Colourless oil, IR (cm^{-1}): 1740, 1230 (C=CCO$_2$Ph, OAc, CO$_2$R); MS: M$^+$ *m/e* 404.184 (3%) (C$_{22}$H$_{28}$O$_7$); − C$_4$H$_7$CO$_2$H 304 (30); C$_4$H$_9$CO$^+$ 85 (12); C$_4$H$_7$CO$^+$ 83 (100).

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REFERENCES

1. Bohlmann, F. and Zdero, C. (1970) *Tetrahedron Letters* 3575.
2. Bohlmann, F. and Grenz, M. (1979) *Phytochemistry* **18,** 177.
3. Bohlmann, F. and Abraham, W. R. (1979) *Phytochemistry* **18,** 668.
4. Aleiva, S., Abdullaev, U., Telezhenetkaya, M. and Yumusov, S. (1976) *Khim. Prir. Soedin.* 194.

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NEW SESQUITERPENES FROM *SENECIO* SPECIES*

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Key Word Index—*Senecio pseudoorientalis; S. vitalis;* Compositae; furanoeremophilane; germacrene derivative.

As a continuation of our investigations of *Senecio* species [1] we have studied the constituents of *S. pseudoorientalis* Schischk. The roots contain β-farnesene (**1**), furanoeremophil-1(10)-ene (**11**) [2], 6β-isobutyryloxy-furanoeremophil-1(10)-ene-9-one (**12**) [2], furanoeremophil-1(2)-en-3-one (**13**) [3, 4], 6α-angeloyloxy-furanoeremophil-9-en-1-one (**14**) [5], 6β-hydroxy-furanoeremophil-9-en-1-one (**15**) [2], 6β-isobutyryloxy-furanoeremophil-9-en-1-one (**16**) [2]. The 6α-isomer of 6β-isobutyryloxy-furanoeremophil-9-en-1-one (**16**) [2] was also obtained and was assigned structure **17** by comparing the ^{1}H NMR chemical shifts of the C-6 proton in 6β-isobutyryloxy-furanoeremophil-9-en-1-one (**16**) [2] and **17** (Table 1). The aerial parts also contained β-farnesene (**1**), furanoeremophil-1(2)-en-3-one (**13**) [3, 4] and 6β-isobutyryloxy-furanoeremophil-9-en-1-one (**16**) [5] as well as the diterpene hydrocarbon 9-geranyl-α-terpinene (**5**) [6]. The polar fraction afforded two compounds, which most probably are artifacts formed by oxidation in methanolic solution. The crystalline compound was obviously identical to 8β-hydroxy-8α-methoxy-3-oxo-eremophil-1,7(11)-dien-12-oic acid lactone (**18**) [7], already isolated from another *Senecio* species. The ^{1}H NMR data are fully in agreement with those reported for 8β-hydroxy-8α-methoxy-3-oxo-eremophil-1,7(11)-dien-12-oic acid lactone (**18**) [7]. The second compound was identified as the corresponding acid **19**. No molecular ion could be detected in the MS, however, a fragment at *m/e* 263 (C$_{15}$H$_{19}$O$_4$) indicated a probable loss of ·OMe. Consequently lactonization of **19** yielded 8β-hydroxy-8α-methoxy-3-oxo-eremophil-1,7(11)-dien(12-oic acid lactone (**18**) [7]. The roots of *S. vitalis* N.E.Br. afforded the hydrocarbons germacrene D (**2**), germacrene C (**3**) and bicyclogermacrene (**4**), the triterpenes oleanoic aldehyde (**6**) [8], oleanoic acid (**7**) [8], lupenone (**8**) [9] and the germacrene derivative 6β-acetoxy-3β-angeloyloxy-4,5-epoxygermacr-1(10)-ene (**20**) [2], while the aerial parts yielded germacrene D (**2**), bicyclogermacrene (**4**), lupenone (**8**) [9], lupeol (**9**) [8], lutin-5(6)-en-3β-ol (**10**) [10] and the germacrene derivatives 6β-acetoxy-3β-angeloyloxy-4,5-epoxygermacr-1(10)-ene (**20**) [2], 3β-angeloyloxy-4,5-epoxy-6β-hydroxygermacr-1(10)-ene (**22**) [11], 4,5-epoxy-6β-hydroxy-3β-senecioyloxygermacr-1(10)-ene (**23**) [11] and 4,5-epoxy-6β-hydroxy-3β-tigloyloxygermacr-1(10)-ene (**24**) [2] together with the corresponding ester **21** as deduced from the differences in the ^{1}H NMR spectra (Table 1). While all signals were more or less identical to those of 6β-acetoxy-3β-angeloyloxy-4,5-epoxygermacr-1(10)-ene (**20**) [2] the typical signals at δ 5.72, 2.16 and 1.73 clearly indicated the nature of the ester group. Acetylation of 4,5-epoxy-6β-hydroxy-3β-senecioyloxygermacr-1(10)-ene (**23**) [11] afforded an acetate, which was identical to the isolated acetate, **21**.

While *S. vitalis* belongs to the succulent species, where the absence of furanoeremophilanes is typical, *S. pseudoorientalis* seems to be closely related to *S. nemorensis*.

EXPERIMENTAL

IR: CCl$_4$ or CHCl$_3$; ^{1}H NMR: 270 MHz, CDCl$_3$, TMS as int. standard; MS: 70 eV; optical rotation: CHCl$_3$. The fresh plant material was chopped and extracted with Et$_2$O–petrol (1:2). Extracts of aerial parts were first treated with MeOH to remove saturated hydrocarbons. The resulting extracts were separated first by CC (Si gel, grade II) and then by

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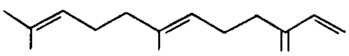
[*] Part 271 in the series "Naturally Occurring Terpene Derivatives". For Part 270 see Bohlmann, F., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19** (in press).



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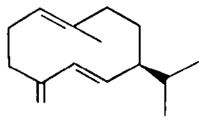

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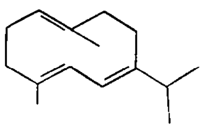

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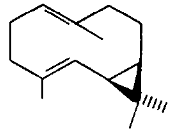

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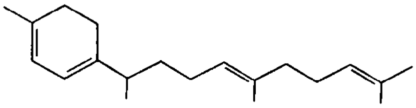

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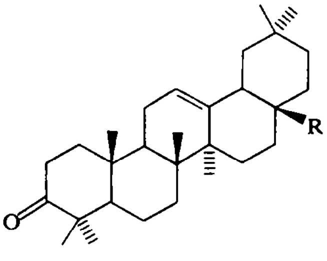
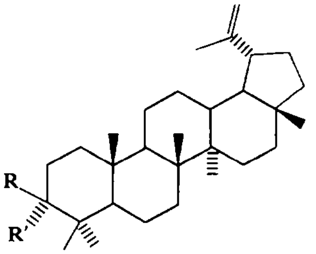
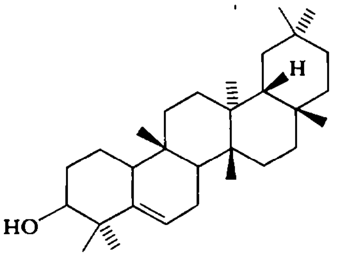


6 R = CHO
7 R = CO_2H



8 R,R^1 = O
9 R = OH R^1 = H



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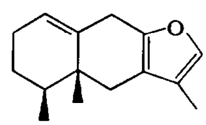

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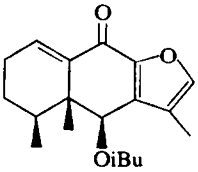

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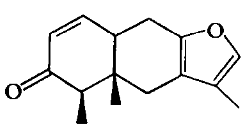

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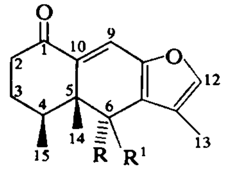
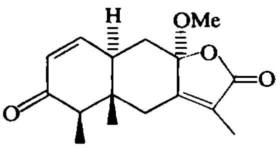


	14	**15**	**16**	**17**
R	OAng	H	H	OiBu
R^1	H	OH	OiBu	H



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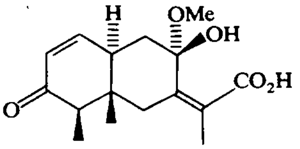

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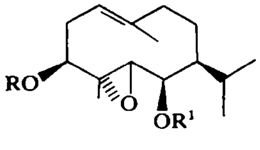

	20	**21**	**22**	**23**	**24**
R	Ang	Sen	Ang	Sen	Tigl
R'	Ac	Ac	H	H	H

Table 1. ^{1}H NMR data of compounds **17–19** and **21** (270 MHz, $CDCl_3$, TMS as internal standard)

	17	**18**	**19**	**21**
1-H		6.54 *dd*	6.53 *dd*	5.24 *m*
2-H	2.65 *ddd* 2.40 *ddd*	6.07 *dd*	6.03 *dd*	2.0 *m*
3-H	1.83 *m*	—	—	5.72 *dd*
4-H	2.28 *m*	2.50 *q*	2.45 *q*	—
5-H	—	—	—	2.96 *d*
6-H 6′-H	5.84 *s*	2.66 *d* 2.16 *d*(*br*)	2.41 *d* 1.88 *d*(*br*)	5.29 *d*(*br*)
9-H 9′-H	7.43 *s*	2.46 *dd* 1.72 *dd*	2.26 *dd* 1.62 *dd*	2.0 *m*
10-H	—	3.02 *ddd*	2.95 *ddd*	
12-H	7.25 *s*(*br*)	—	—	1.16 *d*
13-H	2.07 *s*(*br*)	1.89 *d*	1.76 *s*(*br*)	1.09 *d*
14-H	1.02 *s*	0.65 *s*	0.60 *s*	1.54 *s*(*br*)
15-H	1.02 *d*	1.16 *d*	1.11 *d*	1.73 *s*
OCOR	2.46 *qq*	—	—	5.72 *s*(*br*)
	1.14 *d*	—	—	2.16 *s*(*br*)
	1.09 *d*	—	—	1.73 *s*(*br*)
OMe	—	3.16 *s*	3.19 *s*	—

J(Hz): **16**: 2, 2′ = 17; 2, 3 = 2, 3′ = 3.5; 2′, 3 = 10; 2′, 3′ = 7; 4, 15 = 7; **18** and **19**: 1, 2 = 9.5; 1, 10 = 2, 3; 2, 10 = 3; 4, 15 = 7; 6, 6′ = 13; 6, 13 = 1.5; 9.9′ = 14; 9, 10 = 3.3; 9′, 10 = 14; **21**: 2, 3 = 5; 2, 3′ = 11; 5, 6 = 7; 6, 7 = 1.5; 11, 12 = 11, 13 = 7.

repeated TLC (Si gel GF 254). Known compounds were identified by comparison of their IR and ^{1}H NMR spectra with those of authentic compounds.

Senecio vitalis (*Kew Gardens*) Roots (10 g) afforded afforded 10 mg **1**, 25 mg **11**, 20 mg **12**, 20 mg **13**, 5 mg **14**, 10 mg **15**, 10 mg **16**, and 5 mg **17** (C_6H_6–CH_2Cl_2, 1:1). Aerial parts (200 g) yielded 10 mg **1**, 10 mg **5**, 300 mg **13**, 10 mg **16**, 1.5 mg **18** and 2 mg **19** (Et_2O–petrol, 1:1). Compounds **18** and **19** were dissolved in 1 ml MeOH and neutralized by addition of dil NaOH in order to separate **18** from **19**. However, after addition of dil H_2SO_4, 3 mg of **18** were obtained.

Senecio vitalis (*Kew Gardens*). Roots (10 g) afforded 2 mg **2**, 2 mg **3**, 10 mg **4**, 10 mg **6**, 10 mg **7**, 10 mg **8**, and 20 mg **20**. Aerial parts (100 g) gave 1 mg **2**, 10 mg **4**, 10 mg **8**, 10 mg **9**, 10 mg **10**, 60 mg **20**, 5 mg **21** (Et_2O–petrol, 1:3), 40 mg **22**, 20 mg **23** and 40 mg **24**.

6α-Isobutyryloxy-furanoeremophil-9-en-1-one (**17**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735 (CO_2R), 1680 (C=C—C=O), 1575, 1535 (furan); MS *m/e* (rel. int.): 316.167 (M^+, 17)($C_{19}H_{24}O_4$); 301($M^+ - \cdot Me$, 4); 246 ($M^+ - O{=}C{=}CMe_2$, 24); 229($M - \cdot OCOC_3H_7$, 100); 71 ($C_3H_7CO^+$, 26).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \qquad 578 \qquad 546 \qquad 436\,\text{nm}}{+100.0 \qquad +101.8 \qquad +120.0 \qquad +209.4}\ (c = 0.17).$$

8β-Hydroxy-8α-methoxy-3-oxo-eremophil-1,7(11)-*dien* (12)-*oic acid* (**19**). Obtained as colourless gum containing some **18**; IR $\nu_{max}^{CHCl_3}$ cm ^{1}; 3500–3000, 1720 ($C{=}CCO_2H$), 3540 (OH). MS *m/e* (rel. int.): 263 ($M^+ - \cdot OMe$, 13); 245 ($263 - H_2O$, 62); 217 (245 – CO, 90); 41 ($C_3H_5^+$, 100).

6β-Acetoxy-4,5-epoxy-3β-senecioyloxy-germacr-1(10)-*ene* (**21**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1230 (OAc), 1710, 1655 ($C{=}CCO_2R$); MS *m/e* (rel. int.): 378 (M^+, 0.2) ($C_{22}H_{34}O_5$); 83 ($C_4H_7CO^+$, 100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \qquad 578 \qquad 546 \qquad 436\,\text{nm}}{-47.8 \qquad -50.0 \qquad -58.7 \qquad -113.0}\ (c = 0.2).$$

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REFERENCES

1. Bohlmann, F., Zdero, C., Berger, D., Suwita, A., Mahanta, P. K. and Jeffrey, C. (1979) *Phytochemistry* **18**, 79.
2. Bohlmann, F., Knoll, K.-H., Zdero, C., Mahanta, P. K., Grenz, M., Suwita, A., Ehlers, D., LeVan, N., Abraham, W.-R. and Natu, A. A. (1977) *Phytochemistry* **16**, 965.
3. Bohlmann, F. and Zdero, C. (1978) *Phytochemistry* **17**, 1135.
4. Takahashi, T. (1967) *Chem. Abstr.* 99985u.
5. Bohlmann, F. and Zdero, C. (1978) *Phytochemistry* **17**, 1161.
6. Bohlmann, F., Zdero, C., Hoffmann, E., Mahanta, P. K. and Dorner, W. (1978) *Phytochemistry* **17**, 1917.
7. Jizba, I., Samek, Z., Novotny, C., Majadenova, E. and Boeva, A. (1978) *Collect Czech. Chem. Commun.* **43**, 1113.
8. Halsall, T. G. and Aplin, R. T. (1964) *Fortschr. Chem. Org. Naturst.* **22**, 153.
9. Chatterjee, A., Mukherjee, R., Srimany, S. K. and Bhattacherjee, S. (1966) *J. Indian Chem. Soc.* 63.
10. Taylor, D. A. H. (1967) *J. Chem. Soc.* 490.
11. Bohlmann, F. and Ziesche, J. (1979) *Phytochemistry* **18**, 1489.