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LUMIYOMOGIN, FERREYRANTHOLIDE, FRUTICOLIDE AND OTHER SESQUITERPENE LACTONES FROM *FERREYRANTHUS FRUTICOSUS*

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Key Word Index—*Ferreyranthus fruticosus*, Compositae, sesquiterpene lactones, eudesmanolides, rearranged eudesmanolides; dimeric sesquiterpene lactone, sesquiterpene derivative.

Abstract—The investigation of the aerial parts of *Ferreyranthus fruticosus* afforded yomogin, encelin, 1α-hydroxypinnatifidin and 10 new eudesmanolides, a precursor of yomogin and three rearranged compounds as well as a dimeric sesquiterpene lactone The structures were elucidated by high field NMR techniques and by a few chemical transformations

INTRODUCTION

Chemical investigations of representatives of the small tribe Liabeae with only 185 species have shown that sesquiterpene lactones are widespread This fact, and also the nature of the polyacetylenes, support the separation of this group from the Senecioneae where these genera were placed previously We have reinvestigated *Ferreyranthus fruticosus* (Muschler) Robinson in more detail and the results are discussed in this paper.

RESULTS AND DISCUSSION

F. fruticosus is a small tree with yellow ray and disc florets The aerial parts of a collection from Peru, above Rio Maranon, altitude *ca* 2700 m, afforded a very complex mixture of sesquiterpene lactones. Finally encelin (**2**) [1], yomogin (**5**) [2], 1α-hydroxypinnatifidin (**8**) [3], the eudesmanolides **1**, **3**, **4**, **6**, **7** and **9–14** as well as the rearranged lactones **15–17**, the dimeric lactone **18** and the methyl ester **19** were obtained

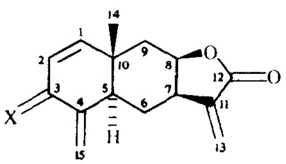
The structures of **1** and **3** followed from the ^{1}H NMR spectra (Table 1) which were in part close to that of **2** The absence of the keto group caused the expected shifts The relative position of the hydroxy group was deduced from the chemical shifts of H-2 and H-3, respectively. In the spectrum of **4** (Table 1) the missing H-5 signal and the molecular formula indicated a 5-hydroxy derivative of **3** The unchanged couplings required the presence of a *trans*-decalin derivative. Accordingly, a 5α-hydroxy group must be proposed. The configuration at C-1 in **3** and **4** followed from the NOE's between H-14, H-1 (10%), H-9β (4%) and H-6β (7%) while those between H-8, H-7 (10%) and H-9α (10%) as well as between H-15 and H-3 (10%) established the remaining stereochemistry The ^{13}C NMR data of **1** and **4** (Table 2) further supported the structures The 3-epimer of **1** has been isolated previously [4].

The structure of **6** followed from the ^{1}H NMR spectrum (Table 1) and its configuration was determined by NOE's between H-8, H-7 (10%) and H-11 (4%) as well as between H-14, H-6β (7%), H-9β (4%) and H-1 (5%). Furthermore, boranate reduction of **5** afforded exclusively **6** Inspection of a model showed that this only agrees with an 11α-H configuration. The ^{13}C NMR spectrum of **6** was close to that of **5** (Table 2)

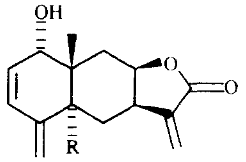
The spectral data of **7** (Table 1) indicated the presence of an eudesmanolide with an enone moiety (δ6.64 *d* and 5 87 *d*) and a methyl singlet at δ1 33 Together with the molecular formula this data required a tertiary hydroxy group most likely at C-4. Clear NOE's between H-15, H-3 (5%) and H-6β (5%), between H-8, H-7 (9%), H-9α (8%) and H-9β (4%), as well as between H-14, H-6β (5%) and H-9β (3%), established the stereochemistry and the position of the double bond. Furthermore this assumption was supported by a *W*-coupling between H-9α and H-14.

The ^{1}H NMR spectrum of **9** (Table 1) was close to that of **8** Again the presence of a hydroxy group at C-5 followed from the absence of a H-5 signal and from the molecular formula while the unchanged couplings of H-6 to H-9 required a *trans*-decalin derivative The configurations of the remaining chiral centers were deduced from the observed results of NOE difference spectroscopy. Clear effects were obtained between H-14, H-1 (5%), H-9β (3%) and H-6β (7%), as well as between H-1, H-9β (5%) and H-14 (5%) The presence of a *W*-coupling between H-6β and the C-5 hydroxyl indicated a hydrogen bridge between the hydroxyls at C-1 and C-5

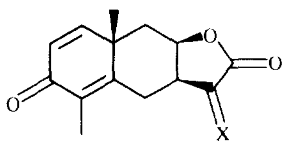
The ^{1}H NMR spectrum of **10** (Table 1) again showed that an alantolactone derivative was present Three signals at δ2.84, 3.44 and 3 09 with small couplings favoured the presence of a diepoxide Spin decoupling indicated that these functions only could be placed at C-1–C-4. The stereochemistry was determined by the observed NOE's Especially clear effects between H-14, H-1 (8%), H-3 (3%), H-6β (8%) and H-9β (4%), between H-1, H-9β (5%), H-14 (6%) and H-2 (20%), between H-8, H-7 (10%), H-9α (10%) and H-9β (6%), as well as between H-15, H-3 (14%), H-6α (4%) and H-6β (4%), established the proposed configurations. This was also supported by an interesting long range coupling between H-1 and H-6α as well as by the ^{13}C NMR data (Table 2) where the signals were assigned by 2D-shift correlation.



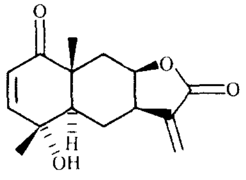
1 X = αOH H
2 X = O



3 R = H
4 R = OH



5 X = CH_2
6 X = βMe,H



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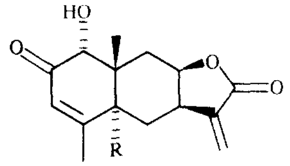
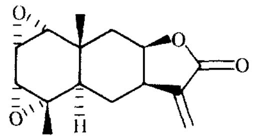


8 R = H
9 R = OH



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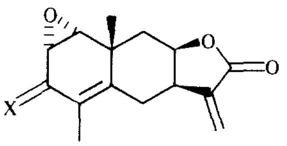
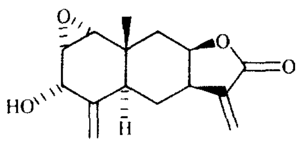


11 X = αOH,H
12 X = O



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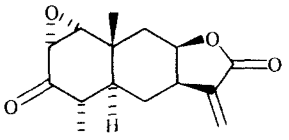

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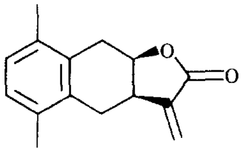

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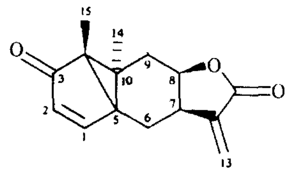

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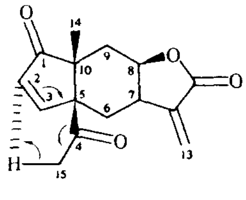

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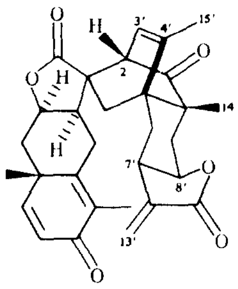

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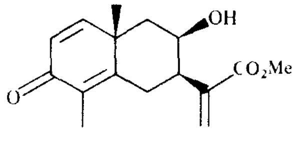

19

The ^{1}H NMR spectra of **11** and **12** (Table 1) again showed that epoxy eudesmanolides were present. However, several couplings differed from those of **7**–**10** indicating a changed conformation The position of the double bond was deduced from the down field shift of H-6 and from the presence of an olefinic methyl signal. Manganese dioxide oxidation of **11** afforded a ketone which was identical with the natural compound **12** Thus **11** was the corresponding alcohol where the stereochemistry followed from the observed NOE's between H-14, H-9β (5%), H-6β (4%), H-1 (5%) and H-3 (2%) as well as between H-15, H-6 (8%) and H-3 (5%) Again the ^{13}C NMR data

Table 1. ^{1}H NMR spectral data of compounds **1**, **3**, **4**, **6**, **7** and **9–14** ($CDCl_3$, 400 MHz, δ-values)

H	**1**	**3**	**4**	**6***	**7**	**9†**	**10**	**11‡**	**12**	**13**	**14§**
1	5.77 *br d*	3.60 *br d*	3.66 *br d*	6.72 *d*	—	3.72 *br s*	2.84 *br d*	3.17 *d*	3.48 *d*	3.07 *d*	3.29 *br d*
2	5.69 *dd*	5.87 *br dd*	5.95 *br dd*	6.24 *d*	5.87 *d*	—	3.44 *dd*	3.49 *dd*	3.52 *d*	3.49 *dd*	3.37 *d*
3	4.43 *br d*	6.23 *br d*	6.17 *br d*	—	6.64 *d*	5.87 *dq*	3.09 *d*	4.26 *br d*	—	4.35 *br d*	—
5	2.44 *dddd*	2.44 *dddd*	—	—	2.02 *dd*	—	1.80 *dd*	—	—	2.34 *br d*	1.80 *m*
6α	1.87 *ddd*	2.10 *ddd*	2.12 *dd*	2.81 *dd*	2.09 *ddd*	2.12 *dd*	1.96 *br dddd*	2.85 *dd*	3.06 *dd*	1.76 *ddd*	1.80 *m*
6β	1.53 *ddd*	1.41 *dd*	1.65 *ddd*	2.07 *br dd*	1.54 *ddd*	1.48 *ddd*	1.39 *ddd*	1.96 *br dd*	2.24 *br dd*	1.45 *ddd*	1.19 *m*
7	3.07 *br ddd*	3.01 *br ddd*	3.34 *br ddd*	2.50 *m*	2.97 *br dddd*	3.49 *br ddd*	2.97 *br ddd*	3.06 *ddddd*	3.18 *ddddd*	3.00 *br ddd*	2.99 *br ddd*
8	4.56 *ddd*	4.64 *ddd*	4.69 *ddd*	4.51 *ddd*	4.57 *ddd*	4.71 *ddd*	4.50 *ddd*	4.66 *ddd*	4.76 *ddd*	4.59 *ddd*	4.60 *ddd*
9α	1.71 *br dd*	2.38 *br dd*	2.82 *br dd*	1.60 *br dd*	1.75 *br dd*	2.82 *br dd*	1.86 *br dd*	2.18 *dd*	2.41 *dd*	1.97 *br dd*	1.98 *br dd*
9β	2.29 *dd*	1.93 *dd*	1.93 *dd*	2.49 *dd*	2.55 *dd*	1.88 *dd*	2.23 *dd*	1.74 *dd*	1.93 *dd*	2.30 *dd*	2.33 *dd*
13	6.17 *d*	6.16 *d*	6.18 *d*	1.32 *d*	6.18 *d*	6.20 *d*	6.16 *d*	6.28 *d*	6.37 *d*	6.16 *d*	6.17 *d*
13′	5.64 *d*	5.63 *d*	5.64 *d*		5.65 *d*	5.66 *d*	5.64 *d*	5.64 *d*	5.73 *d*	5.63 *d*	5.63 *d*
14	0.86 *s*	0.81 *s*	0.93 *s*	1.33 *s*	1.20 *s*	1.06 *s*	1.06 *s*	1.09 *s*	1.25 *d*	0.90 *s*	1.03 *s*
15	5.21 *br s*	5.05 *br s*	5.24 *br s*	1.96 *d*	1.33 *s*	2.04 *d*	1.20 *s*	1.80 *br s*	1.87 *d*	5.15 *br s*	1.19 *d*
15′	4.83 *br s*	4.98 *br s*	5.12 *s*							4.80 *br d*	

*H-11 2.93 *dq*

†1-OH 3.28 *br s*, 5-OH 4.29 *d*

‡OH 2.02 *br d*

§H-5 1.80 *m*, in C_6D_6 1.33 *ddd* (3, 12, 12)

J[Hz] Compounds **1**, **3**, **4**, **6**, **7**, **9**, **10**, **13** and **14** 6α, 6β ≈ 13.5, 6α, 7 ≈ 7.5, 6β, 7 ≈ 12, 7, 8 = 8, 9α = 4.5, 7, 13 = 7, 13′ ~ 1.2, 8, 9β = 1.5, 9α, 9β = 15, compounds **1** 1, 2 = 9.5, 2, 3 = 4, compound **1** and **3** 5, 6α = 5.15 ~ 2, 5, 6β = 12.5, compound **3** and **4** 1, 2 = 5, 2, 3 = 9.5, compound **6** 1, 2 = 10, 6β, 15 = 0.7, 7, 11 = 11, 13 = 7, compound **7** 2, 3 = 10, 5, 6α = 2, 5,6β = 12.5, compound **9** 1, 3 = 3, 15 = 1.5, 6β, OH = 3, compound **10** 1, 2 = 4, 2, 3 = 3, 5, 6α = 3.5, 5, 6β = 13; compounds **11** and **12** 6α, 6β = 6β, 7 = 13, 6α, 7 = 7, 7, 8 = 7.5, 7, 13 = 2.5; 7, 13′ = 2.2, 8, 9α = 4.5, 8, 9β = 9.5; 9α, 9β = 13.5, compound **11** 1, 2 = 4.5, 2, 3 = 2.5, compound **12**· 1, 2 = 4; compound **13** 1, 2 = 2, 3 = 4, 5, 6α = 2.5, 5, 6β = 12, compound **14** 1, 2 = 4, 4, 5 = 5, 6β = 12, 4, 15 = 7; 5, 6α = 3.

Table 2 ^{13}C NMR spectral data of compounds **1**, **4–6**, **10–13** and **15** ($CDCl_3$, δ-values)

C	**1**	**4**	**5**	**6**	**10***	**11**	**12**	**13**	**15**
1	124 5 *d*	73 0 *d*	155 2 *d*	155 4 *d*	60 5 *d*	61 1 *d*	54 0 *d*	63 6 *d*	131 8 *s*
2	142 4 *d*	128 8 *d*	126 3 *d*	126 0 *d*	48 0 *d*	55 0 *d*	59 9 *d*	55 4 *d*	128 1 *d*
3	69 6 *d*	127 7 *d*	185 5 *s*	185 6 *s*	56 0 *d*	68 3 *d*	195 1 *s*	68 8 *d*	128 2 *d*
4	148 7 *s*	145 8 *s*	131 0 *s*	131 2 *s*	53 4 *s*	130 1 *s*	126 8 *s*	146 1 *s*	132 1 *s*
5	40 4 *d*	73 8 *s*	154 4 *s*	155 3 *s*	37 2 *d*	125 1 *s*	151 2 *s*	34 5 *d*	134 2 *s*
6	26 8 *t*	33 1 *t*	29 9 *t*	24 5 *t*	25 7 *t*	28 1 *t*	29 7 *t*	25 9 *t*	30 1 *t*
7	40 6 *d*	37 2 *d*	41 8 *d*	41 8 *d*	40 4 *d*	39 7 *d*	38 8 *d*	40 1 *d*	37 4 *d*
8	76 6 *d*	76 9 *d*	75 3 *d*	76 3 *d*	75 8 *d*	75 7 *d*	74 6 *d*	76 4 *d*	76 9 *d*
9	38 4 *t*	29 4 *t*	38 8 *t*	38 9 *t*	36 2 *t*	39 0 *t*	39 2 *t*	36 3 *t*	29 8 *t*
10	36 5 *s*	37 6 *s*	38 5 *s*	38 8 *s*	33 4 *s*	36 0 *s*	37 9 *s*	34 3 *s*	133 6 *s*
11	141 6 *s*	141 9 *s*	140 3 *s*	42 1 *d*	141 4 *s*	139 4 *s*	138 6 *s*	141 5 *s*	139 2 *s*
12	170 3 *s*	170 5 *s*	169 6 *s*	178 3 *s*	170 1 *s*	170 3 *s*	169 6 *s*	170 1 *s*	170 2 *s*
13	120 7 *t*	120 4 *t*	121 9 *t*	9 4 *q*	120 8 *t*	122 3 *t*	123 3 *t*	120 7 *t*	122 5 *t*
14	19 2 *q*	22 7 *q*	25 6 *q*	25 3 *q*	17 3 *q*	25 0 *q*	26 7 *q*	16 6 *q*	19 4 *q*
15	111 7 *t*	114 4 *t*	10 7 *q*	10 7 *q*	19 5 *q*	14 2 *q*	12 0 *q*	114 3 *t*	19 2 *q*

Multiplicity estimated by DEPT spectra
*2D shift correlated

(Table 2) nicely agreed with the structures of **11** and **12**

The ^{1}H NMR spectrum of **13** (Table 1) clearly showed the presence of an eudesmanolide in the usual conformation as in **7**–**10**. Signals at δ3 07 and 3 49 with small vicinal couplings were an indication of an epoxide while a broadened doublet at δ4 35 most likely was due to a proton under an allylic hydroxyl As signals for two pairs of exomethylene protons were visible an isotelekin derivative was most likely Accordingly, the ^{1}H NMR data were similar The additional epoxy group could be placed only at C-1 and C-2 The stereochemistry again was determined by NOE difference spectroscopy Clear effects were observed between H-14, H-1 (10%), H-6β (7%) and H-9β (3%), between H-3, H-2 (12%) and H-15 (10%), as well as between H-8, H-7 (12%) and H-9β (8%) The proposed structure also was supported by its ^{13}C NMR spectrum (Table 2)

The ^{1}H NMR data of **14** (Table 1) were close to those of hymeyoshin [5] However, the presence of a 4α-methyl group followed from the observed coupling $J_{4,5} = 12$ Hz which only could be observed in C_6D_6 Furthermore, the stereochemistry at C-5 and C-10 was supported by *W*-couplings between H-14 and H-9α as well as a long range coupling between H-1 and H-6β The precursor of the epoxide, the Δ^1-derivative has been reported from a *Greenmanniella* species [6]

The ^{1}H NMR (Table 3) and ^{13}C NMR data (Table 2) of **15** clearly showed that a tetrasubstituted aromatic compound was present where two hydrogens were in ortho position to each other Furthermore, from the spectra two aromatic methyls and a methylene lactone moiety could be deduced All data therefore only agreed with the presence of the rearranged eudesmanolide **15** which has been prepared by proton catalysed rearrangement of the corresponding diol related to **8** [3]. Perhaps **15** is formed by proton catalysed isomerization of **3**.

The ^{1}H NMR spectrum of **16** (Table 2) again indicated the presence of an enone system As, however, the vicinal coupling was 5 5 Hz a cyclopentenone part must be present Accordingly, a rearranged system as in lumisantonin [7] was very likely and therefore the same stereochemistry also could be proposed This was established by the observed NOE's between H-14, H-8 (7%), H-9α (5%) and H-2 (2%), between H-15, H-6β (6%) and H-9β (8%) as well as between H-8, H-7 (5%), H-9α (8%) and H-14 (5%). The structure was further supported by photoisomerization of **5** which afforded in good yield the cyclopropyl ketone **16** which we have named lumiyomogin

The ^{1}H NMR spectrum of **17** (Table 3) also indicated the presence of a cyclopentenone derivative However, a methyl singlet at δ2 21 together with a ketene elimination in the mass spectrometer required a methyl ketone group As the remaining signals could be assigned by spin decoupling only a rearranged lactone like **17** or an isomer with a keto group at C-3 was possible The structure and the stereochemistry were established by the observed NOE's Clear effects were present between H-14, H-15 (6%), H-9α (5%) and H-9β (5%), between H-15, H-14 (5%), H-6β (4%) and H-3 (8%), as well as between H-3, H-6α (4%) and H-15 (4%) These effects required a *cis*-anellation of the rings and an olefinic proton at C-3 The elimination of ketene most likely is a cyclic process as indicated on structure **17** The carbon skeleton of **17** seems to be rare. So far we have isolated a glucoside from an *Iphionia* species [8] and an acid from *Dittrichia viscosa* [9] We have named lactone **17** ferreyrantholide

The molecular formula of the last compound ($C_{30}H_{32}O_6$) required most likely a dimeric lactone and the ^{1}H NMR spectrum (Table 3) supported this assumption Two sets of signals could be correlated by spin decoupling, one with the typical signals of an exomethylene group, similar in part to the spectra of eudesmanolides, and in second part which showed similarities to that of yomogin However, the exomethylene signals were missing and replaced by a pair of doublets (δ2 09 and 1 85) These facts required the presence of a Diels–Alder-adduct with yomogin as dienophil and an anhydro derivative of **7** as diene The stereochemistry was established by the NOE's between H-14, H-6β (6%), H-9β (6%)

Table 3. ^{1}H NMR spectral data of compounds **15**–**19** ($CDCl_3$, 400 MHz, δ-values)

H	**15**	**16**	**17**	**18a***	**18b***	**19†**
1	—	7.41 *d*	—	6.78 *d*	—	6.78 *d*
2	6.96 *br d*	5.93 *d*	6.47 *d*	6.25 *d*	3.27 *d*	6.20 *d*
3	6.93 *br d*	—	7.69 *d*	—	5.73 *dq*	—
6α	2.40 *br dd*	2.36 *dd*	1.93 *dd*	2.77 *dd*	1.92 *d*	2.60 *br d*
6β	2.34 *br dd*	1.47 *dd*	2.38 *dd*	2.06 *br dd*		2.78 *br dd*
7	2.95 *ddddd*	3.38 *ddddd*	2.77 *ddddd*	2.19 *ddd*	3.28 *ddd*	2.84 *br d*
8	5.04 *ddd*	4.76 *ddd*	4.38 *ddd*	4.81 *ddd*	4.66 *ddd*	4.14 *br s*
9α	2.38 *br dd*	2.32 *dd*	2.48 *dd*	1.60 *br dd*	1.47 *br dd*	1.60 *br dd*
9β	2.60 *br dd*	1.37 *br dd*	1.73 *dd*	2.52 *dd*	2.49 *dd*	2.16 *dd*
13	6.23 *d*	6.37 *d*	6.32 *d*	2.09 *d*	6.26 *d*	6.49 *br s*
13′	5.70 *d*	5.72 *d*	5.62 *d*	1.85 *d*	5.71 *d*	5.81 *br s*
14′	2.30 *br s*	1.15 *s*	1.04 *s*	1.29 *s*	1.17 *s*	1.46 *s*
15	2.26 *br s*	1.28 *s*	2.21 *s*	1.90 *br s*	1.88 *d*	1.93 *s*

*(a) dienophil, (b) dien part

†OMe 3.78 *s*.

J [Hz]: Compound **15**. 2, 3 = 8; 6α, 6β = 9α, 9β = 15, 6α, 7 = 6β, 7 = 6; 7, 8 = 9, 7, 13 = 2.5, 7, 13′ = 2.2, 8, 9α = 8, 9β = 5, compound **16**: 1, 2 = 5.5; 6α, 6β = 15; 6α, 7 = 7; 6β, 7 = 13, 7, 8 = 8.5, 7, 13 = 2.5, 7, 13′ = 2, 8, 9α = 6, 8, 9β = 11.5, 9α, 9β = 13.5, compound **17** 2, 3 = 6, 6α, 6β = 6β, 7 = 14, 6α, 7 = 5.5; 7, 8 = 8.5, 7, 13 = 2.7, 7, 13′ = 2.5, 8, 9α = 6, 8, 9β = 11.5; 9α, 9β = 13.5, compound **18a** 1, 2 = 10, 6α, 6β = 6β, 7 = 13; 6α, 7 = 6; 7, 8 = 8, 9α = 4.5, 8, 9β = 1.5, 9α, 9β = 15, 13, 13′ = 14, compound **18b** 2, 3 = 6; 3, 15 = 1.5, 6α, 7 = 6β, 7 = 6β, 7 = 9; 7, 8 = 8, 9α = 4.5; 7, 13 = 7, 13′ ≈ 1.2, 8, 9β = 1, 9α, 9β = 15, compound **19** 1, 2 = 10; 6α, 6β = 6β, 7α ≈ 13, 8, 9α = 3.5, 8, 9β = 2.5, 9α, 9β = 14.

and H-1 (10%) in both parts, as well as between H-8 from the dienone part with H-2 (15%) of the other part. The *cis*-lactone configuration was further established by NOE's between H-8 and H-7 (10%) in both parts. The anhydro-derivative of **7**, which was not present in the extract, would not be a good diene. Therefore **18** most likely is not an artifact. We have named this dimer fruticolide.

The methyl ester **19** displayed a ^{1}H NMR spectrum (Table 3) which was in part close to that of **5**. Spin decoupling allowed the assignment of all signals thus indicating the presence of the methyl ester of the precursor of **5**. Perhaps this compound is an artifact formed by methanolysis of **5** during separation

The overall picture of the chemistry of this *Ferreyranthus* species is very uniform as all compounds are closely related to each other. A previous investigation of this species gave only germacradien-12,8-olides [10] while other representatives of the tribe also afforded germacradien-12,6-olides and guaianolides. Eudesmanolides have been reported from a *Bishopanthus* species [11], *F. rugosus* [10], *F. verbascifolius* [10] and a *Liabum* species [12].

EXPERIMENTAL

The air-dried plant material (295 g, collected in October 1984 in Peru *ca* 18 km E of Celendin on the road to Balsas, Ceje de la Montana above Rio Maranon, altitude *ca* 2700 m, voucher M O Dillon et M. Whalen 4045, deposited in the Herbarium of the Field Museum of National History, Chicago, U.S A) was extracted and worked-up as reported previously [13] The non-polar CC fractions gave caryophyllene epoxide and the polar ones (Fr 1 Et_2O–petrol, 1:1 and Et_2O, Fr 2 Et_2O–MeOH, 9:1 and Fr 3: Et_2O–MeOH, 3:1) gave mixtures which were further separated TLC of CC fraction 1 (CH_2Cl_2) gave 100 mg **15** and a mixture which together with CC fraction 2 was separated first by medium pressure chromatography (MPC) (CH_2Cl_2 with raising amounts of Et_2O) affording 20 mg **15** and four mixtures (2.2–2.5). Similar CC fraction 3 gave by MPC (CH_2Cl_2–Et_2O) five fractions (3.1–3.5) Fractions 2.2 and 3.2 in Et_2O gave crystals which were separated by HPLC (always RP 8 *ca* 100 bar) affording 80 mg **10** and 400 mg **5** The mother liquors gave by TLC and HPLC 18 mg **5**, 3 mg **6**, 5 mg **10**, 5 mg **16** and 1 mg **17** TLC and HPLC of fraction 2.3 gave 7 mg **1** and 5 mg **11**. TLC of fraction 2.4 afforded 25 mg **13** and TLC and HPLC of fraction 2.5 6 mg **4**, 17 mg **11** and 25 mg **13** Separation of fraction 3.1 by HPLC gave 2 mg **2**, 6 mg **5**, 3 mg **10**, 2 mg **12** and 3 mg **14** while fraction 3.2 afforded by HPLC 2 mg **3**, 3 mg **5**, 4 mg **13** and 2 mg **18** TLC and HPLC of fraction 3.4 gave 3 mg **4**, 5 mg **9**, 21 mg **11**, 20 mg **13** and 3 mg **19**. TLC and HPLC of fraction 3.5 gave 3 mg **4**, 5 mg **7**, 2 mg **8**, 4 mg **9** and 5 mg **13** (solvents and R_f values Table 4, amounts are surely reduced due to the difficult separation) Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material

CD values (MeCN) **6** $\Delta\varepsilon_{323}$ −0.18, **11** $\Delta\varepsilon_{259}$ −3.2; **12**: $\Delta\varepsilon_{330}$ +4.7, $\Delta\varepsilon_{260}$ −6.6, **13** $\Delta\varepsilon_{258}$ −2.26, **15** $\Delta\varepsilon_{281}$ −0.11, $\Delta\varepsilon_{293}$ −0.14, $\Delta\varepsilon_{308}$ −0.11

Reduction of yomogin (**5**) To 10 mg **5** in 2 ml MeOH at 0° 10 mg $NaBH_4$ was added After 30 min usual work-up and TLC afforded 8 mg **6**, identical with the natural product

Photoisomerization of **5** Compound **5** (50 mg) in 20 ml EtOH was irradiated for 3 days with UV light Usual work-up and TLC gave 30 mg **16**, identical with the isolated lactone

Oxidation of **11** Compound **11** (10 mg) in 3 ml Et_2O was stirred for 60 min with 100 mg MnO_2 TLC afforded 7 mg **12**, identical with the natural lactone

Table 4 Physical data of the new compounds

Compound	*mp	IR (cm^{-1})		A $CHCl_3$ B CCl_4			MS fragments (*m/z*, rel int)						R_t(min)†
1	oil	3620	1760	A	$C_{15}H_{18}O_3$	246 126 calc	231,	228,	135,	105,	91		5 7 (HP3)
						246 126 found (55)	(25)	(12)	(100)	(50)	(78)		
3	oil	3600	1780	B	$C_{15}H_{18}O_3$	246 126 calc	231,	228,	204,	188,	91		6 8 (HP1)
						246 126 found (50)	(15)	(10)	(100)	(40)	(70)		
4	oil	3600	1775	B	$C_{15}H_{18}O_4$	262 121 calc	244,	229,	216,	105,	91		6 0 (HP1)
						262.120 found (10)	(30)	(33)	(25)	(75)	(100)		
6	167°	1765	1660	A	$C_{15}H_{18}O_3$	246.126 calc	231,	218,	173,	145,	144,	105	7.3 (HP2)
						246 126 found (100)	(16)	(20)	(100)	(80)	(70)	(200)	
7	117°	3450	1760	A	$C_{15}H_{18}O_4$	262 121 calc	247,	244,	165,	98			5 1 (HP1)
		1680				262 121 found (33)	(15)	(6)	(37)	(100)			
9	oil	3400	1770	A	$C_{15}H_{18}O_5$	278 115 calc	260,	232,	227,	150,	111		6 0 (HP1)
		1680				278 115 found (8)	(8)	(20)	(10)	(20)	(200)		
10	192°	1765		A	$C_{15}H_{18}O_4$	262 121 calc	247,	220,	219,	173,	53		5 3 (HP2)
						262 121 found (2)	(35)	(33)	(35)	(53)	(100)		
11	166°	3450	1780	B	$C_{15}H_{18}O_4$	262 121 calc	247,	244,	178,	151,	98		4 7 (HP3)
						262 121 found (30)	(15)	(5)	(20)	(55)	100)		
12	176°	1760	1670	A	$C_{15}H_{16}O_4$	260 105 calc	245,	231,	217,	122,	91		5 1 (HP1)
						260 105 found (100)	(20)	(75)	(80)	(94)	(96)		
13	144°	3450	1785	B	$C_{15}H_{18}O_4$	262 121 cacl	244,	229,	199,	159,	99		4 3 (HP3)
						262 121 found (5)	(18)	(26)	(64)	(70)	(100)		
14	185°	1760	1690	A	$C_{15}H_{18}O_4$	262 121 calc	244,	233,	159,	105,	91		5 5 (HP1)
						262 120 found (10)	(20)	(20)	(40)	(100)	(84)		
15	122°	1780		B	$C_{15}H_{16}O_2$	228 115 calc	183,	156,	143,	132			(R_f 0 54
						228 115 found (67)	(14)	(16)	(24)	(100)			(CH_2Cl_2))

16	94°	1765	1700	A	$C_{15}H_{16}O_3$	244.110 calc. 244.109 found (78)	229, (8)	216, (13)	120, (50)	105 (100)	6.6 (HP2)
17	oil	1775	1720	A	$C_{15}H_{16}O_4$	+1 261(100) (CI)	218, (100)	174, (60)	(EI)		6.5 (HP2)
18	oil	1770 1665	1720	A	$C_{30}H_{32}O_6$	488.220 calc. 488.220 found (100)	245, (60)	244, (62)	174, (60)	159 (55)	8.3 (HP3)
19	oil	3600 1660	1725	A	$C_{16}H_{20}O_4$	276.136 calc. 276.136 found (20)	258, (63)	243, (44)	183, (83)	83 (100)	7.8 (HP1)

*Names assigned to new compounds are as follows:

1 1,2-3α-Hydroxy-dehydro-isoalantolactone
3 2,3-Dehydro-1-epi-asperilin
4 1α-Hydroxy-2.3-dehydrotelekin
6 11α,13 Dihydroyomogin
7 4α-Hydroxy-1-oxo-eudesma-2,11(13)-diene-12,8β-olide
9 1α,5α-Dihydroxypinnatifidin
10 1α,2α,3α,4α-Bisepoxy-5α,6-dihydroalantolactone
11 1α,2α-Epoxy-3α-hydroxyeudesm-4-ene-12,8β-olide
12 1α,2α-Epoxyyomogin
13 1α,2α-Epoxy-3α-hydroxy-isoalantolactone
14 1α,2α-Epoxy-4β,15-dihydroyomogin
15 10-Desmethyl-1-methyl-5,6-dihydroeudesma-1,3,5(10)-triene-12,8β-olide
16 lumiyomogin
17 Ferreyrantholide
18 Fruticolide
19 Yomoginic acid methylester or 2β-Hydroxy-3β-(1-carbomethoxy ethenyl)-7-oxo-6,10-dimethyl-1,2,4,5-tetradehydrodecalin

†HP1 MeOH–H_2O (3:2); HP2 MeOH–H_2O (1:1); HP3 MeOH–H_2O (11:9).

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