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OPLOPANE DERIVATIVES FROM *ACRISIONE DENTICULATA**

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Key Word Index—*Acrisione denticulata*; Compositae; sesquiterpenes; oplopane derivatives; diterpenes; furolabdane.

Abstract—A new furolabdane and 11 new oplopane derivatives have been isolated from the extract of aerial parts of *Acrisione denticulata* (= *Senecio yegua*) in addition to known compounds. The structures were established by high field ^{1}H NMR spectroscopy. The chemistry supports the placement of this newly described genus near the cacaloid genera *Rugelia* and *Arnoglossum* in the subtribe Tussilagininae.

INTRODUCTION

The small new genus *Acrisione* [1] comprises two species from Central Chile, both formerly placed in the large very heterogeneous genus *Senecio*. The genus *Acrisione* morphologically belongs to the cacaloid complex in the tribe, i.e. subtribe Tussilagininae. As the chemistry of several other representatives of this complex has been studied we have investigated *A. denticulata* (H. et A.) B. Nord. to see whether relationships are visible.

RESULTS AND DISCUSSION

The extracts of the aerial parts from plants collected in different locations in Chile were shown to be identical by comparative TLC and therefore were worked-up together. After the usual separation techniques germacrene D, eremophilene, fukinone, phytol and (−)-manoyl oxide [2] were identified by comparing the spectral data with those of authentic samples. Furthermore, the furolabdane **1** and the oplopane derivatives **2**–**7** and **9**–**13** were obtained.

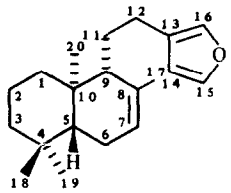
The ^{1}H NMR spectrum (Experimental) of compound **1** clearly showed that a β-substituted furan was present. The other signals were close to those of 17-hydroxyisopolyalthin where only the olefinic methyl signal is replaced by a hydroxy methylene group [3]. As (−)-manoyloxide was present the furan derivative **1** was probably an *ent*-labdane.

The structure of **2** followed from its ^{1}H NMR spectrum (Table 1) which was similar to that of sesquiterpenes from *Arnoglossum atriplicifolium* and related species [4–12]. Spin decoupling indicated that oxygen functions were at C-2, C-6, C-7 and C-14. As in other 14-acetoxyoplopanones in the mass spectrum a favoured elimination of acetic acid was observed. Accordingly, the angelate residue was at C-7. In agreement with this assumption the corresponding chemical shifts (H-7 and H-14) were nearly identical with those of other diesters with an unsaturated ester group at C-7 and an acetate group at C-14. The presence of a 6-hydroxy group followed from the decoupling experiments and the stereochemistry was deduced from the observed couplings and comparison of the values with those of 6-*epi*-derivatives [4].

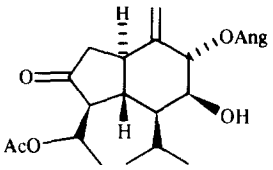
The ^{1}H NMR spectrum of **3** (Table 1) indicated that the keto group was replaced by an acetoxy group and that a 3(14)-double bond was present as followed from the results of spin decoupling. The configuration at C-2 was deduced from the observed couplings which differed from those of a similar **2**-angeloyloxy derivative [4]. Inspection of a model nicely agreed with these assignments. The ^{1}H NMR spectrum of **4** (Table 1) showed that the isomeric 6β-angeloyl derivative was present while that of **5** (Table 1) indicated that it was the 7α-[4-methylsenecioate]. Accordingly, all signals of the latter, except those of the ester group, were nearly identical with those of **3**.

The ^{1}H NMR data of **6** (Table 1) showed that this compound only differed from **3**–**5** by the absence of an ester group at C-6 or C-7. The observed couplings indicated identical configurations of the hydroxy groups at C-6 and C-7.

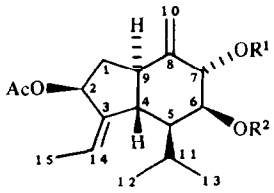
The ^{1}H NMR spectrum of **7** (Table 1) was similar to that of a ketone isolated from *Kleinia neriifolia* (syn. *Senecio kleinia*) [7]. However, a pair of double doublets at δ2.50 and 2.21 obviously were due to a methylene group with a neighbouring keto group. Accordingly, no ester group was at C-1. Identical substitution at C-6 and C-7, as in compound **5**, followed from the corresponding signals and the nature of the ester group was deduced from the typical signals of a 4-methyl senecioate. The configuration of the 3(14)-double bond followed from the chemical shift of H-14 (δ5.98) which differed characteristically from the shift in the corresponding *E*-isomers (see compounds **12** and **13**). Acetylation of **7** gave the acetate **8** its ^{1}H NMR spectrum further supported the structure of the natural compound **7**.



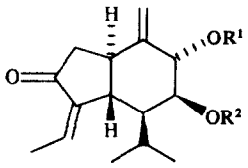
1



2



	3	**4**	**5**	**6**
R^1	Ang	H	Mesen	H
R^2	H	Ang	H	H



	7	**8**	**9**	**10**	**11**	**12**	**13**
R^1	Mesen	Mesen	Sen	Ang	H	Ang	H
R^2	H	Ac	H	H	Ang	H	Ang
						$\Delta^{3(14)}$	*E*

Inspection of the ^{1}H NMR spectrum (Table 1) of the ketones **9** and **10** indicated that also the 7α-senecioyloxy and angeloyloxy derivatives were present. The spectrum of **11** (Table 1) showed that this compound was the 6β-angeloyloxy isomer of **10**. Accordingly, the H-6 signal was shifted more downfield (δ 5.18 *dd*).

The ^{1}H NMR spectra of **12** and **13** (Table 1) clearly showed that we were dealing with the 3(14) *E*-isomers of **10** and **11**. Accordingly, the H-14 signal are shifted downfield (δ 6.60 *dq*). For the corresponding hydrocarbon we propose the name oplopane.

In all cases the signals were assigned by spin

Table 1. ^{1}H NMR spectral data of compounds

H	**2**	**3***	**4**	**5**	**6**	**7**
1α	2.44 *m*	1.44 *ddd*	1.46 *ddd*	1.44 *ddd*	1.42 *ddd*	2.50 *dd*
1β	2.13 *dd*	2.60 *ddd*	2.66 *ddd*	2.60 *ddd*	2.58 *ddd*	2.18 *dd*
2	—	5.69 *br t*	5.70 *br t*	5.69 *br t*	5.69 *br t*	—
3	2.44 *m*	—	—	—	—	—
4	1.46 *q*	2.00 *m*	2.05 *m*	2.01 *m*	1.93 *m*	2.17 *m*
5	1.91 *m*	1.80 *ddd*	1.93 *m*	1.81 *ddd*	1.85 *m*	1.92 *m*
6	3.87 *br d*	3.87 *dd*	5.11 *dd*	3.85 *br s*	3.75 *dd*	3.91 *dd*
7	5.61 *d*	5.54 *d*	4.41 *br s*	5.47 *br d*	4.24 *d*	5.53 *br d*
9	2.58 *br ddd*	2.18 *m*	2.16 *m*	2.19 *m*	2.21 *m*	2.73 *br ddd*
10	5.23 *br s*	5.12 *br s*	5.18 *br s*	5.11 *br s*	5.07 *br s*	5.15 *br s*
10'	4.91 *br s*	4.90 *br s*	4.88 *br s*	4.89 *br s*	4.81 *br s*	4.91 *br s*
11	2.27 *dqq*	2.18 *m*	2.16 *m*	2.19 *m*	2.21 *m*	2.06 *m*
12	0.98 *d*	0.99 *d*	0.91 *d*	0.98 *d*	0.95 *d*	0.99 *d*
13	1.21 *d*	1.16 *d*	1.14 *d*	1.17 *d*	1.18 *d*	1.16 *d*
14	5.07 *dq*	5.54 *m*	5.51 *br q*	5.54 *br q*	5.54 *tq*	5.98 *dq*
15	1.23 *d*	1.66 *dd*	1.66 *dd*	1.66 *dd*	1.66 *dd*	2.11 *dd*
OAc	2.09 *s*	2.06 *s*	2.07 *s*	2.06 *s*	2.06 *s*	
OCOR	6.15 *qq*	6.12 *qq*	6.12 *qq*	5.73 *tq*	—	5.74 *tq*
	2.02 *dq*	2.01 *dq*	2.01 *dq*	2.19 *br q*	—	2.20 *br q*
	1.92 *dq*	1.91 *dq*	1.90 *dq*	1.08 *t*	—	1.08 *t*
				2.18 *br s*		2.19 *br s*

*$CDCl_3/C_6D_6$ H-7 5.47 *d*, H-14 5.44 *tq*.

J [Hz]: 5,11 = 2; 11,12 = 11,13 = 7; compound **2**: 1α,1β = 16.5; 1α,9 ~ 8; 1β,9 = 13; = 12; 1β,2 = 8; 1β,9 = 6; 3,14 = 4,14 = 2; 4,5 = 10; 5,6 = 7; 6,7 = 3; compounds **7**–**13**: **12** and **13**: 5,6 = 6,7 = 3; 5,11 = 1.5; 7,10 = 9,10 ~ 1.7).

decoupling and the observed couplings indicated that the stereochemistry at C-4 to C-7 and C-9 was always the same. The absolute configuration is not settled, the proposed one is that of oplopanone [13]. Some flavones were reported [14, 15] previously from this species (under the old name *S. yegua*).

The isolation of oplopane derivatives from a *Acrisione* species agrees with the morphological features and these compounds are also present in *Rugelia* [12] and *Arnoglossum* [4]. Both of these genera also belong to the cacaloid complex, or subtribe Tussilagininae. The systematic position of *Acrisione* in this subtribe is now well established. However, this type of sesquiterpene has been reported also from *Kleinia* (incl. *Notonia*) [8–10] and two *Senecio* species [5, 11], and also from one species of *Tephroseris* [6]. In the latter cases the typical furoeremophilanes are missing.

Oplopane derivatives, although rare, are thus found in three different subtribes of the Senecioneae, viz. Tussilagininae, Senecioninae and Tephroseridinae. Further information is necessary to establish the value of these compounds as chemotaxonomic markers.

EXPERIMENTAL

The air-dried plant material (1.8 kg, collected in different places in Chile from November 1981 to May 1982; vouchers E. Bayer 200, 237, 337, 478, 973, deposited in the Herbaria of the Institute of Systematic Botany, Munich, and the Swedish Museum of Natural History, Stockholm, Sweden) was extracted with Et_2O–MeOH–petrol (1:1:1) and the extract obtained was worked-up and separated as reported previously [16]. The CC fractions were combined to three fractions (Fr. 1: petrol–Et_2O–petrol, 1:3; Fr. 2: Et_2O–petrol, 1:1, and Fr. 3: Et_2O and Et_2O–MeOH, 9:1). TLC (silica gel, PF 254, Et_2O–Petrol, 49:1) of fr. 1 gave 4 mg eremophilene, 3 mg germacrene D and 8 mg phytol. TLC of fr. 2 (Et_2O–petrol, 1:9) yielded 4 mg **1**, 12 mg (−)-manoyloxide and 8 mg fukinone. HPLC (MeOH − H_2O, 7:3, RP8, *ca* 100 bar) of one-sixth of fr. 3 gave six fractions (3/1–3/6). TLC of fr. 3/1 (Et_2O–petrol, 2:3) gave 10 mg **2** (R_f 0.5) and 1.5 mg **6** (R_f 0.33). TLC of fr. 3/2 (Et_2O–petrol, 2:3) afforded 19 mg **10** (R_f 0.7), 6 mg **9** (R_f 0.6), 4 mg **13** (R_f 0.4) and a mixture which gave by TLC (Et_2O–petrol–CH_2Cl_2, 1:2:1) 2 mg **12** (R_f 0.6) and 4.5 mg **11** (R_f 0.5). TLC of fr. 3/3 (Et_2O–petrol, 2:3) yielded 8 mg **12** (R_f 0.5) and of fr. 3/4 (Et_2O–petrol, 1:1) 6 mg **7** (R_f 0.7). TLC of fr. 3/5 (Et_2O–petrol, 3:7) gave 15.5 mg **3** (R_f 0.75) and of fr. 3/6 (Et_2O–petrol, 2:3) 5 mg **5** (R_f 0.75) and 2 mg **4** (R_f 0.5).

15,16-*Epoxy*-ent-*labda*-7,13(16),14-*triene* (**1**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1600 (C=C), 875 (furan); MS *m/z* (rel. int): 286.230 $[M]^+$ (8) (calc. for $C_{20}H_{30}O$: 286.230), 205 $[C_{15}H_{25}]^+$ (43), 204 $[C_{15}H_{24}]^+$ (52), 109 $[C_8H_{13}]^+$ (61), 82 $[C_5H_6O]^+$ (96), 81 $[C_5H_5O]^+$ (100); $[\alpha]_D^{24°}$ +3.2° ($CHCl_3$; *c* 0.74); ^1H NMR ($CDCl_3$, 400 MHz): 5.43 (*br s*, H-7), 6.29 (*br s*, H-14), 7.36 (*t*, H-15, *J* = 1.5 Hz), 7.24 (*br s*, H-16), 1.75 (*br s*, H-17), 0.89, 0.87, 0.77 (*s*, H-18, 19, 20).

14-*Acetoxy*-7α-*angeloyloxy*-6β-*hydroxyoplopan*-8(10)-*en*-2-*one* (**2**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1745 (OAc), 1710 (C=CCO_2R); MS *m/z* (rel. int.): 392 $[M]^+$ (0.3), 332.199 $[M-HOAc]^+$ (1.5) (calc. for $C_{20}H_{28}O_4$: 332.199), 314 $[332-H_2O]^+$ (1.5), 232 $[332-RCO_2H]^+$ (12), 83 $[RCO]^+$ (100); $[\alpha]_D^{24°}$ +8° ($CHCl_3$; *c* 0.76).

2β-*Acetoxy*-7α-*angeloyloxy*-6β-*hydroxyoplopa*-3(14)Z,8(10)-*diene* (**3**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1730 (OAc, C=CCO_2R); MS *m/z* (rel. int.): 376 $[M]^+$ (1), 316.204 $[M-HOAc]^+$ (2.5) (calc. for $C_{20}H_{28}O_3$: 316.204), 298 $[316-H_2O]^+$ (4), 216 $[316-RCO_2H]^+$ (18), 83 $[RCO]^+$ (100); $[\alpha]_D^{24°}$ +27° ($CHCl_3$; *c* 0.69).

2–13 ($CDCl_3$, 400 MHz, δ-values)

8	9	10	11	12	13
2.54 *dd*	2.51 *dd*	2.51 *dd*	2.57 *dd*	2.58 *dd*	2.62 *dd*
2.20 *dd*	2.19 *dd*	2.19 *dd*	2.21 *dd*	2.18 *dd*	2.20 *dd*
—	—	—	—	—	—
—	—	—	—	—	—
2.20 *m*	2.15 *m*	2.15 *m*	2.20 *m*	2.33 *ddd*	2.15 *m*
1.95 *m*	1.90 *m*	1.90 *ddd*	2.00 *m*	2.24 *ddd*	2.15 *m*
5.12*dd*	3.92 *dd*	3.94 *dd*	5.18 *dd*	4.00 *t*	5.36 *t*
5.69 *br s*	5.53 *br d*	5.60 *br d*	4.46 *br d*	5.67 *br s*	4.47 *br s*
2.75 *br ddd*	2.72 *br ddd*	2.71 *br ddd*	2.81 *br ddd*	2.91 *br ddd*	2.87 *m*
5.17 *br s*	5.16 *br s*	5.18 *br s*	5.29 *br s*	5.19 *br t*	5.23 *br s*
4.91 *br s*	4.92 *br s*	4.93 *br s*	4.92 *br s*	5.01 *br t*	4.99 *br s*
2.10 *m*	2.10 *m*	2.07 *m*	2.05 *m*	2.11 *dq*	2.11 *m*
0.96 *d*	0.99 *d*	1.00 *d*	0.96 *d*	1.05 *d*	1.00 *d*
1.12 *d*	1.16 *d*	1.16 *d*	1.16 *d*	1.18 *d*	1.21 *d*
5.97 *dq*	5.98 *dq*	5.98 *dq*	5.95 *dq*	6.60 *dq*	6.60 *dq*
2.13 *dd*	2.12 *dd*	2.21 *dd*	2.11 *dd*	1.90 *dd*	1.87 *dd*
2.04 *s*	—	—	—	—	—
5.69 *br s*	5.77 *qq*	6.15 *qq*	6.13 *qq*	6.18 *qq*	6.13 *qq*
2.19 *br q*	2.20 *d*	2.02 *dq*	2.00 *dq*	2.04 *dq*	2.00 *dq*
1.08 *t*	1.93 *d*	1.94 *dq*	1.89 *dq*	1.96 *dq*	1.88 *dq*
2.17 *d*					

3,4 = 4,5 = 4,9 = 11; 5,6 = 8; 6,7 = 3; compounds **3**–**6**: 1α,1β = 13; 1α,2 = 6; 1α,9 1α,1β = 17; 1α,9 = 6.5; 1β,9 = 4,9 = 12; 4,14 = 2.5; 5,6 = 5.5; 6,7 = 3; (compounds

2β-Acetoxy-6β-angeloyloxy-7α-hydroxyoplopa-3(14)Z,8(10)-*diene* **(4)**. Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1725 (OAc, $C=CCO_2R$); MS *m/z* (rel. int.): 376.225 $[M]^+$ (0.7) (calc. for $C_{22}H_{32}O_5$: 376.225), 316 $[M-HOAc]^+$ (1), 276 $[M-RCO_2H]^+$ (4), 216 $[276-HOAc]^+$ (22), 83 $[RCO]^+$ (100).

2β-Acetoxy-6β-hydroxy-7α-[4-methyl senecioyloxy]-oplopa-3(14)Z,8(10)-*diene* **(5)**. Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1725 (OAc, $C=CCO_2R$); MS *m/z* (rel. int.): 390 $[M]^+$ (0.2), 330 $[M-HOAc]^+$ (0.7), 312 $[330-H_2O]^+$ (2.5), 276 $[M-RCO_2H]^+$ (1.5), 216 $[276-HOAc]^+$ (21), 97 $[RCO]^+$ (100); $[\alpha]_D^{24}$ +20° ($CHCl_3$; *c* 0.49).

2β-Acetoxy-6β,7α-dihydroxyoplopa-3(14)Z,8(10)-*diene* **(6)**. Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3530 (OH), 1725 (OAc); MS *m/z* (rel. int.): 294 $[M]^+$ (1.5), 234.162 $[M-HOAc]^+$ (10) (calc. for $C_{15}H_{22}O_2$: 234.162), 216 $[234-H_2O]^+$ (34), 173 $[216-CHMe_2]^+$ (100).

6β-Hydroxy-7α-[4-methylsenecioyloxy]-oplopa-3(14)Z,8(10)-*dien*-2-*one* **(7)**. Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520 (OH), 1720, 1645 ($C=CCO_2R$, C=CC=O); MS *m/z* (rel. int.): 346.214 $[M]^+$ (2) (calc. for $C_{21}H_{30}O_4$: 346.214), 232 $[346-RCO_2H]^+$ (14), 97 $[RCO]^+$ (100); $[\alpha]_D^{24}$ −104° ($CHCl_3$; *c* 0.1). To 3 mg **7** in 1 ml $CHCl_3$ 10 mg DMAP and 50 mg Ac_2O were added. After 1 hr refluxing 3 mg **8** was obtained (^1H NMR see Table 1).

6β-Hydroxy-7α-senecioyloxy oplopa-3(14)Z,8(10)-*dien*-2-*one* **(9)**. Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1705, 1640 ($C=CCO_2R$, C=CC=O); MS *m/z* (rel. int.): 332.199 $[M]^+$ (1) (calc. for $C_{20}H_{28}O_4$: 332.199), 232 $[M-RCO_2H]^+$ (8), 214 $[232-H_2O]^+$ (3), 83 $[RCO]^+$ (100).

7α-Angeloyloxy-6β-hydroxyoplopa-3(14)Z,8(10)-*dien*-2-*one* **(10)**. Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1715, 1630 ($C=CCO_2R$, C=CC=O); MS *m/z* (rel. int.): 332.199 $[M]^+$ (8) (calc. for $C_{20}H_{28}O_4$: 332.199), 314 $[M-H_2O]^+$ (5), 232 $[M-RCO_2H]^+$ (26), 83 $[RCO]^+$ (100); $[\alpha]_D^{24}$ −129° ($CHCl_3$; *c* 1.94).

6β-Angeloyloxy-7α-hydroxyoplopa-3(14)Z,8(10)-*dien*-2-*one* **(11)**. Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520 (OH), 1715, 1645 ($C=CCO_2R$, C=CC=O); MS *m/z* (rel. int.): 332.199 $[M]^+$ (1) (calc. for $C_{20}H_{28}O_4$: 332.199), 232 $[M-RCO_2H]^+$ (22), 83 $[RCO]^+$ (100).

7α-Angeloyloxy-6β-hydroxyoplopa-3(14)E,8(10)-*dien*-2-*one* **(12)**. Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1710, 1650 ($C=CCO_2R$, C=CC=O); MS *m/z* (rel. int.): 332.199 $[M]^+$ (1.5) (calc. for $C_{20}H_{28}O_4$: 332.199), 314 $[M-H_2O]^+$ (1), 232 $[M-RCO_2H]^+$ (12), 214 $[232-H_2O]^+$ (11), 83 $[RCO]^+$ (100); $[\alpha]_D^{24}$ −62° ($CHCl_3$; *c* 0.8).

6β-Angeloyloxy-7α-hydroxyoplopa-3(14)E,8(10)-*dien*-2-*one* **(13)**. Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1710 ($C=CCO_2R$, C=CC=O); MS *m/z* (rel. int.): 332.199 $[M]^+$ (1.5) (calc. for $C_{20}H_{28}O_4$: 332.199), 232 $[M-RCO_2H]^+$ (19), 83 $[RCO]^+$ (100).

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