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GERMACRENE DERIVATIVES AND OTHER SESQUITERPENES FROM *SENECIO* SPECIES AND *LORDHOWEA INSULARIS**

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Key Word Index—*Senecio galpinii*; *S. coronatus*; *S. pleistocephalus*; *Lordhowea insularis*; Compositae; sesquiterpenes; germacrene derivatives; farnesol angelate; cadinene derivative.

Abstract—From *Senecio galpinii* six new highly oxygenated germacrene derivatives were isolated, while *S. coronatus* afforded in addition to known cacalol derivatives two new ones. This species also contained a rare tricyclic sesquiterpene angelate, so far only isolated from one species. From the aerial parts of *S. pleistocephalus* an angelate derived from cadinene was isolated, while *Lordhowea insularis* (Benth.) B. Nord. afforded farnesyl angelate, which was reported previously. The structures were elucidicated mainly by high field ^{1}H NMR spectroscopy.

INTRODUCTION

In continuation of our investigation of *Senecio* and related species we now have studied the constituents of three further species from Transvaal and one *Lordhowea* species from Lord Howe Island. The results are discussed in this paper.

RESULTS AND DISCUSSION

The aerial parts of *Senecio galpinii* Hook. f. afforded in addition to squalene, lupenone and friedelin a very complex mixture of sesquiterpene esters, which could only be separated with difficulty. Even after repeated TLC and HPLC a few compounds could not be obtained completely pure. The least polar fractions contained the already known diepoxides **6–8**[1]. Careful spin decoupling at 400 MHz, however, showed that the position of the oxygen functions at C-8 and C-9 had to be changed. In the 270 MHz spectrum of **8** some signals were still overlapped, but irradiation of the signal of H-7 in the spectrum of **8** clearly showed that this proton was coupled with the downfield-shifted broadened doublet at δ 5.39. Accordingly the angelate residue was at C-8 in the diepoxides **6** and **8**. A further tri-ester could be separated from **6** and **7** by HPLC (reversed phase). The ^{1}H NMR spectrum (Table 1) showed that the angelate at C-8 was replaced by senecioate (**9**). A changed position with the acetate group at C-8 could be excluded as the spectra of **6** and **7** clearly indicated that the chemical shifts of H-8 and H-9 respectively were influenced by the nature of the acid. The unsaturated ester caused a downfield shift as in similar cases, thus allowing a clear decision. The ^{1}H NMR spectral data of a further senecioate (Table 1) showed that also the corresponding 9-hydroxy derivative **10** was present. Consequently the ^{1}H NMR spectrum was similar to that of **8**, only the H-8, H-9 and H-13 signals being shifted upfield. The most polar fractions finally gave the monoepoxides **11–14**. The angelate **13** and the senecioate **14**, however, could not be separated, while the corresponding acetates showed slightly different retention times on HPLC using a mixture of methanol and water as the eluent. The ^{1}H NMR spectrum of the mixture of **13** and **14** (Table 1) was in part close to the corresponding 8-(2-methylbutyrate) with an angelate residue at C-9[2]. In particular the couplings observed were identical, indicating the same substitution pattern and identical stereochemistry. While the spectrum in deuteriochloroform could not be interpreted completely, in deuteriobenzene all signals could be assigned by spin decoupling, though the signals of H-2 and H-6 in part were overlapped multiplets. Starting with the clear H-9 doublet the sequence H-5–H-9 could be established, while irradiation of the H-1 signal, its chemical shift clearly showing that this proton was that of an epoxide, allowed the assignment of H-2, which was coupled with a proton displaying a triplet at δ 5.74. The latter obviously was that of H-3. Thus the structures of **13** and **14** were established. The ^{1}H NMR spectra of **11** and **12** (Table 1) showed that we were dealing with the corresponding 5-*O*-acetates of **13** and **14** respectively. Accordingly the H-5 signals were at lower fields, while those of H-6 and H-7 were shifted upfield. Again spin decoupling allowed the assignment of all signals. Furthermore small amounts of the fragmented toxol derivative **24** were present[3]. The roots also contained **9**, **11** and **12**. The aerial parts of *Senecio coronatus* (Thunb.) Harv. afforded germacrene D, bicyclogermacrene, α-humulene and 2β-angeloyloxy-8β-hydroxypresilphiperfol-5-one (**2**), which recently was isolated from an *Ursinia* species[4], while a corresponding acetate was present in a *Senecio* species[4]. Furthermore a complex mixture of cacalohastin derivatives was isolated. In addition to **15**[5] and **18**[6] two new esters, the isobutyrate **16** and the propionate **17** were present.

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*Part 455 in the series "Naturally Occurring Terpene Derivatives". For Part 454 see Bohlmann, F. and Zdero, C. (1982) *Phytochemistry* **21**, 2543.

Table 1. ^{1}H NMR spectral data of compounds **9–14** (400 MHz, TMS as internal standard)

	9	**10**	**11**	**12**	**13**	**13**(C_6D_6)	**14**	**14**(C_6D_6)
H-1	2.74 *dd*	2.77 *dd*	2.76 *t*	2.72 *t*	2.77 *t*	2.64 *t*	2.74 *t*	2.62 *t*
H-2	2.0 *m*	2.0 *m*	2.0 *m*	2.0 *m*	*	2.07 *m*	*	2.07 *m*
H-2′	1.85 *m*	1.88 *m*	1.9 *m*	1.9 *m*	*	1.89 *m*	*	1.89 *m*
H-3	5.37 *dd*	5.38 *dd*	5.49 *dd*	5.45 *dd*	5.50 *m*	5.74 *t*	5.52 *m*	5.74 *t*
H-5	3.20 *d*	3.21 *d*	5.53 *br dd*	5.51 *br dd*	3.90 *br s*	3.81 *br dd*	3.90 *br s*	3.78 *br dd*
H-6	2.13 *dd*	2.13 *dd*	2.35 *ddd*	2.34 *ddd*	*	2.56 *ddd*	*	2.45 *ddd*
H-6′	2.02 *m*	2.0 *m*	1.77 *ddd*	1.77 *ddd*	*	1.70 *m*	*	1.70 *m*
H-7	2.44 *br dd*	2.37 *br dd*	2.85 *br d*	2.81 *br d*	3.04 *br d*	3.31 *br d*	3.00 *br d*	3.27 *br d*
H-8	5.31 *br d*	5.31 *br d*	5.04 *dd*	5.02 *dd*	5.50 *m*	5.99 *br dd*	5.50 *m*	5.93 *br dd*
H-9	5.24 *d*	3.97 *dd*	5.13 *d*	4.99 *d*	5.20 *d*	5.56 *d*	5.07 *d*	5.49 *d*
H-12	1.29 *s*	1.27 *s*	1.27 *s*	1.25 *s*	1.27 *s*	1.40 *s*	1.26 *s*	1.39 *s*
H-13	5.21 *s*	5.21 *s*	5.31 *s*	5.26 *s*	5.30 *s*	5.26 *s*	5.26 *s*	5.21 *s*
H-13′	5.04 *s*	5.01 *s*	5.06 *s*	5.05 *s*	5.08 *s*	5.14 *s*	5.06 *s*	4.97 *s*
H-14	1.27 *s*	1.43 *s*	1.25 *s*	1.23 *s*	1.27 *s*	1.12 *s*	1.26 *s*	1.11 *s*
H-15		1.27 *s*	1.24 *s*	1.12 *s*	1.23 *s*	1.10 *s*	1.23 *s*	1.10 *s*
OCOR	6.11 *qq*	6.11 *qq*	6.11 *qq*	6.11 *qq*	6.13 *qq*	6.13 *qq*	6.13 *qq*	5.82 *qq*
	1.99 *dq*	1.99 *dq*	2.00 *dq*	1.99 *dq*	2.00 *dq*	2.10 *dq*	1.97 *dq*	2.10 *dq*
	1.86 *dq*	1.90 *dq*	1.86 *dq*	1.90 *dq*	1.92 *dq*	2.02 *br s*	1.85 *dq*	2.02 *br s*
	5.71 *qq*	5.71 *qq*	6.11 *qq*	5.63 *qq*	6.11 *dq*	6.13 *qq*	5.63 *qq*	5.56 *br s*
	2.12 *d*	2.13 *d*	2.00 *dq*	2.12 *d*	2.00 *dq*	2.12 *dq*	2.11 *d*	2.02 *d*
	1.93 *d*	1.88 *d*	1.90 *dq*	1.89 *d*	1.92 *dq*	1.91 *dq*	1.88 *d*	1.38 *d*
OAc	2.05 *s*	—	2.09 *s*	2.09 *s*	2.04 *s*	1.79 *s*	2.02 *s*	1.60 *s*
			2.04 *s*	2.06 *s*	—		—	
OH	—	2.27 *d*	3.26 *s*	3.44 *s*	3.30 *s*	—	3.15 *s*	—

*Overlapping multiplets.

J(Hz): Compounds **9** and **10**: 1,2 = 6; 1,2′ = 5; 2,3 = 8; 2′, 3 = 6; 5,6 = 4; 6,6′ = 13; 6,7 = 12; 6′, 7 = 6; 7,8 ~ 1; 8,9 = 3.5 (9, OH = 9.5); compounds **11** and **12**: 1,2 = 6; 2,3 = 8; 2′, 3 = 6; 5,6′ = 2.5; 6,6′ = 6,7 = 14; 6′,7 = 7,8 = 8,9 = 2.5; compounds **13** and **14**: 1,2 = 6; 2,3 = 7; 5,6 = 5,6′ = 6′,7 = 7,8 = 8,9 = 2.5; 6,6′ = 6,7 = 14.

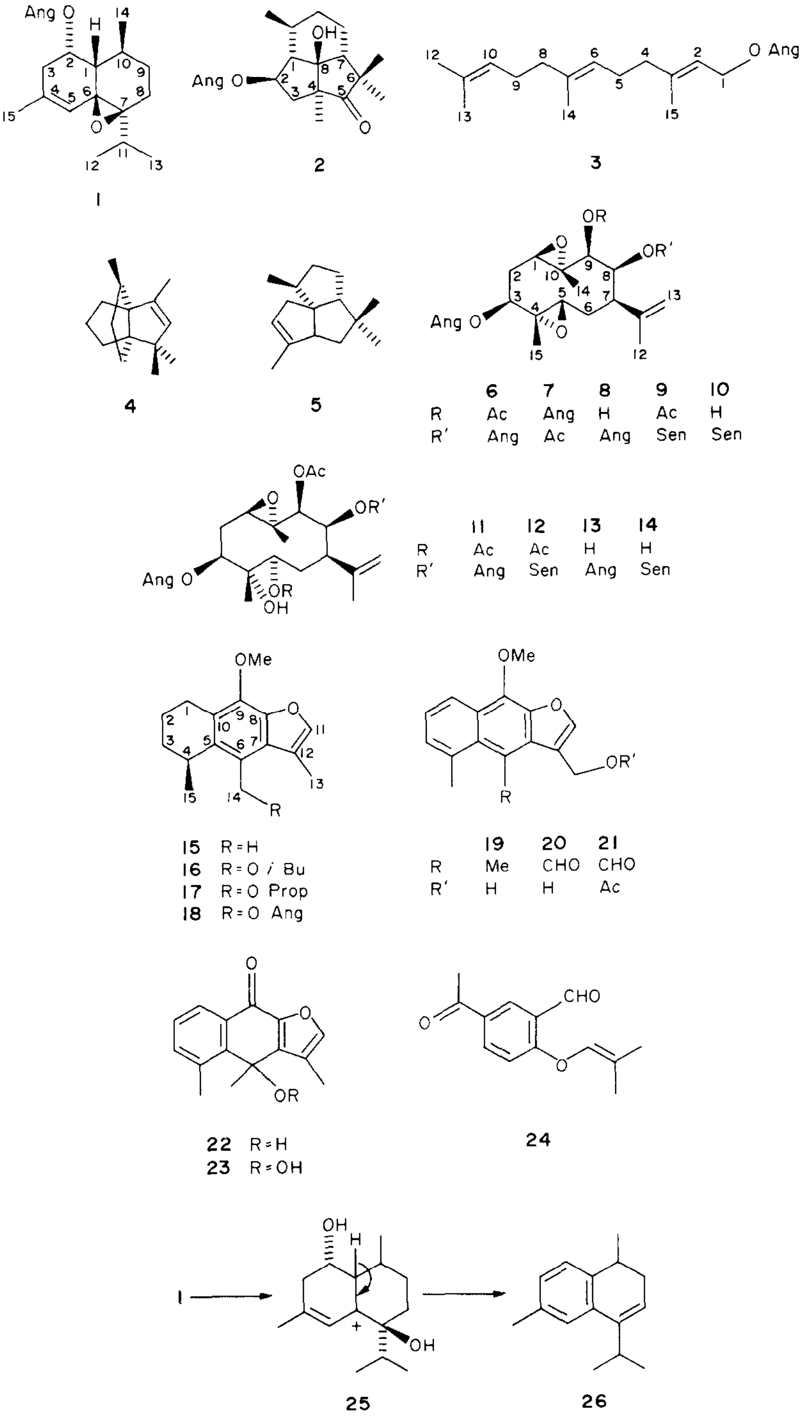
The structures could be easily deduced from their ^{1}H NMR spectra (Table 2), which were similar to those of **18**. The nature of the ester groups also followed from the typical ^{1}H NMR signals. Furthermore dehydrocacalohastin (**19**)[7] and the aldehydes **20**[8] and **21**[9] as well as cacalonol (**22**)[5] and peroxy cacalonol (**23**)[5] were isolated. The roots also contained **15** and **19–21**. The aerial parts of *Senecio pleistocephalus* S. Moore afforded in addition to germacrene D, bicyclogermacrene, α-humulene, lupeyl acetate and lupenone the angelate **1** or its enantiomer. While the mass spectrum even under CI conditions gave no molecular ion, the ^{1}H NMR spectral data clearly showed (Table 3) that an angelate of a sesquiterpene was present, which contained a further oxygen function as followed from the mass spectrum, which showed a strong fragment, *m*/*z* 218 ($C_{15}H_{22}O$), obviously formed by loss of angelic acid. The ^{1}H NMR spectrum, however, did not clearly indicate the presence of an oxygen function. Short reduction with alanate followed by treatment with acid, however, gave **26**, obviously formed via **25** by opening of the epoxide followed by elimination of water (see Scheme 1). Thus the presence of an epoxide group was established. In the ^{1}H NMR spectrum in deuteriobenzene all signals could be assigned by spin decoupling. Starting with the signal of the proton under the angeloyloxy group the signals of the neighbouring protons (H-3) could be assigned, which obviously were allylic. Accordingly the latter were coupled with the olefinic proton, which only showed an additional allylic coupling with the olefinic methyl, while H-3 also was coupled with a proton, which itself showed a coupling with the signal (H-1), which was coupled with one of the secondary methyls. Further spin decoupling led to the assignment of the

Table 2. ^{1}H NMR spectral data of compounds **16** and **17** (400 MHz, $CDCl_3$, TMS as internal standard)

	16	**17**
H-1	6.92 *dd*	6.91 *dd*
H-2	5.94 *ddd*	5.94 *ddd*
H-3	2.54 *dddd*	2.54 *dddd*
H-3′	2.23 *ddd*	2.23 *ddd*
H-4	3.32 *br dq*	3.33 *br dq*
H-12	7.36 *q*	7.36 *q*
H-13	2.31 *d*	2.31 *d*
H-14	5.40 *d*	5.42 *d*
H-14′	5.34 *d*	5.37 *d*
H-15	1.08 *d*	1.08 *d*
OCOR	2.57 *qq*	2.36 *q*
	1.16 *d*	1.14 *t*
	1.15 *d*	

J(Hz): 1,2 = 10; 1,3 = 3.3; 2,3 = 2.5; 2,3′ = 6.5; 3,3′ = 17.5; 3,4 = 7; 3′,4 = 1.5; 4,15 = 7; 12,13 = 1; 14,14′ = 12; 2′, 3′ = 7.5.

signals of H-8 and H-9, while that of H-11 only was coupled with the two further secondary methyls. Accordingly the only possible structure was that of **1**. Inspection of a model showed that the proposed stereochemistry would lead to angles which would agree well with the couplings observed, while a model with an α-orientated epoxide showed that the couplings should be different. Compound **1** is an epoxy angeloyl derivative of the hitherto unknown cadina-4,6-diene. The roots also contained bicyclogermacrene and **1**. *Senecio insularis* Benth. has been placed in the separate monotypic genus *Lordhowea* [10]. Investigation of the aerial parts gave in addition to modhephene (**4**)[11], senoxydene (**5**)[12] and sitosteryl acetate a small amount of an angelate, which turns out to be farnesyl angelate (**3**) as clearly followed from the ^{1}H NMR spectrum (see Experimental), which was similar to that of the corresponding



1 2 3 4 5

	6	7	8	9	10
R	Ac	Ang	H	Ac	H
R'	Ang	Ac	Ang	Sen	Sen

	11	12	13	14
R	Ac	Ac	H	H
R'	Ang	Sen	Ang	Sen

15 R=H
16 R=O *i* Bu
17 R=O Prop
18 R=O Ang

	19	20	21
R	Me	CHO	CHO
R'	H	H	Ac

22 R=H
23 R=OH

24

1 → 25 → 26

Scheme I.

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

	1		**26**
	CDCl$_3$	C$_6$D$_6$	
H-1	2.0 *m*	2.16 *dd*	—
H-2	5.74 *ddd*	6.05 *ddd*	7.08 *d*
H-3	2.31 *br dd*	2.23 *br dd*	6.98 *ddq*
H-3′	2.22 *br dd*	2.05 *br dd*	
H-5	5.52 *br s*	5.41 *br s*	7.14 *dq*
H-8	1.89 *ddd*	1.85 *m*	5.77 *br t*
H-8′	1.64 *m*	1.56 *ddd*	
H-9	1.39 *ddd*	1.23 *dddd*	2.38 *dddd*
H-9′	1.31 *m*	1.01 *m*	2.03 *dddd*
H-10	1.44 *m*	1.35 *dddq*	2.78 *ddq*
H-11	2.0 *m*	1.85 *qq*	2.95 *br qq*
H-12	1.05 *d*	1.08 *d*	1.13 *d*
H-13	0.96 *d*	0.97 *d*	1.12 *d*
H-14	1.04 *d*	1.16 *d*	1.16 *d*
H-15	1.76 *br s*	1.52 *br s*	2.33 *br s*
OCOR	6.03 *qq*	5.78 *qq*	
—	2.00 *dq*	2.09 *dq*	
	1.88 *dq*	1.91 *dq*	

J(Hz): Compound **1**: 1,2 = 3.3; 1,10 = 11; 2,3 = 6; 2,3′ = 11.5; 3,3′ = 17; 3,5 ~ 1; 3,5′ ~ 1.5; 5,15 ~ 1; 8,8′ = 13; 8,9 = 3; 8,9 = 13; 8′, 9 = 3; 8′, 9′ = 15; 9,9′ = 15; 10, 14 = 11, 12 = 11, 13 = 7; OAng: 3′, 4′ = 7: 3′, 5′ = 4′, 5′ = 1.5; compound **26**: 2,3 = 8; 3,5 = 3,15 ~ 1;8,9 = 8,9′ = 4.5; 8,11 ~ 1; 9,9′ = 17;9,10 = 6; 9′10 = 6; 9,11 = 1.5; 9′, 11 = 1; 10,14 = 7.

acetates. Although **5** had been isolated from a *Senecio* species, no close relationship to other groups of the large genus *Senecio* was indicated.

EXPERIMENTAL

The air-dried plant material, collected in Transvaal (except *Lordhowea insularis*, which was collected on Lord Howe Island) was extracted with Et$_2$O–petrol (1 : 2) and the resulting extracts were separated first by CC (SiO$_2$) and further by repeated TLC (SiO$_2$). Known compounds were identified by comparison of the high field ^{1}H NMR spectra, the IR spectra and MS with those of authentic material. Voucher specimens were deposited in the Botanic Research Institute, Pretoria, and in the Swedish Museum of National History, Stockholm.

Senecio galpinii (*voucher* 81/132). The aerial parts (450 g) gave 5 mg squalene, 5 mg lupenone, 5 mg friedelin, 20 mg **6**, 20 mg **7**, 80 mg **8**, 3 mg, **9**, 45 mg **10**, 3 mg **11**, 3 mg **12**, 5 mg **13**, 5 mg **14** and 5 mg **24**, while the roots afforded 5 mg **9**, 80 mg **11** and 10 mg **12**. The esters **6–14** were separated first by repeated TLC (C$_6$H$_6$–CHCl$_3$–Et$_2$O, 2:2:1) and those compounds (**7** and **9**, **8** and **10** as well as **8** and **11–14**) which were not separated completely, were further separated by HPLC (reversed phase, MeOH–H$_2$O, 3 : 1).

β-Angeloyloxy-9β-acetoxy-8β-senecioyloxy-1β,10α,4α, 5-β-diepoxy germacr-11-ene (**9**). Colourless gum. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1240 (OAc), 1720, 1650 (C=CRO$_2$R); MS *m/z* (rel. int.): 490.257 [M]$^+$ (0.5) (C$_{27}$H$_{38}$O$_8$), 391 [M − OCOR]$^+$ (5), 390 [M − RCO$_2$H]$^+$ (5), 331 [391 − AcOH]$^+$ (2), 231 [331 − RCO$_2$H]$^+$ (12), 83 [C$_4$H$_7$CO]$^+$ (100); CI (*iso*-butane): 491 [M + 1]$^+$ (17), 391 [491 − RCO$_2$H]$^+$ (100), 331 [391 − HOAc]$^+$ (38), 231 [331 − RCO$_2$H]$^+$ (31).

3β-Angeloyloxy-9β-hydroxy-8β-hydroxy-8β-senecioyloxy-1β, 10α, 4α. 5β-diepoxy germacr-11-*ene* (**10**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3585 (OH hydrogen bonded), 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 433 [M − Me]$^+$ (5), 349.202 [M − OCOR]$^+$ (0.3) (C$_{20}$H$_{29}$O$_5$), 348 [M − RCO$_2$H]$^+$ (0.3), 248 [348 − RCO$_2$H] (1), 230 [248 − H$_2$O]$^+$ (1), 83 [C$_4$H$_7$CO]$^+$ (100), 55 [83 − CO]$^+$ (35).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-16 \quad -16 \quad -19 \quad -35} \qquad \text{CHCl}_3;\ c = 0.54.$$

3β, 8β-Diangeloyloxy-5α,9β-diacetoxy-4α-hydroxy-1β, 10α-epoxygermacr-11-*ene* (**11**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1755, 1235 (OAc), 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 550.278 [M]$^+$ (0.1) (C$_{29}$H$_{42}$O$_{10}$), 490 [M − HOAc]$^+$ (0.1), 390 [490 − RCO$_2$H]$^+$ (0.2), 291 [390 − OCOR]+ (0.5), 231 [291 − HOAc]$^+$ (1), 83 [C$_4$H$_7$CO]$^+$ (100), 55 [83 − CO]$^+$ (48).

3β-Angeloyloxy-5α,9β-diacetoxy-4α-hydroxy-8β-senecioyloxyl-1β, 10α-epoxygermacr-11-*ene* (**12**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1760, 1240 (OAc), 1725, 1655 (C=CCO$_2$R); MS *m/z* (rel. int.) 550.278 [M]$^+$ (0.2) (C$_{29}$H$_{42}$O$_{10}$), 450 [M − RCO$_2$H]$^+$ (1), 390 [450 − HOAc]$^+$ (0.4), 350 [450 − RCO$_2$H]$^+$ (1.4), 290 [350 − HOAc]$^+$ (0.5), 230 [290 − HOAc]$^+$ (2), 83 [C$_4$H$_7$CO]$^+$ (100), 55 [83 − CO]$^+$ (58).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-56 \quad -57 \quad -66 \quad -116} \qquad \text{CHCl}_3;\ c\ 0.62.$$

3β-Angeloyloxy-9β-acetoxy-8β-(angeloyloxy- and senecioyloxy)-4α,5α-dihydroxy-1β.10α-epoxygermacr-11-*ene* (**13** *and* **14**). Colourless gum, which could not be separated, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3570 (OH), 1750, 1235 (OAc), 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 508.267 [M]$^+$ (0.3) (C$_{27}$H$_{40}$O$_9$), 409 [M − OCOR]$^+$ (1), 408 [M − RCO$_2$H]$^+$ (1), 390 [408 − H$_2$O]$^+$ (0.6), 308 [408 − RCO$_2$H]$^+$ (1.2), 249 [308 − OAc]$^+$ (1.8), 231 [249 − H$_2$O]$^+$ (1.4), 83 [C$_4$H$_7$CO]$^+$ (100), 55 [83 − CO]$^+$ (42).

Senecio coronatus (*voucher* 81/222). The aerial parts (330 g) afforded 3 mg germacrene D, 2 mg bicyclogermacrene, 3 mg α-humulene, 2 mg **2**, 2 mg **15**, 3 mg **16** (Et$_2$O–petrol, 1 : 3), 2 mg **17** (Et$_2$O–petrol, 1 : 3), 1 mg **18**, 5 mg **19**, 2 mg **20**, 2 mg **21**, 1 mg **22** and **22** and 0.5 mg **23**, while the roots (130 g) gave 3 mg **15**, 15 mg **19**, 5 mg **20** and 25 mg **21**.

14-*Isobutyryloxycacalohastin* (**16**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO$_2$R), 3050, 1605 (C=C); MS *m/z* (rel. int.): 328.167 [M]$^+$ (51) (C$_{20}$H$_{24}$O$_4$), 242 [C$_{15}$H$_{14}$O$_3$]$^+$ (17), 241 [M − OCOR]$^+$ (55), 225 [242 − Me]$^+$ (100).

14-*Propioyloxycacalohastin* (**17**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO$_2$R), 3050, 1605 (C=CCO$_2$R); MS *m/z* (rel. int.) 314.152 [M]$^+$ (45) (C$_{19}$H$_{22}$O$_4$), 242 [C$_{15}$H$_{14}$O$_3$]$^+$ (7), 241 [M − OCOR]$^+$ (41), 225 [242 − Me]$^+$ (100).

Senecio pleistocephalus (*voucher* 81/134). The aerial parts (410 g) afforded 20 mg germacrene D, 2 mg bicyclogermacrene, 5 mg α-humulene, 50 mg lupeyl acetate, 10 mg lupenone and 12 mg **1**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720, 1650 (C=CCO$_2$R); MS (CI, *iso*-butane) *m/z* (rel. int.): 219 [M + 1 − RCO$_2$H]$^+$ (100), 201 [219 − H$_2$O]$^+$ (2), 158 [201 − CHMe$_2$]$^+$ (2).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-12 \quad -12 \quad -16 \quad -31} \qquad \text{CHCl}_3;\ c\ 0.5.$$

Lordhowea insularis. The aerial parts (100 g) gave 5 mg sitosteryl acetate, 2 mg **4**, 2 mg **5** and 2 mg **3** (Et$_2$O-petrol, 1:10), colourless gum. IR $\nu_{max}^{CCl_4}$ cm^{-1}; 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 304.240 [M]$^+$ (0.5) (C$_{20}$H$_{32}$O$_2$), 204 [M −

$RCO_2H]^+$ (6), 189 $[204-Me]^+$ (6), 136 $[C_{10}H_{16}]^+$ (15), (McLafferty), 135 $[C_{10}H_{15}]^+$ (10), 83 $[C_4H_7CO]^+$ (47), 69 $[C_5H_9]^+$ (100); ^{1}H NMR ($CDCl_3$): 4.65 *br d* (H-1), 5.38 *br t* (H-2), 2.10 *br t* (H-4), 2.05 *m* (H-5, H-8), 5.09 *br t* (H-6), 1.96 *m* (H-9), 5.07 *br t* (H-10), 1.66 *br s* (H-12), 1.58 *br s* (H-13, H-14), 1.71 *br s* (H-15), 6.03 *qq*, 1.96 *dq*, 1.88 *dq* (OAng) [*J* (Hz): 1, 2 = 5, 6 = 9, 10 = 7; OAng: 3′, 4′ = 7; 3′, 5′ = 1.5].

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