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EREMOPHILANE-, BISABOLANE- AND SHIKIMIC ACID-DERIVATIVES FROM PORTUGESE *SENECIO* SPECIES

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Key Word Index—*Senecio lividus*, *S. pyrenaicus* ssp. *caespitosus*, *S. doronicum*; Compositae; sesquiterpenes; eremophilanes; furoeremophilanes; bisabolanes; shikimic acid derivatives.

Abstract—The aerial parts of *Senecio lividus* afforded four triesters of shikimic acid, four eremophilanes and two bisabolene epoxides. The roots of *S. pyrenaicus* ssp. *caespitosus* gave a known furoeremophilane while the aerial parts afforded a new one with a rare substitution pattern. *S. doronicum* contained known furoeremophilanes. The structures were elucidated by various high field NMR techniques.

INTRODUCTION

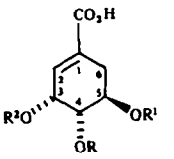
The large genus *Senecio* is rich in many different types of natural products. In a continuation of our chemotaxonomic studies [1, 2], which have already led to some grouping of the species [3, 4], we have now studied three species from Portugal *S. lividus*, L., *S. pyrenaicus* ssp. *caespitosus* (Brot.) Franco. and *S. doronicum* L.

RESULTS AND DISCUSSION

The Portugese annual *S. lividus* had not been investigated chemically. The extract of the aerial parts afforded four new shikimic acid derivatives (**1–4**), four eremophilane derivatives (**5–8**) and the bisabolene derived esters **9** and **10**.

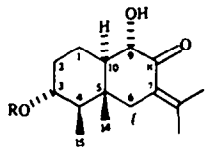
The ^{1}H NMR spectra of the methyl esters of **1–4** (Table 1) established that different esters of shikimic acid were present as all signals could be assigned by spin decoupling. Similar compounds had been reported from several other *Senecio* species [1, 2]. The nature of the ester groups followed from the ^{1}H NMR spectra and the mass spectra. However, the relative position of the ester groups could not be deduced from the spectra. The fragment $[M - OCOC_3H_7]^+$ (*m/z* 409) was the first indication that in compound **1** a 3-O-methylbutyrate was present. As the other fragments were formed by loss of acids, the formation of *m/z* 409 was most likely due to an allylic position of the methylbutyrate. After assignment of the ^{13}C NMR signals by 2D-correlated spectra (Table 2) this assumption was verified by selective INEPT spectra through long range couplings (typical parameters: J_{13}, ^{1}H ~ 3.5 Hz, 30 DB under 0.2 W, 90° (^{13}C) 7 μs, 90° (sel. ^{1}H 7.5 ms). By irradiation of the α-methyl signal of the methylbutyrate the corresponding ^{13}C-carbonyl signal was assigned. Irradiation of H-3 and H-5 indicated the presence of a long range coupling with this carbonyl carbon, while a similar coupling between H-4 and the carbonyl carbon of the decanoyl residue was present. Further long range couplings were observed between H-3, C-1 and C-4, H-5, C-1 and C-3, and H-4 and C-3.

From these clear-cut results the relative position of the ester groups in compounds **2a–4a** was deduced from the chemical shifts of H-3–H-5 when compared with those of **1a** and from the appearance of allylic ions at *m/z* 395 and 381 respectively.

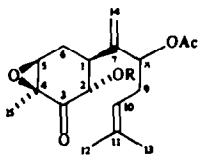


	1	2	3	4
R	A*	B*	A	A
R¹	Mebu	Mebu	iBu	iBu
R²	Mebu	Mebu	iBu	Mebu

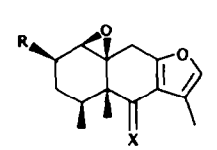
1a–4a are the methylesters



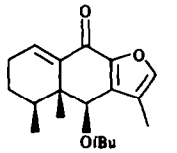
	5	6	7	8
R	C*	D*	C	D
			Δ⁹	Δ⁹



	9	10
R	Ang	Sen



	11	12	13	14
R	OAc	H	H	H
X	βOAng,H	H,	βOAc,H	=O



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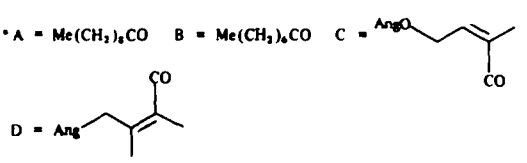

Table 1. ^{1}H NMR spectral data of compounds **1a–4a** ($CDCl_3$, 400 MHz, δ-values)

	1a	**2a**	**3a**	**4a**
H-2	6.75 *ddd*	6.77 *ddd*	6.76 *ddd*	6.76 *ddd*
H-3	5.73 *dd br*	5.75 *dd br*	5.75 *dd br*	5.74 *dd br*
H-4	5.24 *dd*	5.26 *dd*	5.27 *dd*	5.26 *dd*
H-5	5.30 *ddd*	5.31 *ddd*	5.30 *ddd*	5.30 *dd*
H-6_1	2.95 *dd br*	2.96 *dd br*	2.94 *dd br*	2.95 *dd br*
H-6_2	2.37 *m*	2.37 *m*	2.40 *dd br*	2.39 *m*
OMe	3.78 *s*	3.78 *s*	3.78 *s*	3.78 *s*
O-*i*Bu (Mebu)	2.37 *m*	2.37 *m*	2.56 *qq* (2.53 *qq*)	2.53 *qq* 2.38 *m*
	1.67 *m*	1.68 *m*	1.19 *d* (1.18 *d*)	1.17 *d* 1.47 *m*
	1.47 *m*	1.47 *m*	1.17 *d* (1.16 *d*)	1.16 *d* 1.48 *m*
	1.14 *d* (1.12 *d*)	1.16 *d* (1.14 *d*)		1.16 *d*
	0.92 *t* (0.90 *t*)	0.93 *t* (0.91 *t*)		0.93 *t*
OR	2.23 *t*	2.25 *t*	2.25 *t*	2.25 *t*
	1.57 *tt*	1.59 *tt*	1.58 *tt*	1.58 *tt*
	1.26 *m*	1.26 *m*	1.26 *m*	1.26 *m*
	0.87 *t*	0.88 *t*	0.89 *t*	0.89 *t*

J[Hz]: 2,3 = 3,4 = 4; $2,6_1 = 2,6_2 = 2$; 4,5 = 8.5; $5,6_1 = 5,6_2 = 5.5$; *i*Bu: 2,3 = 2,4 = 7; Mebu: 2,5 = 3,4 = 7; OR: 2,3 = 3,4 = 7,8 = 9,10 = 7.

Table 2. ^{13}C NMR spectral data of compounds **1** and **2** ($CDCl_3$, 67.9 MHz, δ-values*)

	1	**2**
C-1	131.4 *s*	131.5 *s*
C-2	132.7 *d*	132.8 *d*
C-3	65.6 *d*	65.7 *d*
C-4	66.3 *d*	66.3 *s*
C-5	68.1 *d*	68.2 *d*
C-6	29.2 *t*	29.1 *t*
C-7	165.9 *s*	166.0 *s*
OMe	52.2 *q*	52.2 *q*
*i*Bu (Mebu)	175.5 (×2) *s*	175.5 (×2) *s*
	41.0 (40.95) *d*	41.1 (41.0) *d*
	26.6 (×2) *t*	26.6 (×2) *t*
	16.4 (×2) *q*	16.4 (×2) *q*
	11.5 (×2) *q*	11.6 (×2) *q*
OR	172.5 *s*	172.6
	34.0 *s*	34.0
	24.7 *t*	24.7
	29.0 *t*	28.9
	29.3 *t*	29.1
	29.2 *t*	31.6
	29.1 *t*	22.6
	31.8 *t*	14.0
	22.6 *t*	
	14.0 *q*	

*Signals assigned by 2D-correlated spectra.

Table 3. ^{1}H NMR spectral data of compounds **5–8** ($CDCl_3$, 400 MHz, δ-values)

	5 **6**	**7** **8***
H-3	4.85, 4.80 *ddd*	4.92, 4.87 *ddd*
H-6	2.93, 2.92 *d*	2.91, 2.92 *d*
H-6′	1.88 *m*	2.15 *m*
H-9	3.84, 3.83 *d*	—
H-12	1.93 *d*	2.18 *d*
H-13	1.81 *d*	1.91 *d*
H-14	0.96, 0.95 s	1.04, 1.03 *s*
H-15	0.96, 0.94 d	1.00, 0.98 *d*
OR	6.05 *tq*, 5.79 *tq*	6.10 *m*, 5.81 *tq*
	5.12 *dq*, 5.32 *s br*	5.11 *dq*, 5.34 *s br*
	1.92 *d br*, 1.93 *s br*	1.92 *d br*, 1.91 *s br*
	6.09 *qq*, 6.11 *qq*	6.10 *m*, 6.10 *m*
	2.00 *dq*, 2.00 *dq*	2.00 *dq*, 2.00 *dq*
	1.91 *dq*, 1.90 *dq*	1.91 *dq*, 1.91 *dq*

*H-1 3.06 *m*; H-1′ 2.15 *m*; OH 6.56 *s br*;
J[Hz]: 2,3 = 4.5; 2′,3 = 3,4 = 11; 4,15 = 7; 6′,12 = 6′,13 = 1.5; compounds 5 and 6: 1,10 = 11; Ang OAng: 3,4 = 5; 3,5 = 4,5 = 1.5; 3′,4′ = 7; 3′,5′ = 4′,5′ = 1.5; Sen OAng: 2,4 = 2,5 = 1.5; 3′,4′ = 7: = 4′,5′ = 1.5; Sen OAng: 2,4 = 2,5 = 1.5; 3′,4′ = 7: 3′,5′ = 4′,5′ = 1.5.

The separation and the structure elucidation of the eremophilones **5–8** caused some difficulties, especially as unusual ester groups were attached to the sesquiterpene moiety. The ^{1}H NMR spectra of compounds **5** and **6** which could not be separated (Table 3) were close to those of related 9α-hydroxyeremophil-7(11)-en-8-ones [2]. The nature of the ester residues was deduced from the molecular formulae and from the ^{1}H NMR signals which required in compound **5** an angelate with a 5′-angeloyloxy group and in compound **6** a senecioate with a 5′-angeloyloxy group. Thus in the spectrum of **5** two β-proton signals of angelates and a doublet quartet at δ5.12 were visible while in that of **6** the signal of an α-proton of a senecioate (δ5.79) and a broadened singlet at δ5.32 (2H, H-5′) were present. As in similar cases the H-3 signal was at lower fields in the spectrum of **5** [2]. The position of the angelate in the senecioate followed from the shift of the methyl group of the latter [δ1.93 *s*(*br*)]. As the chemical shift of the sesquiterpene protons were in part slightly different all signals could be assigned and the concentrations of **5** and **6** in the mixture determined.

The ^{1}H NMR spectra of compounds **7** and **8**, which like compounds **5** and **6** could not be separated (Table 3), differed from those of **5** and **6** by the absence of the H-9 signal, a downfield shift of the H-12 signal and by the appearance of a hydroxy signal at δ6.56 typical for a hydrogen bonded hydroxyl group. In agreement with the molecular formulae therefore the corresponding $^9\Delta$-derivatives of **5** and **6** were present. The signals of the ester residues were identical with those of **5** and **6**. Again only small shift differences were visible for the protons of the sesquiterpene parts of the molecules.

The ^{1}H NMR spectrum of the mixture of **9** and **10** (Table 4) in agreement with those of **5** and **6** differed only in the signals of the ester residues which were typical for angelates and senecioates respectively. Spin decoupling allowed the assignment of all signals. Together with the couplings and the molecular formulae the structures could be assigned as similar compounds had been isolated from *Senecio* species [2]. The relative position of the ester groups followed from the chemical shifts of H-2 and H-8 when compared with those of the diangelate [5]. Furthermore, the shift of H-8 was identical in both ketones while that of H-2 was different indicating the acetoxy group at C-8.

The roots of *S. pyrenaicus* ssp. *caespitosus* afforded adenostylone (**15**) [6]. All data were identical with those of authentic material. From the aerial parts the furoeremophilane **11** was isolated. The ^{1}H NMR spectral data (see Experimental) were close to those of 6β-angeloyloxyeuryopsin epoxide, the corresponding 2-desacetoxy derivative [7]. The presence of an ester group at C-2 followed from the result of spin decoupling while the stereochemistry and the relative position of the ester group was determined by NOE difference spectroscopy. Saturation of H-14 gave NOE's with H-15, H-3β, H-9β and the angelate methyl signal (H-5'), H-1 gave NOE's with H-9α and H-2, H-2 with H-3α and H-1 while H-6 gave an effect with H-3α. Accordingly, H-1, H-2 and H-6 were α-orientated and the angelate had to be placed at C-6.

Table 4. ^{1}H NMR spectra data of compounds **9** and **10** ($CDCl_3$, 400 MHz, δ-values)

	9	**10**
H-1	2.77 *ddd br*	2.75 *ddd br*
H-2	5.85 *d*	5.76 *d*
H-5	3.43 *d*	3.42 *d*
H-6α	2.56 *ddd*	2.53 *ddd*
H-6β	2.18 *dd*	2.18 *dd*
H-8	5.04 *t br*	5.04 *t br*
H-9	2.31 *dd br*	2.31 *dd br*
H-10	5.02 *t br*	5.02 *t br*
H-12	1.68 *s br*	1.69 *s br*
H-13	1.61 *s br*	1.63 *s br*
H-14	5.24 *s br* 5.10 *s br*	5.24 *s br* 5.12 *s br*
H-15	1.47 *s*	1.46 *s*
OAc	2.03 *s*	2.05 *s*
OC OR	6.06 *qq*	5.68 *qq*
	1.97 *dq*	2.15 *d*
	1.88 *dq*	1.90 *d*

J[Hz]: 1,2 = 13.5; 1,6α = 7,5; 1,6β = 10.5; 5,6α = 4; 6α,6β = 16; 8,9 = 9,10 = 6.5; OAng: 3,4 = 7; 3,5 = 4,5 = 1.5; OSen: 2,4 = 2,5 = 1.5.

The ^{13}C NMR spectrum also supported the structure.

The aerial parts of *S. doronicum* afforded the furoeremophilanes **12** [7], **13** [7] and **14** [8].

The isolation of **1**–**10** from *S. lividus* supports its placement in the sect. Senecio as so far all the other species of this section gave no furoeremophilanes which are otherwise widespread in the genus [1–3]. Especially close is its relationship to the annual *S. sylvaticus* which contains similar eremophilanes [8].

S. pyrenaicus is placed in the section Crociseris [9] together with *S. doronicum* both containing epoxy-furoeremophilanes while *S. paludosus* also placed in this section, afforded aromatic furoeremophilones [8].

EXPERIMENTAL

The air-dried plant material was extracted with MeOH–Et_2O–petrol (1:1:1), and the extract obtained worked-up as reported previously [10]. The extract of 350 g of aerial parts of *S. lividus* (collected near Porto, Portugal, all voucher specimens from this study deposited in the herbarium of the Dept. of Botany, Porto) was first separated by CC (Silica gel) into two fractions (1:Et_2O–petrol, 1:2 and 1:1; 2:Et_2O and Et_2O–MeOH, 9:1). PTLC (Silica gel PF 254, Et_2O–petrol, 2:3) of fraction 1 gave 2 mg **7** and **8** (R_f 0.6), which could not be separated even by HPLC, and a mixture (R_f 0.4) which gave by HPLC (RP 8, MeOH–H_2O, 4:1, ca. 100 bar) 3.5 mg **9** and **10** (R_t 7.0 min.) and 10 mg **5** and **6** (R_t 9.9 min.). The ^{1}H NMR spectrum of fraction 2 indicated the presence of a mixture of shikimic acid derivative. After methylation with CH_2N_2, HPLC (RP 8, MeOH–H_2O, 17:3) of fraction 2 afforded 2.5 mg **2a** (R_t 14.3 min.), 2 mg **3a** (R_t 15.5 min.), 13 mg **4a** (R_t 18.8 min.) and 33 mg **1a** (R_t 12.6 min.).

The extract from 470 g of the aerial parts of *S. pyrenaicus* (collected in the Serra Estrela) gave by CC and PTLC (Et_2O–petrol, 3:7) 68 mg **11** while the extract of 300 g roots gave 500 mg **15**.

The extract from 120 g of the aerial parts of *S. doronicum* (grown from seeds from the Botanic Garden, Coimbra) gave by CC and PTLC 200 mg **12**, 50 mg **13** and 150 mg **14**. Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

3-O,5-O-Di-[2-*methylbutyryl*]-4-O-*decanoyl-shikimic acid methyl ester* (**1a**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (CO_2R); MS *m/z* (rel. int.): 510.318 [M]$^+$ (3) (calc. for $C_{28}H_{46}O_8$: 510.318), 409 [M – $OCOC_4H_9$]$^+$ (2.6), 408 [M – $C_4H_9CO_2H$]$^+$ (2.5), 338 [M – RCO_2H]$^+$ (9), 254 [338 – O=C=C(Me)Et]$^+$ (20), 155 [$C_9H_{19}CO$]$^+$ (12), 85 [C_4H_7CO]$^+$ (78), 57 [85 – CO]$^+$ (100).

3-O,5-O-Di-[2-*methylbutyryl*]-4-O-*octanoyl-skikimic acid methyl ester* (**2a**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R); MS *m/z* (rel. int.): 482.288 [M]$^+$ (1.2) (calc. for $C_{26}H_{42}O_8$: 482.289), 381 [M – $OCOC_3H_7$]$^+$ (1.1), 338 [M – RCO_2H]$^+$ (4), 254 (10), 127 [$C_7H_{15}CO$]$^+$ (14), 85 [C_4H_7CO]$^+$ (63), 57 [85 – CO]$^+$ (100).

3-O,5-O-*Diisobutyryl*-4-O-*decanoyl-shikimic acid methyl ester* (**3a**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}; 1740 (CO_2R); MS *m/z* (rel. int.): 482 [M]$^+$ (10), 395 [M – OCOR]$^+$ (4), 394 [M – $C_3H_7CO_2H$]$^+$ (3), 310 [M – $C_9H_{19}CO_2H$]$^+$ (19), 240 [310 – O=C=CMe_2]$^+$ (26), 155 [RCO]$^+$ (24), 71 [C_3H_7CO]$^+$ (100).

3-O- [2-*Methylbutyryl*-5-O-*isobutyryl*-4-O-*decanoyl-shikimic acid methyl ester* (**4a**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (CO_2R); MS *m/z* (rel. int.): 496.304 [M]$^+$ (13) (calc. for $C_{27}H_{44}O_8$: 496.304), 408 [M – $C_3H_7CO_2H$]$^+$ (3), 395 [M – $OCOC_4H_7$]$^+$ (5), 324 [M – RCO_2H]$^+$ (22), 254 [324 – O=C=CMe_2]$^+$ (13), 240 [324 – O=C=C(Me)Et]$^+$ (20), 155 [RCO]$^+$

(22), 85 $[C_4H_7CO]^+$ (75), 71 $[C_3H_7CO]^+$ (56), 57 $[85 - CO]^+$ (100).

9β-Hydroxy-3β-[4'-angeloyloxy-angeloyloxy- and 5'-angeloyloxy senecioyloxy respectively]-10αH-eremophil-7(11)-en-8-one (**5** and **6**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1710 (CO_2R, C=O); MS *m/z* (rel. int.): 432.251 $[M]^+$ (12) (calc. for $C_{25}H_{36}O_6$: 432.251), 234 $[M - RCO_2H]^+$ (19), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (98).

9-Hydroxy-3β-[4'-angeloyloxy-angeloyloxy- and 4'-angeloyloxy senecioyloxy respectively]-eremophil-7(11)-9-dien-8-ones (**7** and **8**). Colourless oil; MS *m/z* (rel. int.): 430.236 $[M]^+$ (5) (calc. for $C_{25}H_{34}O_6$: 430.236), 232 $[M - RCO_2H]^+$ (88), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (88).

2α-[Angeloyloxy and senecioyloxy respectively]-8-acetoxy-4β,5β-epoxybisabola-7(11),10-dien-3-one (**9** and **10**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1725 (CO_2R, C=O); MS *m/z* (rel. int.): 390.204 $[M]^+$ (0.6), (calc. for $C_{22}H_{30}O_6$: 390.204), 330 $[M - HOAc]^+$ (5), 230 $[330 - RCO_2H]^+$ (18), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (38).

2β-Acetoxy-6β-angeloyloxy-1β, 10β-epoxyfuroeremophilane (**11**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (OAc), 1730, 1645 (C=CCO_2R); MS *m/z* (rel. int.): 388.189 $[M]^+$ (0.5) (calc. for $C_{22}H_{28}O_6$: 388.189), 306 $[M - O{=}C{-}C(Me)CH{=}CH_2]^+$ (0.6), 288 $[M - RCO_2H]^+$ (9), 228 $[288 - HOAc]^+$ (9), 199 $[228 - CHO]^+$ (15), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (39); ^1H NMR ($CDCl_3$): δ3.36 (*d*, H-1), 5.19 (*ddd*, H-2), 2.05 and 1.57 (*m*, H-3), 1.64 (*m*, H-4), 6.23 (*sbr*, H-6), 3.26 and 2.37 (*dbr*, H-9), 7.06 (*sbr*, H-12), 1.82 (*d*, H-13), 1.22 (*s*, H-14), 1.12 (*d*, H-15), 2.08 (*s*, OAc), OAng: 6.16 *qq*, 2.01 *dq*, 1.92 *dq* (*J*[Hz]: 1,2 ≈ 2,3 = 3.5; 2,3' = 6; 4,15 = 7; 9,9' = 16; 12,13 = 1; OAng: 3,4 = 7; 3,5 = 4,5 = 1, ^{13}C NMR ($CDCl_3$, C-1–C-15): 61.4 *d*, 68.1 *d*, 30.2 *t*, 32.8 *d*, 40.8 *s*, 69,4 *d*, 117.1 *s*, 148.0 *s*, 30.3 *t*, 65.9 *s*, 119.5 *s*, 139.0 *d*, 8.3 *q*, 15.3 *q*, 17.3 *q*; OAc: 170.5 *q*, 21.0 *q*: OAng: 167.4 *s*, 127.2 *s*, 139.6 *d*, 15.8 *q*, 20.6 *q* (assigned by 2D-correlated spectra).

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