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EREMOPHILANE, GERMACRANE AND SHIKIMIC ACID DERIVATIVES FROM CHILEAN *SENECIO* SPECIES

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Key Word Index—*Senecio* spp.; Compositae; sesquiterpenes; eremophilanes, furoeremophilanes; eremophilanolides; germacranes, cadinanes; eudesmanes; oplopanones; shikimic acid derivatives.

Abstract—From 11 Chilean *Senecio* species eight new furoeremophilanes and eremophilanolides, eight eremophilane, one cadinane, five germacrane, one oplopanone and five shikimic acid derivatives were isolated in addition to known compounds. The structures were elucidated by high field NMR techniques and the chemotaxonomic aspects are discussed briefly.

INTRODUCTION

Very little is known about the chemistry of Chilean *Senecio* species. As a continuation of our studies of this and related genera we have investigated 11 species from this region.

RESULTS AND DISCUSSION

The extract of the aerial parts of *S. algens* Wedd. afforded axerophthene and the furoeremophilanes **1a** [1], **2a** [2], **2b** [3], **2d** [1] and **2e** [2], while that of *S. behnii* Ric. et Martic gave 3-senecioyl-*p*-hydroxyacetophenone [4], 2,2-dimethyl-6,7-dimethoxychromene [5] and the furoeremophilanes **1b** [6], **c** [7], **d** [8], **e** [8], **f** [7], **2d** [1], **f** [7], **g** [1], **h** [9] and **3c** [10]. The aerial parts of *S. candollii* Wedd. gave in addition to eremophilene [8], the furoeremophilanes **2f** [7], **h** [9], **i** [1], **l** [2], **m** [1] and **k**. The structure of the latter followed from its ^{1}H NMR spectrum (Table 1) which was similar to that of **2l**. The nature of the changed ester group followed from the typical ^{1}H NMR signals. As in similar cases the H-6 signal was shifted slightly upfield.

The aerial parts of *S. dryophyllus* Meyen et Walp. gave *E*- and *Z*-biformene, viridiflorene, α-zingibirene, curcumene, spathulenol, sitosterol and the furoeremophilanes **1b** [6], **c** [8], **d** [8], **2d** [1], **f** [7], **g** [1], **h** [9], **i** [1], **3a** [11] and **b**. The structure of the latter followed from its ^{1}H NMR spectrum (Table 1). It differed typically from that of **3c** [10]. Due to the shielding effect of the furan ring one of the angelate methyls is shifted a long way upfield (δ1.54). Similarly in the isomer **3c** the acetate methyl is shifted upfield.

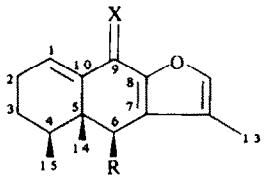
In addition to 5,3′,4′-trihydroxy-3,7-dimethoxyflavone and its 3′-methyl ether the furoeremophilanes **2c** [12] and **6** [6] and the eremophilanolides **5a** [6], **b** [6] and **c** were isolated from the aerial parts of *S. cachinalensis* Phil. The structure of compound **5c** was deduced from its ^{1}H NMR spectrum (Table 2) which was close to that of **5b**. Thus, the methoxy group at C-8 has the same configuration.

Several flavones have been isolated [13] from *S. glaber* Less. We obtained the carbinol **1a** as the main compound [1]. Furthermore, the oxygenated derivatives **4a**, **b** [14], **4c–e** were present. The molecular formula of **4c–e** were identical ($C_{15}H_{20}O_3$) indicating the presence of isomeric compounds. The ^{1}H NMR spectra (Table 2) showed that the lactones **4c** and **d** only differ in the stereochemistry at C-8. In the case of **4d** H-8 was deshielded by the 6β-hydroxy group. Accordingly, the chemical shifts of H-8 differed remarkably (δ5.22 and 4.66). The ^{1}H NMR spectrum of **4e** differed from those of **4c** and **d** (Table 2). While obviously H-8 was absent, a methyl doublet at δ1.38 replaced the olefinic methyl signal. Spin decoupling indicated that a 7,8-double bond must be present. Thus H-11 showed homoallylic couplings with H-9. Furthermore, the chemical shifts of H-9 (δ3.14 and 2.71) required two neighbouring sp^2 carbons. The configuration at C-11 followed from the observed NOE between H-6 and H-13 (6%).

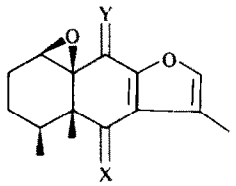
Senecio nutans Sch. Bip. only gave γ- and δ-cadinene as well as 3-prenyl-*p*-hydroxyacetophenone [15].

Senecio almeydae Phil. afforded senkirkin [16], neopetasitenin [17], the eremophilanolides **5b** [6] and **5d** as well as the eremophilanes **7a**, **b–e** [2], **f** [18], **g–i**. The structure of **5d** can be easily deduced from its ^{1}H NMR spectrum (Table 2) which differed from that of **5b** only by the signals of the ester residue. The structure of **7a** followed from its ^{1}H NMR spectrum (Table 3). Spin decoupling allowed the assignment of all signals and the stereochemistry was deduced from the couplings and from the observed NOEs [H-7 with H-8 (5%) and H-9 (4%), H-14 with H-7 (6%) and H-9 (7%)]. The ^{1}H NMR data of **7b–d** were identical with those reported previously [2]. The configuration at C-7 for these compounds are corrected [19].

The structure of **7g** also followed from its ^{1}H NMR spectrum (Table 3) which was similar to that of **7b–d**. The upfield shift of H-3 indicated the presence of the corresponding diol. The stereochemistry was again determined by NOED. Clear effects were observed between H-9 and



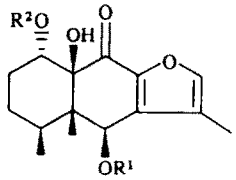
	1a	1b	1c	1d	1e	1f	1g
R	OH	OAc	OAc	O*i*Bu	OAng	O*i*Val	H
X	H_2	H_2	=O	=O	=O	=O	=O



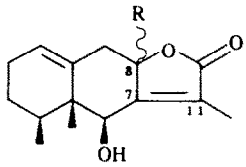
	2a	2b	2c	2d	2e	2f
X	O	H_2	H_2	βOAc,H	βOH,H	βO*i*Bu,H
Y	H_2	H_2	H_2	H_2	H_2	H_2
			1,10*epi*			

	2g	2h	2i	2k
X	βOAc,H	βO*i*Bu,H	βOAng,H	βO*i*Bu,H
Y	=O	=O	=O	βOH,H

	2l	2m
X	βOAng,H	βOAng,H
Y	βOH	H_2



	3a	3b	3c
R^1	*i*Bu	Ang	Ac
R^2	Ac	Ac	Ang



	4a	4b	4c	4d	4e
R	αOH	αOMe	αH	βH	Δ^7
					7,11 - dihydro

Table 1. ^{1}H NMR spectral data of compounds **2k** and **3b** (400 MHz, $CDCl_3$, δ-values)

H	2k	3b
1	3.24 *br d*	4.84 *br s*
2	1.70 *m*	1.70 *m*
2'		
3		2.32 *m*
4	1.46 *ddq*	1.70 *m*
6	6.33 *s*	7.05 *s*
9	4.04 *d*	—
12	7.19 *br s*	7.43 *br s*
13	1.88 *br s*	1.92 *br s*
14	1.30 *s*	1.00 *s*
15	1.06 *d*	1.18 *d*
OH	2.46 *d*	3.99 *s*
OAc	—	2.21 *s*
OCOR	2.66 *qq*	5.95 *qq*
	1.26 *d*	1.54 *dq*
	1.23 *d*	1.90 *dq*

J [Hz]: Compound **2k**: 1,2 = 4,5; 3,4 = 3.5; 3',4 = 4,15 = 7; 9,OH = 2.5; 2',3' = 2',4' = 7; compound **3b**: 4,15 = 7; 3',4' = 7; 3',5' = 4',5' = 1.5.

H-7 (5%), between H-14, H-7 (8%), H-9 (7%), H-6β (3%), H-3 (5%) and H-1β (5%), between H-15, H-6β (3%) and H-3 (3%). The ^{1}H NMR spectrum of **7h** (Table 3) indicated that an isomer of **7g** was present. The signals of the isopropenyl group were replaced by a pair of doublets at δ 1.93 and 1.80 indicating a conjugated 8-keto group. The couplings of H-3 and H-9 required identical configurations as in **7g**. This was confirmed by NOED [H-9 with H-14 (4%), H-3 with H-14 (6%) and H-15 (3%), H-15 with H-6β (4%) and H-14 with H-15 (6%), H-9 (7%), H-6β (3%) and H-1β (4%)].

The ^{1}H NMR spectrum of **7i** (Table 3) showed that this compound is also an isomer of **7g**. Spin decoupling allowed the assignment of all signals. The resulting sequences required a changed position of the keto group and the couplings of H-7, H-8 and H-10 a different stereochemistry. The couplings of H-7 showed that a normal H-7α configuration must be present while the coupling $J_{7,8}$ requires a 8α-hydroxy group. The small couplings of H-10 already indicated a *cis*-decalin derivative. This was established by the NOEs [H-14 with H-10 (5%) and H-6β (3%) and H-3 (5%)].

Senecio serratifolius (Meyen et Walp.) Cuatr. has been studied previously [20]. A reinvestigation of the aerial parts gave in addition to **1g** [9] and **2h** [9] the epimeric

Table 2. ^{1}H NMR spectral data of compounds of **4a**, **c–e**, **5c** and **d** (400 MHz, $CDCl_3$, δ-values)

H	4a	4c	4d	4e*	5c†	5d‡
1	5.72 *dt*	5.77 *dt*	5.33 *dt*	5.65 *dt*	5.25 *dt*	5.24 *dt*
2	1.50 *m*	†	†	†	†	†
4	1.41 *m*	†	†	†	†	†
6	4.59 *br s*	4.48 *br s*	4.67 *br s*	4.33 *br s*	2.74 *d* †	2.74 *d* †
8	—	4.46 *ddq*	5.22 *ddq*	—		—
9	2.67 *d*	2.75 *dd*	2.37 *dd*	3.14 *br d*	2.40 *dd*	2.33 *dd*
9′	2.48 *dq*	2.13 *dddq*	3.04 *dddq*	2.71 *ddd*	2.19 *br d*	2.19 *br d*
10		—	—	—	2.20 *dt*	2.27 *dt*
12	—	—			—	—
13 13′	2.01 *d*	2.06 *d*	1.84 *d*	1.38 *d*	1.86 *br s*	1.82 *br s*
14	0.90 *s*	0.92 *s*	1.08 *s*	0.99 *s*	1.12 *s*	1.12 *s*
15	1.14 *d*	1.11 *d*	1.00 *d*	1.04 *d*	0.82 *d*	0.82 *s*

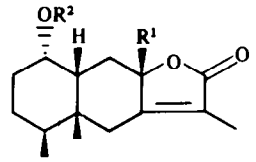
*H-11 3.32 *ddq*.

†OAng 6.07 *qq*, 1.98 *dq*, 1.87 *dq*, OMe 3.10 *s*.

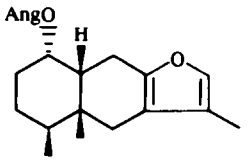
†Overlapped multiplets.

‡OH 2.92 *br s*, OTigl 6.84 *qq*, 1.80 *br d*, 1.82 *br s*.

J [Hz]: 4,15 = 7; 6,13 ~ 1; 9,9′ = 13.5; compound **4a**: 1,9′ = 3; 1,2 ~ 3; compound **4c**: 1,2 = 1,9′ ~ 3; 8,9 = 6; 8,9′ ~ 2; 8,13 = 1.5; compound **4d**: 1,2 ~ 3; 1,9′ ~ 2; 8,9 = 2.5; 8,9′ = 7; 9′,13 ~ 2; compound **4e**: 1,2 ~ 4; 6,9 = 6,9′ = 9,11 = 9′,11 ~ 2; 11,13 = 7; compound **5c**: 1,2 = 11; 1,2′ = 5; 1,10 = 5; 6,6′ = 9,9′ = 14; 9,10 = 4; 9′,10 = 9; compound **5d**: 1,2 ~ 3; 6,6′ = 9,9′ = 14; 9,10 = 4; 9′,10 = 10.



	5a	5b	5c	5d
R^1	H	OH	OMe	OH
R^2	Ang	Ang	Ang	Tigl



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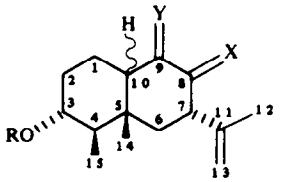


	7a	7b	7c	7d	7e	7f	7g	7h	7i
X	αOH,H	O	O	O	O	O	O	O	αOH,H
Y	αOH,H	αOH,H	αOH,H	αOH,H	αOH,H	αOH,H	αOH,H	αOH,H	O
10 H	α	α	α	α	β	β	α	α	β
R	H	Tigl	Sen	Ang	Ang	Tigl	H	H	H
					$\Delta^{7(11)}$	$\Delta^{7(11)}$		$\Delta^{7(11)}$	7αH

dilactones **8a/b** and the isomeric acetates **9a** and **b**. The structures of the latter clearly followed from their ^{1}H NMR spectra (Table 4) which were close to that of the corresponding desacetoxy derivative **9c** [21]. The position of the acetoxy group followed from the chemical shift of the olefinic methyl.

The ^{13}C NMR spectra of **8a/b** (Table 4) indicated that we were dealing with eremophilanolides with a further carbonyl carbon. The ^{1}H NMR data showed that it has to be placed at C-9 as H-1 was shifted downfield (δ 7.17 *t*). A broadened singlet at δ 5.84 was due to H-8. In agreement with this assumption, in the ^{13}C NMR spectrum a pair of

Table 3. ^{1}H NMR spectral data of compounds **7a** and **g–i** (400 MHz, $CDCl_3$, δ-values)

H	**7a** (MeOD)	**7g**	**7h**	**7i**
1α	1.92 *m*	2.05 *m*	2.06 *m*	2.16 *m*
1β	1.20 *m*	1.44 *dt*	1.42 *m*	1.65 *m*
2α	1.29 *m*	1.32 *m*	1.33 *m*	1.58 *m*
2β	2.05 *dddd*	2.14 *m*	2.12 *m*	1.91 *m*
3	3.37 *dt*	3.52 *dt*	3.47 *dt*	3.50 *dt*
4	1.14 *dq*	1.16 *dq*	1.22 *dq*	1.25 *m*
6α	1.43 *m*	2.10 *dd*	1.83 *br d*	1.91 *dd*
6β	1.48 *m*	1.59 *t*	2.91 *d*	1.56 *dd*
7	2.20 *br dd*	3.24 *br dd*	—	2.40 *ddd*
8	3.92 *t*	—	—	4.02 *br d*
9	3.39 *dd*	3.96 *ddd*	3.82 *dd*	—
10	1.45 *m*	1.36 *dt*	1.52 *dt*	2.28 *dd*
12	1.80 *br s*	1.79 *br s*	1.93 *d*	1.82 *br s*
13	4.85 *dq*	5.00 *dq*	1.80 *d*	4.93 *dq*
13′	4.75 *br s*	4.79 *br s*		4.89 *q*
14	0.78 *s*	1.09 *s*	0.88 *s*	1.06 *s*
15	0.97 *d*	1.03 *d*	1.06 *d*	0.96 *d*
OH		3.51 *d*	3.77 *d*	3.74 *d*

J [Hz]: 4,15 = 7; 7,13 = 13,13′ = 1; compound **7a**: 1β,2α = 2α,2β = 2α,3α ~ 12; 1β,2β = 2β,3 ~ 3; 3,4 = 12; 6α,7 = 11; 6β,7 = 4; 7,8 = 8,9 = 2.5; 9,10 = 11; 9,OH = 2.5; compound **7g**: 1α,1β = 1β,10 = 1β,2α = 2α,3 = 3,4 ~ 12; 1α,10 = 1β,2β = 2β,3 ~ 3; 6α,7 = 13.5; 6β,7 = 5; 9,10 = 11.5; 9,OH = 3; compound **7h**: 1α,10 = 3; 1β,10 = 12; 2β,3 = 3,4 = 12; 2α,3 = 4.5; 6α,6β = 14; 6α,12 = 6α,13 = 2; 9,10 = 11; 9,OH = 2.5; compound **7i**: 2α,3 = 5; 2β,3 = 3,4 = 12; 6α,6β = 14; 6α,7 = 3; 6β,7 = 13; 7,8 = 12; 8,OH = 3; 1α,10 = 2; 1β,10 = 4.

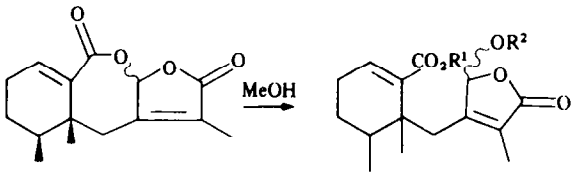
signals at δ98.1 and 98.0 were visible. Both in the ^{1}H and in the ^{13}C NMR spectra several signals were split due to the presence of the 8-epimers. This was supported by methanolysis of the mixture of **8a**/**b** which afforded the epimers **8c**/**d** and **8e**/**f**. Methylation of the mixture of **8c**/**d** gave the acetals **8g**/**h** which could be separated by HPLC. The NMR spectral data (Table 4) further support the structures of **8a**/**b**, named serratifolide A and B, respectively, and which are formed by oxidation of **1g**.

From aerial parts of *S. reicheanus* Cabr. caryophyllene, the eremophilones **9c** [21], **d** and **e** and the shikimic acid derivatives **10a**–**e** were isolated. The ^{1}H NMR spectral data of **9e** (Table 5) required the presence of a hydroperoxide and a cross conjugated keto group. Spin decoupling allowed the assignment of all the signals. The resulting sequences led to the proposed structure. The data of **9d** (Table 5) showed that the corresponding 11-hydroxy derivative was present. The differences in the chemical shifts of H-6, H-12 and H-13 are characteristic for a pair of hydroxy and hydroperoxy derivatives.

The acids **10a–c** were isolated as their methyl esters. The ^{1}H NMR spectra (Table 6) showed that we were dealing with shikimic acid derivatives esterified with acetic acid and two other acids. Inspection of the ^{1}H NMR signals indicated that these acids are propionic, 2-methylbutyric and 3-methylvaleric acid. In the cases of **10c** and **e** two identical ester groups are present in each compound. COLOC experiments with the ester **10e** showed a long-range coupling of the acetate carbonyl with H-3 and the acetate methyl indicating the position of the acetate group. Furthermore, in the mass spectrum a fragment due to loss of acetoxy seems to be characteristic as this was found in all five compounds. This is probably due to the preferred formation of an allylic ion. In the esters **10a**, **b** and **d** the position of the ester residues at C-4 and C-5 could not be determined.

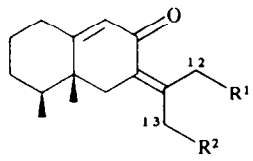
The aerial parts of *S. adenophyllus* Meyen et Walp. gave γ- and δ-cadinene, the methyl ether **11a**, the germacrane derivatives **12a**, **b** [22] and **c**–**g**, the eudesmanes **13a** [23] and **b** [24] as well as oplopanone (**14a**) [25] and its 3α-acetoxy derivative **14b**.

The ^{1}H NMR spectrum of **11a** (see Experimental) was very similar to that of α-cadinol. A singlet at δ3.20 indicated the presence of the methyl ether. The hydroxy acetate **12b** has been isolated previously. All the data agree with those reported [22]. The corresponding diol **12a** has been prepared previously from the acetate [22]. The ^{1}H NMR spectrum of **12e** (Table 6) indicated that it is a hydroperoxide derived from **12a** by an ene-reaction with oxygen. A NOE between H-1 and H-3 (5%) showed that both hydrogens were α-orientated. H-15 gave a NOE with H-3 (4%) and H-5 (5%). As the couplings of H-3 were the same as in **12a** both hydroxy groups are β-orientated. Inspection of a model indicates that a conformation with H-14 below and H-15 in the plane agrees with all the data. The ^{1}H NMR spectrum of **12d** (Table 7) was close to that of **12d** while that of **12f** (Table 7) differed from that of **12e** mainly by the downfield shift of H-3. The ^{1}H NMR spectrum of **12f** again was close to that of **12d** and **e**. All signals could be assigned by spin decoupling. Inspection of models indicated that the observed couplings of H-1 agree with the presence of a 1β-hydroxy derivative. Obviously the germacranes and the eudesmanes are all biogenetically closely related. The carbinol

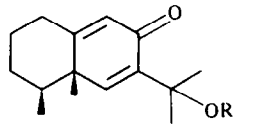


8a/b

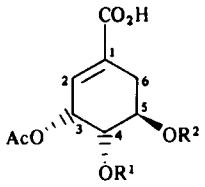
8c/d R^1 = H, R^2 = Me
8e/f R^1 = H, R^2 = H
8g/h R^1 = R^2 = Me



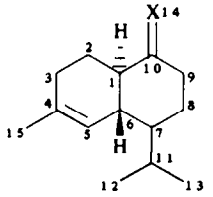
	9a	9b	9c
R^1	H	OAc	H
R^2	OAc	H	H



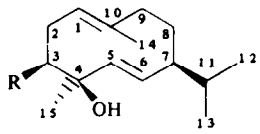
9d R = H
9e R = OH



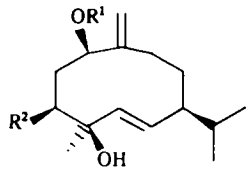
	10a	10b	10c	10d	10e
R^1	Prop	Prop	MeBu	MeBu	MeVal
R^2	MeBu	MeVal	MeBu	MeVal	MeVal



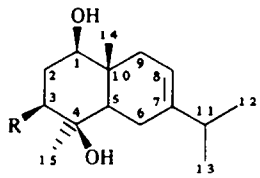
11a X = βMe,OMe
11b X = CH_2



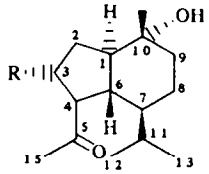
12a R = OH
12b R = OAc
12c R = H



	12d	12e	12f	12g
R^1	H	OH	H	H
R^2	OH	OH	OAc	H



13a R = H
13b R = OAc



14a R = H
14b R = OAc

12c is probably the precursor of all compounds. This assumption further supports the proposed stereochemistry of the new compounds.

The structure of **14b** also followed from its ^{1}H NMR spectrum (see Experimental) which was in part close to that of oplopanone (**14a**). The 3α-position of the acetoxy group followed from the couplings of H-3.

The results of the investigation of 11 Chilean *Senecio* species show again that this large genus is chemically and probably morphologically not very homogeneous. Again most species contain furoeremophilanes which are in some species replaced by the corresponding lactones. Although present in other species the eremophilanes such as **7a–i** are not very common in nature and they are probably the precursors for furoeremophilanes. This is true also for **9a–e**. The presence of shikimic acid derivatives may be of chemotaxonomic interest as the accumulation of these esters is restricted to *Senecio* species [6, 19, 26–29]. The constituents of *S. adenophyllus* are unusual. Some South African species contain highly oxygenated germacrane derivatives. Again in these species no furoeremophilanes or eremophilanes are present. It would be of interest to study the Chilean *Senecios* morphologically to see whether the chemical aspects agree with possible groupings.

EXPERIMENTAL

The air-dried aerial parts were extracted with MeOH–Et_2O–petrol (1:1:1). The defatted extracts were separated by CC, TLC and HPLC (RP 8, flow rate 3 ml min^{-1}) as reported previously [30]. Vouchers are deposited in the Herbarium of the University of Chile, Santiago. The compounds isolated are summarized in Table 8 and the conditions for the final purification of new compounds are given together with the spectral data (HP1 MeOH–H_2O, 17:3, HP2 MeOH–H_2O, 1:1, HP3 MeOH–H_2O, 7:3, HP4 MeOH–H_2O, 3:1, HP5 MeOH–H_2O, 4:1, HP6 MeOH–H_2O, 3:2) (TLC1 Et_2O–petrol, 3:7, TLC2

Table 4a. ^{1}H spectral data of compounds **8a–h** ($CDCl_3$, δ-values)

H	**8a/b***	**8c**	**8d**	**8e/f**	**8g**	**8h**	Multiplicity
1	7.17	7.20	7.18	6.99 (6.98)	7.00	7.00	*t*
2	2.18	2.17	2.17	2.14	2.12	2.13	*m*
3	1.80	1.85 *dddd* 1.73 *dddd*	1.86 *m* 1.74 *m*	1.87 *m* 1.70 *m*	1.86 *dddd* 1.71 *dddd*	1.89 *dddd* 1.71 *dddd*	*m*
4	1.40	1.42	1.42	1.40	1.40	1.40	*tq*
6	2.77	2.87	2.84	2.72 *m*	2.85	2.82	*br d*
6′	2.55 (2.53)	2.73	2.73		2.74	2.75	*br d*
8	5.84	5.53	5.50	5.82 *d*	5.53	5.48	*br s*
13	2.03 (2.01)	1.97	1.98	2.02 (1.98)	1.96	1.97	*s*
14	1.22 (1.21)	1.20	1.20	1.17 (1.16)	1.17	1.17	*s*
15	0.93	0.93	0.92	0.89	0.91	0.90	*d*
OMe		3.48	3.51	3.70 (3.69)	3.71	3.72	s
					3.48	3.51	*s*

*In parentheses differing values of epimers.
J [Hz]. 1,2 = 4; 2,3 = 7; 2,3′ = 2′,3 ~ 3; 2′,3′ = 7; 3,3′ = 14; 3,4 = 3′,4 = 4,15 = 7, 6,6′ = 14.

Table 4b. ^{13}C NMR spectral data of compounds **8a–c** and **8e–h**

C	**8a/b**	**8c**	**8e/f**	**8g**	**8h**
1	144.4	144.4	141.8 (141.7)	141.6	141.4
2	32.4 (32.3)	31.8	32.4 (32.3)	31.7	31.8
3	24.3	24.3	23.8	23.9	23.9
4	36.0 (35.8)	35.2	35.7 (35.5)	35.0	34.9
5	40.7 (40.6)	40.8	40.9 (40.8)	41.0	40.9
6	25.3	25.3	25.3	25.3	25.3
7	158.8	157.1	158.6	157.1	157.0
8	98.1 (97.9)	103.4	98.1 (98.0)	103.4	103.5
9	172.8 (172.7)	172.4	168.2 (168.0)	167.7	167.7
10	134.8 (134.6)	135.0	135.6 (135.2)	135.7	135.7
11	128.3	129.1	128.2	129.1	129.0
12	171.7 (171.6)	171.7	170.8	172.4	172.3
13	12.4	12.5	12.5	12.4	12.6
14	15.7	15.7	15.6	15.7	15.7
15	21.6 (21.5)	21.3	21.5	21.3	21.3
OMe	–	55.8	51.4	51.3	51.3
				55.8	56.2

Et_2O–petrol, 7:3, TLC3 Et_2O–petrol, 1:1, TLC4 Et_2O–petrol, 2:3). Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

6β-Isobutyryloxy-9β-hydroxy-1β,10β-epoxyfuroeremophilane (**2k**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CO_2R); MS *m/z* (rel. int.): 334.178 $[M]^+$ (6) (calc. for $C_{19}H_{26}O_5$: 334.178), 246 $[M-RCO_2H]^+$ (44), 231 $[246-Me]^+$ (24), 217 $[246-CHO]^+$ (46), 189 $[217-CO]^+$ (96), 109 (60), 71 $[RCO]^+$ (100). TLC2: R_f 0.7.

1α-Acetoxy-6β-angeloyloxy-10β-hydroxy-furoeremophil-9-one (**3b**). Crystals, mp 152°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3460 (OH hydrogen bonded), 1760 (OAc), 1730 (CO_2R), 1680 (C=O); MS *m/z* (rel. int.): 404.184 $[M]^+$ (0.5) (calc. for $C_{22}H_{28}O_7$: 404.184), 362 $[M-ketene]^+$ (0.2), 344 $[M-HOAc]^+$ (2.5), 321 $[M-RCO]^+$ (2), 262 $[362-AngOH]^+$ (11), 178 (50), 83 $[RCO]^+$ (100); $[\alpha]_D^{24}$ −27° ($CHCl_3$; *c* 0.3), TLC1: R_f 0.7.

6β,8α-Dihydroxyeremophil-1(10),7(11)-dien-12,8β-olide (**4a**). Oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3480 (OH), 1770 (γ-lactone); MS *m/z* (rel. int.): 264.013 $[M]^+$ (14) (calc. for $C_{15}H_{20}O_4$: 264.013), 246 $[M-H_2O]^+$ (42), 123 (100); $[\alpha]_D^{24}$ - 32° ($CHCl_3$; *c* 1.3); HP3: R_t 2.8 min.

6β-Hydroxyeremophil-1(10),7(11)-dien-12,8β-olide (**4c**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 248 $[M]^+$ (9), 230 $[M-H_2O]^+$ (56), 185 (41), 123 (92), 122 (76), 107 (100), 93 (60), 81 (61), 69 (60); HP4: R_t 8.4 min.

6β-Hydroxyeremophil-1(10),7(11)-dien-12,8α-olide (**4d**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3440 (OH), 1780 (γ-lactone); MS *m/z* (rel. int.): 248 $[M]^+$ (31), 230 $[M-H_2O]^+$ (14), 123 (100), 109 (92), 107 (66), 81 (72), 69 (66). HP4: R_t 4.5 min.

6β-Hydroxy-11βH-eremophil-1(10),7-dien-12,8-olide (**4e**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1820 (γ-lactone); MS *m/z* (rel. int.): 248.141 $[M]^+$ (42) (calc. for $C_{15}H_{20}O_3$: 248.141), 220 $[M-CO]^+$ (12), 205 $[220-Me]^+$ (21), 177 $[205-CO]^+$ (18), 123 (51), 109 (100), 81 (54); HP4: R_t 11 min.

1α-Angeloyloxy-8β-methoxyeremophil-7(11)-en-12,8α-olide (**5c**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1720, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 362.209 $[M]^+$ (9) (calc. for $C_{21}H_{30}O_5$: 362.209), 330 $[362-MeOH]^+$ (6), 262 [M

$-RCO_2H]^+$ (4), 234 $[262-CO]^+$ (56), 203 $[234-OMe]^+$ (24), 175 $[203-CO]^+$ (22), 83 $[RCO]^+$ (100), 55 $[83-CO]^-$ (77); HP3: R_t 19.5 min.

1α-*Tigloyloxy*-8β-*hydroxyeremophil*-7(11)-*en*-12,8α-*olide* (**5d**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1780 (γ-lactone), 1715, 1650 (C=CCO$_2$R); MS *m/z* (rel. int.): 348.194 $[M]^+$ (0.4) (calc. for $C_{20}H_{28}O_5$: 348.194), 330 $[M-H_2O]^+$ (1.6), 248 $[M-RCO_2H]^+$ (12), 230 $[248-H_2O]^+$ (17), 220 $[248-CO]^+$ (7), 123 (18), 83 $[RCO]^+$ (100); HP3: R_t 11.0 min.

3α,8α-*Dihydroxy*-7β,10α-H-*eremophil*-11(13)-*ene* (**7a**). Crystals, mp 159°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 236.178 $[M-H_2O]^+$ (18) (calc. for $C_{15}H_{24}O_2$: 236.178), 218 $[236-H_2O]^+$ (100), 203 $[218-Me]^+$ (19), 200 $[218-H_2O]^+$ (14), 189 (31), 121 (76), 109 (90), 107 (76), 95 (86); $[\alpha]_D^{24°}-19°$ (MeOH; *c* 0.36); HP2: R_t 12.5 min.

3α,9α-*Dihydroxy*-7β,10αH-*eremophil*-11(13)-*en*-8-*one* (**7g**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1710 (C=O); MS *m/z* (rel. int.): 252.173 $[M]^+$ (64) (calc. for $C_{15}H_{24}O_3$: 252.173), 234 $[M-H_2O]^+$ (28), 205 (41), 191 (51), 179 (70), 155 (70), 137 (67), 123 (100), 109 (90), 95 (80); $[\alpha]_D^{24°}-44°$ ($CHCl_3$; *c* 0.49); HP1: R_t 5.6 min.

3α,9α-*Dihydroxy*-10αH-*eremophil*-11(13)-*en*-8-*one* (**7h**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3480 (OH hydrogen bonded), 1690 (C=CC=O); MS *m/z* (rel. int.): 252.173 $[M]^+$ (46) (calc. for $C_{15}H_{24}O_3$ 252.173), 234 $[M-H_2O]^+$ (10), 216 $[234-H_2O]^+$ (8), 206 $[234-CO]^+$ (62), 191 $[206-Me]^+$ (100), 137 (51), 109 (95), 107 (46), 95 (56); $[\alpha]_D^{24°}-143°$ ($CHCl_3$; *c* 0.32); R_t 6.3 min.

3α,8α-*Dihydroxy*-7α,10βH-*eremophil*-11(13)-*en*-9-*one* (**7i**). Crystals, mp 149°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1720 (C=O); MS *m/z* (rel. int.): 234.162 $[M-H_2O]^+$ (28) (calc. for $C_{15}H_{22}O_2$: 234.162), 216 $[234-H_2O]^+$ (10), 205 (37), 123 (34), 109 (100), 107 (56), 95 (44); $[\alpha]_D^{24°}+24°$ ($CHCl_3$; *c* 0.5); HP1: R_t 7.5 min.

Serratifolide A and B (**8a/b**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1730 (C=CCO$_2$R); MS *m/z* (rel. int.): 262.121 $[M]^+$ (10) (calc. for $C_{15}H_{18}O_4$: 262.121), 153 (100), 135 (98), 107 (97), 93 (60), 69 (51); HP5; R_t 5.0 min.

On standing overnight 25 mg **8a/b** in MeOH were transformed to a mixt. of **8c/d** and **8e/f** which gave by HP4 only one fr. (R_t 6.3 min). TLC (Et_2O–petrol, 1:1, ×10) gave 4 mg **8c** (R_f 0.35), 10 mg **8c/d** (R_f 0.38) and 10 mg **8e/f** (R_f 0.3). To 10 mg **8c/d** in Et_2O excess of CH_2N_2 was added. TLC (Et_2O–petrol, 3:7, ×2) gave 3 mg **8g** (R_f 0.50) and 3 mg **8h** (R_f 0.45). **8g**: MS *m/z* (rel. int.): 308.162 $[M]^+$ (0.2) (calc. for $C_{17}H_{24}O_5$: 308.162), 276 $[M-MeOH]^+$ (6), 245 $[276-OMe]^+$ (2), 244 $[276-MeOH]^+$ (4), 167 (66), 166 (42), 142 (46), 135 (100), 110 (36), 107 (96), 93 (28), 91 (24). **8h**: MS *m/z* (rel. int.): 308.162 $[M]^+$ (0.4) (calc. for $C_{17}H_{24}O_5$: 308.162), 276 (6), 245 (2), 244 (2), 167 (64), 166 (37), 142 (46), 135 (100), 110 (36), 107 (96), 93 (26), 91 (20).

Table 5. ^1H NMR spectral data of compounds **9a**, **b**, **d** and **e** (400 MHz, $CDCl_3$, δ-values)

H	**9a**	**9b**	**9d**	**9e**
1	2.30 *m*	2.30 *m*	2.40 *m*	2.40 *m*
1′	2.25 *m*	2.25 *m*	2.32 *m*	2.32 *m*
4	1.50 *m*	1.50 *m*	1.48 *m*	1.48 *m*
6	2.91 *d*	2.87 *d*	6.93 *s*	7.19 *s*
6′	2.20 *br d*	2.18 *br d*		
9	5.77 *br s*	5.76 *d*	6.06 *d*	6.05 *d*
12	2.07 *d*	5.17 *dd*	1.44 *s*	1.56 *s*
		4.83 *dd*		
13	4.68 *s*	1.81 *d*		1.52 *s*
14	0.99 *s*	0.98 *s*	1.12 *s*	1.13 *s*
15	0.94 *d*	0.94 *d*	1.96 *d*	1.09 *d*
OAc	2.08 *s*	2.05 *s*		—

*OOH 8.59 *s*.

J [Hz]: Compound **9a**: 4,15 = 7; 6,6′ = 14; 6,12 = 2; compound **9b**: 1,9 = 1.5; 4,15 = 7; 6,6′ = 14; 6′,12 = 1; 6′,12′ = 2.5; 6′,13 = 1.5; 12,12′ = 14; compounds **9d** and **9e**: 1,9 = 1; 4,15 = 7.

Table 6. ^1H NMR spectral data of the methyl esters of **10a–e** (400 MHz, $CDCl_3$, δ-values)

H	**10a**	**10b**	**10c**	**10d**	**10e**	Multiplicity
2	6.77	6.76	6.77	6.77	6.76	*dt*
3	5.74	5.77	5.72	5.73	5.72	*dt*
4	5.26	5.28	5.26	5.27	5.27	*m*
5	5.30	5.30	5.30	5.30	5.30	*m*
6	2.91	2.91	2.90	2.92	2.91	*ddt*
6′	2.43	2.42	2.40	2.40	2.41	*ddt*
OAc	2.06	2.06	2.05	2.07	2.06	*s*
OCOR	2.33 *q*	2.33 *q*	2.35 *tq*	2.37 *tq*	2.30 *dd*	
	1.14 *t*	1.13 *t*	1.64 *m*	1.65 *ddq*	2.11 *dd*	
			1.45 *m*	1.45 *ddq*	1.84 *ttq*	
			0.83 *t*	0.87 *t*	1.34 *dq*	
			1.13 *d*	1.13 *d*	0.87 *t*	
					0.92 *d*	
OCOR′	2.36 *tq*	2.28 *dd*	2.34 *tq*	2.28 *dd*	2.27 *dd*	
	1.65 *ddq*	2.12 *dd*	1.64 *m*	2.11 *dd*	2.11 *dd*	
	1.44 *ddq*	1.84 *ttq*	1.45 *m*	1.84 *ttq*	1.84 *ttq*	
	0.90 *t*	0.88 *t*	0.83 *t*	1.35 *dq*	1.34 *dq*	
	1.12 *d*	0.93 *d*	1.11 *d*	0.89 *t*	0.86 *t*	
				0.92 *d*	0.91 *d*	
OMe	3.78	3.77	3.77	3.77	3.77	*s*

J [Hz]: 2,3 = 4; 2,4 = 2; 2,6 = 2,6′ ~ 1.5; 3,4 = 5,6 = 5,6′ ~ 5; 6,6′ = 19; OProp: 2,3 = 7.5; OMebu: 2,2′ = 14; 2,3 = 2,5 = 3,4 = 7; OMeVal: 2,2′ = 15; 2,3 = 2′,3 = 3,4 = 3,6 = 4,5 ~ 7.

Table 7. ^{1}H NMR spectral data of **12a** and **d–g** (400 MHz, $CDCl_3$, δ-values)

H	12a	12d*	12e	12f‡	12g
1	5.01 *br d*	4.08 *dd*	4.17 *dd*	4.30 *dd*	3.94 *dd*
2	2.54 *dt*	2.53 *dt*	2.36 *ddd*	2.63 *ddd*	1.92 *m*
2′	2.34 *m*	1.80 *m*	1.75 *m*	1.90 *m*	1.61 *m*
3	3.44 *dd*	3.44 *br d*	3.60 *d*	4.43 *dd*	1.84 *m* 1.43 *m*
5	5.18 *d*	5.11 *d*	5.27 *d*	4.96 *d*	5.21 *d*
6	5.25 *dd*	5.37 *dd*	5.40 *dd*	5.45 *dd*	5.29 *dd*
7	1.99 *dddd*	1.85 *m*	1.80 *m*	1.85 *m*	1.84 *m*
8	1.21 *m*	†	1.97 *m*	†	1.96 *m*
8′	1.13 *m*	†	1.45 *m*	†	1.55 *m*
9	2.36 *m*	†	2.47 *br dd*	†	2.26 *br dd*
9′	2.30 *dt*	†	1.75 *m*	†	1.84 *m*
11	1.33 *dqq*	1.50 *m*	1.52 *dqq*	1.50 *m*	1.49 *dqq*
12	0.73 *d*	0.90 *d*	0.88 *d*	0.89 *d*	0.89 *d*
13	0.69 *d*	0.85 *d*	0.86 *d*	0.84 *d*	0.84 *d*
14	1.52 *br s*	5.16 *br s* 4.88 *br s*	5.25 *br s* 5.12 *br s*	5.18 *br s* 4.85 *br s*	5.12 *br s* 4.89 *br s*
15	1.18 *s*	1.33 *s*	1.36 *s*	1.24 *s*	1.27 *s*

*OOH 8.06 *br s*.

†Obscured multiplets.

‡OAc 2.12 *s*.

J [Hz]: 11,12 = 11,13 = 7; compound **12a**: 1,2 = 2,2′ = 2,3 = 11; 2′,3 = 4; 5,6 = 15; 6,7 = 9; 7,8 = 2.5; 7,8′ = 12; 7,11 = 6; 8,9′ = 9,9′ = 12.5; 8′,9′ = 3; Compound **12d**: 1,2 = 8; 1,2′ = 2.5; 2,2′ = 14; 2,3 = 8; 5,6 = 15; 6,7 = 9; compound **12e**: 1,2 = 5; 1,2′ = 3; 2,2′ = 14; 2,3 = 10; 2′,3 = 2; 5,6 = 15; 6,7 = 10; 7,11 = 7; 8,9 = 8; 9,9′ = 14; compound **12f**: 1,2 = 10; 1,2′ = 3; 2,2′ = 15; 2,3 = 7; 2′,3 = 1; 5,6 = 15; 6,7 = 10; compound **12g**: 1,2 = 9; 1,2′ = 3; 5,6 = 15; 6,7 = 10; 8,9 = 10; 8′,9 = 3; 9,9′ = 14.

13-*Acetoxyeremophil*-7(11),9-*dien*-8-*one* (**9a**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745 (OAc), 1670 (C=CC=O); MS *m/z* (rel. int.): 276.173 $[M]^+$ (24) (calc for $C_{17}H_{24}O_3$: 276.173), 234 [M − ketene]$^+$ (100), 216 [M − HOAc]$^+$ (78), 159 (86), 145 (88), 91 (27); $[\alpha]_D^{24}$ +174° ($CHCl_3$; *c* 0.23); HP5: R_t 12.3 min; TLC3: R_f 0.70.

12-*Acetoxyeremophil*-7(11),9-*dien*-8-*one* (**9b**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (OAc), 1670 (C=CC=O); MS *m/z* (rel. int.): 276.173 $[M]^+$ (16) (calc. for $C_{17}H_{24}O_3$: 276.173), 234 [M − ketene]$^+$ (100), 216 [M − HOAc]$^+$ (34), 205 (62), 159 (42), 145 (52); $[\alpha]_D^{24}$ +120° ($CHCl_3$; *c* 1.65); HP5: R_t 12.3 min; TLC3: R_f 0.65.

11-*Hydroxyeremophil*-6,9-*dien*-8-*one* (**9d**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH); 1670, 1630 (C=CC=O); MS *m/z* (rel. int.): 234.162 $[M]^+$ (68) (calc. for $C_{15}H_{22}O_2$: 234.162), 219 [M − Me]$^+$ (100), 216 [M − H_2O]$^+$ (78), 201 [216 − Me]$^+$ (82), 175 (84), 163 (85), 161 (82), 145 (76), 135 (76), 121 (79), 91 (76); $[\alpha]_D^{24}$ −19° ($CHCl_3$; *c* 1.0); HP4: R_t 6.4 min; TLC4: R_f 0.4.

11-*Hydroperoxyeremophil*-6,9-*dien*-8-*one* (**9e**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3560 (OH), 1675, 1645 (C=CC=O); MS *m/z* (rel. int.): 234.162 [M − O]$^+$ (7) (calc. for $C_{15}H_{22}O_2$: 234.162), 233 [M − OH]$^+$ (20), 219 [234 − Me]$^+$ (75), 217 [M − O_2H]$^+$ (72), 201 [219 − H_2O]$^+$ (58), 177 (76), 175 (78), 161 (100), 135 (56), 121 (52), 91 (54); $[\alpha]_D^{24}$ −7° ($CHCl_3$; *c* 1.2); HP4: R_t 6.4 min; TLC4: R_f 0.5.

3-O-*Acetyl*-4,5-O-[2-*methylbutyryl*]- *and propionylshikimic acid* (**10a**). Isolated as its methyl ester; oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (CO_2R), 1730 (C=CCO_2R); MS *m/z* (rel. int.): 370.163 $[M]^+$ (1) (calc. for $C_{18}H_{26}O_8$: 370.163), 311 [M − OAc]$^+$ (0.5), 296 [M − $EtCO_2H$]$^+$ (0.5), 268 [M − $C_4H_9CO_2H$]$^+$ (2), 236 [268 − MeOH]$^+$ (1), 226 [268 − ketene]$^+$ (2), 212 [268 − O =C=CHMe]$^+$ (15), 170 [212 − ketene]$^+$ (15), 152 [212 − HOAc]$^+$ (30), 85 [RCO]$^+$ (51), 57 (RCO)$^+$ (100); HP5: R_t 7.5 min.

3-O-*Acetyl*-4,5-O-[3-*methylvaleryl*]- *and propionylshikimic acid* (**10b**). Isolated as its methyl ester; oil; IR $\nu_{max}^{CCl_4}$cm^{-1}: 1750 (CO_2R), 1730 (C=CCO_2R); MS *m/z* (rel. int.): 384.178 $[M]^+$ (19) (calc. for $C_{19}H_{28}O_8$: 384.178), 325 [M − OAc]$^+$ (4), 310 [M − $EtCO_2H$]$^+$ (6), 268 [M − $C_5H_{11}CO_2H$]$^+$ (40), 236 [268 − MeOH]$^+$ (9), 226 [268 − ketene]$^+$ (16), 212 (100), 170 (37), 152 (60), 99 [RCO]$^+$ (35); $[\alpha]_D^{24}$ −140° ($CHCl_3$; *c* 0.42); HP5: R_t 9.5 min.

3-O-*Acetyl*-4,5-O-*di*-[2-*methylbutyryl*]-*shikimic acid* (**10c**). Isolated as its methyl ester; oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (CO_2R), 1730 (C=CCO_2R); MS *m/z* (rel. int.): 398.194 $[M]^+$ (0.5) (calc. for $C_{20}H_{30}O_8$: 398.194), 339 [M − OAc]$^+$ (0.2), 296 [M − RCO_2H]$^+$ (1), 212 (10), 170 (10), 152 (16), 85 [RCO]$^+$ (53), 57 [85 − CO]$^+$ (100); $[\alpha]_D^{24}$ −99° ($CHCl_3$; *c* 0.45); HP5: R_t 11.6 min.

3-O-*Acetyl*-4,5-O-[3-*methylvaleryl*]-*and* [2-*methylbutyryl*]-*shikimic acid* (**10d**). Isolated as its methyl ester; oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (CO_2R), 1730 (C=CCO_2R); MS *m/z* (rel. int.): 412.210 $[M]^+$ (20) (calc. for $C_{21}H_{32}O_8$: 412.210), 353 [M − OAc]$^+$ (5), 310 [M − $C_4H_9CO_2H$]$^+$ (18), 296 [M − $C_5H_{11}CO_2H$]$^+$ (37), 254 [296 − ketene]$^+$ (24), 212 (62), 170 (54), 152 (72), 99 [RCO]$^+$ (92), 85 [RCO]$^+$ (80), 71 [99 − CO]$^+$ (72), 57 [85 − CO]$^+$ (100); $[\alpha]_D^{24}$ −142° ($CHCl_3$; *c* 2.95); HP5: R_t 15.2 min.

3-O-*Acetyl*-4,5-O-*di*-[3-*methylvaleryl*]-*shikimic acid* (**10e**). Isolated as its methyl ester; oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (CO_2R), 1730 (C=CCO_2R); MS *m/z* (rel. int.): 426.225 $[M]^+$ (2) (calc. for $C_{22}H_{34}O_8$: 426.225), 367 [M − OAc]$^+$ (0.2), 310 [M − RCO_2H]$^+$ (7), 212 (60), 170 [212 − ketene]$^+$ (35), 152 [212 − HOAc]$^+$ (77), 99 [RCO]$^+$ (100), 71 [99 − CO]$^+$ (95); ^{13}C NMR ($CDCl_3$, C-1–C-7): δ 131.0, 132.8, 66.1, 67.3, 66.5, 28.5, 165.9; OMe 52.2; OAc 20.7, 169.8; OMeVal 172.1 (172.0), 41.3 (41.1), 31.9 (31.8), 29.2 (29.1), 19.2 (19.1), 11.2 (assigned by 2D techniques).

α-*Cadinol methyl ether* (**11a**). Oil; MS *m/z* (rel. int.): 236.214

Table 8. Isolated compounds from the investigated species

Senecio species (voucher and locality)		Constituents
S. almeydae (AH5, December 1988 region de Atacana)	170 g	5 mg **7a**, 100 mg **7b**, 30 mg **7c**, 30 mg **7d**, 150 mg **7e**, 50 mg **7f**, 8 mg **7g**, 6 mg **7h**, 5 mg **7i**, 15 mg **5b**, 3 mg **5d**, 20 mg senkirkin, 8 mg neopetasitenin
S. adenophyllus (89102, July 1989 region de Tarapaca)	330 g	40 mg δ-cadinene, 120 mg **11a**, 300 mg **12a**, 1 g **12b**, 15 mg **12c**, 50 mg **12d**, 100 mg **12e**, 80 mg **12f**, 80 mg **12g**, 150 mg **13a**, 150 mg **13b**, 200 mg **14a**, 100 mg **14b**, 15 mg γ-cadinene
S. algens (8993, May 1989 region de Tarapaca)	770 g	0.3 g **2a**, 1.2 g **2b**, 220 mg **2d**, 100 mg **1a**, 220 mg **2e**, 10 mg axerophthene
S. behnii (8961, May 1989 region de Tarapaca)	270 g	7 mg **1b**, 10 mg **1c**, 10 mg **1d**, 10 mg **1e**, 5 mg **1f**, 10 mg 6,7-dimethoxy-2,2-dimethylchromene, 5 mg 3-senecioyl-p-hydroxyacetophenone, 30 mg **2d**, 20 mg **2f**, 10 mg **2g**, 10 mg **2h**, 25 mg **3c**
S. cachinalensis (AH12, December 1908 region de Atacana)	100 g	25 mg **2c**, 40 mg **5a**, 130 mg **5b**, 10 mg **5c**, 150 mg **6**, 200 mg 5,4'-dihydroxy-3,7,3'-trimethoxyflavone, 5,3',4'-trihydroxy-3,7-dimethoxyflavone
S. candollii (8997, May 1989 region de Tarapaca)	360 g	50 mg eremophilane, 120 mg **2f**, 200 mg **2k**, 150 mg **2l**, 20 mg **2h**, 20 mg **2i**, 120 mg **2m**
S. dryophyllus (89108, May 1989 region de Tarapaca)	175 g	60 mg **1b**, 40 mg **1c**, 50 mg **1d**, 40 mg **2d**, 30 mg **2f**, 30 mg **2g**, 30 mg **2h**, 30 mg **2i**, 60 mg **3a**, 80 mg **3b**, 80 mg viridiflorene, 50 mg α-curcumene, 60 mg α-zingibirene, 20 mg spathulenol, 50 mg each *E*- and *Z*-biformene, 10 mg sitosterol
S. glaber (8915, February 1989 region del Liberator Bernardo O'Higgins)	360 g	1 g **1a**, 200 mg **4a**, 10 mg **4b**, 5 mg **4c**, 5 mg **4d**, 15 mg **4e**
S. nutans (8999, May 1989 region de Tarapaca)	340 g	250 mg γ-cadinene, 250 mg δ-cadinene, 7 g 3-prenyl-4-hydroxyacetophenone
S. reicheanus (8972, May 1989 region de Tarapaca)	360 g	15 mg caryophyllene, 1.35 g **9c**, 25 mg **9d**, 12 mg **9e**, 25 mg **10a**, 15 mg **10b**, 150 mg **10c**, 80 mg **10d**, 30 mg **10e**
S. serratifolius (8991, May 1989 region de Tarapaca)	100 g	80 mg **1g**, 20 mg **2h**, 30 mg **8a/b**, 15 mg **9a**, 15 mg **9b**

$[M]^+$ (23) (calc. for $C_{16}H_{28}O$: 236.214), 221 $[M-Me]^+$ (28), 205 $[M-OMe]^+$ (24), 204 $[M-MeOH]^+$ (62), 189 $[204-Me]^+$ (33), 161 (66), 151 (52), 121 (54), 85 (100); ^1H NMR ($CDCl_3$): δ 1.98 and 1.91 (*m*, H-3), 5.51 (*br s*, H-5), 2.15 (*dqq*, H-11), 0.91 and 0.76 (*d*, H-12, H-13), 1.06 (*s*, H-14), 1.66 (*br s*, H-15), 3.20 (*s*, OMe); *J* [Hz]: 7,11 = 3; 11,12 = 11,13 = 7; $[\alpha]_D^{24^\circ} - 49^\circ$ ($CHCl_3$; *c* 3.42); TLC: Et_2O–petrol, 1:19; R_f 0.65.

3β,4β-Dihydroxygermacra-1(10)E,5E-diene (**12a**). Crystals, mp 120°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 238.193 $[M]^+$ (2) (calc. for $C_{15}H_{26}O_2$: 238.193), 220 $[M-H_2O]^+$ (6), 205 $[220-Me]^+$ (4), 195 $[M-C_3H_7]^+$ (5), 177 $[195-H_2O]^+$ (14), 159 (20), 123 (45), 97 (45), 81 (100); $[\alpha]_D^{24^\circ} - 178^\circ$ ($CHCl_3$; *c* 0.55); HP3: R_t 14.3 min.

1β,3β,4β-Trihydroxygermacra-5E,10(14)-diene (**12d**). Gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 236.178 $[M-H_2O]^+$ (10) (calc. for $C_{15}H_{24}O_2$: 236.178), 177 (66), 139 (53), 109 (74), 97 (83), 71 (100); HP3: R_t 6.3 min.

1β-Hydroperoxy-3β,4β-dihydroxygermacra-5E,10(14)-diene (**12e**). Gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 252.173 $[M-H_2O]^+$ (6) (calc. for $C_{15}H_{24}O_3$: 252.173), 236 $[M-H_2O_2]^+$ (27), 221 $[236-Me]^+$ (24), 218 $[236-H_2O]^+$ (22), 193 (52), 123 (94), 109 (96), 97 (96), 71 (100); $[\alpha]_D^{24^\circ} - 25^\circ$ ($CHCl_3$; *c* 0.96); HP4: R_t 5.3 min.

1β,4β-Dihydroxy-3β-acetoxygermacra-5E,10(14)-diene (**12f**). Gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1735 (OAc); MS *m/z* (rel. int.): 296.199 $[M]^+$ (1) (calc. for $C_{17}H_{28}O_4$: 296.199), 236 $[M-HOAc]^+$ (32), 218 $[236-H_2O]^+$ (14), 193 $[236-C_3H_7]^+$ (55), 175 $[193-H_2O]^+$ (58), 139 (80), 109 (88), 97 (80), 81 (75), 71 (100); $[\alpha]_D^{24^\circ} - 54^\circ$ ($CHCl_3$; *c* 0.8); HP4: R_t 7.1 min.

1β,4β-Dihydroxygermacra-5E,10(14)-diene (**12g**). Crystals, mp 119°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 238.193 $[M]^+$ (6) (calc. for $C_{15}H_{26}O_2$: 238.193), 220 $[M-H_2O]^+$ (22), 177 $[220-C_3H_7]^+$ (50), 159 $[177-H_2O]^+$ (48), 107 (76), 97 (83), 81 (100), 71 (78); HP6: R_t 19.5 min.

3α-Acetoxyoplopanone (**14b**). Oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745 (OAc), 1725 (C=O); MS *m/z* (rel. int.): 296.199 $[M]^+$ (0.8) (calc. for $C_{17}H_{28}O_4$: 296.199), 281 $[M-Me]^+$ (0.9), 236 $[M-HOAc]^+$ (12), 193 $[236-C_3H_7]^+$ (61), 175 $[193-H_2O]^+$ (30), 109 (100); ^1H NMR ($CDCl_3$): δ 2.35 and 1.50 (*m*, H-2), 5.38 (*ddd*, H-3), 2.96 (*t*, H-5), 1.98 (*q*, H-6), 1.35 (*m*, H-11), 0.89 and 0.70 (*d*, H-12, H-13), 1.22 (*s*, H-14), 2.17 (*s*, H-15), 2.00 (*s*, OAc); *J* [Hz]: 1,6 = 6,7 = 10; 2,3 = 2',3 ~ 7; 3,5 = 5,6 = 9.5; 11,12 = 11,13 = 7; $[\alpha]_D^{24^\circ} - 43^\circ$ ($CHCl_3$; *c* 0.58); HP6: R_t 12.5 min.

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