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SHORT REPORTS

TWO SESQUITERPENES FROM *SENECIO* SPECIES*

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Key Word Index—*Senecio ochoanus*; *S. conrathii*; *S. balbinifolius*; *S. microglossus*; Compositae; sesquiterpenes; eremophilane derivative; eudesmane derivative.

Abstract—The investigation of further *Senecio* species gave, in addition to known compounds, two new sesquiterpenes, an eremophilane and a eudesmane derivative.

In continuation of our investigations of the large genus *Senecio* we have studied the constituents of one species from Peru and three from Transvaal, South Africa. The aerial parts of *Senecio ochoanus* Cuatr. afforded phytadiene, lupeol and its Δ^{12}-isomer, stigmasterol, sitosterol, β-amyrin, spathulenol, the eremophilane **2** [1] and its previously unknown isomer, **1**.

The structure of **1** followed from the ^{1}H NMR spectrum (Table 1) which was close to that of the corresponding angelate [1] except that the H-3β signal was slightly shifted upfield in the spectrum of **1** if compared with the shift in that of the angelate. The roots also contained stigmasterol, sitosterol, and **1** and **2**.

The aerial parts of *Senecio conrathii* N.E. Br. only afforded **14**, while the roots gave β-farnesene and the furoeremophilane derivatives **7** [2], **8** [3], **9** [4], **10** [3], **11** [5] and **12** [6].

The aerial parts of *Senecio balbinifolius* DC. afforded lupeol and its Δ^{12}-isomer as well as the germacrene angelate, **13** [1], while the roots gave lupeol and its Δ^{12}-isomer.

The roots of *Senecio microglossus* DC. afforded stigmasterol, sitosterol, dammaradienol, its 3-epimer and the angelate, **5** [7], while the aerial parts gave germacrene D, γ- and δ-cadinene, bisabolol, the angelate **3** [8], **4** [9], the diol **6** and **14**–**17**. The structure of the diol, **6**, followed from the ^{1}H NMR spectrum (Table 1). The positions of the hydroxyl groups were assigned by spin decoupling. The broadened doublet at δ 1.77 was coupled with the vinyl protons and with the proton which displayed a double doublet at 3.73 and this permitted the assignments of H-5 and H-6. As the second lowfield signal was at δ 3.25 an allylic position at C-3 could be excluded. Accordingly a 1β- and 6α-hydroxyl were present. The stereochemistry followed from the couplings of H-1 and H-6. The remaining signals were similar to those of **3**.

This investigation shows that only *S. conrathii* contains the furanoeremophilanes typical of many plants of the genus *Senecio* and related species [1]. It may be of chemotaxonomic interest that the species from Peru, *S. ochoanus*, contains the same eremophilane derivative as *S. gerardii* [1] from South Africa, while the constituents of *S. balbinifolius* indicate relationships to the succulent species [10].

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

	1	**6**
H-1α	2.08 *ddd*	3.25 *dd*
H-1β	1.50 *m*	—
H-2α	1.38 *ddd*	1.87 *dddd*
H-2β	2.17 *ddd*	*
H-3	4.80 *ddd*	2.10 *ddd*
H-4	1.56 *dq*	—
H-5	—	1.77 *br d*
H-6α	1.87 *d*	—
H-6β	2.92 *d*	3.73 *dd*
H-9α	3.84 *dd*	*
H-10β	1.57 *ddd*	—
H-12	1.82 *s*	0.90 *d*
H-13	1.94 *s*	1.00 *d*
H-14	0.98 *s*	0.75 *s*
H-15	0.96 *d*	5.03 *br s*
H-15′		4.76 *br s*
OTigl	6.85 *qq*	—
	1.85 *dq*	—
	1.81 *dq*	—
OH	3.77 *d*	*

* Not assigned.

J (Hz): Compound **1**: 1α, 1β = 12; 1α, 2α = 1α, 2β = 1α, 10β ~ 3; 1β, 10β = 10; 2α, 2β = 13; 2α, 3β = 11; 2β, 3β = 4.5; 3β, 4α = 10.5; 4α, 15 = 6.5; 6α, 6β = 13.5; 9α, 10β = 11; 9α, OH = 2.5; compound **6**: 1α, 2α = 5; 1α, 2β = 11; 2α, 2β = 12; 2α, 3α = 2α, 3β ~ 2.5; 2β, 3α = 13; 3α, 3β = 14; 5α, 6β = 10; 6β, 7α = 10; 11, 12 = 11, 13 = 7.

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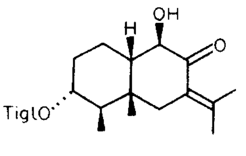
*Part 479 in the series "Naturally Occurring Terpene Derivatives". For Part 478 see Khafagy, S. M., Al-Yahya, M. A., Ziesche, J. and Bohlmann, F. (1983) *Phytochemistry* **22** (in press).



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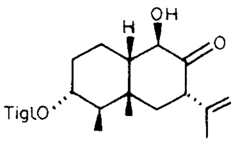

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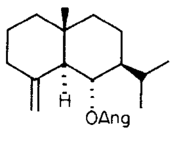

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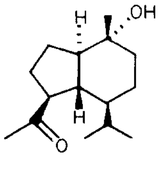

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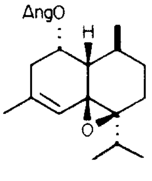

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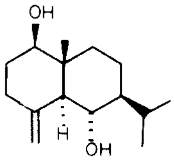

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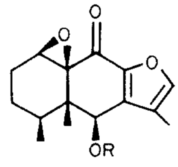
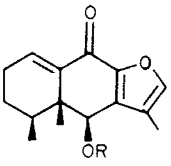
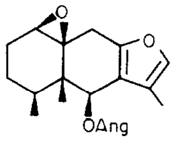


7 R = Ang
8 R = *i*Val



9 R = Ang
10 R = *i*Val
11 R = Prop



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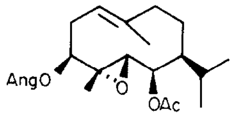

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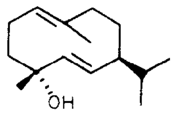

14

$HOCH_2CH{=}CH(C{\equiv}C)_2(CH{=}CH)_2(CH_2)_4CH{=}CH_2$
t *tt* **15**
t *ct* **16**

$HOCH_2CH{=}CH(C{\equiv}C)_2CH_2CH{=}CH(CH_2)_5CH{=}CH_2$
c
17

EXPERIMENTAL

The air-dried plant material was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by CC (Si gel) and further by TLC (Si gel). Known compounds were identified by comparing the high field ^{1}H NMR spectra with those of authentic material.

Senecio ochoanus (*voucher RMK* 9041, *collected in January* 1982 *in Peru*). The roots (120 g) afforded 10 mg stigmasterol, 10 mg sitosterol, 25 mg **1** (Et_2O–petrol, 1:1) and 26 mg **2**, while the aerial parts (250 g) gave 5 mg phytadiene, 18 mg β-amyrin, 6 mg lupeol, 12 mg lup-12-en-3β-ol 7.5 mg stigmasterol, 7.5 mg sitosterol, 6 mg spathulenol, 3.5 mg **1** and 5.5 mg **2**.

Senecio conrathii (*voucher* 81/258, *collected in February* 1981 *in Transvaal*). The roots (60 g) gave 20 mg β-farnesene, 12 mg **7**, 12 mg **8**, 5 mg **9**, 2 mg **10**, 8 mg **11** and 80 mg **12**, while the aerial parts (200 g) gave 8 mg **14**.

Senecio balbinifolius (*voucher* 81/158, *collected in February* 1981 *in Transvaal*). The roots (50 g) gave 120 mg lupeol and 120 mg lup-12-en-3β-ol, while the aerial parts (50 g) afforded 60 mg lupeol, 60 mg lup-12-en-3β-ol and 12 mg **13**.

Senecio microglossus (*voucher* 81/99, *collected in February* 1981 *in Transvaal, South Africa*). The roots (260 g) gave 8 mg dammaradienol, 3 mg of its 3-epimer, 4 mg sitosterol, 4 mg stigmasterol and 3 mg **5**, while the aerial parts (310 g) afforded 135 mg germacrene D, 1.5 mg γ- and 1.5 mg δ-cadinene, 4 mg bisabolol, 7 mg **3**, 17 mg **4**, 2 mg **6** (Et_2O), 150 mg **14**, 25 mg **15**, 30 mg **16** and 30 mg **17**.

*9β-Hydroxy-3α-tigloyloxyeremophil-*7(11)*-en-*8*-one* (**1**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3460 (OH), 1705, 1650 ($C{=}CCO_2R$), 1680 ($C{=}CC{=}O$); MS *m/z* (rel. int.): 334.214 $[M]^+$ (28) ($C_{20}H_{30}O_4$), 234 $[M-RCO_2H]^+$ (7), 216 $[234-H_2O]^+$ (8), 206 $[234-CO]^+$ (40), 191 $[206-Me]^+$ (37), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (20).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-85 \quad -88 \quad -103 \quad -193} \ (CHCl_3;\ c\ 0.35).$$

*1β,6α-Dihydroxyeudesm-*4(15)*-ene* (**6**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 220.183 [M

$-H_2O]^+$ (6) ($C_{15}H_{24}O$), 205 $[220-Me]^+$ (3), 177 $[220-C_3H_7]^+$ (8), 57 $[C_4H_9]^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+7 \quad +9 \quad +10 \quad +16} \; (\text{CHCl}_3;\ c\ 0.1).$$

Acknowledgements—We thank Dr. B. de Winter and Miss M. Welman, Botanic Research Institute, Pretoria, South Africa, for their help during plant collection and identification of the material and the Deutsche Forschungsgemeinschaft for financial support.

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FLAVONOIDS FROM *RHAMNUS PALLASII*

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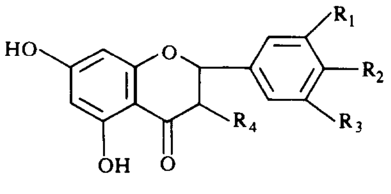
Key Word Index—*Rhamnus pallasii*; Rhamnaceae; flavonoids; pallasiin; 2,3-dihydromyricetin 4′-*O*-methyl ether; kaempferol; quercetin; isorhamnetin; mearsetin; aromadendrin; eriodictyol; taxifolin.

Abstract—A new dihydroflavonol, pallasiin, together with kaempferol, quercetin, isorhamnetin, mearnsetin, aromadendrin, eriodictyol and taxifolin, has been isolated from the bark of *Rhamnus pallasii* and its structure elucidated as 2,3-dihydromyricetin 4′-*O*-methyl ether.

Rhamnus species (Rhamnaceae) are known to be rich sources of anthraquinones and to produce flavonols, i.e. kaempferol, quercetin and their methyl ethers [1]. There is, however, no report on the constituents of *Rhamnus pallasii* Fisch. et Meg., a species from Turkey, as far as we know. The present paper describes the isolation of seven known flavonoids, kaempferol (**1**), quercetin (**2**), isorhamnetin (**3**), mearnsetin (**4**), aromadendrin (**5**), eriodictyol (**6**) and taxifolin (**7**), and a new flavonoid, pallasiin (**8**), from the bark of *Rhamnus pallasii*.

Compounds **1–3**, and **5–7** were identified by direct comparison with respective authentic samples. The spectral data (UV, ^{1}H NMR and mass spectra) of **4** were in good agreement with those of mearnsetin (myricetin 4′-*O*-methyl ether) in the literature [2].

Furthermore, the structure of **4** was confirmed by correlating its ^{13}C NMR chemical shifts with those of myricetin (Table 1). This represents the first report of a myricetin-type flavonol in this genus.



5 $R_1 = R_3 = H,\ R_2 = R_4 = OH$
6 $R_1 = R_2 = OH,\ R_3 = R_4 = H$
7 $R_1 = R_2 = R_4 = OH,\ R_3 = H$
8 $R_1 = R_3 = R_4 = OH,\ R_2 = OMe$

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