gel (10 g Merck, 70–230 mesh) eluting with MeOH. The appropriate fractions were collected together and, after removal of the solvent, melittoside (*ca* 0.075%) was crystallized from MeOH–EtOH (2:1).

Melittoside (**1**), mp 157–159°, $[\alpha]_D^{20}$ −41.9° (c = 1.03, MeOH); ^{1}H NMR (360 MHz, D_2O): δ 6.51 (1 H, *d*, J = 6.5 Hz, H-3), 5.86 (1 H, *dd*, J = 1.8/2.0 Hz, H-7), 5.44 (1 H, *d*, J = 5.4 Hz, H-1), 5.16 (1 H, *d*, J = 6.5 Hz, H-4), 4.58 (1 H, *s* (*br*), (H-6), 4.28/4.25 (2 H, AB-syst., J = 15.2 Hz, 2 H-10), 3.35 (1 H, *d*, J = 5.4 Hz, H-9); ^{13}C NMR (CD_3OD); aglycone: δ 94.18 (C-1), 143.42 (C-3), 105.26 (C-4), 80.06 (C-5), 79.92 (C-6), 128.21 (C-7), 147.34 (C-8), 50.55 (C-9), 60.94 (C-10); glucose: δ 99.69 (C-1′), 98.15 (C-1″), 74.90/75.11 (C-2′/2″), 78.22/78.43 (C-3′/3″ or C-5′/5″), 70.83/71.67 (C-4′/4″), 77.19/78.11 (C-5′/5″ or C-3′/3″), 62.12/62.74 (C-6′/6″).

Melittoside decaacetate (**1a**) was obtained (pyridine and Ac_2O) as an amorphous powder. $[\alpha]_D^{20}$ −43.4° (c = 1.1, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$): δ 6.37 (1 H, *d*, J = 6.7 Hz, H-3), 5.77 (1 H, *dd*, J = 1.8/2 Hz, H-7), 5.38 (1 H, *dd*, J = 2/2 Hz, H-6), 5.28 (1 H, *d*, J = 1.6 Hz, H-1), 5.27 (1 H, *d*, J = 6.7 Hz, H-4), 4.70 (2 H, *s* (*br*), 2 H-10), 3.82 (1 H, *s* (*br*), H-9), 4.74 (1 H, *d*, J = 8.2 Hz, H-1′), 4.87 (1 H, *d*, J = 8.6 Hz, H-1″), 3.71–3.78 and 3.90–3.97 (2 H, *m*, H-5′/5″), 4.09–4.17 and 4.22–4.34 (4 H, *m*, 2 H-6′/6″), 4.70–5.50 (H-2′/3′/4′/5′ and H-2″/3″/4″/5″), 1.94–2.19 (10 × OCOMe); ^{13}C NMR ($CDCl_3$); aglycone: δ 93.99 (C-1), 142.63 (C-3), 109.90 (C-4), 77.01 (C-5), 82.83 (C-6), 127.18 (C-7), 141.06 (C-8), 54.91 (C-9), 60.92 (C-10); glucose: 96.92 (C-1′), 95.80 (C-1″), 70.50/71.08 (C-2′/2″), 72.70/72.49 (C-3′/3″ or C-5′/5″), 68.10/68.47 (C-4′/4″), 72.35/71.37 (C-5′/5″ or C-3′/3″), 61.52 (62.06 (C-6′/6″), 169.47–170.72 ($\underline{\mathrm{C}}\mathrm{OMe}$), 20.54–20.71 ($\mathrm{CO}\underline{\mathrm{C}}\mathrm{H}_3$).

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NOTONIPETRONE-LIKE SESQUITERPENES FROM *SENECIO KLEINIA**

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Key Word Index—*Senecio kleinia*; Compositae; sesquiterpenes; notonipetrone derivatives.

Abstract—Five new notonipetrone-like sesquiterpenes have been isolated from the roots of *Senecio kleinia* and their structures elucidated.

Only pyrrolizidin alkaloids [1] and quercetin [2] have been isolated from *Senecio kleinia* Less., a plant which is widespread on the Canary Islands. A re-investigation of the aerial parts showed that in addition to caryophyllene and γ-humulene, large amounts of **7** [3] and **8** [4] were present. The roots contained a complex mixture of sesquiterpene esters, which could be separated only with difficulty. Finally six compounds were obtained, but only one of them, the ketone notonipetrone (**1**) [4], has been isolated previously. The structures **2**–**6** of the other sesquiterpenes followed from the ^{1}H NMR data (Table 1), which were in part similar to those of **1**. The ^{1}H NMR spectrum of **2** obviously only differed in the signals of the ester residue at C-7. The signals of the isovalerate were replaced by the typical signals of a 4-methyl senecioate. Compound **3**, however, was a ketone with a free hydroxyl and two ester groups, a 2-methylbutyrate and a 4-methylsenecioate. The ^{1}H NMR data clearly showed that

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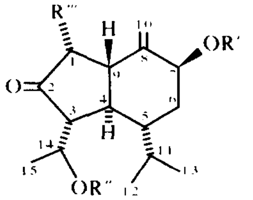
*Part 351 in the series "Naturally Occurring Terpene Derivatives". For Part 350 see Bohlmann, F., Zdero, C., Jakupovic, J., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20** (in press).

Table 1. ^{1}H NMR spectral data of compounds **2–6** (400 MHz, TMS as internal standrd standard)

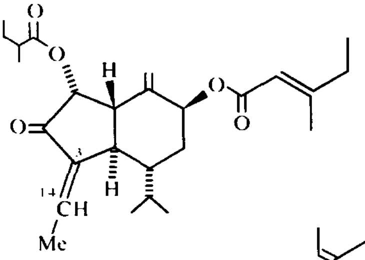
	2 ($CDCl_3$)*	**3** ($CDCl_3$)	**4** (C_6D_6)	**5** ($CDCl_3$)	**6** (C_6D_6)	**6** ($CDCl_3$)
H-1α	2.15 *m*	—	—	—	—	—
H-1β	2.40 *dd*	5.52 *d*	5.60 *d*	5.58 *d*	5.77 *d*	5.52 *br s*
H-3β	2.50 *dd*	2.58 *dd*	2.39 *dd*	—	—	—
H-4α	2.0 *m*	2.0 *m*	1.95 *m*	2.79 *m*	2.81 *br dd*	2.68 *m*
H-5β		1.9 *m*	1.80 *m*	2.15 *m*	1.95 *m*	2.15 *m*
H-6α	1.5 *m*	1.45 *m*	1.18 *ddd*	1.6 *m*	1.2 *m*	1.5 *m*
H-6β	1.95 *m*	2.0 *m*	1.95 *m*	1.95 *m*	1.95 *ddd*	2.01 *ddd*
H-7α	5.57 *br dd*	5.53 *br dd*	5.73 *br dd*	5.56 *br dd*	5.79 *br dd*	5.52 *br s*
H-9β	2.60 *m*	2.63 *br d*	2.39 *br dd*	2.79 *m*	2.59 *br d*	2.68 *m*
H-10	5.16 *br s*	5.18 *br s*	5.30 *br s*	5.23 *br s*	5.33 *br s*	5.18 *br s*
H-10′	4.80 *br s*	4.76 *br s*	4.99 *br s*	4.86 *br s*	5.07 *br s*	4.81 *br s*
H-11	2.31 *m*	2.33 *m*	2.45 *dd q*	2.35 *m*	2.27 *m*	2.32 *ddq*
H-12	1.00 *d*	0.96 *d*	0.92 *d*	1.03 *d*	0.83 *d*	1.00 *d*
H-13	0.80 *d*	0.78 *d*	0.67 *d*	0.88 *d*	0.72 *d*	0.88 *d*
H-14	5.11 *dq*	4.10 *br dq*	5.26 *dq*	6.72 *dq*	6.08 *dq*	6.40 *dq*
H-15	1.22 *d*	1.19 *d*	1.31 *d*	1.96 *dd*	2.10 *dd*	2.20 *dd*
OCOR	5.64 *br s*	5.62 *q*	5.89 *q*	5.68 *br s*	5.84 *br s*	5.64 *br s*
	2.18 *br q*	2.18 *br q*	1.87 *br q*	2.18 *br q*	1.82 *br q*	2.18 *br q*
	1.08 *t*	1.07 *t*	0.85 *t*	1.10 *t*	0.83 *t*	1.09 *t*
	2.16 *br s*	2.16 *br q*	2.23 *br s*	2.28 *br s*	2.21 *br s*	2.16 *br s*
	—	2.38 *tq*	2.20 *tq*	2.38 *tq*	2.27 *tq*	2.39 *tq*
	—	1.68 *ddq*	1.64 *ddq*	1.65 *ddq*	1.64 *ddq*	1.68 *ddq*
	—	1.45 *ddq*	1.27 *ddq*	1.47 *ddq*	1.47 *ddq*	1.47 *ddq*
	—	0.87 *t*, 1.14 *d*	0.80 *t*, 1.02 *d*	0.90 *t*, 1.14 *d*	0.81 *t*, 1.05 *d*	0.94 *t*, 1.15 *d*
OAc	2.11 *s*	—	1.85 *s*	—	—	—

*270 MHz.

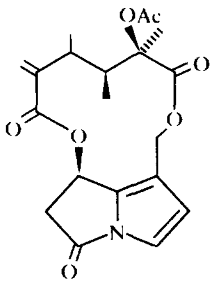
J (Hz): 1β,9 = 4; 3β,4α = 10; 3β,14 = 3; 5β,6α = 12; 5,11 = 3; 6α,6β = 15; 6α,7α = 6β,7α = 3.5; 11,12 = 11,13 = 14,15 = 7; compound **2**: 1α,1β = 17; 1β,9 = 6; compounds **5** and **6**: 1β,9 = 4, 4α,5β = 11; 4α,9 = 10; 4α,14 = 4α,15 = 2; OMesen: 4′,5′ = 7; OMeBu: 2′,3′ = 2′,5′ = 3′,4′ = 7; $3'_1,3'_2 = 14$.



	1	**2**	**3**	**4**
R′	iVal	Mesen*	Mesen	Mesen
R″	Ac	Ac	H	Ac
R‴	H	H	OMebu	OMebu



5 3,14-*E*
6 3,14-*Z*



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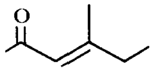
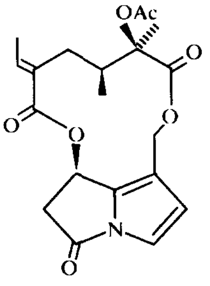
* Mesen =





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the free hydroxyl had to be placed at C-14 and the ester groups at C-1 and C-7, as the H-14 signal was shifted upfield and the H-1 double doublet was replaced by a doublet, which was coupled with a multiplet at δ 2.00. The observed couplings also established the stereochemistry at C-1 and C-7. Acetylation of **3** afforded **4**, identical with the natural acetate. Spin decoupling in C_6D_6 at 400 MHz allowed the assignment of nearly all signals, though the signals of H-4, H-5 and H-6β were still multiplets. The ^{1}H NMR data of **5** and **6** (Table 1) showed that these ketones were closely related to **3** and **4**. However, the C-14 oxygen function was missing and the presence of a 3,14-double bond was indicated by the additional olefinic signals and those of olefinic methyls. Their chemical shifts easily allowed the assignment of the stereochemistry of the double bond. Similar compounds with an additional ester group were isolated from *Senecio implexus* [5]. Again spin decoupling allowed the assignment of all signals, though again some were multiplets. The relative position of the ester group in compounds **3–6** was deduced from biogenetic considerations and from the chemical shifts of H-7α, which were nearly identical with those in the spectrum of **2**. Usually a saturated ester group would cause an upfield shift of the corresponding signal. We have given the name notonipetranone to the parent compound of **2–4** without oxygen functions at C-1, C-7 and C-14.

The compounds isolated show a close relationship of *S. kleinia* to the *Kleinia* group, which is characterized by highly oxygenated sesquiterpenes, while the typical furanoeremophilanes are missing [6].

EXPERIMENTAL

The air-dried plant material (collected near Garachico, Tenerife, voucher 80/1469) was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing their IR and ^{1}H NMR spectra with those of authentic material. The roots (150 g) afforded 20 mg **1**, 15 mg **2**, 25 mg **3**, 40 mg **4**, 3 mg **5** and 10 mg **6** (all separated with Et_2O–petrol, 1:1, several times), while the aerial parts (400 g) afforded 20 mg caryophyllene, 20 mg γ-humulene, 600 mg **7** and 150 mg **8**.

14-*Acetoxy-7β-[3'-ethyl crotonoyloxy]-notonipetranone* (**2**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750, 1255 (OAc), 1740 (CO), 1720, 1655 (C=CCO$_2$R); MS *m/z* (rel. int.): 390.241 $[M]^+$ (1) ($C_{23}H_{34}O_5$), 330 $[M - HOAc]^+$ (3), 276 $[M - RCO_2H]^+$ (3), 216 $[276 - AcOH]^+$ (18), 97 $[C_5H_9CO]^+$ (100), 69 $[97 - CO]^+$ (12).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-40 \quad -43 \quad -54 \quad -134}\ (c = 1.0,\ \text{CHCl}_3).$$

7β-[3'-Ethyl crotonoyloxy]-14-hydroxy-1α-[2'-methylbutyryloxy]-notonipetranone (**3**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3530 (OH, hydrogen-bonded), 1745 (CO$_2$R, C=O), 1715, 1640 (C=CCO$_2$R); MS *m/z* (rel. int.): 448 $[M]^+$ (0.1), 346.214 $[M - C_4H_9CO_2H]^+$ (0.5) ($C_{21}H_{30}O_4$), 328 $[M - C_5H_9CO_2H]^+$ (0.3), 232 $[346 - C_5H_9CO_2H]^+$ (7), 97 $[C_5H_9CO]^+$ (100), 85 $[C_4H_9CO]^+$ (23), 69 $[97 - CO]^+$ (30), 57 $[85 - CO]^+$ (93).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{-72 \quad -77 \quad -91 \quad -215}\ (c = 2.5,\ \text{CHCl}_3).$$

14-*Acetoxy-7β-[3'-ethyl crotonoyloxy]-1α-[2'-methylbutyryloxy]-notonipetranone* (**4**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1255 (OAc), 1745 (CO$_2$R, C=O), 1720, 1660 (C=CCO$_2$R); MS *m/z* (rel. int.): 430 $[M - HOAc]^+$ (0.1), 388 $[M - C_4H_9CO_2H]^+$ (0.2), 376 $[M - C_5H_9CO_2H]^+$ (0.3), 328.204 $[388 - HOAc]^+$ (1) ($C_{21}H_{28}O_3$), 316 $[430 - C_5H_9CO_2H]^+$ (1), 214 $[316 - C_4H_9CO_2H]^+$ (7), 97 $[C_5H_9CO]^+$ (100), 85 $[C_4H_9CO]^+$ (11), 69 $[97 - CO]^+$ (5), 57 $[85 - CO]^+$ (42).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-124 \quad -133 \quad -159 \quad -390}\ (c = 4.0,\ \text{CHCl}_3).$$

7β-[3'-Ethyl crotonoyloxy]-1α-[2'-methylbutyryloxy]-3,14-dehydro-E-notonipetranone (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (CO$_2$R), 1725, 1660 (C=CCO, C=CCO$_2$R); MS *m/z* (rel. int.): 430 $[M]^+$ (0.2), 328.204 $[M - C_4H_9CO_2H]^+$ (2) ($C_{21}H_{28}O_3$), 316 $[M - C_5H_9CO_2H]^+$ (2), 214 $[328 - C_5H_9CO_2H]^+$ (15), 171 $[214 - {}^{\cdot}CHMe_2]^+$ (17) 97 $[C_5H_9CO]^+$ (100), 85 $[C_4H_9CO]^+$ (14), 69 $[97 - CO]^+$ (10), 57 $[85 - CO]^+$ (93).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-95 \quad -103 \quad -126 \quad -322}\ (c = 0.2,\ \text{CHCl}_3).$$

7β-[3'-Ethyl crotonoyloxy]-1α-[2'-methylbutyryloxy]-3,14-dehydro-Z-notonipetranone (**6**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (CO$_2$R), 1720, 1660 (C=CC=O, C=CCO$_2$R); MS *m/z* (rel. int.): 430 $[M]^+$ (0.2), 328.204 $[M - C_4H_9CO_2H]^+$ (2) ($C_{21}H_{28}O_3$), 316 $[M - C_5H_9CO_2H]^+$ (2), 214 $[316 - C_4H_9CO_2H]^+$ (20), 171 $[214 - {}^{\cdot}CHMe_2]^+$ (20), 97 $[C_5H_9CO]^+$ (100), 85 $[C_4H_9CO]^+$ (14), 69 $[97 - CO]^+$ (12), 57 $[85 - CO]^+$ (77).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-125 \quad -135 \quad -164 \quad -494}\ (c = 1.0,\ \text{CHCl}_3).$$

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