(hexane–C_6H_6, 9:1). IR ν_{max}^{KBr} cm^{-1}: 3480, 3420, 2920, 2855, 1740, 1465, 1170, 725, 715. ^1H NMR: δ0.85 (6H, *t*, 2Me, $J = 10$ Hz), 1.20 (82H, *br s*, 41CH_2), 1.56 (8H, *s*, 2 CH_2–CH(OH)–CH_2–), 2.23 (4H, *t*, –CH_2COCH_2–, $J = 8$ Hz), 4.0 (2H, *t*, 2CH–OH, $J = 7$ Hz). MS *m/z* (rel. int.) 762 $[M]^+$ $C_{51}H_{102}O_3$ (12), 734 (86), 726 (20), 719 (12), 705 (71), 691 (9), 677 (50), 675 (4), 661 (5), 649 (21), 535 (3), 505 (2), 370 (12), 342 (26), 314 (12), 285 (9), 257 (38), 227 (2), 138 (10), 124 (13), 110 (26), 101 (4), 95 (42), 87 (39), 86 (30), 85 (48), 71 (9), 67 (62), 58 (20), 57 (100), 43 (67).

Acetylation of compound **1**. Compound **1** (15 mg) was dissolved in pyridine and Ac_2O (1 ml each) and warmed slightly. On usual work-up it afforded a solid diacetate derivative (4 mg). Mp 65°. TLC (silica gel G) R_f 0.82 (hexane–C_6H_6, 9:1). MS *m/z* (rel. int.): 846 $[M]^+$ $C_{55}H_{106}O_5$ (2), 818 (6), 789 (36), 775 (20), 726 (45), 724 (78), 717 (25), 703 (65), 591 (4), 577 (7), 505 (10), 355 (11), 341 (10), 269 (9), 255 (16), 143 (25), 129 (60), 86 (65), 71 (60), 61 (60), 60 (50), 58 (50), 57 (100), 43 (86).

Compound **2**. Frs 10–30 of the hexane–C_6H_6 (3:1) eluate yielded a residue (MeOH) (155 mg). Mp 85–86°. TLC (silica gel G) R_f 0.25 (hexane–C_6H_6, 1:1). IR ν_{max}^{KBr} cm^{-1}: 3500, 2920, 2860, 1470, 1265, 1100, 800, 730, 720. ^1H NMR: δ0.9 (3H, *t*, 1Me, $J = 9$ Hz), 1.2 (60H, *br s*, 30 CH_2), 1.50 (2H, *s*, CH_2–CH_2OH), 1.8 (1H, *m*, CH_2–OH), 3.46 (2H, *t*, CH_2–OH, $J = 7$ Hz). MS *m/z* (rel. int.) 480 $[M]^+$ $C_{33}H_{68}O$ (2), 449 (24), 435 (4), 423 (5), 421 (12), 409 (2), 407 (3), 395 (2), 393 (4), 367 (2), 113 (7), 99 (2), 85 (48), 73 (2), 71 (57), 59 (3), 57 (100).

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FUROEREMOPHILANES AND RELATED COMPOUNDS FROM *SENECIO PACHYPHYLLOS*

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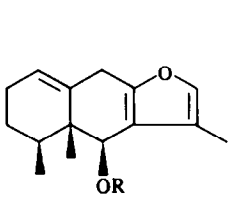
Key Word Index—*Senecio pachyphyllos*; Compositae; sesquiterpenes; furoeremophilanes, oxygenated furoeremophilanes.

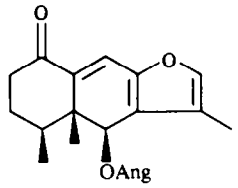
Abstract—In addition to known compounds, a new furoeremophilane and two pairs of epimeric acetals with an eremophilane skeleton have been isolated from *Senecio pachyphyllos*. The structures were elucidated by high field ^1H NMR techniques.

Senecio pachyphyllos Remy, native in Chile, has not previously been studied chemically. From the aerial parts, we obtained germacrene D, *p*-hydroxyacetophenone, the furoeremophilanes **1** [1], **2** [2], **3**, **4** [3], **5** [4] and **6** [5], the *seco* compound **7** [5] and two epimeric pairs of acetals (**8**–**11**).

The structure of **3** followed from its ^1H NMR spectrum (Experimental). It differed from that of **4** only by the



1 R = Ac
2 R = Meacr



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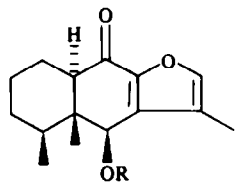
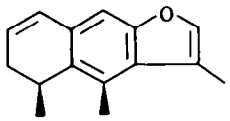


3 R = Prop
4 R = *i*Bu



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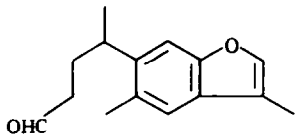

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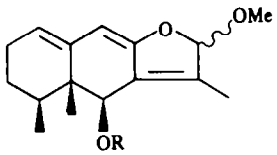

	8	**9**	**10**	**11**
R	*i*Bu	*i*Bu	Prop	Prop
12	αH	βH	αH	βH

signals of the ester part. Due to the neighbouring chiral centre the signal of the methylene group of the propionate was split.

The spectra of the epimers **8** and **9** (Table 1) differed slightly. Only one epimer could be obtained in pure form. The assignment of the stereochemistry at the acetal carbon was not possible. However, the signal could be assigned as the concentrations of the epimers was different.

The ^{1}H NMR spectrum of the mixture of **10** and **11** (Table 1) showed that the corresponding epimeric propionates were present. Again several signals differed in the spectra of the epimers. As the plant material was extracted with a mixture containing methanol, compounds **8–11** may be artifacts. It is, however, interesting to note that the isolated compounds are similar to those from South African *Senecio* species [6].

Table 1. ^{1}H NMR spectral data of compounds **8–11** (400 MHz, $CDCl_3$, δ-values)

H	**8**	**9**	**10**	**11**
1	5.52 *br t*		5.52 *br t*	
6	5.74 *br s*	5.79 *br s*	5.75 *br s*	5.79 *br s*
9	5.84 *dq*	5.89 *dq*	5.85 *dq*	5.90 *dq*
12	5.33 *br s*	5.35 *br s*	5.33 *br s*	5.35 *br s*
13	1.71 *br s*	1.73 *br s*	1.71 *br s*	1.72 *br s*
14	0.96 *d*	0.95 *d*	0.95 *d*	0.94 *d*
15	1.10 *s*	1.04 *s*	1.10 *s*	1.03 *s*
OCOR	2.68 *qq*	2.67 *qq*	2.40 *q*	
	1.26 *d*	1.25 *d*	1.21 *t*	
OMe	3.39 *s*	3.29 *s*	3.38 *s*	3.29 *s*

J[Hz]: 1, 2 = 1, 2′ = 4; 1, 9 = 9, 13 = 1.5; 4, 14 = 7; O*i*Bu: 2, 3 = 2, 4 = 7; OProp: 2, 3 = 7.5.

EXPERIMENTAL

The air-dried plant material (600 g, voucher Niemeyer 8928, deposited in the Herbarium of the University of Chile, collected in February 1989 in Region del Maule, Chile) was extracted and the extract worked-up as reported previously [7]. CC and repeated TLC finally gave 50 mg germacrene D, 40 mg *p*-hydroxyacetophenone, 10 mg **1**, 3 mg **2**, 5 mg **3** (HPLC: MeOH–H_2O, 4:1), 2 mg **4**, 5 mg **5**, 3 mg **6**, 5 mg **7**, 15 mg of a mixture which on repeated TLC afforded 5 mg **8** or **9** and 10 mg **8/9** (petrol–Et_2O, 1:10) and 7 mg **10/11** (petrol–Et_2O, 1:10). Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

6β-Propionyloxy-10αH-furoeremophil-9-one (**3**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (CO_2R), 1700 (C=O); MS *m/z* (rel. int.): 304.168 $[M]^+$ (3) (calc. for $C_{18}H_{24}O_4$: 304.168), 248 $[M-O=C=CHMe]^+$ (75), 230 $[M-RCO_2H]^+$ (24), 57 $[RCO]^+$ (100); ^{1}H NMR (400 MHz, $CDCl_3$): δ6.36 (*s*, H-6), 2.37 (*dd*, H-10, *J* = 3.5, 12 Hz), 7.33 (*q*, H-12, *J* = 1 Hz), 1.88 (*d*, H-13, *J* = 1 Hz), 0.87 (*d*, H-14, *J* = 7 Hz), 0.91 (*s*, H-15); OCOR 2.45 (*dq*, CH_2), 1.21 (*t*, Me).

6β-Isobutyryloxy-12α- and 12-β-methoxy respectively-8,12-epoxyeremophila-1(10),7(11),8-triene (**8** and **9**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R); MS *m/z* (rel. int.): 332.199 $[M]^+$ (9) (calc. for $C_{20}H_{28}O_4$: 332.199), 317 $[M-Me]^+$ (7), 244 $[M-RCO_2H]^+$ (10), 229 $[244-Me]^+$ (28), 71 $[RCO]^+$ (100).

6β-Propionyloxy-12α- and 12β-methoxy respectively-8,12-epoxyeremophila-1(10),7(11)8-triene (**10** and **11**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R); MS *m/z* (rel. int.): 318.184 $[M]^+$ (4) (calc. for $C_{19}H_{26}O_4$: 318.183), 244 $[M-RCO_2H]^+$ (17), 229 $[244-Me]^+$ (20), 57 $[RCO]^+$ (100).

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DENNSTOSIDE A, AN ANALOGUE OF PTAQUILOSIDE, FROM *DENNSTAEDTIA SCABRA*

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Key Word Index—*Dennstaedtia scabra*; Pteridaceae; illudane-type sesquiterpene glycoside; dennstoside A.

Abstract—A new illudane-type sesquiterpene glycoside, named dennstoside A, was isolated from *Dennstaedtia scabra* and characterized as an analogue of ptaquiloside, the carcinogenic principle of *Pteridium aquilinum*, on the basis of spectral analyses and chemical conversion to pterosin A.

INTRODUCTION

Ptaquiloside (aquilide A) (**1**) is a carcinogen and bovine bracken poison which has been isolated from bracken fern (*Pteridium aquilinum*), and characterized as a novel glycoside of a *nor*-illudane-type sesquiterpene [1–3]. Using biological and chemical methods for the assay of ptaquiloside (**1**) and related compounds, *ca* 30 species of the Pteridaceae have been examined and the widespread occurrence of such compounds revealed [4, 5]. In a previous paper [6], we have reported the isolation of ptaquiloside (**1**) from *Pteris cretica* and *Histiopteris incisa*, as well as the isolation and the structure determination of several analogues, hypolosides A (**2**), B (**3**) and C (**4**) from *Hypolepis punctata*, and B and C from *Dennstaedtia hirsta*. We now report the isolation and characterization of a further ptaquiloside analogue from *Dennstaedtia scabra*.

RESULTS AND DISCUSSION

In the course of chemotaxonomical work on the Pteridaceae by Murakami's group [7], the indan-1-one-type sesquiterpenes (2*S*)-pterosin A (**5**), (2*S*)-4-hydroxypterosin A (onitisin) and pterosin V were isolated and pterosins K and F were detected by GC-MS from the terrestial part of *Dennstaedtia scabra*. The application of our screening test to this fern [5] suggested the presence of a ptaquiloside-like substance. This compound, named dennstoside A (**6**), was isolated by a modification of the method used for hypolosides [6], using TLC [5] for monitoring. The molecular formula of **6** was established as $C_{23}H_{34}O_{10}$, having one more oxygen atom than hypoloside A (**2**), by the examination of FAB-MS and other spectral data. The ^1H and ^{13}C NMR signals (Tables 1 and 2) of dennstoside A (**6**) were nearly the same as those of hypoloside A (**2**) except for those due to C-2, C-3, C-10a and C-10b. The presence of a hydroxymethyl group instead of the methyl group at C-10 was clearly demonstrated by DEPT experiments. These facts showed that one of the methyl groups at C-10 of **2** is replaced by a hydroxymethyl group. On treatment with acid, alkali, heat or on standing at room temperature, dennstoside A (**6**) gave pterosin A (**5**), an indan-1-one [8], as in the case of the formation of pterosin B (**7**) from ptaquiloside (**1**) [2, 3] and pterosin Z (**8**) from hypolosides (**2**–**4**) [6]. Thus, the plane structure of **6** was established.

The absolute configuration of (−)-pterosin A (**5**) has been established as 2*S* [8]. The optical rotation of pterosin A (**5**) ($[\alpha]_D^{20}-36.9°$) obtained from **6** clearly showed 2*S*-configuration. Among the two methylene protons at C-3 (δ1.85 and 2.67), NOE was observed between the higher field proton and the C-10b methyl and