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ERIOLANOLIDES, EUDESMANOLIDES AND A REARRANGED SESQUITERPENE FROM *ERIOPHYLLUM* SPECIES*

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Key Word Index—*Eriophyllum lanatum*; *E. staechadifolium*; Compositae; sesquiterpene lactones; eriolanolides; eudesmanolides; tricyclic sesquiterpene alcohol; unusual carbon skeleton.

Abstract—The investigation of two *Eriophyllum* species afforded, in addition to numerous known compounds, eight new sesquiterpene lactones related to eriolanin, two eudesmanolides and a new type of sesquiterpene alcohol. The structures were elucidated by spectroscopic methods and a few chemical transformations. The chemotaxonomic situation of this genus, the placement of which is still in doubt, is discussed briefly.

INTRODUCTION

The placement of the N. American genus *Eriophyllum* is still a problem. Earlier a member of the tribe Helenieae, its genera have now been relegated to different tribes and subtribes, mainly belonging to the Heliantheae [1]. It was proposed as a member of a new subtribe Eriophylliinae in the tribe Senecioneae, which was in contradiction with the results of the chemical investigations of the three species investigated so far. The occurrence of sesquiterpene lactones of different types [2–6] and of the thiophenacetylene **13** and the corresponding dithio derivative **14** [7], have never been reported from any member of the Senecioneae. We have re-investigated in more detail the constituents of two species, *E. lanatum* (Pursh.) Forbes and *E. staechadifolium* Lag. In addition to already known compounds, ten new sesquiterpene lactones and a new type of a sesquiterpene alcohol were isolated, again showing that the placement of the genus has to be corrected.

RESULTS AND DISCUSSION

The aerial parts of *E. lanatum* had been reported to contain the secoeudesmanolides eriolanin (**1**) and eriolangin [2]. We have now isolated in addition to lupeyl acetate, the isomeric matricarional acetates **15a** and **15b** [7], germacrene D and the sesquiterpene lactone **12** [8], a complex mixture of further sesquiterpene lactones, the eriolanin-like compounds **2**–**9** and the eudesmanolides **10** and **11**. The main compound was the lactone **2**, which on acetylation afforded **5**, which was found to be identical with a further lactone isolated from the mixture. The ^{1}H NMR data of **2** and **5** (Table 1) showed that we were dealing with compounds related to eriolanin. However, the isobutyrate had to be placed at C-14 as the chemical shifts of the H-14 signals were nearly the same in the spectra of **2** and **5**. Careful spin decoupling starting with the H-7 signal allowed the assignment of the signals of H-6–H-9. Also, the stereochemistry at C-6–C-8 followed from the couplings observed. Further spin decoupling led to the sequence of the side chain at C-5, while the presence of the 5,10 double bond followed from the chemical shifts of H-6 and H-14 and the absence of additional couplings for these signals, thus indicating the same carbon skeleton as in **1**, which itself was not detected. Minor amounts of not completely pure methacrylates (**6**–**9**), however, were present. Their ^{1}H NMR data (Table 1) showed that they were 14-methacryloyloxy compounds. Consequently, in the spectra of **6**–**9** the H-14 signals were shifted slightly downfield, compared with the shifts in **2**–**5**. Acetylation of **6**–**8** afforded the diacetate **9**, identical with the natural lactone. The isomeric acetates **3** and **4** also gave the diacetate **5**. Therefore, the structures of all these lactones were settled. The stereochemistry at C-4, however, was assigned only by analogy to that of eriolanin, where the configuration was established by X-ray [9]. We propose the name eriolanolide for the compound without oxygen functions at C-1, C-6 and C-14.

The structures of the isomeric eudesmanolides **10** and **11** were determined from the ^{1}H NMR data (Table 1). Starting with the signal of H-7, spin decoupling allowed the assignment of the signals of H-6–H-9 in the spectrum of **10**. The stereochemistry at C-8 followed from the couplings observed, especially if compared with those of alantolactone. Also the sequence of H-1–H-4 could be deduced by spin decoupling, while the configurations at C-1, C-2 and C-4 followed from the couplings observed. $J_{1,2}$ and $J_{2\beta,3\alpha}$ being large, both oxygen functions must be equatorial, while the methyl at C-4 was axial orientated as $J_{3\alpha,4}$ was 6 Hz only. **10**, therefore, was the 2α-acetoxy derivative of the known 1β-hydroxy alantolactone [10]. Although only 0.3 mg of the second eudesmanolide was available, careful ^{1}H NMR investigations clearly established the proposed structure. Again by spin decoupling all signals could be assigned. The couplings

* Part 350 in the series "Naturally Occurring Terpene Derivatives". For Part 349, see Bohlmann, F., Ahmed, M., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 2027.

Table 1. ^{1}H NMR spectral data of compounds **2**–**11** (270 MHz, TMS as internal standard)

	2($CDCl_3$)	**3**($CDCl_3$)	**4**(C_6D_6)*	**5**(C_6D_6)*	**6**($CDCl_3$)	**7**($CDCl_3$)	**8**(C_6D_6)*	**10**		**11**
								10($CDCl_3$)*	$CDCl_3$–C_6D_6 (2:1)	**11**($CDCl_3$)*
H-1	3.55 *ddd*	3.53 *ddd*	4.03 *ddd*	4.03 *ddd*	3.55 *ddd*	3.53 *ddd*	4.03 *ddd*	3.23 *dd*	3.03 *dd*	3.55 *dd*
H-1′	3.42 *ddd*	3.43 *ddd*	3.96 *ddd*	3.95 *ddd*	3.42 *ddd*	3.43 *ddd*	3.96 *ddd*			
H-2	1.4 *m*	1.33 *m*	1.25 *m*	1.25 *m*		1.33 *m*	1.25 *m*	5.15 *ddd*	5.03 *ddd*	5.02 *dd*
H-3	1.1 *m*	1.08 *m*	1.03 *m*	1.06 *m*		1.1 *m*	1.03 *m*	1.91 *ddd*	1.76 *ddd*	2.67 *dd* (*br*)
								1.61 *ddd*	1.44 *ddd*	2.06 *dd* (*br*)
H-4	2.80 *m*	2.79 *m*	2.53 *ddq*†	2.58 *m*	2.80 *m*	2.79 *m*	2.53 *ddq*	2.60 *dq*(*br*)	2.35 *dq*(*br*)	—
H-6	4.24 *s*(*br*)	5.25 *d*	3.75 *d*	5.27 *d*	4.24 *s*(*br*)	5.25 *d*	3.75 *d*	5.30 *d*	5.00 *d*	2.87 *dd*
										2.00 *dd*(*br*)
H-7	3.55 *m*	3.51 *dddd*	2.88 *dddd*	3.01 *dddd*	3.55 *m*	3.51 *dddd*	2.88 *dddd*	3.59 *dddd*	3.16 *dddd*	3.09 *ddddd*
H-8	5.08 *ddd*	5.01 *ddd*	4.41 *ddd*	4.28 *ddd*	5.08 *ddd*	5.01 *ddd*	4.41 *ddd*	4.84 *ddd*	4.44 *ddd*	4.49 *ddd*
H-9	2.78 *dd*	2.76 *dd*	2.50 *m*	2.57 *dd*	2.78 *dd*	2.76 *dd*	2.50 *m*	2.66 *dd*	2.48 *dd*	2.38 *dd*
H-9′	2.68 *dd*	2.63 *dd*		2.33 *dd*	2.68 *dd*	2.63 *dd*		1.56 *dd* (*br*)	1.26 *dd* (*br*)	1.50 *dd*
H-13	6.33 *d*	6.39 *d*	6.08 *d*	6.26 *d*	6.33 *d*	6.39 *d*	6.07 *d*	6.24 *d*	6.06 *d*	6.31 *d*
H-13′	5.80 *d*	6.01 *d*	4.98 *d*	5.52 *d*	5.80 *d*	6.01 *d*	4.97 *d*	5.65 *d*	5.28 *d*	5.64 *d*
H-14	4.75 *d*	4.70 *d*	4.56 *d*	4.58 *d*	4.83 *d*	4.80 *d*	4.62 *d*	1.25 *s*	1.14 *s*	1.09 *s*
H-14′	4.50 *d*	4.60 *d*	4.36 *d*	4.43 *d*	4.56 *d*	4.67 *d*	4.39 *d*			
H-15	1.14 *d*	0.92 *d*	0.86 *d*	0.84 *d*	1.14 *d*	0.92 *d*	0.84 *d*	1.19 *d*	1.01 *d*	1.68 *s* (*br*)
OAc	—	2.06 *s*	1.83 *s*	1.83 *s*	—	2.07 *s*	1.82 *s*	2.10 *s*	1.85 *s*	2.12 *s*
	—	—	—	1.60 *s*	—	—	—	—	—	—
OCOR	2.58 *qq*	2.59 *qq*	2.47 *qq*	2.47 *qq*	6.16 *s* (*br*)	6.18 *s* (*br*)	6.30 *s* (*br*)	—		
	1.19 *d*	1.19 *d*	1.18 *d*	1.17 *d*	5.62 *dq*	5.63 *s* (*br*)	5.32 *s* (*br*)	—	—	
	—	1.18 *d*	1.16 *d*	1.16 *d*	1.97 *s* (*br*)	1.18 *s* (*br*)	1.94 *s* (*br*)	—	—	—
OH	—	—	—	—	—	—	—	2.20 *d*	1.98 *d*	2.18 *d*

* 400 MHz.

† J = 7,5,7.

J (Hz): Compounds **2**–**9**: 1,1′ = 12; 1,2 = 1,2′ = 1′,2 = 1′,2′ ~ 6; 4,15 = 7; 6,7 = 1.5; 7,8 = 7.5; 7,13 = 2.5; 8,9 = 2; 8,9′ = 3.5; 9,9′ = 16; 14,14′ = 12; compound **9**: ($CDCl_3$)*: H-14, 4.79 and 4.62 (*d*, J = 12 Hz), 6.16 *s* (*br*), 5.61 *s* (*br*), 1.96 *s* (*br*), other signals identical with those of **5**, compound **10**: 1,2 = 10; 1,OH = 4; 2,3 = 4.5; 2,3′ = 3,3′ = 12; 3,4 = 1.6; 3′,4 = 6; 4,15 = 7.6; 6,7 = 4; 7,8 = 6.5; 7,13 = 1.5; 8,9 = 8,9′ = 3; 9,9′ = 15; compound **11**: 1,2 = 10; 1,OH = 3.8; 2,3 = 7.5; 2,3′ = 10; 3,3′ = 17; 6,6′ = 13.5; 6,7 = 7.5; 6′,7 = 10; 7,8 = 10; 8,9 = 4.5; 8,9′ = 11; 9,9′ = 14; 7,13 = 2.8; 7,13′ = 2.5.

observed required a changed stereochemistry at C-8. In particular, the couplings $J_{7,13}$, $J_{7,8}$ and $J_{8,9}$ were those of an 8,12-*trans* eudesmanolide. Consequently, the data were close to those of 8-epiivangustin [10]. The roots afforded **3**, **5**, **12**, **13** and **14**.

The aerial parts of *E. staechadifolium*, from which eupatoriopicrin (**24**) was isolated in an earlier study [3], afforded germacrene D, bicyclogermacrene, **13**, **14**, the thymol derivatives **16**–**22** and in addition to **24** the corresponding alcohol eupatolide (**23**) [11], hiyodorilactone (**25**) [12], the corresponding ester **26** [13], ligustin (**27**) [14], inuviscolide (**28**) [10] and a sesquiterpene alcohol, which turned out to be **29**. Careful spin decoupling using mixtures of solvents and shift reagents allowed the assignment of nearly all signals (Table 2). The most important point, however, was the transformation of **29** by heating with acetic anhydride to the known hydrocarbon silphiperfol-6-ene (**30**) [15], obviously formed via the ion **29a** by double Wagner–Meerwein rearrangement. In addition, the non-rearranged hydrocarbon **31** was isolated, which afforded two epoxides **32**, only one of which could be isolated pure. The ^{1}H NMR signals of **31** and **32**, however, could not be interpreted completely. Those, which could be assigned, agreed with the proposed structures of **31** and **32**. The ^{13}C NMR spectrum of **29** (Table 2) also supported the proposed structure. Though the stereochemistry at C-7 and C-8 was not rigorously established, the proposed structure was most likely as the observed rearrangement is easier to understand if a *trans* orientation of the hydroxyl and the 7,11-bond was assumed. **29** has been isolated from *Flourensia heterolepis* together with the closely related hydrocarbons silphinene [15] and silphiperfol-6-ene [15]. **29** most probably is the hydroxy derivative of **37**, an important intermediate in the biogenesis of a group of tricyclic hydrocarbons [15]. **37** could be formed via **33**, the first cyclization product of farnesyl pyrophosphate, and **34**–**36**.

The compounds isolated so far from *Eriophyllum* species show that this genus cannot be placed in the tribe Senecioneae. However, a clear decision as to which tribe they belong is difficult. As the genus seems to be related to *Picradeniopsis* [1], the occurrence of secoeudesmanolides in the latter [16] is of interest. Here also the acetylenic thio compounds like **14** and the thymol derivative **20** are present [17]. The rare dithio compounds of type **14** have so far only been isolated from genera belonging to Heliantheae and Helenieae, most of them transferred to Heliantheae [7]. However, most of the lactones isolated from *E. staechadifolium* are present in *Eupatorium* species. But similar lactones were isolated from representatives of the Heliantheae, too. Thymol derivatives also are present in both tribes. Therefore only the dithio acetylenes would be an indication that a placement of the Eriophylliinae in the Heliantheae is more likely. This is also supported by the occurrence of anthochlors [18].

EXPERIMENTAL

The air-dried plant material, collected in California in 1980, was extracted with Et_2O–petrol (1:2) and the resulting extracts, after treatment with MeOH to remove long-chain hydrocarbons, were separated first by CC (Si gel) followed by TLC (Si gel) and HPLC (reversed phase, RP 2 and RP 18, MeOH–H_2O, 3:2). Known compounds were identified by comparison of their IR and ^{1}H NMR spectra with those of authentic materials.

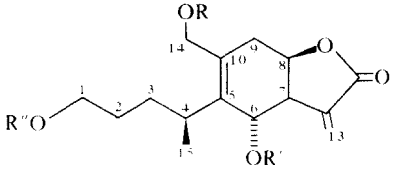
Eriophyllum lanatum (*voucher RMK* 8418 *and* 8423). The aerial parts (440 g) afforded 1 mg germacrene D, 30 mg lupeyl acetate, 30 mg **2**, 20 mg **3**, 15 mg **4**, 20 mg **5**, 2 mg **6**, 1 mg **7**, 4 mg **8**, 1 mg **9**, 4 mg **10**, 0.3 mg **11**, 2 mg **12**, 1 mg **15a** and 1 mg **15b**, while the roots

Table 2. ^{1}H NMR spectral data of compounds **29** and **31** (400 MHz, C_6D_6, TMS as internal standard)

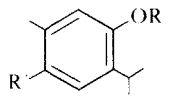
	29	**29** + Eu(fod)$_3$	**31**		**29** (^{13}C NMR, $CDCl_3$)*
H-1	1.3 *m*	2.77 *dd* (*br*)	2.01 *m*	C-1	49.7 *d*
H-2α	1.83 *dddd*	2.40 *dddd*		C-2	32.9 *t*
H-2β	2.35 *ddd*	3.01 *ddd*		C-3	33.7 *t*
H-3α	2.12 *ddd* (*br*)	3.43 *ddd* (*br*)		C-4	56.3 *s*
H-3β	1.05 *m*	1.84 *m*		C-5	49.2 *t*
H-5α	2.18 *d* (*br*)	3.26 *d* (*br*)	1.87 *d*	C-6	47.9 *s*
H-5β	1.2–1.3 *m*	1.84 *m*	1.83 *d*	C-7	52.0 *d*
H-7	1.5 *m*	2.90 *dd* (*br*)	—	C-8	97.1 *s*
H-9	1.3 *m*		1.59 *m*	C-9	36.2 *d*
H-10α				C-10	37.4 *t*
H-10β	1.2–1.3 *m*	1.84 *m*		C-11	26.9 *t*
H-11α			1.94 *m*	C-12	21.6 *q*
H-11β	1.03 *m*	1.27 *dddd*	2.12 *ddd*	C-13	27.8 *q*
H-12	1.16 *dd*	1.67 *dd*	1.17 *s*	C-14	34.3 *q*
H-13	1.21 *s*	1.54 *s*	1.21 *s*	C-15	28.0 *q*
H-14	1.42 *s*	1.77 *s*	1.35 *s*		
H-15	0.88 *d*	0.99 *d*	0.99 *d*		

* Assignment may be partly interchangeable.

J (Hz): Compound **29**: 1,2α ~ 9; 1,2β ~ 3; 1,9 ~ 10; 2α,2β = 13; 2α,3α = 9; 2α,3β = 8; 2β,3α = 9; 2β,3β = 9; 3α,3β = 11; 5α,5β = 12; 7,11α = 8; 7,11β = 12; 9,15 = 7; compound **31**: 5α,5β = 12; 9,15 = 6.5; 10α,11β = 9; 10β,11β = 2; 11α,11β = 17.



	1	2	3	4	5	6	7	8	9
R	H	iBu	iBu	iBu	iBu	Meacr	Meacr	Meacr	Meacr
R'	Meacr	H	Ac	H	Ac	H	Ac	H	Ac
R''	H	H	H	Ac	Ac	H	H	Ac	Ac



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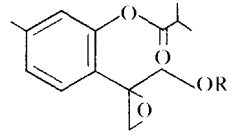
17 R = iBu, R' = OMe
18 R = Me, R' = H
19 R = iBu, R' = H



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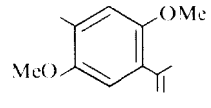
21 R = Mebu



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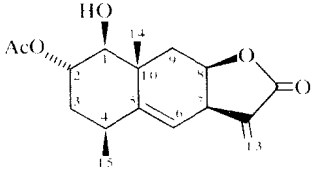

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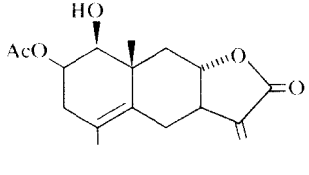

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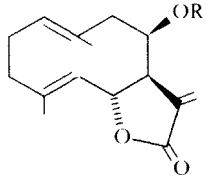

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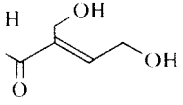
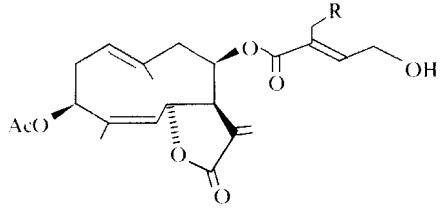
24 R = 



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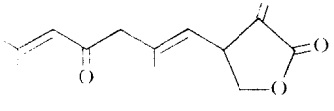

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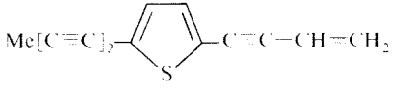

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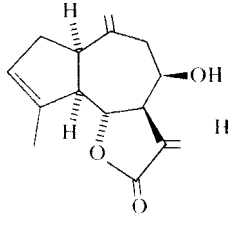

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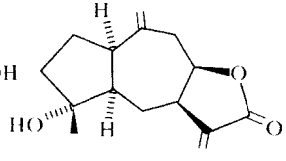

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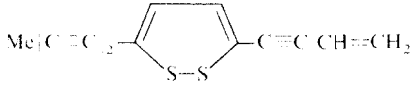
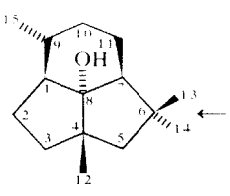


14

Me CH=CH[C≡C]$_2$ CH=CH CH$_2$OAc

t *t* **15a**
c *t* **15b**



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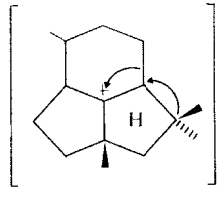

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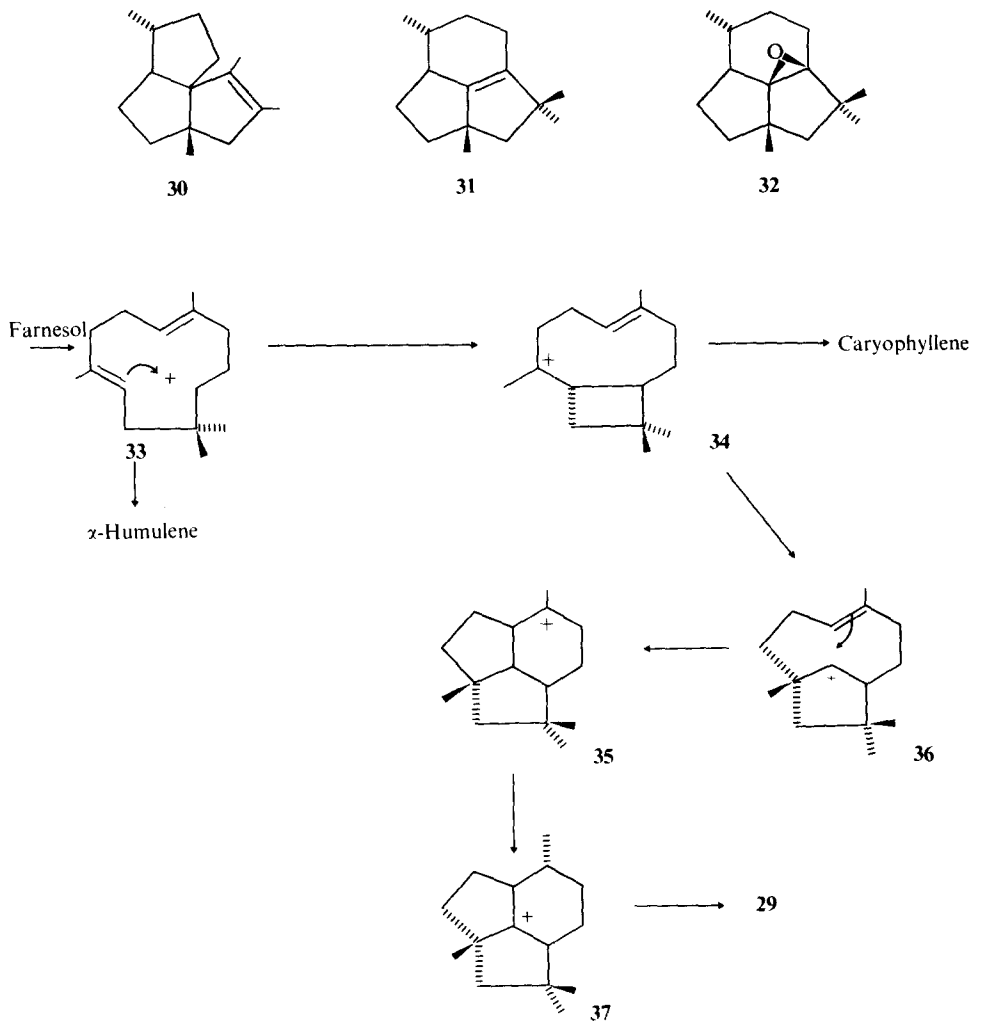

(70 g) gave 2 mg **3**, 3 mg **5**, 3 mg **12**, 1 mg **13** and traces of **14**.

Eriophyllum staechadifolium (*voucher RMK* 8406 *and* 8412). The aerial parts (930 g) afforded 25 mg germacrene D, 25 mg bicyclogermacrene, 30 mg **13**, 5 mg **14**, 500 mg **16**, 40 mg **17**, 300 mg **18**, 10 mg **19**, 80 mg **20**, 200 mg **21**, 3 mg **22**, 2 mg **23**, 100 mg **24**, 10 mg **25**, 100 mg **26**, 3 mg **27**, 3 mg **28** and 50 mg **29**, while the roots (50 g) gave 3 mg **13**, traces of **14**, 10 mg **16** and 10 mg **20**.

Isolation of **29** *from* Flourensia heterolepis. The aerial parts (100 g) afforded 20 mg silphinene [15], 5 mg silphiperfol-6-ene [15] and 8 mg **29**.

1,6α-*Dihydroxy*-14-*isobutyryloxyeriolanolide* (**2**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620, 3520 (OH), 1760 (γ-lactone), 1730 (CO_2R); MS *m/z* (rel. int.): 334.178 (M − H_2O) ($C_{19}H_{26}O_5$), 316 (334 − H_2O, 1), 264 (M − RCO_2H, 8), 246 (334 − RCO_2H, 22), 231 (246 − Me, 15), 202 (231 − CHO, 20), 71 ($C_3H_7CO^+$, 100). To 10 mg **2** in 1 ml $CHCl_3$ were added 10 mg 4-pyrrolidinopyridine [19] and 50 mg Ac_2O. After standing at room temp. for 12 hr MeOH was added. The reaction product was isolated with Et_2O, washed with dil. H_2SO_4 and $NaHCO_3$ soln, evapd and purified by TLC (Et_2O–petrol, 3:1) to give 10 mg **5**, identical with the natural compound.

6α-*Acetoxy*-1-*hydroxy*-14-*isobutyryloxyeriolanolide* (**3**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620, 3530 (OH), 1770 (γ-lactone), 1740 (OAc, CO_2R); MS *m/z* (rel. int.): 334.178 (M − HOAc, 2) ($C_{19}H_{26}O_5$), 316 (334 − H_2O, 0.5), 306 (M − RCO_2H, 3), 264 (306 − ketene, 6), 246 (264 − H_2O, 78), 231 (246 − Me, 52), 71 ($C_3H_7CO^+$, 100);

$$[\alpha]_{24°}^{\lambda} = \frac{\begin{matrix}589 & 578 & 546 & 436 & 365\,nm\\ -16 & -18 & -22 & -56 & -131\end{matrix}}{CHCl_3)} \quad (c = 1.07,$$

5 mg **3** were acetylated as above yielding 4 mg **5**, identical with the natural lactone.

1-*Acetoxy*-6α-*hydroxy*-14-*isobutyryloxyeriolanolide* (**4**). Colourless crystals, mp 94° (Et_2O–petrol); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH), 1775 (γ-lactone), 1745 (OAc, CO_2R); MS *m/z* (rel. int.): 394 (M^+, 1), 376 (M − H_2O, 1), 306.147 (M − RCO_2H, 35) ($C_{17}H_{22}O_5$), 288 (306 − H_2O, 7), 264 (306 − ketene, 12), 246 (306 − HOAc, 40), 71 ($C_3H_7CO^+$, 100);

$$[\alpha]_{24°}^{\lambda} = \frac{\begin{matrix}589 & 578 & 546 & 436 & 365\,nm\\ +85 & +89 & +101 & +171 & +262\end{matrix}}{CHCl_3)} \quad (c = 0.53,$$

5 mg **4** were acetylated as above yielding 4 mg **5**, identical with the natural compound.

1,6α-*Diacetoxy*-14-*isobutyryloxyeriolanolide* (**5**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1740 (OAc, CO_2R); MS *m/z* (rel. int.): 376.189 (M − HOAc, 2) ($C_{21}H_{28}O_6$), 306 (376 − O=C=CMe_2, 60), 71 ($C_3H_7CO^+$, 100).

1,6α-*Dihydroxy*-14-*methacryloyloxyeriolanolide* (**6**). Colourless gum, not free from **2**; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1760 (γ-lactone), 1730, 1645 (C=CCO$_2$R); MS *m/z* (rel. int.): 332 (M − H$_2$O, 0.5), 246 (M − RCO$_2$H, 25), 69 ($C_3H_5CO^+$, 100). 2 mg **6** on acetylation afforded **9**.

6α-*Acetoxy*-1-*hydroxy*-14-*methacryloyloxyeriolanolide* (**7**). Colourless gum, not free from **3**; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1745 (OAc), 1730, 1645 (C=CCO$_2$R): MS *m/z* (rel. int.): 332 (M − H$_2$O, 0.5), 246 (M − RCO$_2$H, 5), 69 ($C_3H_5CO^+$, 100). 1 mg **7** on acetylation afforded **9**.

1-*Acetoxy*-6α-*hydroxy*-14-*methacryloyloxyeriolanolide* (**8**). Colourless gum, not free from **4**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1775 (γ-lactone), 1745 (OAc), 1730 (C=CCO$_2$R); MS *m/z* (rel. int.): 392 (M$^+$, 0.5), 306 (M − RCO$_2$H, 41), 69 ($C_3H_5CO^+$, 100). 1 mg **8** on acetylation afforded **9**, colourless gum, not free from **5**, ^{1}H NMR (see Table 1).

1,6α-*Diacetoxy*-14-*methacryloyloxyeriolanolide* (**9**). Colourless gum, not free from **5**; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1745 (OAc), 1730 (C=CCO$_2$R); MS *m/e* (rel. int.): 374.178 (M − HOAc, 3) ($C_{21}H_{26}O_6$), 69 ($C_3H_5CO^+$, 100).

2α-*Acetoxy*-1β-*hydroxyalantolactone* (**10**). Colourless crystals, mp 170°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1770 (γ-lactone), 1740, 1245 (OAc); MS *m/z* (rel. int.): 306.147 (M$^+$, 5) ($C_{17}H_{22}O_5$), 246 (M − HOAc, 100), 228 (246 − H$_2$O, 54), 213 (228 − Me, 22);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,\text{nm}}{+112 \quad +117 \quad +135 \quad +247 \quad +436} \quad (c = 0.23, CHCl_3).$$

2α-*Acetoxy*-8-*epiivangustin* (**11**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1780 (γ-lactone), 1750 (OAc); MS *m/z* (rel. int.): 306.147 (M$^+$, 3), 246 (M − HOAc; 70), 231 (246 − Me, 75), 213 (231 − H$_2$O, 45), 203 (231 − CO, 100);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+50 \quad +54 \quad +60 \quad +87} \quad (c = 0.03, CHCl_3).$$

8α-*Hydroxy*-*presilphiperfolene* (**29**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 3020, 1460, 1450, 1380, 1160, 1120, 980; MS *m/z* (rel. int.): 222.204 (M$^+$, 10) ($C_{15}H_{26}O$), 207 (M − $\dot{M}e$, 24), 204 (M − H$_2$O, 28), 189 (204 − Me, 61), 161 (204 − $C_3\dot{H}_7$, 38), 55 (C_4H_7, 100);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-18.4 \quad -25.3 \quad -28.6 \quad -46.5} \quad (c = 3.6, CHCl_3).$$

10 mg **29** in 0.5 ml Ac$_2$O were heated for 90 min at 70°. TLC (petrol) afforded 3 mg **30** and 3 mg **31**. The ^{1}H NMR data of **30** were identical with those of silphiperfol-6-ene [15]. 3 mg **31** were oxidized in 1 ml $CHCl_3$ with 10 mg *m*-chloroperbenzoic acid for 2 hr in the presence of NaHCO$_3$ soln. TLC (Et$_2$O–petrol, 1:20) afforded a mixture of epoxides and **32**, ^{1}H NMR [C_6D_6, Eu(fod)$_3$-induced shifts in parentheses]: 0.96 (*s*, H-14, 0.04), 1.07 (*s*, H-13, 0.06), 1.11 (*s*, H-12, 0.06), 0.98 (*d*, H-15, *J* = 7 Hz, 0.01), 1.36 (*m*, H-9), 1.54 (*d*, 0.02) and 1.43 (*d*, H-5, *J* = 14 Hz, 0.02), 1.24 (*m*, 1), 1.43 (*m*), 1.65 (*m*), 1.77 (*m*), 1.95 (*m*), 1.97 (*m*) (definitive assignments of the multiplets were not possible).

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