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EREMOPHILANE DERIVATIVES AND OTHER CONSTITUENTS FROM *SENECIO* SPECIES

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Key Word Index—*Senecio* species; Compositae; sesquiterpenes; cacalol derivatives; eremophilanes; bisabolene derivatives; shikimic acid ester; cumol derivatives.

Abstract—The investigation and reinvestigation respectively of 23 *Senecio* species afforded 11 further cacalol derivatives, a furoeremophilone, 17 eremophilanes, 4 bisabolene derivatives, a shikimic acid derivative, a *bis*-prenylated *p*-hydroxybenzaldehyde, menth-2-en-1,7-diol and a cumol derivative. The configuration of some eremophilanes have been revised. Structures were elucidated by spectroscopic methods. The results are summarized in a table. The chemotaxonomic aspects agree with those of previous investigations.

INTRODUCTION

Many species of the large genus *Senecio* have been studied chemically by several groups of workers. So far the results show that this taxonomically very diverse genus is also chemically diverse. Although some types of natural products such as the pyrrolizidine alkaloids and the furoeremophilanes are very common in the genus, large parts of it do not contain such compounds. On the other hand, both furoeremophilanes and pyrrolizidine alkaloids have also been reported from neighbouring genera. Accordingly, even the generic limits are not really clear [1, 2]. We have studied, therefore, several chemically uninvestigated species and have also reinvestigated a number of others. The results are discussed in this paper.

RESULTS AND DISCUSSION

Senecio lydenburgensis Hutch. et Burtt. Davy contains several derivatives of cacalol [3, 4]. A reinvestigation of the aerial parts gave the further propionyl cacalol derivatives **1**–**6**. The structures of **1**–**6** could easily be deduced from the spectroscopic data. The common presence of 9-*O*-propionates followed from their mass spectra, which all showed elimination of methyl ketene, typical for phenol propionates. The nature and the position of the oxygen function in the cacalol propionates was deduced from the ^{1}H NMR spectra (Table 1). In the spectrum of **1** the presence and the position of acetoxy groups at C-13 and C-14 followed from the methylene singlet at δ5.21 and the pair of doublets at δ5.53 and 5.34 as well as from the singlets at δ2.08 and 2.07. The ^{1}H NMR spectra of **2**–**6** were close to that of the corresponding acetate [3] except the signals of the ester moieties. Neither compounds **2** and **3** nor **5** and **6** could be separated. However, since the concentration of the esters in both mixtures were different, all the ^{1}H NMR signals could be assigned and therefore the assigned structures are probably correct.

From the roots of *S. inaequidens* DC., which was investigated previously [2], a further cacalohastin derivative, the angelate **7**, was isolated. The structure could be deduced easily from the ^{1}H NMR spectrum (Table 1) which differed from that of the isomeric diester [5] in the expected way. The H-3 signal was slightly more down field and the H-14 doublets more up field as compared with the shifts observed in the spectrum of the 14-*O*-acetate [5].

The aerial parts and the roots of *S. heliopsis* Hilliard et Burtt gave 3β-acetoxycacalohastin [6] and 6β-isobutyryloxyfuroeremophil-1(10)-en-9-one [7] while the roots also afforded 1α-hydroxy-6β-isobutyryloxy-10αH-furoeremophil-9-one [6], **8** and **12**. The ^{1}H NMR spectrum of **8** (Table 1) indicated the presence of an aldehyde. The down field shifts of H-1–H-3 clearly showed that the aldehyde was placed at C-4, while the down field shift of H-12 required a hydroxy group at C-13. Accordingly, a broadened two proton singlet at δ4.73 was present. The chemical shift of the methyl singlet (δ2.83) agreed nicely with the expected chemical shift at H-14.

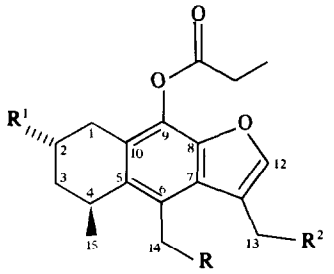
The ^{1}H NMR spectrum of **12** (Table 2) and its molecular formula ($C_{19}H_{26}O_4$) indicated the presence of a keto ester of a furoeremophilane. Spin decoupling allowed the assignment of all signals and the structure **12** was determined directly from these results. The stereochemistry was deduced from the couplings observed and by comparison with the data from similar compounds [2]. The nature of the ester group followed from the typical ^{1}H NMR signals.

The aerial parts of *S. coronatus* (Harv.) Thunb. gave dehydrocacalohastin [8], 14-angeloyloxy-3β-acetoxy cacalohastin [5] and the methyl ether **9**. The same compounds also were present in the roots. However, in addition to the methyl ether **9**, the long chain ethers **10** and **11** were isolated. The structures of **9**–**11** clearly followed from the spectral data. While the ^{1}H NMR spectra (Table 1) were close to that of dehydrocacalohastin,

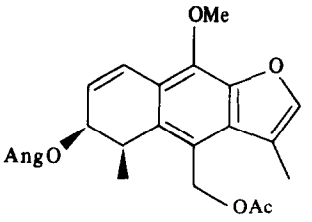
Table 1. ^{1}H NMR spectral data of compounds **1–11** (400 MHz, $CDCl_3$, TMS as internal standard)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10/11**
H-1	2.85 *br dd* 2.59 *ddd*	3.25 *br dd* 2.50 *dd*		3.25 *br dd* 2.50 *m*	3.25 *br dd* 2.49 *dd*		7.22 *d*	7.44 *br d*	7.28 *d*	7.30 *d*
H-2		4.34 *m*		4.33 *m*	4.34 *m*		6.13 *br dd*	7.39 *dd*	8.24 *t*	8.23 *t*
H-3	1.8 *m*	2.06 *br d* 1.86 *m*		2.06 *br d* 1.86 *ddd*	2.06 *br d* 1.85 *m*		5.28 *dd*	8.27 *dd*	7.28 *d*	7.30 *d*
H-4	3.46 *ddq*	3.61 *m*		3.59 *m*	3.58 *ddq*		3.54 *br q*	—	—	—
H-12	7.62 *br s*	7.32 *br s*		7.32 *q*	7.32 *q*		7.40 *q*	7.77 *br s*	7.45 *q*	7.47 *q*
H-13 H-13′	5.21 *br s*	2.30 *d*	2.29 *d*	2.29 *d*	2.29 *d*		2.34 *d*	4.73 *br s*	2.52 *d*	2.56 *d*
H-14	5.53 *d*	5.53 *d*	5.46 *d*	5.47 *d*	5.47 *d*		5.42 *d*	2.83 *br s*	5.02 *s*	5.04 *s*
H-14′	5.34 *d*	5.40 *d*	5.34 *d*	5.33 *d*	5.33 *d*		5.36 *d*			
H-15	1.22 *d*	1.27 *d*		1.40 *d*	1.26 *d*		1.14 *d*	10.78 *s*	3.04 *br s*	3.03 *br s*
OCOR	2.72 *q* 1.33 *t*	2.73 *q* 1.33 *t*		2.72, 2.35 *q* 1.33, 1.14 *t*	2.72 *q* 1.33 *t*		5.93 *m* 1.73 *br s*			
		6.07 *qq*	5.68 *qq*		2.11 *d*	2.73 *tq*				
		1.94 *dq*	2.19 *d*		2.08 *tqq*	1.66 *m*				
		1.85 *dq*	1.88 *d*		0.95 *d*	1.46 *m*				
						0.88 *t*				
						1.13 *d*				
OAc	2.08 *s* 2.07 *s*						2.05 *s*			
OR							4.18 *s*	4.45 *s*	4.27 *s* 3.54 *s*	4.26 *s* 3.64 *t* 1.69 *tt* 1.27 *m* 0.85 *t*

J (Hz): Compound **1**: 1, 1′ = 16; 1, 2 = 4; 3, 4 = 5; 3′, 4 = 10; 4, 15 = 7; 14, 14′ = 13; compounds **2–6**: 1, 1′ = 16; 1, 2 = 7; 1′, 2 = 10; 2, 3 = 3.5; 2, 3′ = 12; 3, 3′ = 12; 3, 4 = 2.5; 3′, 4 = 5; 12, 13 = 1; 14, 14′ = 13; compound **7**: 1, 2 = 10; 2, 3 = 6; 3, 4 = 2; 4, 15 = 7; 12, 13 = 1; 14, 14′ = 13; compound **8**: 1, 2 = 7.5; 1, 3 = 1; 1, 14 ~ 0.5; 2, 3 = 8; compounds **9–11**. 1, 2 = 2, 3 = 6; 12, 13 = 1.5; (compounds **10/11**: 1′, 2′ = 6.5; 15′, 16′ and 17′, 18′ = 6.5; OAng: 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1; OSen: 2′, 4′ = 2′, 5′ = 1; OProp: 2, 3 = 7; OiVal: 2′, 3′ = 3′, 4′ = 3′, 5′ = 7, OMebu: 2′, 3′ = 2′, 5′ = 3′, 4′ = 7).



	1	2	3	4	5	6
R	OAc	OAng	OSen	OProp	OiVal	OMebu
R^1	H	OH	OH	OH	OH	OH
R^2	OAc	H	H	H	H	H



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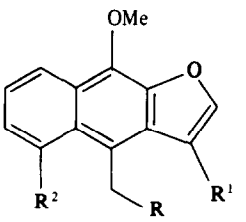
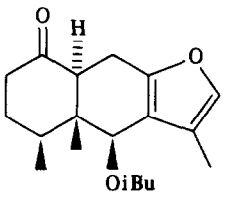


	8	9	10	11
R	H	OMe	$O(CH_2)_{15}Me$	$O(CH_2)_{17}Me$
R^1	CH_2OH	Me	Me	Me
R^2	CHO	Me	Me	Me



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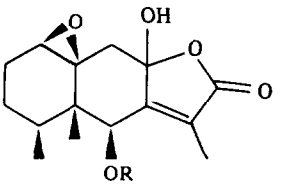
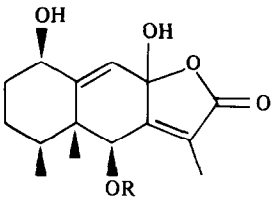
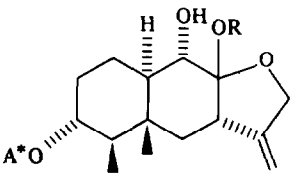


13 Meacr 14 R = Sen 15 R = Ang





16 R = Meacr 17 R = Sen 18 R = H 19 R = Me

the mass spectra showed a base peak at *m/z* 239 formed by loss of the corresponding ether radical. This showed that the long chain ether residue was at C-14 and not at C-9. Although **10** and **11** could not be separated their structures are very probably correct.

The roots of *S. isatideus* DC. have been studied previously. However, only hydrocarbons were reported [2, 9]. A reinvestigation gave 6β-angeloyloxy-, methacryloyloxy- and senecioyloxy-1β,10β-epoxyfuroeremophilanes [10–12], 1β,10β-epoxyfuroeremophil-6-one [13], the lactones **13–17** as well as the eremophilone **30**. The structure of **13** followed from the molecular formula ($C_{19}H_{24}O_6$) and the ^{1}H NMR spectrum (Table 2) together with the results of spin decoupling. The nature of the oxygen functions was deduced from the IR spectrum. The latter showed the presence of a γ-lactone, an ester and a hydroxy group, while the broadened doublet at δ3.20 was due to an epoxy proton. The stereochemistry at C-1, C-4, C-5, C-6 and C-10 followed from comparison of the corresponding chemical shifts with those of similar

Table 2. ^{1}H NMR spectral data of compounds **12–20** (400 MHz, $CDCl_3$, TMS as internal standard)

	12 (C_6D_6)	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
H-1	—	3.20 *br d*	3.20 *br d*	3.18 *br d*	3.85 *br t*	3.85 *br t*	*	*	*
H-2	1.83 *ddd* 2.19 *ddd*	1.98 *m*	1.98 *m*	2.00 *m*	*	*	*	*	*
H-3	1.75 *dddd* 1.67 *m*	2.03 *m* 1.33 *m*	2.03 *m* 1.33 *m*	2.03 *m* 1.33 *m*	*	*	4.77 *ddd*	4.77 *ddd*	4.78 *ddd*
H-4	1.48 *ddq*	1.62 *m*	1.63 *m*	1.64 *m*	*	*	1.42 *m*	1.41 *m*	—
H-6	6.13 *dd*	5.94 *br s*	5.78 *br s*	5.96 *br s*	6.60 *q*	6.57 *q*	1.78 *dd* 0.96 *dd*	1.78 *dd* 0.94 *dd*	2.68 *d* 2.13 *d*
H-7	—	—	—	—	—	—	2.68 *br dd*	2.65 *br dd*	—
H-9 H-9′	3.05 *ddd* 2.66 *br dd*	2.31 *d* 1.80 *d*	2.31 *d* 1.81 *d*	2.32 *d* 1.80 *d*	5.84 *s*	5.81 *s*	3.55 *br d*	3.61 *d*	3.36 *d*
H-10	1.92 *dd*	—	—	—	—	—	1.30 *m*	1.17 *m*	—
H-12 H-12′	6.93 *br s*	—	—	—	—	—	4.49 *br s*	4.52 *br d* 4.34 *br d*	—
H-13 H-13′	1.89 *d*	1.79 *d*	1.81 *d*	1.80 *d*	1.79 *d*	1.82 *d*	5.04 *br s* 4.91 *br s*	4.99 *br s* 4.88 *br s*	1.88 *br s*
H-14	0.68 *s*	1.10 *s*	1.06 *s*	1.11 *s*	1.16 *s*	1.12 *s*	0.87 *s*	0.82 *s*	0.65 *s*
H-15	0.78 *d*	1.02 *d*	0.99 *d*	1.02 *d*	0.83 *d*	0.81 *d*	0.82 *d*	0.81 *d*	0.91 *d*
OH							3.45 *br*†		
OMe								3.42 *s*	3.17 *s*
OCOR	2.36 *qq*	6.23 *br s*	5.78 *qq*	6.30 *qq*	6.22 *br s*	5.73 *qq*	**	**	**
	1.11 *d*	5.75 *dq*	2.18 *d*	2.07 *dq*	5.70 *dq*	2.24 *d*			
	1.09 *d*	2.00 *br s*	1.97 *d*	1.99 *dq*	2.01 *br s*	1.97 *d*			

*Overlapped multiplets; **5.84 *d*, 7.67 *dd*, 6.09 *br d*, 6.15 *d*, 5.95 *dt*, 2.15 *m*, 1.41 *tt*, 1.31 *m* (4H), 0.88 *t*, 1.98 *br s*.

†Disappeared after D_2O addition.

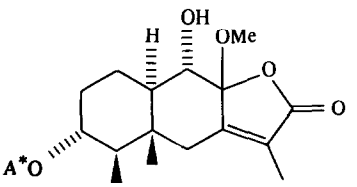
J (Hz): Compound **12**: 2,2′ = 14; 2,3 = 7; 2,3′ = 13; 2′,3 = 4.5; 2′,3′ = 2; 3,3′ = 13; 3,4 = 12; 3′,4 = 3.5; 4,15 = 7; 6,9 = 2; 6,9′ = 1; 12,13 = 1.5; compounds **13–15**: 1,2 = 4.5; 4,15 = 7; 6,13 = 1.5; 9,9′ = 14; compounds **16** and **17**: 1,2 = 1,2′ ~ 3; 4,15 = 7; 6,13 = 2; compounds **18**/**19**: 2,3 = 3,4 = 10; 2′,3 = 5; 4,15 = 7; 6,7 = 7; 6′,7 = 13; 6,6′ = 13; 9,10 = 10 (compounds **19**: 9,OH = 10; 12,12′ = 13).

eremophilanes [2, 14]. The configuration at C-8 could not be established. Types of lactones with both 8α- and 8β-hydroxy groups are known [15, 16], but the chemical shift of H-14 favours a 8β-hydroxy group. The corresponding esters **14** and **15** could not be separated completely. However, since both could be enriched by TLC, all signals in the ^{1}H NMR spectra could be assigned (Table 2) and therefore the structures assigned appear plausible. The angelate residue caused a larger down field shift of H-6 as in the esters in **13** and **14** [2, 14]. The ^{1}H NMR spectra of **16** and **17** (Table 2) only differed by the signals of the ester moiety which indicated the presence of a methacrylate and a senecioate. The signal of the epoxide proton of **13–15** was replaced by a broadened triplet at δ3.85 and the H-9 doublets by down field singlets at δ5.84 and 5.81 respectively. The molecular formulae indicated that **16** and **17** were isomeric with **13** and **14** respectively. All the data agree well with the proposed structures of **16** and **17**. It seems most likely that these compounds were formed by opening of the epoxide ring in **13** and **14** followed by elimination of water. As the chemical shifts of H-14 corresponded to those in **13** and **14**, the configuration at C-8 obviously was the same. It appears reasonable also to postulate that **13–15** are formed by oxidative transformation of the corresponding furoeremophilanes.

The structure of **30** was determined by careful spin decoupling. The ^{1}H NMR signal (Table 3) of H-7 was assigned easily as the signals of the exomethylene protons were sharpened on irradiation at δ2.78. Simultaneously, the signals of H-6 and H-8 could be assigned. As the down field shifted double doublets must be due to protons α to the keto group an eremophil-11(12)-en-9-one was present. The 3α-position of the hydroxyl group also followed from the coupling of the corresponding ^{1}H NMR signal. The aerial parts of *S. isatideus* also gave compounds **13** and **30**.

The aerial parts of *S. erubescens* Ait. var. *erubescens* afforded 3α-angeloyloxy-9α-hydroxy-eremophil-7(11)-en-8-one [14], the corresponding 3α[4-angeloyloxy]-hex-2-enoyloxy derivative [17], as well as the lactone **20**. The structure of the latter was deduced from its ^{1}H NMR spectrum (Table 3) which was similar to that of **23** (see below). However, the signals from H-13 were absent. The γ-lactone band in the IR indicated the presence of an 8,12-lactone. As the H-9 signal was a simple doublet, no hydrogen was present at C-8 and the singlet at δ3.17 agreed with a methoxy group there. Thus **20** is a derivative of **23** formed by oxidation at C-12 followed by production of a lactol which was then stabilized as its methyl ether.

S. speciosus Willd. has been studied previously [17]. From the roots, in addition to compounds isolated previously (**21**, **23**), two further cyclized compounds, the semiacetal **18** and the methyl acetal **19**, were isolated. The structure of **21** could easily be deduced from the ^{1}H NMR spectrum (Table 3) which was very close to that of the isomeric diester [**18**]. However, the different ester group at C-9 caused an up field shift of the H-9 signal, and the nature of the ester group followed from the typical ^{1}H NMR signals. The ^{1}H NMR spectral data of **23** (Table 3) were nearly identical with those of the corresponding angelate [14] except for the signals of the ester side chain. The latter, however, agreed with those of other 5-methyl dodecatrienoates [17]. As in eremophilanes such



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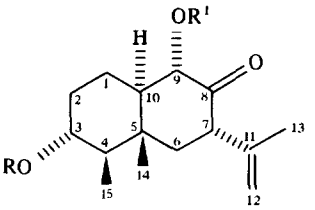
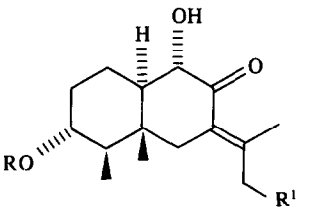
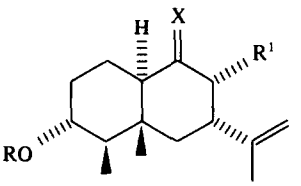


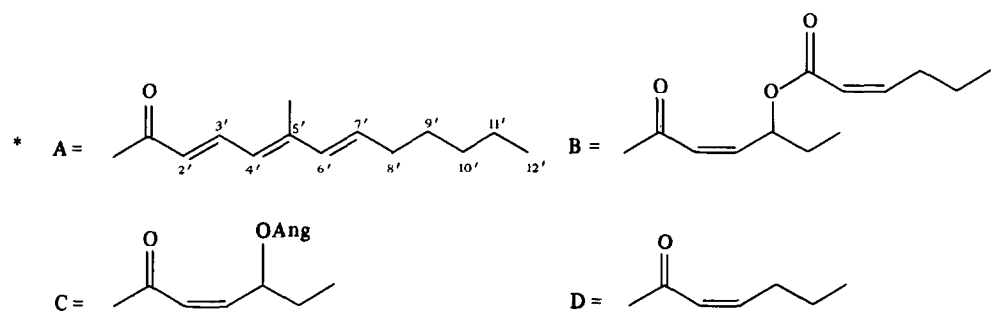
	21	**22**
R	Sen	B*
R^1	Mebu	H



	23	**24**	**25**
R	A*	B*	A*
R^1	H	H	OH



	26	**27**	**28**	**29**	**30**
R	B*	C*	D*	A*	H
R^1	OH	OH	OH	OH	H
X	H,αOH	H,αOH	H,αOD	=O	=O



as **21** [18] with a conjugated 7(11)-double bond, the configurations at C-9 and C-10 have to be changed as a clear NOE was observed between H-14 and H-9. The same is true for the corresponding 8-hydroxy derivatives (**26–29**) where a clear NOE between H-14 and H-7 led to the configuration H-7β, H-8β, H-9β and H-10α. Accordingly, the configurations of the previous reported eremophilanes of this type have to be corrected [14, 17, 19], as the couplings found in all compounds are identical with those of **23–25** and **26–29** respectively. The aerial parts gave the *N*-oxide of 7-*O*-sarracinoyl-retronecin-9-*O*-senecioate [18].

The ^{1}H NMR spectrum of **19** (Table 2) indicated that again a 5-methyldodecatrienoate was present with the ester group at C-3 and a hydroxy group at C-9. The stereochemistry at these centres followed from the couplings. A broadened double doublet was due to H-7, since irradiation sharpened the signals of the exo-methylene protons. Furthermore a pair of double doublets collapsed to doublets (H-6). A pair of broadened doublets at δ4.52 and 4.34 were also coupled with the exo-methylene protons. As H-9 only showed a coupling with H-10, C-8 most likely was a ketal centre. Accordingly, the ^{13}C NMR spectrum (see Experimental) showed a low field singlet at δ106.1 in addition to three further signals which were due to the carbons with an oxygen function (δ74.5 *d*, 74.4 *d* and 68.6 *t*). All data therefore nicely agreed with the proposed structure. The configuration at C-8 was not established, but from the chemical shift of H-14 (see above), a β-methoxy group is the most likely.

All data of compound **18** were close to those of **19**. However, the molecular formula and the missing methoxy signal indicated the presence of the corresponding semi acetal, which surely is the direct precursor of the corresponding furoeremophilane.

Senecio erubescens Ait. var. *crepidifolius* DC. has been investigated previously [2]. A reinvestigation of the aerial parts gave **25**, already isolated as its diacetate [17], and the shikimic acid derivative **36**. The structure of **25** directly could be deduced from the ^{1}H NMR spectrum (Table 3) by comparison with that of the diacetate [17]. As expected the signals of H-9 and H-13 were shifted up field. Compound **36** which was present in large amounts was transformed to the methyl ester **36a**. The structure followed from the ^{1}H NMR spectrum (see Experimental) which was close to those of similar derivatives [18, 20, 21].

Table 3. ^{1}H NMR spectral data of compounds **21–28** and **30** (400 MHz, $CDCl_3$, TMS as internal standard)

	21	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**30**
H-3	4.82 *ddd*	4.87 *ddd*	4.84 *ddd*	4.83 *ddd*	4.82 *ddd*	4.83 *ddd*	4.84 *ddd*	4.81 *dd*	3.35 *dd*
H-4	1.51 *m*	1.45 *m*	1.45 *m*	1.45 *m*	1.43 *m*	1.43 *m*	1.43 *m*	1.45 *m*	1.33 *m*
H-6	2.08 *dd*	2.11 *dd*	2.92 *d*	2.91 *d*	3.00 *d*	2.00 *br d*	2.00 *br d*	2.12 *br d*	1.90 *dd*
H-6′	1.57 *m*	1.60 *dd*	*	*	*	1.50 *dd*	1.48 *m*	*	1.65 *dd*
H-7	3.24 *dd*	3.24 *dd*	—	—	—	2.25 *br dd*	2.25 *br d*	2.30 *br d*	2.78 *dddd*
H-8	—	—	—	—	—	3.98 *br s*	3.97 *br s*	4.07 *br s*	2.45 *dd* 2.35 *dd*
H-9	5.06 *d*	3.98 *dd*	3.84 *dd*	3.81 *d*	3.87 *dd*	3.48 *br dd*	3.47 *br dd*	4.95 *dd*	—
H-10	*	*	1.47 *ddd*	1.48 *ddd*	1.48 *ddd*	1.48 *ddd*	1.50 *m*	1.50 *m*	2.38 *dd*
H-12	4.95 *br s*	5.00 *br s*	1.93 *d*	1.93 *d*	1.98 *br s*	4.99 *br s*	4.99 *br s*	4.98 *br s*	4.79 *br s*
H-12′	4.73 *br s*	4.78 *br s*				4.82 *br s*	4.82 *br s*	4.88 *br s*	4.77 *br s*
H-13	1.75 *br s*	1.78 *br s*	1.81 *d*	1.81 *d*	4.24 *br d* 4.18 *br d*	1.81 *br s*	1.82 *br s*	1.81 *br s*	1.47 *br s*
H-14	1.17 *s*	1.14 *s*	0.93 *s*	0.92 *s*	0.95 *s*	0.79 *s*	0.79 *s*	0.87 *s*	0.71 *s*
H-15	0.93 *d*	0.91 *d*	0.91 *d*	0.93 *d*	0.90 *d*	0.84 *d*	0.85 *d*	0.84 *d*	1.00 *d*
OCOR	5.67 *qq* 2.17 *d* 1.89 *d* 2.47 *tq* 1.6 *m*, 1.42 *m* 0.88 *t*, 1.16 *d*	OH 3.49 *d* ‡	OH 3.76 *d* †	‡	OH 3.66 *d* †	‡	§	¶	

*Overlapped multiplets.

J (Hz): 2,3 = 3,4 = 11; 2′,3 = 5; 4,15 = 7; 9,10 = 11; compounds **21** and **22**: 6,6′ = 14; 6,7 = 14; 6′,7 = 5.5; (compound **22**: 9,OH = 3.5); compounds **23–25**: 6,6′ = 14; (compound **23**: 9,OH = 2.5; compound **26**: 9,OH = 2.5; 13,13′ = 13); compounds **26–28**: 6,6′ = 13; 6,7 = 3; 6′,7 = 13; 7,8 = 8,9 ~ 2; compound **30**: 1,10 = 11; 1′,10 = 3.5; 6,6′ = 15; 6,7 = 7; 6′,7 = 10; 7,8 = 5; 7,8′ = 10.5; 8,8′ = 17.5.

^{1}H NMR spectral data of **A**, **B**, **C**, **D**.

†OCOR: 5.84 *d* (H-2), 7.67 *dd* (H-3), 6.09 *br d* (H-4), 6.15 *d* (H-6), 5.95 *dt* (H-7), 2.15 *br dt* (H-8), 1.41 *tt* (H-9), 1.31 *m* (H-10, H-11), 0.88 *t* (H-12), 1.98 *br s* (H-13) [*J* (Hz): 2,3 = 15; 3,4 = 12; 6,7 = 15; 7,8 = 8,9 = 11,12 ~ 7].

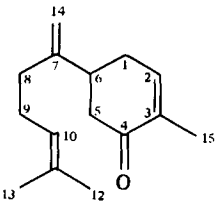
‡OCOR: 5.81 *br d* (H-2), 6.10 *dd* (H-3), 6.18 *dt* (H-4), 1.75 *m* (H-5), 0.95 *t* (H-6), 5.76 *dt* (H-2′), 6.23 *dt* (H-3′), 2.60 *br dt* (H-4′), 1.45 *tq* (H-5′), 0.91 *t* (H-6′) [*J* (Hz): 2,3 = 2′,3′ = 11; 3,4 = 7.5; 4,5 = 6; 5,6 = 5′,6′ = 7; 3′,4′ = 4′,5′ = 7].

§5.83 *dd* (H-2), 6.14 *dd* (H-3), 6.22 *ddd* (H-4), 1.50 *m* (H-5), 1.00 *t* (H-6), 6.07 *qq* (H-3′), 1.98 *dq* (H-4′), 1.90 *dq* (H-5′) [*J* (Hz): 2,3 = 11; 2,4 = 0.5; 3,4 = 7.5; 4,5_1 = 6.5; 4,5_2 = 6; 5,6 = 7; 3′,4′ = 7; 3′,5′ = 4′,5′ = 1].

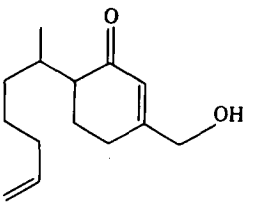
¶OCOR: 5.71 *dt* (H-2), 6.21 *dt* (H-3), 2.61 *ddt* (H-4), 1.5 *m* (H-5), 0.91 *t* (H-6); 8-OCOR: 5.84 *dt* (H-2), 6.28 *dt* (H-3), 2.64 *ddt* (H-4), 1.50 *m* (H-5), 0.92 *t* (H-6) [*J* (Hz): 2,3 = 11; 2,4 = 1.5; 3,4 = 7.5; 4,5 = 5,6 = 7].

However, the unusual nature of one of the ester groups was obvious from the ^{1}H NMR spectrum. Mild methanolysis afforded hexadec-2*E*-enoic acid. Pairs of double doublets at δ2.58 and 2.52 as well as a triplet of triplets at δ5.13 in the spectrum of **36a** indicated a β-acetoxy group in the ester side chain which obviously was eliminated during saponification. In the mass spectrum of **36**, a strong elimination of the long chain acid (*m/z* 240) and only a weak fragment [M − HOAc] (*m/z* 434) was observed, so a 3-position for the C_{16}-acid was favoured, which was strongly supported by the result of the methanolysis since the allylic position should be preferred.

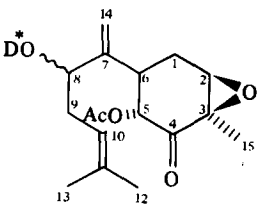
The roots of *S. erubescens* var. *crepidifolius* gave, in addition to compounds isolated previously, manool, **22–29**, **33** and **37**. The structure of **22** clearly followed from the comparison of its ^{1}H NMR spectrum (Table 3) with that of the 4′-angeloyloxy derivative [22] which showed that only the ester part was changed. From the typical signals the nature of the ester group could easily be deduced. The configuration was established by NOE difference spectroscopy. Clear NOEs were observed between H-14 and H-3β, H-9β and H-7β. The ^{1}H NMR spectral data of **24** (Table 3) indicated that this compound only differed from **22** by the position of the double bond. In **24** this clearly was conjugated, as shown by the presence of two olefinic methyl singlets and the absence of a H-7 signal. Accordingly, the spectrum was close to that of the corresponding 4′-angeloyloxy derivative [17]. The spectral data of **25** showed that this compound was the 13-hydroxy derivative of **23**, one of the olefinic methyl signals being replaced by a pair of broadened doublets at δ4.24 and 4.18. The chemical shift of the remaining methyl singlet indicated the position of the allylic hydroxyl group. The ^{1}H NMR spectra of **26** and **27** (Table 3) were close to those of other 8,9-dihydroxyeremophilanes [17]. The nature of the 3-acyloxy groups clearly followed from the ^{1}H NMR signals. NOE difference spectroscopy indicated that the configuration of these compounds had to be changed to H-7β, H-8β, H-9β and H-10α. Thus irradiation



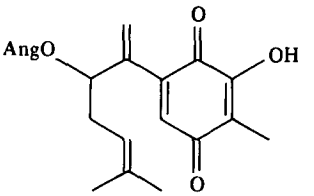
31



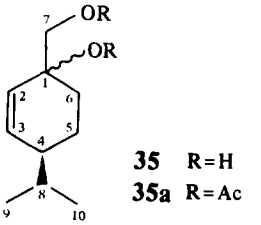
32



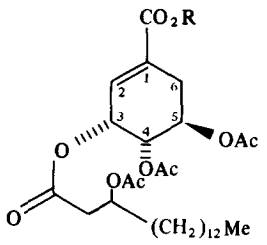
33



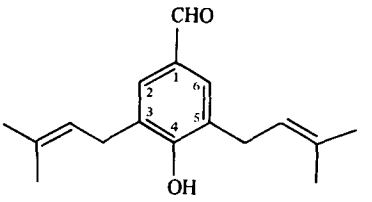
34



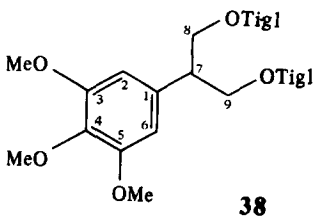
35 R=H
35a R=Ac



36 R=H **36a** R=Me



37



38

of H-14 showed clear NOEs with H-3β, H-7β and H-9β.

The ^{1}H NMR spectrum of **28** (Table 3) showed that an ester group was at C-9. The couplings indicated the same configurations as in **26** and **27**, while the nature of the two ester groups followed from the typical ^{1}H NMR signals. So far, only acyloxy derivatives of hex-2*Z*-enoates have been observed in the *Senecio* species.

The structure of **33** again could be deduced from comparison of its ^{1}H NMR spectrum (Table 4) with those of similar bisabolene derivatives [23]. The configuration at C-5 followed from the large coupling $J_{5,6}$. The relative position of the ester groups could be deduced from the chemical shifts of H-5 and H-8 which characteristically are influenced by the presence of saturated or conjugated ester groups. If the chemical shifts of H-5 and H-8 were compared with those of the corresponding diangelate [23] it was obvious that the large difference for H-5 (0.1 ppm) better agreed with a 5-acetoxy derivative. The structure of **37** directly followed from the molecular formula and the ^{1}H NMR spectrum (see Experimental). The symmetrical structure led to a very simple spectrum with only one aromatic proton singlet. The chemical shift clearly showed the neighbouring aldehyde group thus settling the position of the prenyl groups. So far only similar derivatives of *p*-hydroxyacetophenones were isolated as typical compounds from Compositae.

S. macroglossus DC. has also been studied previously [24]. A reinvestigation of the roots gave, in addition to the bisangelate [24], the bistiglate **38**. The structure could easily be deduced from the spectral data (see Experimental). Furthermore the bisabolone **31** was present, its structure being deduced directly from the ^{1}H NMR spectrum (Table 4). The position of the keto group followed from the chemical shift of H-2 and from the result of spin decoupling as the pair of doublets were coupled with H-6.

S. affinis DC. has been investigated previously [2]. A reinvestigation of the aerial parts gave in addition to compounds isolated previously the norbisabolene derivatives **32** and the 15-desoxy derivative [25] as well as the menthene derivative **35**. The structure of the latter was readily deduced from the spectral data and from those of the monoacetate obtained by mild acetylation (see Experimental). The configuration at C-1 was not determined. The structure of **32** followed from the ^{1}H NMR spectrum (Table 4) which was very similar to that of the desoxy compound [25]. However, the olefinic methyl signal was replaced by a broadened singlet at δ4.24.

The aerial parts of *S. longifolius* L.f. gave the perezone derivative **34** and the corresponding hydroquinone [24]. The structure of **34** directly followed from the ^{1}H NMR spectrum (Table 4) which was close to that of similar perezone derivatives [26]. The position of the hydroxy group was clear since the signals of H-5 and H-15 were sharp singlets. A 5-hydroxy derivative would show corresponding signals with allylic couplings as found in desoxyperezone [27].

Twelve other *Senecio* species were investigated and gave no new compounds. All the results on the 23 species examined are summarized in Table 5.

Table 4. ^{1}H NMR spectral data of compounds **31**–**34** (400 MHz, $CDCl_3$, TMS as internal standard)

	31	**32**	**32a**	**33**	**34**
H-1	2.47 *br ddd* 2.26 *br dd*	—	—	2.53 *ddd* 2.19 *dd*	—
H-2	6.75 *br d*	6.11 *br s*	6.00 *tt*	3.43 *d*	—
H-3	—	—	—	—	—
H-4	—		2.20 *m*	—	—
H-5	2.60 *ddd* 2.35 *dd*	2.2 *m*	2.30 *m*	5.76 *d*	6.67 *s*
H-6	2.69 *br dddd*	2.4 *m*	2.30 *m*	2.78 *ddd*	—
H-7	—	1.97 *m*	1.98 *m*	—	—
H-8	2.06 *br dt*	*	*	5.00 *br t*	5.66 *br t*
H-9	2.12 *dt*	*	*	2.29 *m*	2.42 *br t*
H-10	5.10 *br d*	2.05 *br dt*	2.05 *br dt*	5.00 *br t*	5.02 *tqq*
H-11	—	5.80 *ddt*	5.80 *ddt*	—	—
H-12	1.69 *br s*	4.99 (*t*) *ddt* 4.93 (*c*) *ddt*	4.99 (*t*) *ddt* 4.93 (*c*) *ddt*	1.68 *br s*	1.61 *br s*
H-13	1.61 *br s*	—	—	1.61 *br s*	1.52 *br s*
H-14	4.85 *br s* 4.82 *br s*	0.97 *d*	0.80 *d*	5.22 *s* 5.09 *s*	5.57 *br s* 5.51 *s*
H-15	1.79 *br s*	4.24 *br s*	4.65 *br s*	1.45 *s*	1.94 *s*
OAc	—	—	2.13 *s*	—	—
OCOR	—	—	—	see Table 3	6.08 *qq*, 1.95 *dq* 1.85 *dq*

*Overlapped multiplets.

J (Hz): Compound **31**: 1,2 = 4.5; 1,1′ = 18; 1,6 = 3.5; 1′,6 = 11; 5,5′ = 16; 5,6 = 12; 5′,6 = 3.5; 8,9 = 9, 10 = 7; compounds **32** and **32a**: 2,4 = 2, 15 ~ 1.5; 7,14 = 9, 10 = 10, 11 = 7; 10, 12 = 12, 12′ = 1.5; 11, 12*t* = 17; 11, 12*c* = 10; compound **33**: 1,2 = 4; 1,1′ = 15.5; 1,6 = 7; 1′,6 = 11; 5,6 = 13; 8,9 = 9, 10 = 6.5; compound **34**: 8,9 = 6.5; 9, 10 = 7.5; 10, 12 = 10, 13 = 1; OAng: 3′, 4′ = 7.5; 3′, 5′ = 4′, 5′ = 1.5.

Table 5. *Senecio* species investigated and characteristic constituents isolated (lit. in brackets)

Species with furoeremophilanes	Aerial parts	Constituents	Roots	
Senecio affinis DC. (81/8 Transvaal)	100 g	in addition to previous results [2] 2 mg **32**, 60 mg 15-desoxy **32** [25] 2 mg **35**	110 g	dehydrocacalohastin derivatives [12]
S. atratus Greenm. (RMK 9080, Colorado)	150 g	200 mg 6β-isobutyryloxy-10αH-furoeremophil-9-one [12], 100 mg 6β-isobutyryloxy-1β,10β-epoxyfuroeremophilane [13], 240 mg 6β-isobutyryloxy- and 60 mg 6β-angeloyloxy-1β,10β-epoxyfuroeremophil-9-one [10], 100 mg 6β-isobutyryloxyfuroeremophil-1(10)-en-9-one [7]		
S. bellidifolius HBK (4/84, Mexico, Cerecahui)	120 g	5 mg cacalol [31, 32], 60 mg 6β-angeloyloxy- and 40 mg 6β-isovaleryloxyfuroeremophil-1(10)-en-9-one [13]		
S. coronatus Thunb. (Harv.) (Vincent 218, Natal)	75 g	10 mg dehydrocacalohastin [8], 4 mg 14-angeloyloxy-3β-acetoxycacalohastin [6], 3 mg **9**	40 mg	5 mg dehydrocacalohastin [8], 10 mg 14-angeloyloxy-3β-acetoxycacalohastin [5], 5 mg **9**, 10 mg **10**, 3 mg **11**
S. heliopsis Hilliard et Burtt. (Vincent 201, Natal)	130 g	3 mg 3β-acetoxycacalohastin [6], 500 mg 6β-isobutyryloxyfuroeremophil-1(10)-en-9-one [7]	60 g	2 mg 3β-acetoxycacalohastin [6], 30 mg **8**, 3 mg 1α-hydroxy-6β-isobutyryloxy-10αH-furoeremophil-9-one [6], 2 mg **12**, 2 mg 6β-isobutyryloxyfuroeremophil-1(10)-en-9-one [7]
S. inequidens DC. (81/61, Transvaal)		dehydrocacalohastin derivatives [2]	50 g	In addition to previous results [2] 8 mg **7**
S. isatideus DC. (81/125, Transvaal)	260 g	90 mg 6β-angeloyloxy-1β,10β-epoxyfuroeremophilane [12], 100 mg 1β,10β-epoxyfuroeremophil-6-one [13], 60 mg **13**, 1 mg **30**	150 g	140 mg 6β-angeloyloxy- [10], 500 mg 6β-methacryloyloxy- [11] 300 mg 6β-senecioyloxy-1β,10β-epoxyfuroeremophilane [12], 20 mg 1β,10β-epoxyfuroeremophil-6-one [13], 6 mg **13**, 5.5 mg **14**, 4 mg **15**, 1 mg **16**, 1 mg **17**, 2 mg **30**
S. iydenburgensis Hutch. et Burtt Davy (81/186, Transvaal)	100 g	in addition to previous results [3, 4], 2 mg **1**, 1 mg **2**, 1 mg **3** 1 mg **4**, 1 mg **5**, 1 mg **6**		dehydrocacalohastin derivatives [4]
S. macrocephalus DC. (Vincent 203, Natzl)	30 g	10 mg manool, 20 mg 3α-[5-methyldodeca-2,4,6-trienoyloxy]-10αH-furoeremophilan-9α-ol [17], 5 mg **18**, 5 mg **25**		
S. madagascariensis Poiret (1670/83, Natal)	—		10 g	3 mg 15-angeloyl- and 2 mg isovaleryloxycacalohastin [3], 2 mg 3-methoxy-1-oxo-2,3-dehydrocacalol [14]
S. minesnius Cuatr. (RMK 9078, Peru)	480 g	180 mg 1β-angeloyloxy- [10] and 80 mg 1β-tigloyloxy-10α-hydroxyfuroeremophilane [28]		

Table 5. (*Continued*)

Species with furoeremophilanes	Aerial parts	Constituents	Roots	
(B) Species with eremophilanes				
S. erubescens Ait. var. *crepidifolius* DC. (Vinent 217, Natal)	620 g	30 mg **25** [17], 1.3 g 6β-isobutyryloxyfuroeremophil-1(10)-en-9-one [7]	360 g	In addition to previous results [2] 7 mg manool, 20 mg **22**, 1.5 mg **23**, 1 mg **24**, 7 mg **26**, 2.5 mg **27**, 2 mg **28**, 2.5 mg **33**, 2 mg **37**
S. erubescens var. *erubescens* (Vincent 220, Natal)	70 g	in addition to previous results [2] 2.5 mg **20**, 3 mg 3α-angeloyloxy-9α-hydroxyeremophil-7(11)-en-8-one [14], 6 mg of the corresponding 3α-[4-angeloyloxy]-hex-2-enoyloxy derivative [17]		
S. speciosus Willd. (Vincent 192, Natal)		eremophilanes similar to the roots [17]	48 g	In addition to previous results [17] 8 mg **18**, 5 mg **19**, 3 mg **21**, 3 mg **23**
(C) Further species				
S. acarinus Cabr. (RMK 9102, Peru)	220 g	traces of pyrrolizidine alkaloids	—	
S. adamantinus Bongard (RMK 8482, Brazil)	100 g	5 mg 8α-angeloyloxy-4α-hydroxygermacra-1(10),5-diene [29]	—	
S. brasiliensis (Spreng.) Less (RMK 8561, Brazil)	250 g	25 mg germacrene D, 3 mg bicyclogermacrene	—	
S. cannabifolius Less. (1190/82, grown f. seeds)	150 g	1 mg Me = $\equiv_2 =_2$ $(CH_2)_3OAc$ [30], 10 mg 4α-hydroxygermacra-1(10),5-diene [14]	—	
S. longifolius L. f. (Botanical Garden Berlin)	30 g	15 mg **34** and 40 mg of the corresponding quinone [24]	—	
S. macroglossus DC. (81/131, Transvaal)	370 g	150 mg mixture of triterpenes	10 g	3 mg **31**, 3 mg **38** and 3 mg of the bisangelate [24]
S. murii L. Bol. (81/160, Transvaal)	25 g	150 mg triterpenes, 10 mg α-humulene	—	
S. pohlii, Sch. Bip. ex Baker (RMK 8330, Brazil)	150 g	20 mg squalene	—	
S. venosus Harv. (81/184, Transvaal)	150 g	10 mg germacrene D	80 g	10 mg $H_2C{=}CH(CH_2)_8Me$

The overall picture from these results again shows the diversity of this large genus. Again most species contain furoeremophilanes (Table 5, group A) and a smaller number can be characterized by the occurrence of the precursors, the eremophilanes with an oxygen function at C-8 (group B). For the first time a direct precursor, the semi-acetal **18** was isolated. Finally there is again a group of species which lack these sesquiterpenes (group C). Investigations of more species from the whole tribe will be necessary to get a clear picture both from the chemical and from the taxonomic point of view.

EXPERIMENTAL

The air dried plant materials were extracted with Et_2O–petrol, 1:2, and the extracts were worked-up and separated in the usual fashion [29]. CC (SiO_2) fractions were as follows: 1 (petrol), 2 (Et_2O–petrol, 1:10), 3 (1:3), 4 (1:1), 5 (Et_2O) and 6 (Et_2O–MeOH, 10:1). From each crude fraction a 400 MHz ^1H NMR spectrum was measured. If only saturated proton signals were visible these fractions were not further studied. All the others were separated by repeated TLC (SiO_2, PF 254, Et_2O–petrol mixtures corresponding to the mixtures of the CC fractions). Known compounds were identified by comparison with authentic material (400 MHz ^1H NMR, co-TLC). Separation conditions for the new compounds are described below. HPLC was always achieved using RP 8200 bar, flow rate 3 ml/min. The purity of the compounds isolated was tested by TLC in different solvent mixtures and by their 400 MHz ^1H NMR spectra. Constituents isolated are listed in Table 5.

13,14-*Diacetoxy-cacalol propionate* (**1**). Colourless oil (TLC: Et_2O–petrol, 7:3, R_f 0.4); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (PhOCOR), 1745 (OAc); MS *m/z* (rel. int.): 402.168 $[M]^+$ (11) (calc. for $C_{22}H_{26}O_7$: 402.168), 346 $[M-O{=}C{=}CHMe]^+$ (42), 342 $[M-HOAc]^+$ (8), 286 $[346-HOAc]^+$ (100), 244 $[286-ketene]^+$ (82), 226 $[286-HOAc]^+$ (37), 211 $[226-Me]^+$ (22), 57 $[C_2H_5CO]^+$ (68).

14-*Angeloyloxy and* 14-*senecioyloxy-2α-hydroxy-cacalol propionate* (**2** *and* **3**). Colourless oil (TLC: C_6H_6–Me_2CO, 4:1 and HPLC (MeOH–H_2O, 7:3) R_t = 6.0 min.); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1760 (PhOCOR), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 400.189 $[M]^+$ (3) (calc. for $C_{23}H_{28}O_6$: 400.189), 344 $[M-O{=}C{=}CHMe]^+$ (6), 300 $[M-C_4H_7CO_2H]^+$ (9), 244 $[344-C_4H_7CO_2H]^+$ (100), 226 $[244-H_2O]^+$ (12), 83 $[C_4H_7CO]^+$ (23), 57 $[C_2H_5CO]^+$ (20), 55 $[83-CO]^+$ (22).

14-*Propionyloxy-2α-hydroxy-cacalol propionate* (**4**). Colourless oil (TLC: C_6H_6–Me_2CO, 4:1, HPLC (MeOH–H_2O, 7:3) R_t = 4.5 min.); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (PhOCOR), 1735 (CO_2R); MS *m/z* (rel. int.): 374.173 $[M]^+$ (8) (calc. for $C_{21}H_{26}O_6$), 318 $[M-O{=}C{=}CHMe]^+$ (10), 244 $[318-C_2H_5CO_2H]^+$ (100), 226 $[244-H_2O]^+$ (28), 211 $[226-Me]^+$ (42), 57 $[C_2H_5CO]^+$ (47).

14-*Isovaleryloxy and* 14-[2-*methylbutyryloxy*]-2α-*hydroxy-cacalol propionate* (**5** *and* **6**). Colourless oil (TLC: C_6H_6–Me_2CO, 4:1 HPLC (MeOH–H_2O, 7:3) R_t = 5.2 min); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (PhOCOR), 1735 (CO_2R); MS *m/z* (rel. int.): 402.204 $[M]^+$ (3) (calc. for $C_{23}H_{30}O_6$: 402.204), 346 $[M-O{=}C{=}CHMe]^+$ (7), 300 $[M-RCO_2H]^+$ (8), 244 $[346-RCO_2H]^+$ (100), 226 $[244-H_2O]^+$ (10), 211 $[226-Me]^+$ (12), 85 $[C_4H_9CO]^+$ (8), 57 $[C_2H_5CO]^+$ (25).

3β-*Angeloyloxy*-14-*acetoxy-cacalohastin* (**7**). Colourless oil (TLC: Et_2O–petrol, 1:3, R_f 0.42); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (OAc), 1710 (C=CCO_2R); MS *m/z* (rel. int.): 398.173 $[M]^+$ (8) (calc. for $C_{23}H_{26}O_6$: 398.173), 298 $[M-C_4H_7CO_2H]^+$ (12), 239 $[298-OAc]^+$ (100), 83 $[C_4H_7CO]^+$ (14), 55 $[83-CO]^+$ (20); $[\alpha]_D$ – 168 ($CHCl_3$; *c* 0.8).

13-*Hydroxydehydrocacalohastin*-15-*al* (**8**). Colourless crystals, mp 135° (TLC: Et_2O–petrol, 1:10, R_f 0.35); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 2720, 1675 (CHO); MS *m/z* (rel. int.): 270.089 $[M]^+$ (62) ($C_{16}H_{12}O_4$: 270.089), 253 $[M-OH]^+$ (28), 224 $[253-CHO]^+$ (32), 55 (100).

14-*Methoxydehydrocacalohastin* (**9**). Colourless crystals, mp 127° (TLC: Et_2O–petrol, 1:3, R_f 0.6); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3050, 1630, 1600, 1505 (benzofurane); MS *m/z* (rel. int.): 270.126 $[M]^+$ (25) (calc. for $C_{17}H_{18}O_3$: 270.126), 239 $[M-OMe]^+$ (100), 224 (18), 220 (24).

14-*Hexadecyloxy and* 14-*octadecyloxy-dehydrocacalohastin* (**10** and **11**). Colourless oil (TLC: Et_2O–petrol, 1:10, R_f 0.72); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3050, 1630, 1600 (aromatic); MS *m/z* (rel. int.): 508.391 and 480.360 $[M]^+$ (20 and 41) (calc. for $C_{34}H_{52}O_3$: 508.391 and $C_{32}H_{48}O_3$: 480.360), 239 $[M-OR]^+$ (100), 223 (14).

6β-*Isobutyryloxy*-10α*H-furoeremophil*-1-*one* (**12**). Colourless oil (TLC: Et_2O–petrol, 1:3, R_f 0.35); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1725 (CO_2R, C=O); 1630, 1570 (aromate); MS *m/z* (rel. int.): 318.183 $[M]^+$ (10) (calc. for $C_{19}H_{26}O_4$: 318.183), 248 $[M-O{=}C{=}CMe_2]^+$ (12), 230 $[M-RCO_2H]^+$ (20), 215 $[230-Me]^+$ (38), 124 $[C_7H_8O_2]^+$ (100), 71 $[C_3H_7CO]^+$ (68).

6β-*Methacryloyloxy*-8,8 *dihydroxy*-1β,10β-*epoxyeremophil*-7(11)-*ene*-8,12-*olide* (**13**). Colourless oil (TLC: Et_2O–petrol, 9:1, R_f 0.7); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1775 (γ-lactone), 1730, 1635 (C=CCO_2R); MS *m/z* (rel. int.): 348.157 $[M]^+$ (0.1) (calc. for $C_{19}H_{24}O_6$: 348.157), 262 $[M-RCO_2H]^+$ (7), 244 $[262-H_2O]^+$ (4), 200 $[244-CO_2]^+$ (2), 69 $[C_3H_5CO]^+$ (100); $[\alpha]_D$ – 55, ($CHCl_3$; *c* 0.48).

6β-*Senecioyloxy and* 6β-*angeloyloxy*-8,8 *dihydroxy*-1β,10β-*epoxyeremophil*-7(11)-*ene*-8,12-*olide* (**14** *and* **15**). Colourless oil (TLC: Et_2O–petrol, 9:1, R_f 0.65, not separated by repeated TLC); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1780 (γ-lactone), 1730, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 362.173 $[M]^+$ (0.1) (calc. for $C_{20}H_{26}O_6$: 362.173), 262 $[M-RCO_2H]^+$ (7), 244 $[262-H_2O]^+$ (4), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (52); $[\alpha]_D$ – 55 ($CHCl_3$; *c* 1.13).

6β-*Methacryloyloxy- and* 6β-*senecioyloxy*-1β 8,8 *tri-hydroxy-eremophila*-9,7(11)-*diene*-8,12-*olide* (**16** *and* **17**). Colourless oil (TLC: Et_2O–petrol, 9:1, R_f 0.2, not separated by repeated TLC); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1785 (γ-lactone), 1725, 1640 (C=CCO_2R); MS *m/z* (rel. int.): 362.173 and 348.157 $[M]^+$ (0.6 and 1.7) (calc. for $C_{20}H_{26}O_6$: 362.173 and for $C_{19}H_{24}O_6$: 348.157), 262 $[M-RCO_2H]^+$ (20), 244 $[262-H_2O]^+$ (14), 83 $[C_4H_7CO]^+$ (100), 69 $[C_3H_5CO]^+$ (44), 55 $[83-CO]^+$ (42); $[\alpha]_D$ – 44 ($CHCl_3$; *c* 0.1).

3α-[5-*Methyldodeca*-2E,4E,6E-*trienoyloxy*]-9α,13-*dihydroxy*-10α*H-eremophil*-8-*one-semi acetal* (**18**). Colourless oil (TLC: Et_2O–MeOH, 20:1, R_f 0.65); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3570 (OH); 1705, 1610 (C=CCO_2R); MS *m/z* (rel. int.): 458.303 $[M]^+$ (16) (calc. for $C_{28}H_{42}O_5$: 458.303), 440 $[M-H_2O]^+$ (27), 422 $[440-H_2O]^+$ (6), 250 $[440-O{=}C{=}CHR]^+$ (36), 233 $[440-OCOR]^+$ (100), 232 $[440-RCO_2H]^+$ (92), 215 $[233-H_2O]^+$ (78), 208 $[RCO_2H]^+$ (40), 191 $[RCO]^+$ (36); $[\alpha]_D$ – 67 ($CHCl_3$; *c* 0.8).

3α-[5-*Methyldodeca*-2E,4E,6E-*trienoyloxy*]-9α,13-*dihydro*-10α*H-eremophil*-8-*one*-8-O-*methylacetal* (**19**). Colourless oil (TLC: Et_2O–petrol, 2:1, R_f 0.33); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3570 (OH), 1705, 1605 (C=CCO); MS *m/z* (rel. int.): 472.319 $[M]^+$ (4) (calc. for $C_{29}H_{44}O_5$: 472.319), 440 $[M-MeOH]^+$ (5), 422 $[440-H_2O]^+$ (0.5), 265 $[M-RCO_2]^+$ (9), 233 $[440-RCO_2]^+$ (38), 125 (100); $[\alpha]_D$ – 51 ($CHCl_3$; *c* 0.82).

^{13}C NMR ($CDCl_3$, C-1–C-15): 22.3 *t*, 31.9 *t*, 74.4 *d*, 46.8 *d*, 38.4 *s*, 42.8 *t*, 50.0 *d*, 106.1 *s*, 74.5 *d*, 47.6 *d*, 151.7 *s*, 104.1 *t*, 68.6 *t*, 11.9 *q*, 14.0 *q*; OMe: 51.3 *q*; OCOR: 167.1 *s*, 120.4 *d*, 140.6 *d*, 134.5 *d*, 143.9 *s*, 134.1 *d*, 126.5 *d*, 29.0 *t*, 31.4 *t*, 33.1 *t*, 22.5 *t*, 13.2 *q*.

3α-[5-*Methyldodeca*-2E,4E,6E-*trienoyloxy*]-8,9α-*dihydroxy*-

8-methoxy-10αH-eremophilon-8,12-olide (**20**). Colourless oil (TLC: C_6H_6–CH_2Cl_2–Et_2O, 3:3:2δ and HPLC: MeOH–H_2O, 4:1, R_t = 13.0 min); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1750 (γ-lactone, CO_2R); MS *m/z* (rel. int.): 486.298 $[M]^+$ (6) (calc. for $C_{29}H_{42}O_6$: 486.298), 454 $[M-MeOH]^+$ (1), 279 $[M-RCO_2]^+$ (9), 278 $[M-RCO_2H]^+$ (6), 208 $[RCO_2H]^+$ (21), 191 $[RCO]^+$ (24), 55 (100); $[\alpha]_D$ −12 ($CHCl_3$; *c* 0.2).

3α-Senecioyloxy-9α-[2-methylbutyryloxy]-7β,10αH-eremophil-11-ene-8-one (**21**). Colourless oil (TLC: Et_2O–petrol, 1:2, R_f 0.4); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (C=O), 1720, 1650 (C=CCO_2R), 900 (C=CH_2); MS *m/z* (rel. int.): 418.272 $[M]^+$ (10) (calc. for $C_{25}H_{38}O_5$: 418.272), 316 $[M-C_4H_9CO_2H]^+$ (100), 216 $[316-C_4H_7CO_2H]^+$ (46), 201 $[216-Me]^+$ (14), 85 $[C_4H_9CO]^+$ (40), 83 $[C_4H_7CO]^+$ (82), 57 $[85-CO]^+$ (100), 55 $[83-CO]^+$ (83).

3α-[4-Pent-2E-enoyloxy-pent-2E-enoyloxy]-9α-hydroxy-7β,10αH-eremophil-11-ene-8-one (**22**). Colourless crystals, mp 102° (TLC: C_6H_6–CH_2Cl_2–Et_2O, 3:3:1, then HPLC (MeOH–H_2O, 4:1, R_t = 15.2 min), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3480 (OH), 1730 (C=O, C=CCO_2R); MS *m/z* (rel. int.): 460.283 $[M]^+$ (2.5) (calc. for $C_{27}H_{40}O_6$: 460.283), 442 $[M-H_2O]^+$ (1), 346 $[M-C_5H_9CO_2H]^+$ (3), 235 $[M-OCOR]^+$ (26), 234 $[M-RCO_2H]^+$ (25), 97 $[C_5H_9CO]^+$ (100), 69 $[97-CO]^+$ (30).

3α-[5-Methyldodeca-2E,4E,6E-trienoyloxy]-9α-hydroxy-10αH-eremophil-7(11)-ene-8-one (**23**). Colourless oil (TLC: C_6H_6–CH_2Cl_2–Et_2O, 3:3:1, then HPLC (MeOH–H_2O, 4:1, R_t = 16.0 min), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH), 1720 (C=CCO, C=CCO_2R); MS *m/z* (rel. int.): 442.308 $[M]^+$ (11) (calc. for $C_{28}H_{42}O_4$: 442.308), 414 $[M-CO]^+$ (8), 374 $[M-C_5H_8]^+$ (23), 235 $[M-RCO_2]^+$ (44), 234 $[M-RCO_2H]^+$ (26), 217 $[235-H_2O]^+$ (26), 206 $[234-CO]^+$ (40), 191 $[RCO]^+$ (40), 55 (100); $[\alpha]_D$ −10 ($CHCl_3$; *c* 0.16).

3α-[4-Pent-2E-enoyloxy-pent-2E-enoyloxy]-9α-hydroxy-10αH-eremophil-7(11)-en-8-one (**24**). Colourless oil (TLC: C_6H_6–CH_2Cl_2–Et_2O, 3:3:1, then HPLC, MeOH–H_2O, 4:1, R_t = 7.1 min); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH), 1720 (C=CCO, C=CCO_2R); MS *m/z* (rel. int.): 460.282 $[M]^+$ (1) (calc. for $C_{27}H_{40}O_6$: 460.282), 442 $[M-H_2O]^+$ (0.5), 414 $[442-CO]^+$ (2.5), 346 $[M-C_5H_9CO_2H]^+$ (1.5), 235 $[M-RCO_2]^+$ (26), 234 $[M-RCO_2H]^+$ (32), 206 $[234-CO]^+$ (30), 97 $[C_5H_9CO]^+$ (100), 55 (87).

3α-[5-Methyldodeca-2E,4E,6E-trienoyloxy]-9α,13-dihydroxy-10αH-eremophil-7(11)-en-8-one (**25**). Colourless crystals, mp 148° (TLC: C_6H_6–CH_2Cl_2–Et_2O, 1:1:1, R_f 0.13); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1720 (C=CC=O, C=CCO_2R); MS *m/z* (rel. int.): 458.303 $[M]^+$ (20) (calc. for $C_{28}H_{42}O_5$: 458.303), 440 $[M-H_2O]^+$ (8), 251 $[M-RCO_2]^+$ (26), 233 $[251-H_2O]^+$ (60), 232 $[440-RCO_2H]^+$ (61), 208 $[RCO_2H]^+$ (58), 191 $[RCO]^+$ (26), 55 (100); $[\alpha]_D$ −26 ($CHCl_3$; *c* 4.0).

3α-[4-Pent-2E-enoyloxy-pent-2E-enoyloxy]-8α,9α-dihydroxy-7β,10αH-eremophil-11-ene (**26**). Colourless oil (TLC: Et_2O–petrol, 9:1, then HPLC: MeOH–H_2O, 4:1, R_t = 5.8 min); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3570 (OH), 1725, 1640 (C=CCO_2R); MS *m/z* (rel. int.): 462.298 $[M]^+$ (1) (calc. for $C_{27}H_{42}O_6$: 462.298), 444 $[M-H_2O]^+$ (0.5), 426 $[444-H_2O]^+$ (0.3), 236 $[M-RCO_2H]^+$ (30), 218 $[236-H_2O]^+$ (15), 97 $[RCO]^+$ (100); $[\alpha]_D$ −75 ($CHCl_3$; *c* 0.34).

3α-[4-Angeloyloxy-pent-2E-enoyloxy]-8α,9α-dihydroxy-7β,10αH-eremophil-11-ene (**27**). Colourless oil (TLC: Et_2O–petrol, 9:1, then HPLC: MeOH–H_2O, 4:1, R_t = 5.0 min); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3570 (OH), 1725, 1640 (C=CCO_2R); MS *m/z* (rel. int.): 448.282 $[M]^+$ (1.5) (calc. for $C_{26}H_{40}O_6$: 448.282), 430 $[M-H_2O]^+$ (0.3), 412 $[430-H_2O]^+$ (0.3), 349 $[M-OAng]^+$ (0.4), 348 $[M-AngOH]^+$ (0.4), 236 $[M-RCO_2H]^+$ (18), 218 $[236-H_2O]^+$ (18), 95 $[C_5H_7CO]^+$ (24), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (60).

3α,9α-Di-pent-2E,enoyloxy-8α-hydroxy-7β,10αH-eremophil-11-ene (**28**). Colourless oil (TLC: C_6H_6–CH_2Cl_2, 1:1, then HPLC (MeOH–H_2O, 4:1, R_t = 7.5 min); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3570 (OH), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 446.303 $[M]^+$ (8) (calc. for $C_{27}H_{42}O_5$: 446.303), 332 $[M-RCO_2H]^+$ (4), 218 $[332-RCO_2H]^+$ (100), 200 $[218-H_2O]^+$ (8), 97 $[C_5H_9CO]^+$ (73).

3α-Hydroxy-7β,10αH-eremophil-9-one (**30**). Colourless oil (TLC: Et_2O–petrol, 9:1, R_f 0.4); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1715 (C=O); MS *m/z* (rel. int.): 236.178 $[M]^+$ (18) (calc. for $C_{15}H_{24}O_2$: 236.178), 218 $[M-H_2O]^+$ (42), 203 $[218-Me]^+$ (16), 176 $[218-C_3H_6]^+$ (30), 153 (38), 109 (46), 107 (58), 55 (100); $[\alpha]_D$ −52 ($CHCl_3$; *c* 0.22).

Bisabol-2,7,(14),10-trien-4-one (**31**). Colourless oil (TLC: Et_2O–petrol, 1:1, R_f 0.75); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1670 (C=CC=O); MS *m/z* (rel. int.): 218.167 $[M]^+$ (12) (calc. for $C_{15}H_{22}O$: 218.167), 203 $[M-Me]^+$ (12), 109 $[M-C_8H_{13}]^+$ (68), 93 (98), 69 $[C_5H_9]^+$ (100).

15-Hydroxy-nor-bisabol-2,11-dien-1-one (**32**). Colourless oil (TLC: Et_2O–petrol, 3:1, R_f 0.55); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1670 (C=CC=O); CIMS (isobutane) *m/z* (rel. int.): 223 (100) ($C_{14}H_{22}O_2+1$); Acetylation (30 min heating with 0.1 ml Ac_2O, 70°) gave **32a**, colourless oil (TLC: Et_2O–petrol, 1:3, R_f 0.6); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1230 (OAc), 1670 (C=CC=O); MS *m/z* (rel. int.): 264.173 $[M]^+$ (0.5) (calc. for $C_{16}H_{24}O_3$: 264.173), 168 $[C_9H_{12}O_3$, McLafferty$]^+$ (20), 108 $[168-HOAc]^+$ (100); $[\alpha]_D$ −10 ($CHCl_3$; *c* 0.12).

5-Acetoxy-8-pent-2E-enolyoxy-2,3-epoxybisabol-7(14),10-dien-4-one (**33**). Colourless crystals, mp 130° (TLC: C_6H_6–CH_2Cl_2–Et_2O, 3:3:1, then HPLC: MeOH–H_2O, 4:1, R_t = 5.2 min); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (OAc), 1730 (C=O), 1720, 1640 (C=CCO_2R); MS *m/z* (rel. int.): 404 $[M]^+$ (0.05), 344.199 $[M-HOAc]^+$ (1.5) (calc. for $C_{21}H_{28}O_4$: 344.199), 230 $[344-C_5H_9CO_2H]^+$ (10), 97 $[C_5H_9CO]^+$ (100), 55 (43); $[\alpha]_D$ −22 ($CHCl_3$; *c* 0.23).

8-Angeloyloxy-2-hydroxy-5-desoxy-7,14-dehydroperezone (**34**). Orange crystals, mp 73° (TLC: Et_2O–petrol, 1:3, R_f 0.57); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3420 (OH, hydrogen bonded), 1720, 1640 (C=CCO_2R), 1665 (quinone); MS *m/z* (rel. int.): 344.162 $[M]^+$ (0.2) (calc. for $C_{20}H_{24}O_5$: 344.162), 244 $[M-RCO_2H]^+$ (30), 229 $[244-Me]^+$ (14), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (70); $[\alpha]_D$ +40 ($CHCl_3$; *c* 0.72).

Menth-2-ene-1,7-diol (**35**). Colourless oil (TLC: Et_2O–petrol, 1:1, R_f 0.35); MS *m/z* (rel. int.): 139 $[M-CH_2OH]^+$ (100), 121 $[139-H_2O]^+$ (62), 109 (85), 81 (74), 69 (70); Acetylation (30 min, Ac_2O, 70°) gave **35a**, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1745, 1240 (OAc); MS *m/z* (rel. int.): 139.112 $[M-CH_2OAc]^+$ (100) (calc. for $C_9H_{15}O$: 139.112), 121 $[139-H_2O]^+$ (48), 69 (68); $[\alpha]_D$ −9 ($CHCl_3$; *c* 0.11); ^1H NMR ($CDCl_3$): 5.86 *br d* (H-2), 5.67 *ddd* (H-3), 1.84 *ddd* (H-4), 4.06 and 3.96 *d* (H-7), 1.65 *m* (H-8), 0.96 *d* (H-9), 0.89 *d* (H-10), 2.12 *s* (OAc); [*J* (Hz): 2,3 = 10.5; 3, 4 = 1.5; 3, 5 = 2; 4, 5 = 10; 4, 8 = 4.5; 7, 7′ = 11; 8, 9 = 8, 10 = 7].

3-O-[3-Acetoxypalmitoyl]-shikimic acid-4,5-O-acetate (**36**). Colourless oil (CC: Et_2O, TLC: Et_2O–petrol, 3:2, R_f 0.3); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2700, 1720 (CO_2H), 1760 (OAc), 1720 (CO_2R); MS *m/z* (rel. int.) 494.288 $[M-HOAc]^+$ (3) (calc. for $C_{27}H_{42}O_8$: 494.288), 434 $[494-HOAc]^+$ (8), 374 $[434-HOAc]^+$ (2), 240 $[M-RCO_2H]^+$ (64), 237 $[C_{13}H_{27}CH{=}CHCO]^+$ (100), 198 $[240-$ketene$]^+$ (76), 138 $[198-HOAc]^+$ (60); $[\alpha]_D$ −50 ($CHCl_3$; *c* 15.2); addition of CH_2N_2 in Et_2O gave **36a**, colourless oil; ^1H NMR ($CDCl_3$): 6.73 *dt* (H-2), 5.70 *dd* (H-3), 5.26 *dd* (H-4, H-5), 2.89 *br d* (H-6), 2.42 *br d* (H-6′), 2.07 and 2.06 *s* (OAc), 3.77 *s* (OMe), 2.58 and 2.52 *dd* (H-2′), 5.13 *tt* (H-3′), 1.57 (H-4′), 1.24 *m* (H-5′–H-15′), 0.84 *t* (H-16) [*J* (Hz): 2, 3 = 4; 2, 6 = 2, 6′ ~ 1.5; 3, 4 = 4; 3, 6

= 2; 3,6′ = 3; 5,6 = 5,6′ ~ 3; 6,6′ = 18; 2′,2′ = 16; 2′,3′ = 3′,4′ = 15′,16′ = 7]. Reaction of 27.5 mg **36a** with two equivalents of NaOMe gave 10 mg *hexadec-2E-enoic acid*; ^{1}H NMR ($CDCl_3$): 6.76 *br d* (H-2), 6.97 *dt* (H-3), 2.20 *br dt* (H-4), 1.43 *m* (H-5), 1.25 *m* (H-6–H-15), 0.87 *t* (H-16) (*J* [Hz]: 2,3 = 15; 3,4 = 15,16 = 7).

3,5-Bis-[3,3-*dimethyl allyl*]-p-*hydroxybenzaldehyde* (**37**). Colourless crystals, mp 118° (TLC: C_6H_6–CH_2Cl_2, 1:1, then HPLC: MeOH–H_2O, 4:1, R_t = 4.0 min); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2700, 1670 (vinylogic acid); MS *m/z* (rel. int.): 258.162 $[M]^+$ (100) (calc. for $C_{17}H_{22}O_2$: 258.162), 229 $[M-CHO]^+$ (18), 203 $[M-C_4H_7]^+$ (65), 187 (52), 173 (40); ^{1}H NMR ($CDCl_3$): 7.53 *s* (H-2, H-6), 9.82 *s* (H-7), 6.01 *s* (OH), 3.49 *br d* (*J* = 7 Hz), 5.30 *tqq* (*J* = 7, 1, 1 Hz), 1.79 and 1.77 *br s* ($CH_2CH{=}CMe_2$).

3,4,5-*Trimethoxy*-8,9-*dihydroxycumol-ditiglate* (**38**). Colourless oil (TLC: Et_2O–petrol, 1:1, R_f 0.45); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1700 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 406.199 $[M]^+$ (4) (calc. for $C_{22}H_{30}O_7$: 406.199), 306 $[M-C_4H_7CO_2H]^+$ (53), 83 $[C_4H_7CO]^+$ (66), 55 $[83-CO]^+$ (100); ^{1}H NMR ($CDCl_3$): 6.49 *s* (H-2, H-6), 3.34 *tt* (H-7, *J* = 7, 7 Hz), 4.43 and 4.39 *dd* (H-8, H-9, *J* = 11, 6 Hz), 3.83 *s* (3H, OMe), 3.84 *s* (6H, OMe), 6.83 *qq* (*J* = 7.5, 1 Hz), 1.78 *dq* (*J* = 7.5, 1 Hz), and 1.81 *dq* (*J* = 1, 1 Hz, OTigl).

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