[M − AngOH]$^+$ (0.6), 344 [M − $C_4H_9CO_2H$]$^+$ (0.9), 244 [344 − AngOH]$^+$ (5), 326 [344 − H_2O]$^+$ (1), 85 [C_4H_9CO]$^+$ (31), 83 [C_4H_7CO]$^+$ (100), 57 [85 − CO]$^+$ (68), 55 [83 − CO]$^+$ (52).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+10 \quad +17 \quad +19 \quad +38} (\text{CHCl}_3;\ c\,0.4).$$

11,13-*Epoxy*-11,13H-*budlein A* (**15**). Colourless crystals, mp 93°, IR $\nu_{\max}^{\text{CCl}_4}$ cm^{-1}: 3620 (OH), 1800 (γ-lactone), 1720 (C=CCO), 1600 (C=C–OR); MS *m/z* (rel. int.): 390.132 [M]$^+$ (16), 291 [M − OCOR]$^+$ (2), 273 [291 − H_2O]$^+$ (1), 83 [C_4H_7CO]$^+$ (100), 55 [83 − CO]$^+$ (98); $[\alpha]_D = -27°$.

11β-*Hydroxy*-13-*chloro*-11,13H-*budlein A* (**16**). Colourless gum, IR $\nu_{\max}^{\text{CCl}_4}$ cm^{-1}: 3580 (OH), 1780 (γ-lactone), 1720 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 426.103 [M]$^+$ (5) ($C_{20}H_{23}O_8Cl$), 390 [M − HCl]$^+$ (10), 327 [M − OCOR]$^+$ (1), 291 [327 − HCl]$^+$ (1), 83 [C_4H_7CO]$^+$ (100), 55 [83 − CO]$^+$ (94).

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EREMOPHILENE AND GERMACRENE DERIVATIVES FROM *SENECIO GLANDULOSO-PILOSUS*[*]

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Key Word Index—*Senecio glanduloso-pilosus*; Compositae; sesquiterpenes; eremophilene derivative; germacrene hydroperoxide.

Abstract—*Senecio glanduloso-pilosus* afforded in addition to known compounds a new eremophilene derivative and a hydroperoxide derived from germacrene D.

In a continuation of our investigation of *Senecio* species we have studied the constituents of *S. glanduloso-pilosus* Volkens et Muschler. The aerial parts afforded germacrene D, α-humulene, β-farnesene, 5′-angeloyloxysenspeciosone (**1**)[1] and the isomeric ester **2** as well as the hydroperoxide **6**. The structure of **2** followed from the molecular formula and the ^{1}H NMR spectral data (Table 1), which were similar to those of **1** and of the 7,11-isomer of **2**[1]. The nature of the ester residue clearly followed from the typical ^{1}H NMR signals. The three-fold doublet at δ 6.22 was coupled with one of the olefinic protons and with those of a neighbouring CH_2 group, which were also coupled with a methyl group (1.00*t*). The stereochemistry at C-7, C-9 and C-10 followed from the couplings $J_{6,7}$ and $J_{9,10}$, which were identical with those of the isomeric ester isolated previously[1]. Structures **1–5** represent the relative configurations, which are also probably the absolute ones as the configuration at C-7 is normally β. The structure of **6** was deduced from the spectral data. In the mass

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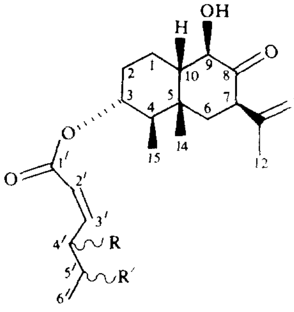
[*] Part 438 in the series "Naturally Occurring Terpene Derivatives". For Part 437 see Bohlmann, F., Gupta, R. K. and Jakupovic, J., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 1665.

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

H-3β	4.89 *dd*	H-2′	5.83 *dd*
H-7α	3.25 *dd*	H-3′	6.14 *dd*
H-9α	3.98 *dd*	H-4′	6.22 *ddd*
H-12	5.01 *dq*	H-5′	1.5 *m*
H-12′	4.80 *br s*	H-6′	1.00 *t*
H-13	1.80 *br s*	OAng	6.08 *qq*
H-14	1.17 *s*		1.99 *dq*
H-15	0.94 *d*		1.90 *dq*
		OH	3.51 *d*

J (Hz): 2α,3β = 3β,4α = 10; 2β,3β = 5; 4α,15 = 6.5; 6α,7α = 5; 5β,7α = 13; 6,12 = 1.5; 9α,10β = 11.5; 9α, OH = 2.5.



1 R = H, R′ = OAng

2 R = OAng, R′ = H

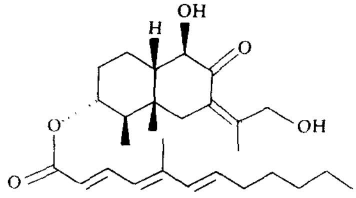


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Table 2. ^{1}H NMR spectral data of compound **6** (400 MHz, $CDCl_3$, TMS as internal standard)

H-1	4.12 *dd*	H-12	0.84 *d*
H-2	2.04 *m*	H-13	0.92 *d*
H-3	2.45 *ddd*	H-14	5.33 *br s*
H-3′	2.28 *dddd*	H-14′	5.20 *br s*
H-5	6.02 *d*	H-15	4.96 *br s*
H-6	5.44 *dd*	H-15′	4.88 *br s*
		-OOH	7.51 *s*

J (Hz): 1,2 = 11.5; 1,2′ = 3.5; 2,3 = 3,3′ = 12; 2,3′ = 4.5; 2′,3 = 5; 2′,3′ = 3; 3,15 = 1.5; 5,6 = 16; 6,7 = 10.5; 11,12 = 11,13 = 7.

spectrum a clear molecular ion was visible leading to the molecular formula $C_{15}H_{24}O_2$. The presence of a hydroperoxide was indicated by loss of hydrogen peroxide and water (*m*/*z* 202 and 218). Accordingly reaction with triphenylphosphine afforded the alcohol **7**, identical with an authentic sample[3]. In the ^{1}H NMR spectrum (Table 2) the signals were similar to those of **7**. However, the chemical shift of H-1 was slightly different. Furthermore a singlet at δ 7.51 in the spectrum of **6** was obviously that of the hydroperoxide proton.

The roots gave germacrene D, bisabolene, the eremophilenes **1–3**[1] and the furanoeremophilanes **4** and **5**[1]. The chemistry of this *Senecio* species is very similar to that of *S. speciosus*[1] and *S. scaposus*[2].

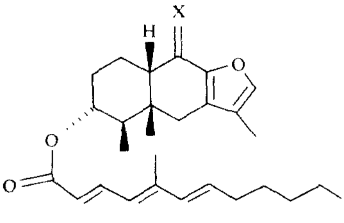
EXPERIMENTAL

The air-dried plant material, collected in February 1981 in Transvaal, (voucher 81/231, deposited in the Botanic Research Institute, Pretoria) was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by CC (Si gel) and further be repeated TLC (Si gel). Known compounds were identified by comparing the ^{1}H NMR spectra with those of authentic material. The aerial parts (35 g) afforded 50 mg germacrene D, 50 mg α-humulene, 10 mg β-farnesene, 50 mg **1**, 20 mg **2** (Et_2O–petrol, 3:1), and 10 mg **6** (Et_2O–petrol, 1:3), while the roots (10 g) gave 5 mg bisabolene, 1 mg germacrene D, 20 mg **1**, 5 mg **2**, 5 mg **3**, 2 mg **4** and 2 mg **5**.

4′-Angeloyloxysenspeciosone (**2**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH, hydrogen bonded), 1740, 1235 (OAc), 1720, 1645 (C=CCO_2R); MS *m*/*z* (rel. int.): 446.267 $[M]^+$ (5) ($C_{26}H_{38}O_6$), 346 $[M - AngOH]^+$ (1), 235 $[M - O_2CR]^+$ (27), 234 $[M - HO_2CR]^+$ (26), 195 $[RCO]^+$ (2), 113 [195 − O=C=C(Me)–CH=CH_2]$^+$ (59), 83 $[C_4H_7CO]^+$ (100).

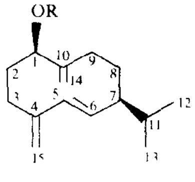
$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\text{ nm}}{-40 \quad -44 \quad -53 \quad -90} (CHCl_3; c\,0.2).$$

1β - *Peroxygermacra* - 4(15),5,10(14) - *triene* (**6**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OOH), 975 (*trans* CH=CH), 895 (C=CH_2); MS *m*/*z* (rel. int.): 236.178 $[M]^+$ (1) ($C_{15}H_{24}O_2$), 218 $[M - H_2O]^+$ (9), 202 $[M - H_2O_2]^+$ (14), 175 [218 −



4 X = O

5 X = α - OH, H



6 R = OH

7 R = H

CHMe$_2$]$^+$ (14), 159 [202 − CHMe$_2$]$^+$ (30), 119 (41), 109 (62), 91 (51), 69 (80), 55 (100); CI (iso-butane): 237 [M + 1]$^+$ (7), 219 [237 − H$_2$O]$^+$ (3), 203 [237 − H$_2$O$_2$]$^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-38 \quad -40 \quad -46 \quad -80} (\text{CHCl}_3;\ c\,0.1).$$

To 3 mg **6** in 0.5 ml CDCl$_3$ 10 mg triphenylphosphine was added. After 5 min the ^{1}H NMR spectrum was identical with that of **7**.

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TEUPOLIN III, A FURANOID DITERPENE FROM *TEUCRIUM POLIUM*

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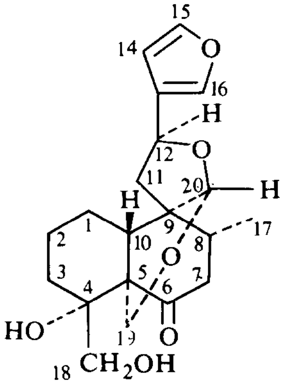
Key Word Index—*Teucrium polium* var. *polium*; Lamiaceae; teupolin III; furanoid diterpene; clerodane.

Abstract—A new clerodane derivative was isolated from *Teucrium polium* var. *polium*. The structure and stereochemistry have been established by detailed studies of the ^{1}H NMR spectra.

We have previously described some clerodane and nor-clerodane derivatives from *Teucrium polium* var. *polium* [1]. In a continuation of this work we have isolated from the same plant a new clerodane diterpene, teupolin III (**1**). The IR spectrum of **1** contained two strong bands for a primary and a tertiary alcohol (1050, 1150, 3420 cm^{-1}), a furan ring (3130, 1600, 1505, 870 cm^{-1}), and a strong band for a carbonyl group (1700 cm^{-1}).

The ^{1}H NMR spectrum (Table 1) showed two AB*q* (δ 3.70, 3.78 and 3.90, 4.60) which we have assigned to H-19 and H-18. The double doublet at δ 5.13 and the singlet at 5.20 were assigned to H-12 and H-20, respectively. The proton of the hydroxyl group at C-4 appeared as a singlet at δ 3.88 (hydrogen bond of OH-4 with 6-keto).

^{1}H NMR spin decoupling studies were particularly informative. A double doublet (δ 3.70) which we have assigned to H-19β, was coupled to a single-proton resonance at δ 1.97 ($^4J_{10\beta,19\alpha}$ = 1 Hz). A double dou-



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