′ = 6.5; compound **3c**: 1,2 = 9; 1,2′ = 7; 5,6 = 6,7 = 10; 7,8 = 8,9′ = 11.5; 7,13 = 8,9 = 3.5; 7,13′ = 3; 9,9′ = 12.5; compounds **3d** and **3e**: 1,2 = 12.5; 1,2′ = 4; 6,7 = 12; 6,15 = 1.5; 7,8 = 8,9 = 2.5; 7,13 = 8,9′ = 3.5; 9,9′ = 14; compounds **3n** and **3o**: 1,2 = 10; 1,2′ = 6; 6,7 = 10; 7,8 = 8,9′ ~ 11.5; 7,13 = 3.5; 7,13′ = 3; 8,9 = 5; 9,9′ = 12.5; compound **3o**: 5,6 = 10; compound **4a**: 1,2c = 10.5; 1,2t = 17; 5,6 = 6,7 = 11.5; 7,8 = 11; 7,13 = 3; 8,9 = 4; 8,9′ = 11; 9,9′ = 13.



**4a**



**4b** **4c** 5.10 *epi*



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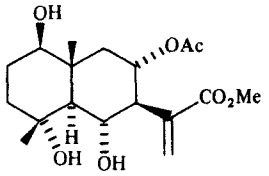
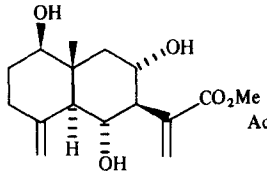
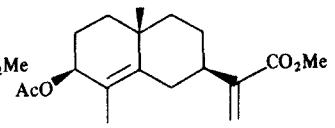


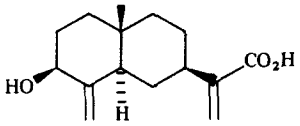
**6a**



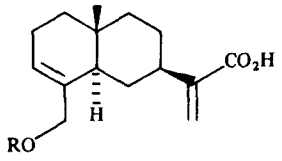
**6b**



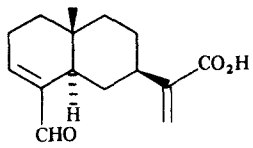
**6c***



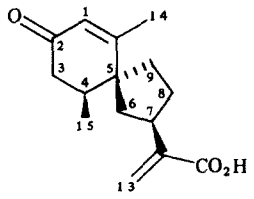
**6d***



| | 6e* | 6f* | 6g* | 6h* | 6i* | 6j | 6k* | 6l* |
|---|---|---|---|---|---|---|---|---|
| R | H | *c*-coumar. | *t*-coumar. | *c*-cinn | *t*-cinn | Prop | *n*Bu | Tigl |



**6m***



**7***

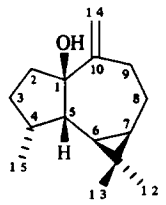
*isolated as their methylesters

presence of an alloaromadendrene derivative with a 1$\beta$-hydroxy group. A clear NOE between H-15 and H-6, as well as between H-12 and H-5, showed that the configuration at the corresponding chiral centres was the same as in the hydrocarbon. It seems most likely that **8** was formed by an ene-reaction of viridiflorene.

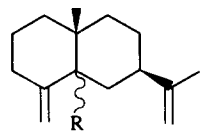
The spectral data of **9a** and **9b** indicated that we were dealing with epimeric hydroxy-$\beta$-selinenes. While the $^1$H NMR spectrum of **9a** (Table 5) was close to that of the latter that of **9b** was highly broadened at room temperature which is typical for *cis*-decalin derivatices. At elevated temperature a clear spectrum was obtained which allowed spin decoupling and assignment of the signals. A NOE between H-14 and H-6$\beta$ further supported the configuration and the conformation.

The $^1$H NMR spectrum of **9c** (Table 5) was similar to that of $\alpha$-eudesmol. The presence of a second hydroxy group was indicated by a pair of doublets at $\delta$3.62 and 3.47. As the signal of H-14 was unchanged, 13-hydroxy-$\alpha$-eudesmol was present. The $^1$H NMR data of **9d** (Table 5) indicated that now a hydroxy group was at C-15. Accordingly, a pair of broadened doublets at $\delta$4.12 and 3.98 were visible. All data agreed well with the presence of 15-hydroxy-$\alpha$-eudesmol. In the spectrum of **9e** these signals were replaced by a singlet at $\delta$9.42 and the H-3 signal was shifted down field ($\delta$6.70 *dt*). Therefore the corresponding aldehyde was present.

The molecular formula ($C_{15}H_{20}O_2$) of **9f** indicated a more unsaturated compound. The $^1$H NMR data (Table 5) showed that a 12-oxo derivative was present,

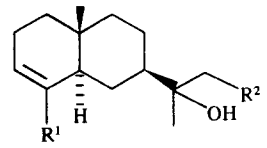


**8**



**9a** **9b**

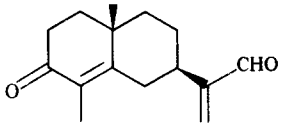
R αOH βOH



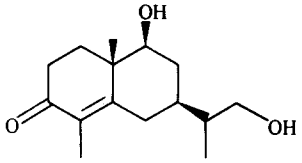
**9c** **9d** **9e**

R¹ Me $CH_2OH$ CHO

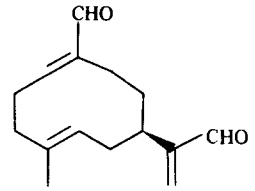
R² OH H H



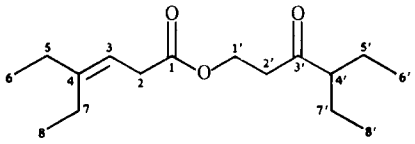
**9f**



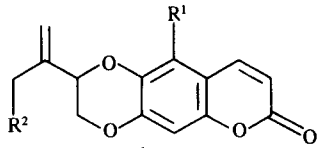
**9g**



**10**



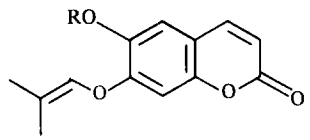
**11**



**12a** **12b** **12c** **12d**

R¹ H OMe OH OMe

R² H H H OH



**12e** **12f**

R H Me

Table 3. $^1$H NMR spectral data of compounds **3j–3m** and **3p** (400 MHz, $CDCl_3$, δ-values)

| H | **3j**($CD_3OD$) | **3k**($CD_3OD$) | **3l** | **3m** | **3p** |
|---|---|---|---|---|---|
| 1 | 3.33 *dd* | 3.41 *dd* | 3.40 *m* | 3.34 *dd* | 3.49 *dd* |
| 5 | 1.86 *d* | 1.60 *d* | 1.90 *d* | 1.50 *d* | 1.81 *d* |
| 6 | 4.61 *dd* | 4.29 *dd* | 4.19 *dd* | 4.33 *dd* | 5.67 *br dd* |
| 7 | 2.80 *dddd* | 2.63 *dddd* | 2.89 *dddd* | 2.83 *dddd* | 2.83 *dddd* |
| 8 | 4.53 *ddd* | 3.99 *ddd* | 5.18 *ddd* | 5.25 *ddd* | 4.02 *ddd* |
| 9 | 2.18 *dd* | 2.37 *dd* | 2.42 *dd* | 2.42 *dd* | 2.54 *dd* |
| 9′ | 1.46 *br d* | 1.46 *dd* | 1.52 *dd* | 1.22 *dd* | 1.50 *br dd* |
| 13 | 6.14 *d* | 6.04 *d* | 6.19 *d* | 6.14 *d* | 6.11 *d* |
| 13′ | 5.59 *d* | 5.90 *d* | 5.60 *d* | 5.53 *d* | 5.37 *d* |
| 14 | 1.18 *s* | 0.97 *s* | 1.07 *s* | 1.22 *s* | 1.06 *s* |
| 15 | 1.39 *s* | 1.37 *s* | 1.38 *s* | 1.48 *s* | 1.31 *s* |
| OAc | — | — | 2.11 *s* | 2.10 *s* | 2.13 *s* |

*J* [Hz]: Compound **3j**: 1,2 = 10; 1,2′ = 5; 5,6 = 6,7 = 11; 7,8 = 7,13 = 7,13′ = 8,9 = 8,9′ ≈ 3; 9,9′ = 14; compounds **3k–m** and **3p**: 5,6 = 6,7 = 10; 7,8 = 8,9′ = 9,9′ = 11.5; 7,13 = 8,9 = 3.5; 7,13′ = 3; compound **3k**: 1,2 = 8.5; 1,2′ = 6; compound **3m**: 1,2 = 11.5; 1,2′ = 4; compound **3p**: 1,2 = 10; 1,2′ = 4.

Table 4. $^1$H NMR spectral data of com-

| H | 6a | 6b | 6c | 6d | 6e | 6f† |
|---|---|---|---|---|---|---|
| 3 | * | * | 5.28 *br dd* | 4.02 *br dd* | 5.64 *br s* | 5.72 |
| 5 | 1.52 *d* | 1.80 *br d* | — | 1.84 *br d* | 2.16 *br d* | 2.12 |
| 6 | 4.39 *t* | 4.08 *t* | 2.64 *ddd* | 2.00 *m* | 1.91 *dddd* | 1.71 |
| 6′ | | | 1.84 *br dd* | * | 1.26 *ddd* | 1.23 |
| 7 | 2.59 *t* | 2.40 *t* | 2.43 *br dddd* | 2.53 *br dddd* | 2.55 *br dddd* | 2.50 |
| 13 | 6.34 *br s* | 6.41 *br s* | 6.19 *br s* | 6.17 *br s* | 6.15 *br s* | 6.14 |
| 13′ | 5.77 *br s* | 5.81 *br s* | 5.58 *br s* | 5.58 *br s* | 5.57 *br s* | 5.55 |
| 14 | 1.07 *s* | 0.80 *s* | 1.14 *s* | 0.74 *s* | 0.83 *s* | 0.80 |
| 15 | 1.37 *s* | 5.00 *br s* | 1.62 *br s* | 5.05 *br s* | 4.08 *br d* | 4.53 |
| 15′ | | 4.72 *brs* | | 4.60 *br s* | 3.96 *br d* | 4.48 |
| OMe | 3.81 *s* | 3.77 *s* | 3.77 *s* | 3.76 *s* | 3.76 *s* | 3.76 |
| OR | 1.96 *s* | | 2.08 *s* | | | 7.54 *d* |
| | | | | | | 6.85 *d* |
| | | | | | | 6.76 *d* |
| | | | | | | 5.88 *d* |
| | | | | | | 5.65 *br s* |

*Obscured; †multiplicity as in **6e**.

*J* [Hz]: Compounds **6a** and **6b**: 5,6 = 6,7 = 7,8 = 10; compound **6c**: 2,3 = 6; 2′,3 = 7; 6,6′ = 13.5; = 7,8 = 3; compounds **6e**–**6l**: 5,6 = 6,7 = 7,8 = 3; 5,6′ = 6,6′ = 6′,7 = 7,8′ = 12; 6,8 = 1.5; 15,15′ = 12; 6,8 = 1; 7,13′ = 13,13′ = 1.

Table 5. $^1$H NMR spectral data of compounds **8**, **9a**–**9g** (400 MHz, $CDCl_3$, $\delta$-values)

| H | 8† | 9a | 9b(60°) | 9c‡ | 9d§ | 9e†† | 9f‖ | 9g¶ | 10**(60°) |
|---|---|---|---|---|---|---|---|---|---|
| 5 | 1.70 *m* | — | — | 1.88 *br d* | 2.06 *br d* | 2.18 *br d* | — | — | 5.26 *br dd* |
| 7 | 0.51 *ddd* | 2.52 *dddd* | 2.35 *m* | * | * | * | 2.61 *m* | * | 2.50 *m* |
| 12 | 1.01 *s* | 1.76 *br s* | 1.78 *br s* | 1.18 *s* | 1.23 *s* | 1.20 *s* | 9.56 *s* | 1.00 *d* | 9.44 *s* |
| 13 | 0.98 *s* | 4.75 *br s* | 4.77 *br s* | 3.62 *d* | 1.24 *s* | 1.22 *s* | 6.34 *d* | 3.67 *br dd* | 6.17 *s* |
| | | 4.73 *br s* | 4.74 *br s* | 3.47 *d* | | | 6.06 *s* | 3.59 *br dd* | 5.90 *s* |
| 14 | 4.99 *br s* | 0.90 *s* | 1.08 *s* | 0.80 *s* | 0.80 *s* | 0.78 *s* | 1.25 *s* | 1.16 *s* | 9.49 *s* |
| | 4.85 *br s* | | | | | | | | |
| 15 | 0.97 *d* | 4.81 *dd* | 4.96 *br s* | 1.61 *br s* | 4.12 *br d* | 9.42 *s* | 1.77 *d* | 1.79 *d* | 1.68 *br s* |
| | | 4.69 *dd* | | | 3.98 *br d* | | | | |

*Obscured; †H-4 2.54 *m*, H-6 0.19 *dd*; ‡H-3 5.32 *br s*; §H-3 5.63 *br s*; ‖H-2 2.53 *ddd*, H-2′ 2.41 *ddd*; H-6 2.77 *ddd*, H-6′ 2.05 *ddq*; ¶H-2 2.44 *dd*, H-6 2.66 *br d*, H-6′ 1.83 *m*, H-9 3.45 *br dd*, H-11 1.68 *m*; **H-1 6.46 *dd*; ††H-3 6.70 *dt*.

*J* [Hz]: Compound **8**: 4,15 = 7; 5,6 = 12; 6,7 = 9; 7,8 = 10; 7,8′ = 6.5; compound **9a**: 3,14 = 3,14′ = 14,14′ = 1.5; 6,7 = 7,8 = 12.5; 6′,7 = 7,8′ = 3.5; compound **9c**: 5,6 = 12; 13,13′ = 10.5; compound **9d**: 5,6 = 12; 15,15′ = 12; compound **9e**: 2,3 = 3,5 = 3; 2′,3 = 4; 5,6 = 12; compound **9f**: 1,2 = 13; 1,2′ = 5; 1′,2 = 5.5; 1′,2′ = 3; 2,2′ = 17; 6,6′ = 14.5; 6,7 = 3; 6,8 = 1.5; 6′,7 = 13; 6′,15 = 1.5; 7,13 = 1; compound **9g**: 1,2 = 4.5; 1′,2 = 10; 6,6′ = 14; 6′,15 = 1.5; 8,9 = 4; 8,9′ = 11.5; 11,12 = 6.5; 11,13 = 11,13′ = 6; 13,13′ = 11; compound **10**: 1,2 = 1,2′ = 8.5; 5,6 = 11; 5,6′ = 4.5.

because the H-13 signals were shifted downfield and a singlet at $\delta$9.56 was visible. Furthermore, spin decoupling indicated that a 3-keto group and a $\Delta^4$-double bond must be proposed. Accordingly, the signals of H-2, H-6 and H-7 were shifted downfield and a narrowly split doublet at $\delta$1.77 was due to H-15. This was established by a homoallylic coupling with H-6′.

The $^1$H NMR data of **9g** (Table 5) were in part close to those of **9f**. However, the situation of ring B was different. A pair of broadened double doublets at $\delta$3.67 and 3.59 required a 12-hydroxy group while spin decoupling showed that an equatorial hydroxy group was at C-9 ($\delta$3.45).

From the $^1$H NMR spectrum of **10** at elevated temperature (Table 5) the presence of a dialdehyde with three double bonds could be deduced. Together with the molecular formula and the flexibility of this system the data suggested that a germacrane derivative was very likely. This was supported by spin decoupling. The chemical shift of H-14 ($\delta$9.49 *s*) required an *E*-configuration for the $\Delta^1$-bond and the $^1$H NMR shifts of H-13 suggested a C-11 aldehyde group. Comparison of the chemical shifts of H-5 and H-15 indicated that a 4*Z*-double bond was most likely.

The unusual ester **11**, molecular formula $C_{16}H_{28}O_3$, showed a $^1$H NMR spectrum which best agreed with the proposed structure (see Experimental). This was further supported by the $^{13}$C NMR spectrum (see Experimental). This type of keto ester seems to be new and it must be the result of a rare biogenetic pathway.

pounds **6a–6m** (400 MHz, $CDCl_3$ $\delta$-values)

| 6g† | 6h† | 6i† | 6j† | 6k† | 6l† | 6m |
|---|---|---|---|---|---|---|
| 5.76 | 5.68 | 5.57 | 5.72 | 5.71 | 5.71 | 6.71 *ddd* |
| 2.20 | 2.11 | 2.22 | 2.15 | 2.15 | 2.15 | 2.29 *ddddd* |
| 1.83 | 1.72 | 1.85 | 1.75 | 1.74 | * | 2.78 *dddd* |
| 1.27 | 1.23 | 1.30 | 1.34 | 1.35 | 1.30 | 1.19 *ddd* |
| 2.56 | 2.50 | 2.57 | 2.54 | 2.54 | 2.54 | 2.59 *br dddd* |
| 6.15 | 6.14 | 6.14 | 6.30 | 6.14 | 6.16 | 6.14 *br s* |
| 5.56 | 5.54 | 5.56 | 5.67 | 5.55 | 5.54 | 5.55 *dd* |
| 0.84 | 0.82 | 0.85 | 0.85 | 0.85 | 0.86 | 0.84 *s* |
| 4.62 | 4.53 | 4.63 | 4.52 | 4.51 | 4.53 | 9.42 *s* |
| 4.55 | 4.48 | 4.55 | 4.41 | 4.40 | 4.50 | |
| 3.72 | 3.74 | 3.72 | — | 3.76 | 3.74 | 3.76 *s* |
| 7.62 *d* | 7.56 *m* | 7.68 *d* | 2.34 *q* | 2.30 *t* | 6.86 *qq* | |
| 7.41 *d* | 7.33 *m* | 7.55 *m* | 1.15 *t* | 1.65 *tq* | 1.84 *dq* | |
| 6.84 *d* | 6.96 *d* | 7.39 *m* | | 0.96 *t* | 1.80 *dq* | |
| 6.33 *d* | 5.97 *d* | 6.45 *d* | | | | |
| 6.30 *br s* | | | | | | |

6,7 = 7,8 = 3; 6,8 = 2; 6′,7 = 7,8′ = 12; compound **6d**: 2,3 = 10; 2′,3 = 6; 5,6 = 6′,7 = 7,8′ = 12; 6,7 = 12; compound **6m**: 2,3 = 2,5 = 2′,5 = 3,5 = 5,6 = 3; 2′,3 = 6,7 = 7,8 = 4; 5,6′ = 6,6′ = 6′,7 = 7,8′

Table 6. Mass spectral data of compounds **1b–1c**, **3a–3f**, **3j–3p** and **4a** [*m/z* (rel. int.), $M^+$ found and calc. identical]

| | |
|---|---|
| 8α-Hydroxyanhydroverlotorin (**1b**) | 262.121 ($C_{15}H_{18}O_4$) (1.4), 244 (27), 97 (95), 80 (100), 69 (72) |
| 8α-Acetoxyartemorin (**1c**) | 246.126 ($C_{15}H_{18}O_3$) $[M-HOAc]^+$ (10), 228 (24), 213 (1), 61 (100) |
| 8β-Hydroxy-α-cyclocostunolide (**3a**) | 248.141 ($C_{15}H_{20}O_3$) (10), 233 (15), 215 (12), 73 (100) |
| 8β-Hydroxysantamarin (**3b**) | 264.136 ($C_{15}H_{20}O_4$) (46), 246 (11), 228 (12), 164 (42), 91 (50), 57 (100) |
| 8α-Hydroxysantamarin (**3c**) | 264.136 ($C_{15}H_{20}O_4$) (24), 246 (26), 228 (24), 97 (100), 91 (76) |
| 1β,3α,8β-Trihydroxyarbusculin B (**3d**) | 280.131 ($C_{15}H_{20}O_5$) (3.5), 262 (6), 247 (6), 97 (40), 57 (100) |
| 8β-Hydroxyarmexifolin (**3e**) | 278.115 ($C_{15}H_{18}O_5$) (2), 263 (2), 260 (2), 97 (54), 71 (68), 57 (100) |
| 8β-Hydroxy-β-cyclocostunolide (**3f**) | 248.141 ($C_{15}H_{20}O_3$) (76), 233 (37), 230 (46), 215 (37), 137 (100), 109 (66) |
| 1β,8β-Dihydroxyarbusculin A (**3j**) | 267.123 ($C_{14}H_{19}O_5$) $[M-Me]^+$ (40), 249 (42), 246 (17), 231 (12), 188 (44), 55 (100) |
| 1β,8α-Dihydroxyarbusculin A (**3k**) | 282 ($C_{15}H_{22}O_5$) (2), 267 (8), 164 (49), 101 (96), 55 (100) |
| 8α-Acetoxy-1β-hydroxyarbusculin A (**3l**) | 309.134 ($C_{16}H_{21}O_6$) $[M-Me]^+$ (4), 267 (8), 249 (3), 97 (44), 57 (100) |
| 8α-Acetoxy-1β-hydroxy-4-epi-arbusculin A (**3m**) | 309.134 ($C_{16}H_{21}O_6$) $[M-Me]^+$ (7), 267 (24), 249 (12), 97 (44), 57 (100) |
| 1α,8α-Dihydroxy-10-*epi*-arbusculin A (**3n**) | 264.136 ($C_{15}H_{20}O_4$) (2), 246 (6), 228 (6), 97 (46), 57 (100) |
| 1α,8α-Dihydroxy-10-*epi*-β-cyclo-costunolide (**3o**) | 264.136 ($C_{15}H_{20}O_4$) (10), 246 (15), 228 (12), 109 (72), 69 (100) |
| 6α-Acetoxy-1β,4α-dihydroxy-eudesm-11(13)-en-12,8α-olide (**3p**) | 309.134 ($C_{16}H_{21}O_6$) $[M-Me]^+$ (0.5), 267 (1), 164 (71), 101 (100) |
| 8α-Acetoxyeleman-12,6α-olide (**4a**) | (CIMS) 291 $[M+1]^+$ (11), 231 (100) |

The overall picture of the chemistry of *Cassinia* indicated that the presence of eudesmanes and the corresponding lactones is characteristic and therefore no relationship to *Helichrysum* is visible where these compounds are not at all common. The rare obliquin derivatives isolated from *C. uncata* and *Actinobole uliginosum* have been isolated from some *Helichrysum* species [20] but they are also reported from *Stoebe* [29] and *Phaenocoma* [30] species. The latter is closely related to *Anaxeton* [1]. But these coumarins are also present in other tribes [31, 32 and lit. cited therein] and therefore these compounds may be not very useful chemotaxonomic markers. From members of the subtribe Gnaphaliineae sesquiterpene lactones have been reported only from a *Calocephalus* species [33]. Further investigations may show whether the chemistry of related genera will led to a more clear picture of the difficult subtribal delineations [1].

## EXPERIMENTAL

The air-dried plant material was extracted with MeOH–$Et_2O$–petrol (1:1:1) and worked-up as reported previously [34]. Vouchers are deposited in the US National Herbarium. The quantities of the obtained compounds (see below) are calculated for the whole extract though in several cases only a part of the corresponding fraction was separated completely. For all new compounds the final conditions of their isolation are given in parenthesis. The compounds are summarized in order of increasing polarity. The mass spectral data of all new sesquiterpenes are given in Tables 6 and 7. All acids except **6j** were isolated as their methyl esters ($CH_2N_2$ in $Et_2O$). TLC (silica gel, PF 254) were

Table 7. Mass spectral data of compounds **6a**–**6m**, **7**, **8**, **9a**–**9g** and **10** [*m/z* (rel. int.), $M^+$ found and calc. identical]

| | |
|---|---|
| **6a** | 356 ($C_{18}H_{28}O_7$) (1), 296 (1), 278 (3), 246 (4), 57 (100) |
| **6b** | 278.152 ($C_{16}H_{22}O_4$) (15), 260 (8), 246 (31), 242 (16), 228 (29), 55 (100) |
| **6c** | 306 (0.4), 246.162 ($C_{16}H_{22}O_2$) $[M-HOAc]^+$ (100), 231 (27) |
| **6d** | 264.173 ($C_{16}H_{24}O_3$) (15), 246 (21), 232 (44), 91 (100) |
| **6e** | 264.173 ($C_{16}H_{24}O_3$) (5), 246 (68), 232 (50), 214 (30), 187 (51), 91 (100) |
| **6f** | 410.209 ($C_{25}H_{30}O_5$) (2), 246 (36), 231 (18), 214 (12), 147 (100) |
| **6g** | 410.209 ($C_{25}H_{30}O_5$) (5), 246 (32), 231 (15), 147 (100) |
| **6h** | 394.214 ($C_{25}H_{30}O_4$) (0.2), 246 (100), 231 (57), 131 (60) |
| **6i** | 394.214 ($C_{25}H_{30}O_4$) (0.7), 246 (96), 231 (38), 131 (100) |
| **6j** | EIMS: 246 $[M-RCO_2H]^+$ (100), 231 (74), 57 (81); CIMS: 307 $[M+1]^+$ (2), 233 (100) |
| **6k** | 334.214 ($C_{20}H_{30}O_4$) (0.1), 303 (1), 264 (5), 246 (100), 231 (82) |
| **6l** | 246.162 ($C_{16}H_{22}O_2$) $[M-RCO_2H]^+$ (42), 231 (27), 161 (31), 95 (40), 83 (64), 55 (66); CIMS: 347 $[M+1]^+$ (5), 247 (100) |
| **6m** | 262.157 ($C_{16}H_{22}O_3$) (34), 247 (8), 231 (30), 230 (100) |
| **7** | 262.157 ($C_{16}H_{22}O_3$) (10), 247 (25), 234 (52), 220 (31), 202 (15), 105 (100) |
| **8** | 220.183 ($C_{15}H_{24}O$) (19), 205 (32), 202 (48), 159 (98), 105 (99), 91 (100) |
| **9a** | 220.183 ($C_{15}H_{24}O$) (7), 205 (18), 202 (23), 187 (53), 55 (100) |
| **9b** | 220.183 ($C_{15}H_{24}O$) (33), 205 (29), 202 (27), 187 (43), 61 (100) |
| **9c** | 238.193 ($C_{15}H_{26}O_2$) (12), 220 (21), 207 (67), 189 (92), 61 (100) |
| **9d** | 238.193 ($C_{15}H_{26}O_2$) (3), 220 (6), 205 (16), 202 (6), 59 (100) |
| **9e** | 236.178 ($C_{15}H_{24}O_2$) (0.5), 221 (5), 218 (7), 203 (10), 178 (100) |
| **9f** | 232.146 ($C_{15}H_{20}O_2$) (100), 217 (92), 189 (34), 91 (66) |
| **9g** | 252.173 ($C_{15}H_{24}O_3$) (21), 138 (100) |
| **10** | 232.146 ($C_{15}H_{20}O_2$) (21), 217 (17), 203 (60), 185 (86), 91 (100) |

performed with the following $Et_2O$–petrol mixtures: Tl (3:1); T2 (1:9); T3 (2:3); T4 (9:1); T5 (4:1). For HPLC (always RP 8, *ca* 100 bar) MeOH–$H_2O$ mixtures were used (H1 4:1; H2 3:2; H3 1:1; H4 2:3; H5 3:7; H6 1:4; H7 7:3; H8 9:1; H9 3:1).

*Cassinia laevis* (850 g aerial parts, collected in Queensland in August 1986, voucher Robinson 86-0189) yielded 5 mg α-copaene, 7 mg δ- and 8 mg γ-cadinene, 10 mg caryophyllene, 16 mg viridiflorene, 5 mg aromadendrene, 3 mg α-calacorene, 8 mg copaborneyl acetate, 7 mg squalene epoxide, 70 mg caryophyllene-1β,10α-epoxide, 260 mg copaborneol, 400 mg spathulenol, 720 mg betulinic acid, 420 mg oleanolic acid, 370 mg **6m** (Tl, $R_f$ 0.80), 200 mg **6d** (H1, $R_t$ 6.5 min), 7.1 g **6e** (H1, $R_t$ 7.2 min), 550 mg **6f** (H1, $R_t$ 11.5 min), 3.6 g **6g** (H1, $R_t$ 13.7 min), 900 mg mikanin, 50 mg astragalin, 450 mg afzelin.

*Cassinia subtropica* (580 g aerial parts, collected in Queensland in August 1986, voucher Robinson 86-0099) yielded 30 mg caryophyllene, 50 mg squalene, 85 mg caryophyllene-1β,10α-epoxide, 30 mg **9a** (T2, $R_f$ 0.70), 13 mg **9b** (H1, $R_t$ 9.8 min), 260 mg spathulenol, 15 mg nerolidol, 10 mg copaborneol, 3 mg **8** (H1, $R_t$ 9.6 min), 5 mg costunolide, 2 mg **4a** (H2, $R_t$ 33.0 min), 285 mg **6c** (T3, $R_f$ 0.95), 370 mg 8α-acetoxycostunolide, 315 mg laurenobiolide, 110 mg desacetyl laurenobiolide, 25 mg **12e**, 1.2 g 8β-hydroxycostunolide, 40 mg 4α,5β-epoxydesacetyl laurenobiolide, 7 mg **2b**, 4 mg **2d**, 10 mg **1d** (H2, $R_t$ 6.2 min), 45 mg **3i**, 7 mg **2c**, 20 mg **2a**, 190 mg **3g**, 50 mg quercetin, 40 mg **3f** (H3, $R_t$ 41.7 min), 280 mg **7** (T4, $R_f$ 0.8), 5 mg **3a** (H2, $R_t$ 14.9 min), 5 mg 8α-hydroxy-4α,5β-epoxycostunolide, 10 mg pinoresinol, 5 mg **2e**, 11 mg **1c** (H3, $R_t$ 9.9 min), 3 mg **3m** (H4, $R_t$ 22.2 min), 10 mg tatridin A, 45 mg **3c** (H4, $R_t$ 18.8 min), 2 mg **6b** (H4, $R_t$ 9.6 min), 50 mg **3h**, 3 mg **1b** (H6, $R_t$ 35.1 min), 2 mg **3n** (H5, $R_t$ 20.2 min), 120 mg **3b** (H4, $R_t$ 19.4 min), 4 mg **1a**, 2 mg **3o** (H5, $R_t$ 18.4 min), 3 mg **3l** (H6, $R_t$ 36.1 min), 5 mg **3p** (H6, $R_t$ 29.0 min), 100 mg **3j** (H5, $R_t$ 5.1 min), 3 mg **6a** (H6, $R_t$ 36 min), 50 mg **3d** (H6, $R_t$ 23.6 min), 5 mg **3p** (H6, $R_t$ 29.0 min), 20 mg **3e** (H6, $R_t$ 27.3 min), 3 mg **3k** (H6, $R_t$ 24.2 min).

*Cassinia uncata* (500 g roots, collected in Queensland in September 1986, voucher RMK 9628). 2 mg **12a**, 8 mg **12b**, 15 mg **10** (H7, $R_t$ 11.6 min), 4 mg **9f** (H7, $R_t$ 9.8 min), 6 mg **12c**, 1 mg **12e**, 1 mg **12f**, 4 mg **12d**, 5 mg ferulylaldehyde, 2 mg **9g** (H3, $R_t$ 13.5 min). Extract of 600 g aerial parts: 25 mg aromadendrene, 15 mg α-copaene, 20 mg caryophyllene, 3 mg δ- and 2 mg γ-cadinene, 10 mg α-selinene, 4 mg viridiflorene, 25 mg bicyclogermacrene, 8 mg squalene, 4 mg caryophyllene-1β,10α-epoxide, 300 mg **11** (T2, $R_f$ 0.3), 30 mg **4c**, 12 mg **4b**, 200 mg desacetoxylaurenobiolide, 30 mg **5**, 5 g **6e**, 6 g **6g**, 0.6 g **6i** (H8, $R_t$ 16.2 min), 150 mg **6h** (H1, $R_t$ 27.3 min), 300 mg **6k** (H8, $R_t$ 10.8 min), 100 mg **6j** (H9, $R_t$ 20.6 min), 15 mg **6l** (H1, $R_t$ 24.6 min), 50 mg betulin, 50 mg **9c** (T5, $R_f$ 0.45), 100 mg **9d** (T5, $R_f$ 0.15), 100 mg pectolinarigenin.

*Actinobole uliginosum* (145 g aerial parts, collected in NW Australia, voucher RMK 9567) yielded 2 mg germacrene D, 2 mg α-humulene, 2 mg spathulenol, 2 mg **12a**, 4 mg **12b**, 1 mg **12c**, 8 mg **12e**, 6 mg 5,4′-dihydroxy-7-methoxyflavanone, 5 mg **9e** (H9, $R_t$ 12.1 min).

*Anaxeton arborescens* (120 g aerial parts, collected in Natal, R.S.A., voucher 77/331) yielded 1 mg **12a** and 5 mg **12e**.

Known compounds were identified by comparing the 400 MHz $^1$H NMR spectra with those of authentic material or by comparison of all spectral data with those in the literature.

*4-Ethyl-3-oxo-hexyl-[4-ethyl hex-3-enoate]* (**11**). Colourless oil; MS *m/z* (rel. int.): 268.204 $[M]^+$ (3) (calc. for $C_{16}H_{28}O_3$: 268.203), 197 $[M-Et_2CH]^+$ (1.5), 127 (28), 124 $[Et_2C{=}CH{-}CH{=}C{=}O]^+$ (100), 96 $[124-CO]^+$ (94), 71 (56); $^1$H NMR ($CDCl_3$): δ 3.02 (*br d*, H-2), 5.23 (*br t*, H-3), 2.04 (*br q*, H-5), 1.02 (*t*, H-6), 2.02 (*br q*, H-7), 0.97 (*t*, H-8), 4.36 (*t*, H-1′), 2.73 (*t*, H-2′), 2.33 (*tt*, H-4′), 1.63 (*ddq*, H-5′$_1$, H-7′$_1$), 1.50 (*ddq*, H-5′$_2$, H-7′$_2$), 0.88 (*t*, H-6′, H-8′); *J* [Hz]: 2,3 = 5,6 = 7,8 = 7; 1′, 2′ = 6; 4′, 5′$_1$ = 8; 4′, 5′$_1$, 5′$_2$ = 14; 5′, 6′ = 7; $^{13}$C NMR ($CDCl_3$, C-1–C-8): δ 172.4, 33.2, 113.6, 146.7, 29.1, 12.9, 23.5, 12.5; C-1′–C-8′: δ 59.5, 40.5, 211.5, 55.8, 23.9 (2×), 11.7 (2×).

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