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EREMOPHILANE DERIVATIVES AND OTHER CONSTITUENTS FROM MEXICAN *SENECIO* SPECIES

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Key Word Index—*Senecio* species, Compositae, sesquiterpenes, furoeremophilanes, eremophilanolides, cadinenes

Abstract—The investigation of six Mexican *Senecio* species gave seven unreported furoeremophilanes, 15 related eremophilanolides and two cadinene derivatives. The structures were elucidated by high field NMR techniques

INTRODUCTION

Some time ago we studied the constituents of two Mexican *Senecio* species As with many species from South Africa they also contained furanoeremophilanes [1]. We have studied now six further species and the results are presented in this paper.

RESULTS AND DISCUSSION

The extract of *Senecio pericalia* Klatt. afforded the furoeremophilanes **1a** and **1b**–**1d** as a mixture and the related eremophilanolides **2a**–**2m** and **3a**–**3c** which also in part could not be separated. The ^1H NMR spectra of **1a**–**1d** (Table 1) only differed in the signals of the ester residues. Their typical signals clearly showed that we were dealing with a 4-methyl senecioate, an angelate, a tiglate and a senecioate. Spin decoupling indicated the presence of furoeremophilanes with a 1(10)-double bond and oxygen functions at C-3 and C-6. The couplings of H-3 required a β-substitution and the chemical shifts showed that the ester groups were at C-3 while a hydroxy group had to be placed at C-6. Comparison of the data with similar 6-hydroxy derivatives [2] indicated a β-orientation of the latter. Accordingly, the spectra were similar to those of the *Euryops* species which have the same substitution pattern.

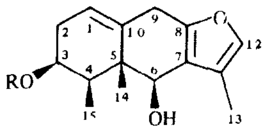
From the ^1H NMR spectra of **2a**–**2m** (Table 1) the presence of eremophilanolides could be deduced. The signal of the ester residues showed that the same groups as in compounds **1a**–**1d** were present. However, the signal of H-12 was missing and the IR spectra exhibited a γ-lactone band. Accordingly, eremophilanolides were present, obviously derived from **1a**–**1d** by further oxidation While in the spectra of **2a**, **2d** and **2g** a low field signal at δ 4.42 was present, this signal was missing in the remaining lactones. Spin decoupling indicated that this signal was due to H-8 which in the other lactones was replaced by a hydroxy and a methoxy group, respectively The spectra therefore were similar to those with the same substitution pattern with a 1,10-epoxide [3] or the 1,10-dihydro derivatives [4]. The proposed stereochemistry of **2a**–**2m** was established by NOE difference spectroscopy with **2a**–**2c** which gave clear effects between H-6, H-3 and H-4 in all cases Compound **2b** gave NOE's between H-OH and H-6 while in the case of **2c** an effect was observed between H-6 and methoxy A NOE of H-6 with H-8 in compound **2a** showed that also H-8 was α-orientated

The ^1H NMR spectra of **3a**–**3c** (Table 1) indicated that again eremophilanolides were present which also must be related to **1b**–**1d** and the corresponding lactones **2e**, **2h** and **2k**. Accordingly, the signals of the same ester residues were observed and the substitution pattern also was the same, except the substitution at C-8. As the H-9 signals were replaced by a low field broadened singlet at δ 6.00 a 8,9-double bond was present Accordingly, the data were close to those of similar trienolides [2] The extract of the aerial parts of *S. aschenbornianus* Schauer gave, in addition to widespread compounds, the furoeremophilanes **4a**–**4c** [5], **4d**, **4e** [6], **4f** [7] and **4h** [8].

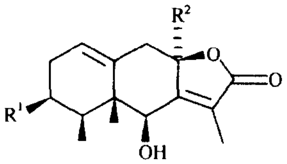
The structures of **4a** and **4b** were deduced from the characteristic ^1H NMR spectra (Table 2) which were similar to that of **4c** [5] The signals of the ester residue of **4a** indicated that an unusual ester group was present. Spin decoupling required a 2-methyl-but-3-enoic acid, an isomer of angelic acid. The spectrum of **4d** (Table 2) indicated that again a 2-methyl-but-3-enoate was present which differed from **4a** by a 1(10)-double bond. Accordingly, the spectrum was close to that of **4e** [6]

The extract of the aerial parts of *S. imparipinnatus* Klatt also gave the furoeremophilane **4g** [8], the chinol ester **9a** [9] and the presilphiperfolane derivative **7** which has been isolated from *S anteuphorbium* [10]. The chinol derivatives **9a** [9], **9b** [11] and **10** [12] as well as the hydroxygermacrene D derivative **8** [13] were isolated from *S confusus* Britt while *S sundbergii* Turner only gave widespread compounds.

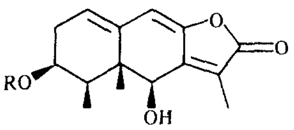
The extract of the aerial parts of *S. tomentosus* Michx gave ferulic acid, the cadinene derivatives **5a** [14] and **5b** [15] as well as the unreported derivatives **5c** and **6**. The structure of **5c** clearly followed from its ^1H NMR spectrum (Table 3) which of course was very close to that of **5b**. The ^1H NMR and the ^{13}C NMR spectra of **6** (Table 3) indicated that a cadinene derivative was present with two oxygen functions The chemical shifts required a 3-keto group while that of H-15 indicated that the methoxy group was at C-4 The stereochemistry was determined by NOE difference spectroscopy. Thus clear effects were

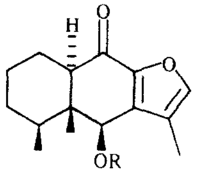


	1	1a	1b	1c	1d
R	OH	Mesen	Ang	Tigl	Sen



2	2	2a	2b	2c	2d	2e	2f	2g	2h	2i	2k	2l	2m
R¹	OH	OMesen	OMesen	OMesen	OTigl	OTigl	OTigl	OSen	OSen	OSen	OAng	OAng	H
R²	H	H	OH	OMe	H	OH	OMe	H	OH	OMe	OH	OMe	OMe

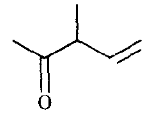


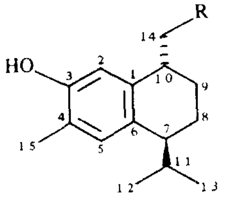


	3a	3b	3c
R	Ang	Tigl	Sen

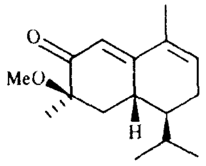
	4a	4b	4c	4d	4e	4f	4g	4h
R	A*	MeBu	Ang	A	MeBu	Ang	iBu	iVal
				$\Delta^{1,10}$	$\Delta^{1,10}$	$\Delta^{1,10}$	$\Delta^{1,10}$	$\Delta^{1,10}$

*A =





	5a	5b	5c
R	H	OH	OAc



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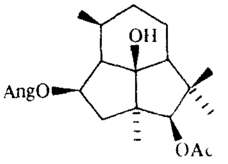

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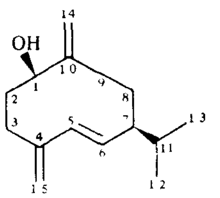

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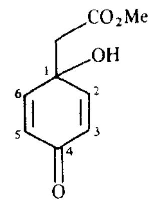
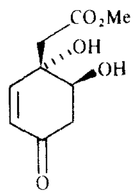


9a

9b 2,3,5,6H



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observed between H-13, H-6 (6%) and H-5 (2%), between H-12, H-7 (5%) and H-8 (3%) as well as between H-15, OMe (10%), H-5 (4%) and H-5′ (5%) These observations indicated that the free rotation of the isopropyl group is hindered The results show again that the large genus *Senecio* is very complex Though again most species afforded the typical furoeremophilanes, there are large numbers of species where these compounds are missing

Table 1 ^{1}H NMR spectral data of compounds **1a–1d**, **2a–2m** and **3a–3c** (400 MHz, CDCl$_3$, δ-values)

H	**1a***	**2a†**	**2b‡**	**2c§**	**2m‖**	**3a¶**
1	5 51 *ddd*	5 65 *br d*	5 61 *br d*	5 58 *br d*	5 70 *br s*	5 79 *br dd*
2	2 20 *m*	2 30 *dddd* 2 22 *ddd*	2 30 *dddd* 2.22 *ddd*	2 30 *br dddd* 2.24 *br ddd*		2 45 *m* 2 20 *m*
3	5 16 *ddd*	5.08 *ddd*	5 08 *ddd*	5 07 *ddd*		5 10 *ddd*
4	2 36 *dq*	2 36 *dq*	2 35 *dq*	2 34 *dq*		2 46 *m*
6	4 85 *br s*	4 71 *br s*	4 79 *br q*	4 61 *br q*	4 42 *br q*	4.80 *br s*
9	3 38 *br d*	2 76 *dd*	2 66 *d*	2 73 *d*	2 77 *d*	6.00 *br s*
9′	3 01 *d*	2 16 *m*	2 50 *br d*	2 39 *br d*	2 41 *dddd*	
13	2 06 *br s*	2 07 *dd*	2 05 *d*	2 11 *d*	2 10 *d*	2 12 *br s*
14	1 05 *s*	0 95 *s*	0 94 *s*	0 96 *s*	0 93 *s*	1 20 *s*
15	0 97 *d*	0 97 *d*	0 98 *d*	1 00 *d*	1 16 *d*	1.23 *d*
OR	5 68 *br s*	5 67 *br s*	5 67 *br s*	5 67 *br s*	—	6 08 *qq*
	2 17 *br q*	2 18 *br q*	2 18 *br q*	2.18 *br q*		1.99 *dq*
	2 16 *br s*	2.15 *br s*	2 15 *br s*	2 16 *br s*		1.89 *dq*
	1 08 *t*	1 09 *t*	1 09 *t*	1 08 *t*		

*H-12 7.04 *br s*, compound **1b** H-3 5 20 *ddd*; OAng 6 17 *qq*, 1 99 *dq*, 1 90 *br s*, compound **1c** H-3 5 17 *ddd*, OTigl 6.87 *qq*, 1 83 *br s*, 1 80 *dq*, compound **1d**· H-3 5 14 *ddd*, OSen 5 69 *br s*, 2.16 *br s*, 1 90 *br s*

†H-8 4 42 *ddq*, compound **2d** H-3 5 10 *ddd*, OTigl 6 88 *qq*, 1 83 *br s*, 1 81 *br d*, compound **2g**: H-3 5 06 *ddd*, OSen 5 69 *qq*, 2.16 *d*, 1.91 *d*.

‡compound **2e** H-3 5 11 *ddd*, OTigl 6 88 *qq*, 1 82 *br s*, 1 81 *br d*, compound **2h**. H-3 5 07 *ddd*, OSen 5 68 *br s*, 2 15 *br s*, 1 91 *br s*, compound **2k** H-3 5 14 *ddd*, OAng: 6 14 *qq*, 1.98 *dq*, 1 87 *dq*.

§OMe 3 14 *s*, compound **2f** H-3 5 09 *ddd*; OTigl: 6 87 *qq*, 1 83 *br s*, 1 81 *br d*, compound **2i** H-3 5 06 *ddd*, OSen: 5 69 *qq*, 2 17 *d*, 1 91 *d*; compound **2l** H-3 5 13 *ddd*; OAng 6 11 *qq*, 1.99 *dq*, 1 89 *dq*

‖OMe 3 26 *s*

¶Compound **3b** H-3 5 10 *m*; OTigl 6 84 *dq*, 1 89 *br s*, 1.80 *br d*; compound **3c** H-3 5 06 *m*, OSen 5 66 *br s*, 2 18 *d*, 1 90 *d*

J[Hz]· Compounds **1a–1d** 1,2 = 5, 1,2′ = 1,9 = 2.5, 2,3 = 7 5, 2′,3 = 8 5, 3,4 = 3 5, 9 9′ = 16.5; compounds **2a–2m** 1,2 = 2,9′ = 3, 1,2′ = 5, 2,2′ = 17, 2,3 = 10; 2′3 = 6; 3,4 = 3 5, 6,13 = 2, compounds **2a**, **2d** and **2g**. 8,9 = 7, 8,9′ = 11, 8,13 = 2, 9,9′ = 12, compounds **2b**, **2e**, **2h**, **2l**· 9,9′ = 13.5, compound **2m** 1,9′ = 2,9′ = 2.5, 6,13 = 2, 9,9′ = 14, compounds **3a–3c** 1,2 = 1,2′ = 4; 2,3 = 5, 2′,3 = 10, 3,4 = 3

Table 2 ^{1}H NMR spectral data of compounds **4a**, **4b** and **4d** (400 MHz, CDCl$_3$, δ-values)

H	**4a**	**4b**	**4d***
4	1 80 m	1 80 m	1 92 m
6	6 35 s	6 35 s	6 35 s
10	2 39 dd	2 40 dd	—
12	7.34 br s	7 35 q	7 40 q
13	1 88 *br s*	1 89 *d*	1.91 *d*
14	0.94 *s*	0 95 *s*	1 13 *s*
15	0 84 *d*	0 88 *d*	0.94 *d*
OR	5 95 *ddd*	2 45 *m*	5 97 *ddd*
	5 19 *br d*	1 23 *d*	5 22 *ddd*
	5 15 *br d*	1 00 *t*	5.18 *ddd*
	3 25 *br dq*		3 30 *dddq*
	1 36 *d*		1 38 *d*

*H-1 6 97 *br dd*, H-2 2 27 and 2 17 *m*, H-3 1.57 and 1 44 *m*

J[Hz]· Compounds **4a** and **4b**. 1,10 = 3 5; 1’,10 = 12, 4,15 = 7, compound **4d**: 1,2 = 1,2′ = 4, 4,15 = 7, 12,13 = 1, OR (**4a** and **4d**)· 2,3 = 8, 2,4c = 2,4t = 4c,4t = 1, 2,5 = 7, 3,4c = 10, 3,4t = 17

EXPERIMENTAL

The air-dried aerial parts were extracted and the extracts were separated as reported previously [16] The aerial parts (400 g) of *S. pericalia* (voucher 8211, collected in Montemoreol, N L., Mexico, Jan. 1987) afforded by CC two crude fractions which were separated by HPLC (MeOH–H$_2$O, 4:1, RP 8, *ca* 100 bar, flow rate, 3 ml/min). Finally 50 mg **1a** (R_t 20.4 min), a mixture of **1b–1d** (R_t 15 3 min, *ca* 2 3 2), 25 mg ferulic acid, 13 mg **2m** (R_t 6 3 min), 14 mg of a mixture of **3a–3c** (*ca* 1:2 2) (R_t 7.0 min), 30 mg of a mixture of **2e**, **2h** and **2k** (*ca* 2.1:1) (R_t 6.8 min), 10 mg **2b** (R_t 8 2 min), 12 mg **2c** (R_t 10.5 min), 9 mg **2a** (R_t 10.5 min), 30 mg of a mixture of **2d** and **2g** (*ca* 5:1) (R_t 8.5 min) and 42 mg of a mixture of **2f**, **2i** and **2l** (*ca* 1 1 1) (R_t 8.8 min) were obtained

The aerial parts (1 kg) of *S. aschenbornianus* (voucher 4081, collected in San Luis Potosi, Dec. 1987) gave by CC and TLC 25 mg α-curcumene, 25 mg β-farnesene, 40 mg of bisabolene-1,4-endoperoxide, 50 mg nerolidol and a mixture which was separated by HPLC affording 16 mg **4d** (R_t 10.5 min), 8 mg **4f**, 13 mg **4c**, 14 mg **4h**, 7 mg **4e**, 5 mg **4b** (R_t 14 min) and 21 mg **4a** (R_t 11 8 min).

The aerial parts (1.2 kg) of *S. imparipinnatus* (voucher 8363, collected in Lampazos, N L, Mexico) gave by CC and TLC 43 mg **7**, 15 mg **4g** and 80 mg **9a**. The aerial parts (520 g) of *S. confusus* (voucher 8072B, collected in Monterrey, Mexico, March.

Table 3 ^{1}H NMR spectral data of compounds **5c** and **6** (400 MHz, CDCl$_3$, δ-values)

H	**5c**	**6**
2	6 62 *br s*	5 87 *br d*
5	6 99 *br s*	2 38 *dd* 1 52 *dd*
6	—	2 71 *dddd*
7	2 58 *br ddd*	1 46 *dddd*
8	1 65 *m*	2 19 *br ddd* 2 05 *m*
9	1 89 *m* 1 74 *m*	6 16 *br d*
10	3 01 *dddd*	
11	2 27 *dqq*	2 05 *m*
12	1 01 *d*	0 94 *d*
13	0 72 *d*	0 86 *d*
14	4 25 *dd* 4 10 *dd*	1 84 *br s*
15	2 21 *br s*	1 30 *s*
OR	2 08 *s*	3 16 *s*

J[Hz] Compound **5c** 7,8 = 7,11 = 11,12 = 11,13 = 7, 9,10 = 9′,10 = 10,14 = 5, 10,14′ = 9, 14,14′ = 11 5, compound **6** 2,6 = 2, 5,5′ = 14, 5,6 = 4, 5′,6 = 12 5, 6,7 = 7,8′ = 11, 7,8 = 7,11 = 4, 8,8′ = 19, 8,9 = 6, 11,12 = 11,13 = 7

1987) gave by CC and TLC 23 mg **8**, 38 mg **9a**, 15 mg **9b** and 12 mg **10** while those of *S sundbergii* (voucher 8211, collected in Borrado Hill, N L, Mexico) gave 20 mg of a mixture of caryophyllene, *ar*-curcumene and *β*-farnesene and 60 mg ferulic acid

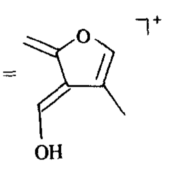
The aerial parts (180 g) of *S tomentosus* (voucher 8228, collected in Arroyo Seco, N L, Mexico, Febr 1987) gave by CC and TLC 9 mg **6** (Et$_2$O–petrol, 1 2, R_f 0 68), 5 mg **5a**, 33 mg **5c** (Et$_2$O-petrol, 2 1, R_f 0 66), 37 mg ferulic acid and 12 mg **5b** Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material

6β-Hydroxy-3β-[4-methylsenecioyloxy]-euryopsin (**1a**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3440 (OH), 1710, 1650 (C=CCO$_2$R), MS *m/z* (rel int) 344 199 $[M]^+$ (2) (calc for $C_{21}H_{28}O_4$ 344 199), 326 $[M-H_2O]^+$ (6), 230 $[M-RCO_2R]^+$ (100), 215 $[230-Me]^+$ (18), 212 $[230-H_2O]^+$ (16), 197 $[215-H_2O]^+$ (30), 124 [B]* (76), 97 $[RCO]^+$ (84), $[\alpha]_D^{24}$ +26° (CHCl$_3$, *c* 0 2)

Tiglate (**1b**), *senecioate* (**1c**) *and angelate* (**1d**) *esters of compound* **1** Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3460 (OH), 1720, 1660 (C=CCO$_2$R), MS *m/z* (rel int.) 330 183 $[M]^+$ (2 5) (calc for $C_{20}H_{26}O_4$ 330 183), 312 $[M-H_2O]^+$ (6), 230 $[M-RCO_2H]^+$ (77), 124 [B]* (78), 83 $[RCO]^+$ (100)

6β-Hydroxy-3β-[4-methylsenecioyloxy]-eremophila-1(10),7(11)-*dien*-12,8*β-olide* (**2a**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1765 (γ-lactone), 1710, 1645 (C=CCO$_2$R), MS *m/z* (rel int) 360 194 $[M]^+$ (1) (calc for $C_{21}H_{28}O_5$ 360 194), 246 $[M-RCO_2H]^+$ (24), 121 $[C_9H_{13}]^+$ (100), 97 $[RCO]^+$ (76), $[\alpha]_D^{24}$ −66° (CHCl$_3$, *c* 0 17)

B =



Tiglate (**2d**) *and senecioate* (**2g**) *esters of compound* **2** Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3460 (OH), 1770 (γ-lactone), 1700, 1650 (C=CCO$_2$R), MS *m/z* (rel int) 346 178 $[M]^+$ (0 6) (calc for $C_{20}H_{26}O_5$ 346 178), 246 $[M-RCO_2H]^+$ (12), 121 $[C_7H_7O_2]^+$ (100), 83 $[RCO]^+$ (70)

6β,8α-Dihydroxy-3β-[4-methylsenecioyloxy]-eremophila-1(10),7(11)-*diene*-12,8*β-olide* (**2b**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3460 (OH), 1770 (γ-lactone), 1710, 1650 (C=CCO$_2$R), MS *m/z* (rel int) 376 189 $[M]^+$ (0 5), 358 $[M-H_2O]^+$ (1), 244 $[358-RCO_2H]^+$ (32), 229 $[244-Me]^+$ (14), 121 [C$_7$H$_7$O$^+$ (87), 106 $[121-Me]^+$ (93) 97 $[RCO]^+$ (100), $[\alpha]_D$ −53° (CHCl$_3$, *c* 0 18)

Tiglate (**2e**) *senecioate* (**2h**) *and angelate* (**2k**) *esters of compound* **2** Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3440 (OH), 1770 (γ-lactone), 1710, 1650 (C=CCO$_2$R), MS *m/z* (rel int) 362 $[M]^+$ (0 2), 344 162 $[M-H_2O]^+$ (1) (calc for $C_{20}H_{24}O_5$ 344 162), 244 $[M-RCO_2H]^+$ (44), 121 $[C_9H_{13}]^+$ (72), 106 $[121-Me]^+$ (80), 83 $[RCO]^+$ (100)

6β-Hydroxy-3β-[4-methylsenecioyloxy]-8α-methoxyeremophila-1(10), 7(11)-*dien*-12,8*β-olide* (**2c**) Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1775 (γ-lactone), 1710, 1650 (C=CCO$_2$R), MS *m/z* (rel int) 390 204 $[M]^+$ (0 2) (calc for $C_{22}H_{30}O_6$ 390 204), 358 $[M-MeOH]^+$ (4), 276 $[M-RCO_2H]^+$ (7), 244 $[276-MeOH]^+$ (16), 121 $[C_9H_{13}]^+$ (65), 106 $[121-Me]^+$ (71), 97 $[RCO]^+$ (100)

Tiglate (**2f**), *senecioate* (**2i**) *and angelate* (**2l**) *ester of compounds* **2** Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1770 (γ-lactone), 1700, 1650 (C=CCO$_2$R), MS *m/z* (rel int) 376 $[M]^+$ (0 1), 344 162 $[M-MeOH]^+$ (1) (calc for $C_{20}H_{24}O_5$ 344 162), 276 $[M-RCO_2H]^+$ (25), 244 $[276-MeOH]^+$ (9) 121 (51), 106 (7), 83 $[RCO]^+$ (100)

6β-Hydroxy-8α-methoxyeremophila-1(10),7(11)-*dien*-12,8*β-olide* (**2m**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3480 (OH), 1770 (γ-lactone), MS *m/z* (rel int) 278 152 $[M]^+$ (14) (calc for $C_{16}H_{22}O_4$ 278 152), 260 $[M-H_2O]^+$ (12), 246 $[M-MeOH]^+$ (44), 231 (32), 123 (74), 107 (76), 55 (100) $[\alpha]_D^{24}$ −8° (CHCl$_3$, *c* 0 32)

6β-Hydroxy-3β-[angeloyloxy, tigloyloxy and senecioyloxy, respectively]-ligularenolide (**3a**–**3c**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3460 (OH), 1770 (γ-lactone), 1710, 1650 (C=CCO$_2$R), MS *m/z* (rel int), 344 162 $[M]^+$ (0 6) (calc for $C_{20}H_{24}O_5$ 344 162), 244 $[M-RCO_2H]^+$ (82), 121 (28), 83 $[RCO]^+$ (100)

6β-[2-methyl-2-vinylacetoxy]-Furoeremophil-9-one (**4a**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1735 (CO$_2$R), 1700 (C=O), MS *m/z* (rel int) 330 183 $[M]^+$ (4 5) (calc for $C_{20}H_{26}O_4$ 330 183), 248 $[M-O=C=C(Me)Et]^+$ (100), 230 $[M-RCO_2H]^+$ (44), 83 $[RCO]^+$ (43), 55 $[83-CO]^+$ (91)

6β-[2-methylbutyryloxy]-Furoeremophil-9-one (**4b**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1730 (CO$_2$R), 1690 (C=O), MS *m/z* (rel int) 332 199 $[M]^+$ (2) (calc for $C_{20}H_{28}O_4$ 332 199), 248 $[M-O=C=C(Me)CH=CH_2]^+$ (52), 230 $[M-RCO_2H]^+$ (20), 85 $[RCO]^+$ (48), 57 $[85-CO]^+$ (100)

6*β*-[2-methyl-2-vinylacetoxy]-Euryopsin-9-one (**4d**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1735 (CO$_2$R), 1685 (C=O), MS *m/z* (rel int) 328 $[M]^+$ (0 4), 228 115 $[M-RCO_2H]^+$ (57) (calc for $C_{15}H_{16}O_2$ 228 115), 83 $[RCO]^+$ (17), 55 $[83-CO]^+$ (100)

14-*Acetoxy-2-hydroxycalamene* (**5c**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1740, 1230 (OAc), MS *m/z* (rel int) 276 173 $[M]^+$ (1) (calc for $C_{17}H_{24}O_3$ 276 173), 216 $[M-HOAc]^+$ (8), 173 $[216-C_3H_7]^+$ (100)

4β-Methoxycadina-1,9-*dien-3-one* (**6**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1660 (dienone), UV $\lambda_{max}^{Et_2O}$ 277 nm, MS *m/z* (rel int) 248 178 $[M]^+$ (2 5) (calc for $C_{16}H_{24}O_2$ 248 178), 205 [M

$-C_3H_7]^+$ (10), 133 (100), ^{13}C NMR ($CDCl_3$, C-1–C-15) 160 5, 119.1, 197.6, 75 2, 40 3, 34 3, 43 8, 25 0, 137 4, 131 4, 26 2, 20 9, 19.3, 14 6, 18.3, OMe 51 4, $[\alpha]_D^{24^\circ}$ +28° ($CHCl_3$, *c* 0 36)

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