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EREMOPHILANOLIDES, EUDESMANOLIDES, GUAIANOLIDES AND OTHER CONSTITUENTS FROM *ONDETIA LINEARIS*

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Key Word Index—*Ondetia linearis*, Compositae; sesquiterpene lactones, eremophilanolides; eudesmanolides; guaianolides; pseudoguaianolides, norsesquiterpenes.

Abstract—The aerial parts of *Ondetia linearis* afforded in addition to known compounds, 13 eremophilanolides, six eudesmanolides, one pseudoguaianolide and two norsesquiterpenes. The structures were elucidated by high field NMR techniques. The chemotaxonomic aspects are discussed briefly.

INTRODUCTION

The monotypic South African genus *Ondetia* is placed in the second group of the subtribe Inulinae (Compositae, tribe Inuleae) together with *Geigeria* [1]. While the chemistry of several species of the latter genus has been studied [2–6] nothing was known on the constituents of *Ondetia linearis* and we therefore studied this South West African species. The results are discussed in this paper.

RESULTS AND DISCUSSION

The extract of the aerial parts gave by careful chromatographic separation techniques the eudesmanolides **1** [7], **2**–**4**, **5** [8], **6**–**8** and **9** [9], the eremophilanolides **10**–**16** and **18**–**23**, the noreremophilanes **24** and **25**, the cyclopropenone **26** [10], the acid **27**, the guaianolides **28** [11] and **29** [12], the pseudoguaianolides **31** [13, 14] as well as the corresponding alcohol **30**, the geigeriolides **32** and **33** [6], the lignane derivative **34** [6], vomifoliol, geranylisobutyrate and selina-4,11-diene.

The structures of **2** and **3** followed from their ^{1}H NMR spectra (Table 1) which were similar to that of **1** [7]. However, the signals of methyl doublets and the absence of methylene proton signals required the presence of 11,13-dihydro derivatives. The observed coupling $J_{7,11}$ did not allow a direct assignment of the stereochemistry at C-11. Boranate reduction of **1** afforded a 1:5 mixture of **2** and **3**. Inspection of a Dreiding model clearly showed that this result was only in agreement with the proposed configurations at C-11 as the attack of boranate from the α-face was favoured.

The ^{1}H NMR spectrum of **4** and of the corresponding acetate obtained by mild acetylation (**4Ac**) (Table 1) indicated that again an eudesmanolide was present. Spin decoupling allowed the assignment of all signals. The obtained sequences required a Δ^3-double bond and a hydroxy group at C-2. The coupling of H-2 indicated a 2α-hydroxy group. Accordingly, the spectrum was in part close to that of the corresponding costic acid derivative [15]. The ^{1}H NMR spectra of **6** and **7** (Table 1) were similar to that of 2α-hydroxyalantolactone (**5**) [8]. Again the observed methyl doublets showed that the corresponding dihydro derivatives isomeric at C-11 may be present. Boranate reduction of **5** gave only the isomer **6**. Therefore, this isomer had an 11β-methyl group. In agreement with this in the case of the lactone **7** the observed NOE's indicated the 11α-methyl configuration. Thus effects between H-13, H-7 (5%) and H-8 (4%), between H-15, H-2 (4%), H-6β (8%) and H-9β (4%) as well as between H-8 and H-7 (8%) were observed.

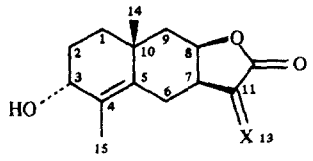
The spectrum of **8** (Table 1) was similar to that of **6**. However, the methyl doublet was replaced by a singlet at δ1.44. In agreement with the molecular formula ($C_{15}H_{22}O_4$) a 11-hydroxy derivative of **6** was proposed. The configuration at C-11 was deduced from the chemical shift of H-8 which was shifted down field by 0.32 ppm if compared with the shift of H-8 in the spectrum of **6**.

The structure of **10** also followed from its ^{1}H NMR spectrum (Table 2) which was in part similar to that of the corresponding 1β,10β-epoxyfuroeremophilane [16]. However, the signals of H-6 to H-9 and H-13 showed that a methylene lactone was present. The configuration at C-1 was assigned from the splitting of H-1 which was a triplet in the α-epoxides while in the β-epoxides a doublet was visible. The configuration at C-8 followed from the splitting of H-8 which was identical with that of H-8 in xanthadiene [17].

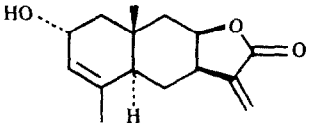
The ^{1}H NMR spectrum of **11** (Table 2) indicated that this lactone was a 11,13-dihydro derivative of compound **10**. Boranate reduction of **10** afforded only one dihydro compound which was identical with the natural product. Inspection of a model indicated that this observation only agreed with the presence of an 11β-methyl derivative.

The structure of **12** followed from its ^{1}H NMR spectrum (Table 2) which was in part very similar to that of compound **10**. The molecular formula ($C_{15}H_{20}O_4$) showed that an additional oxygen function was present. The IR spectrum required a hydroxy group and a ^{1}H NMR signal at δ4.04 was coupled with a doublet at δ3.22 which was due to an epoxide proton. Inspection of a model indicated that the couplings of H-2 best agreed with a 2α-hydroxy derivative.

The spectra of **13** and **14** (Table 2) required the presence of the corresponding 11,13-dihydro derivatives of compound **12**. In the case of compound **14** the observed



	1	2	3
X	CH_2	αMe,H	βMe,H



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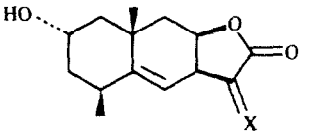
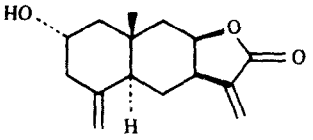


	5	6	7	8
X	CH_2	βMe,H	αMe,H	βMe,OH



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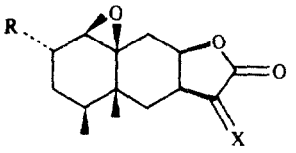
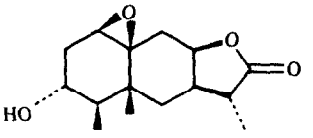
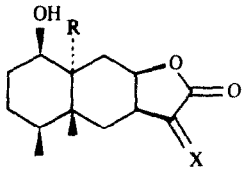


	10	11	12	13	14
R	H	H	OH	OH	OH
X	CH_2	βMe,H	CH_2	αMe,H	βMe.H



15



	16	17	18	19
R	OH	OH	OH	Cl
X	CH_2	βMe,H	αMe,H	CH_2

NOE's established the proposed stereochemistry at all chiral centres. Especially important were effects between H-14, H-2, H-3 and H-9β, between H-7, H-8 and H-11 as well as between H-11, H-7 and H-8. The couplings $J_{7,11}$ in the isomer **13** was 13 Hz which was in good agreement with an 11α-methyl lactone.

All signals in the spectrum of **15** (Table 2) could be assigned by spin decoupling and the stereochemistry was determined by the observed NOE's in deuteriobenzene between H-14, H-3 (7%), H-9β (4%) and H-11 (3%), between H-7 and H-8 (7%) as well as between H-1, H-2α (7%) and H-9α (6%).

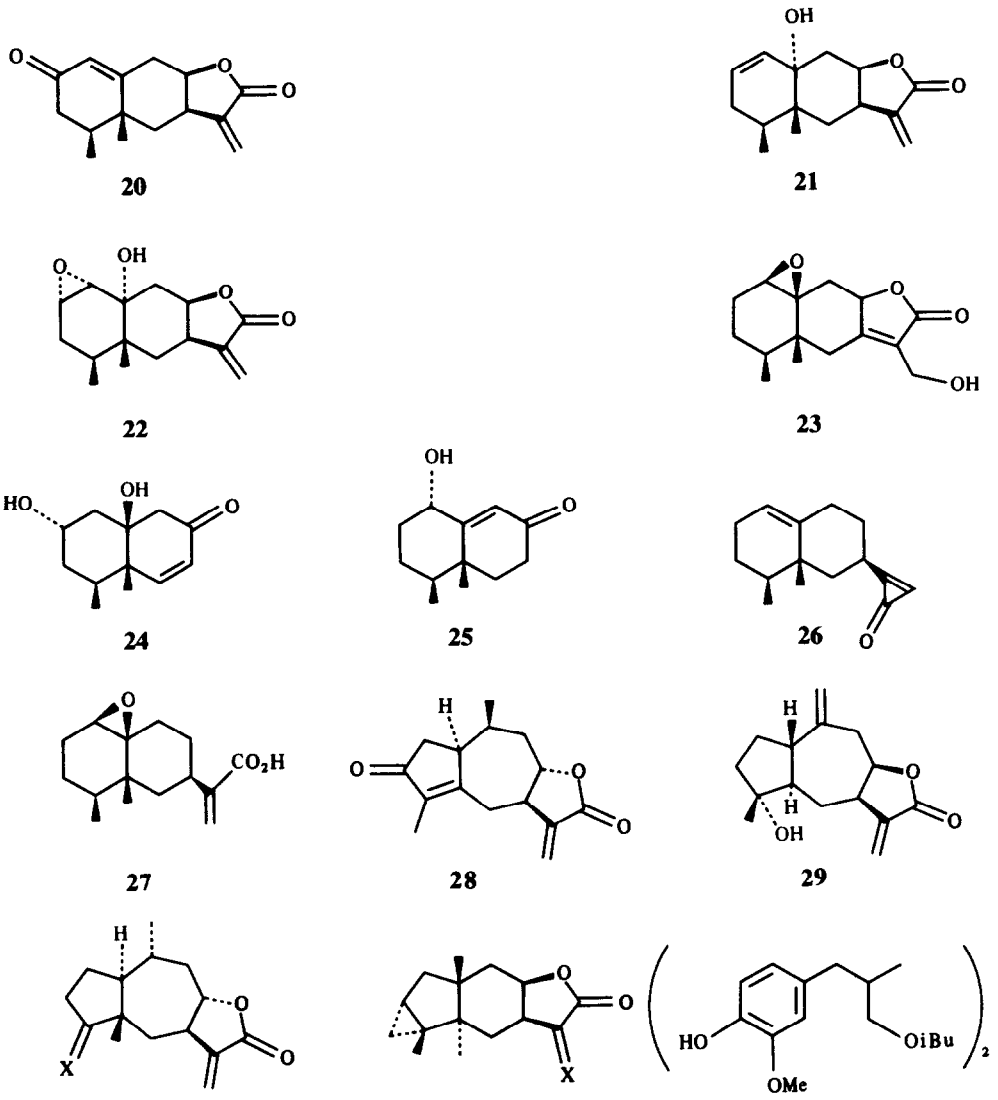
The molecular formula of **16** indicated that this lactone had two hydroxy groups and the ^{1}H NMR spectrum (Table 2) agreed with this assumption. Thus the signals of H-1 and H-9 were double doublets indicating that no hydrogen was located at C-10. An NOE between H-1, H-2α (7%) and H-9α (6%) and between H-14 and H-9β (4%) supported the proposed stereochemistry which was established by acid catalysed hydrolysis of the epoxide **10** which gave a diol identical with the isolated lactone

The ^{1}H NMR spectrum of **19** (Table 2) differed very slightly from that of **16**, only H-2α was shifted downfield. As the couplings in the spectra of **16** and **19** were nearly identical the presence of an isomeric diol could be excluded. Therefore a chlorohydrine was proposed with a chlorine at C-10. This would explain the downfield shift of H-2α as the effect of an axial chloro is stronger than that of a hydroxy group This was established by reaction of the lactone **10** with hydrochloric acid in chloroform which gave the chlorohydrine **19** as the only product, which therefore may be an artifact

The ^{1}H NMR spectral data of **18** (Table 2) showed that we were dealing with a 11,13-dihydro derivative of **16**. Again the assignment of the configuration followed from the result of boranate reduction of **16** which only gave the isomer **17**, due to the preferred α-attack of boranate The product **17** was not identical with **18**.

The ^{1}H NMR spectrum of **20** (Table 3) showed a broadened singlet at δ5.91 Spin decoupling indicated that it was due to H-1 as an allylic coupling with H-9 was observed. The presence of a keto group at C-2 followed from the down field shifts of H-3 which were assigned by irradiation of H-4 The remaining signals were similar to those of the other eremophilanolides

The ^{1}H NMR spectral data of **21** (Table 3) showed that again an eremophilanolide must be present Spin decoupling indicated that the low field signals at δ5 55 and 7 75



4Ac, **6Ac**, **8Ac** and **30Ac** are the corresponding acetates

were due to H-1 and H-2. As the signals of H-9 only were coupled with H-8 a hydroxy group was at C-10. The configuration followed from the chemical shifts of H-14 and H-15 which are not influenced by the hydroxy group as in many other eremophilanes with a *trans*-ring junction.

The ^{1}H NMR spectrum of **22** (Table 3) was very similar to that of **21**. However, the signals of the olefinic protons (H-1 and H-2) were replaced by a doublet at δ2.92 and a double doublet at 3.37 due to epoxide protons. Furthermore, a narrowly split doublet at δ2.84 was visible which showed a *W*-coupling with H-9β. Accordingly, a 10α-hydroxy group was present. The IR band at 3530 cm^{-1} indicated a hydrogen bond. Therefore a 1α,2α-epoxide was present in agreement with the triplet splitting of H-2.

The ^{1}H NMR spectrum of **23** in deuteriobenzene (Table 3) clearly showed that a glaucolide-like lactone was present. A pair of broadened double doublets were due to H-13 as they were coupled with a hydroxy triplet at δ2.01 and sharpened on irradiation of H-8 and H-6. Furthermore the H-6 signals showed only geminal couplings while a doublet at δ2.40 was due to H-1 as followed from spin decoupling. This signal was at δ3.08 in $CDCl_3$. Therefore a 1β,10β-expoxide was present. Most probably lactone **23** was formed biogenetically by oxidation of **10** followed by allylic rearrangement.

The molecular formulae of **24** and **25** indicated that they were norsesquiterpenes. The ^{1}H NMR data of **24** (Table 3) showed that a conjugated ketone was present (δ6.83 and 5.99 *d*). Furthermore a triplet of triplets at

Table 1 ^{1}H NMR spectral data of compounds **2–4**, **4Ac**, **6**, **6Ac**, **7** and **8** ($CDCl_3$, 400 MHz, δ-values)

H	2	3	4	4Ac	6	6Ac	7	8
1α	*	1.50 *m*	*	1 34 *dd*	1 08 *t*	1 17 *t*	1 08 *t*	1 09 *t*
1β	*	1 60 *m*	*	1 99 *m*	1 95 *br d*	1.95 *br d*	1 95 *br d*	1 95 *br d*
2	1 86 *m*	1.78 *m*	4.30 *br t*	5.38 *br t*	4.20 *tt*	5 29 *tt*	4 20 *tt*	4 19 *tt*
2′	1 71 *m*	1 66 *m*						
3α	3 90 *br s*	3 94 *br s*	5 46 *br s*	5 41 *br s*	1.47 *dt*	1.57 *dt*	1 46 *dt*	1 47 *dt*
3β					1 91 *br d*	1 91 *br d*	1 91 *br d*	1 91 *br d*
4	—	—	—	—	1 68 *br dq*	2 70 *br dq*	2 63 *br dq*	2 67 *br dq*
5	—	—	2.01 *br d*	2 05 *br d*	—	—	—	—
6α	1 71 *m*	1 70 *m*	1 95 *m*	1.99 *d*	5 25 *d*	5 26 *d*	2.25 *d*	5 22 *d*
6β	2 67 *dd*	2 44 *dd*	1 25 *m*	1.23 *dd*				
7	2 17 *dddd*	2 35 *dddd*	3 02 *br tt*	3 03 *br tt*	3 08 *ddd*	3.07 *ddd*	2 68 *br dd*	2.93 *dd*
8	4 55 *ddd*	4.45 *ddd*	4 56 *dt*	4 52 *dt*	4 70 *ddd*	4 73 *ddd*	4 87 *ddd*	5 05 *ddd*
9α	1 64 *dd*	1 54 *dd*	1 47 *dd*	1 53 *dd*	1 55 *dd*	1 55 *dd*	1 54 *dd*	1 56 *dd*
9β	2 02 *dd*	2 24 *dd*	2 19 *br d*	2 20 *br d*	2 19 *dd*	2 19 *dd*	2 17 *dd*	2.20 *dd*
11	2 42 *dq*	2 81 *dq*	—	—	2.90 *dq*	2.90 *dq*	2.44 *br q*	—
13	1 30 *d*	1 23 *d*	6 15 *br s*	6.16 *br s*	1.23 *d*	1 23 *d*	1.36 *d*	1 44 *s*
13′			5 62 *br s*	5.63 *br s*				
14	1.10 *s*	1 09 *s*	0 94 *s*	0.99 *s*	1 27 *s*	1 32 *s*	1 28 *s*	1 23 *s*
15	1 79 *br s*	1 80 *br s*	1 67 *br s*	1 69 *br s*	1 17 *d*	1 22 *d*	1 18 *d*	1 15 *d*
OAc	—	—	—	2 05 *s*		2 03 *s*		

*Obscured multiplets.

J [Hz]: Compounds **2** and **3** 2α,3 = 2β,3 ~ 2, 6α,6β = 14, 11,13 = 7 (compound **2**. 6α,7 = 6β,7 = 7,8 ~ 7, 7,11 = 4, 8,9α = 4, 8,9β = 7, 9α,9β = 15, compound **3** 6α,7 = 6; 6β,7 = 12, 7,8 = 4; 7,11 = 7; 8,9α = 4, 8,9β = 2; 9α,9β = 15.5), compounds **4** and **4Ac** 1α,1β = 1α,2 = 12, 1β,2 ~ 7, 2,3 ~ 2, 5,6β = 6α,6β ~ 12; 6α,7 = 6β,7 = 7, 7,8 = 8 9α = 5; 9α,9β = 15, compounds **6** and **6Ac** 1α,1β = 1α,2 = 2, 3α = 12, 1β,2 = 2,3β = 4, 1β,3β = 3β,4 = 1.5; 3α,4 = 6; 4,15 = 11,13 = 7; 6,7 = 3, 7,8 = 5 5, 7,11 = 8, 8,9α = 2 5, 8,9β = 3, 9α,9β = 15, compound **7** 1α,1β = 1α,2 = 2,3α = 12; 1β,2 = 2,3β = 4, 1β,3β = 3β,4 = 1 5, 4,15 = 11,13 = 7, 6,7 = 3, 7,8 = 6, 7,11 ~ 1, 8,9α = 2 5, 8.9β = 3, 9α,9β = 14, compound **8** 1α,1β = 1α,2 = 2,3α = 12, 1β,2 = 2,3β = 4, 3α,4 = 6, 4.15 = 7; 6,7 = 3 5, 7,8 = 6, 8,9α = 2 5, 8,9β = 3, 9α,9β = 15

δ4.14 required an equatorial hydroxy group with two neighbouring methylene groups. Accordingly, a 2α-hydroxy derivative of a noreremophilane was very likely. Spin decoupling supported this proposal. However, the relative position of the keto group had to be determined. This, and the stereochemistry, were established by the observed NOE's. Clear effects were obtained between H-14, H-4 (7%), H-6 (8%) and H-9β (4%) as well as between H-15, H-2 (4%) and H-6 (5%). Thus a Δ^6-double bond had to be assumed. Inspection of a model showed that the NMR data required a *cis*-ring junction.

The ^{1}H NMR spectrum of **25** (Table 3) indicated that again a conjugated ketone must be present. A doublet at δ6.18 showed an allylic coupling with H-1. Accordingly, the double bond was between C-9 and C-10. The couplings of H-1 required an α-hydroxy group and the remaining signals showed that again a noreremophilane was present.

The ^{1}H NMR spectrum of **27** (see Experimental) showed that an eremophilanic acid was present Spin decoupling allowed the assignment of all signals though some were overlapping multiplets. The isolation of **27** is of interest as it may be the precursor of the main constituent **10** which itself is the precursor of nearly all the other eremophilanolides (**11–18**).

The structure of the pseudoguaianolide **30** followed from the ^{1}H NMR data and from those of the corresponding acetate **30Ac** (Table 3) which were in part similar to those of **31** [13]. Spin decoupling and the observed NOE's of **30Ac** established the proposed structure. Clear NOE's were obtained between H-4, H-1 (3%) and H-6α (5%), between H-8 and H-10 (7%) as well as between H-15 and H-8 (4%). The corresponding 2α-acetoxy derivative was isolated from a *Geigeria* species [6]. The ^{1}H NMR spectrum of the latter was similar to that of **30**.

The chemistry of *Ondetia* supports in part the proposed close relationship to *Geigeria* [1] where a variety of sesquiterpene lactones have been isolated. In particular the co-occurrence of the rare lactones of type **32** [6] is remarkable. But eudesmanolides and eremophilanolides are present also in *Geigeria aspera* [6] which contains the guaianolide **29** while further guaianolides and some pseudoguaianolides related to **30** and **31** are reported from other *Geigeria* species [2–6]. However, most remarkable is the extreme variety of lactones in *Ondetia* The lignane **34** was also present in *Geigeria* while the rare cyclopropenone **26** has been isolated only from members of the Inuleae from a *Telekia* species [10] Noreremophilanes of type **24** and **25** are not common They are probably the result of oxidative degradation as this species seems to be very rich in oxidizing enzymes. The proposed relationship of *Geigeria* and *Ondetia* to *Calostephane* and related genera so far is not supported by the chemistry as the latter genus can be characterized by a variety of eudesman-12,6β-olides [18] However, the lactone **33** was isolated [19] from the related genus [1] *Antiphiona*

Table 2. ^{1}H NMR spectral data of compounds **10–19** and **24** (400 MHz, $CDCl_3$, δ-values)

H	10	11	12	13	14	15	16	C_6D_6	17	18	19	24
1	2.94 *br d*	3.04 *t*	3.22 *d*	3.24 *d*	3.25 *d*	3.01 *d*	3.55 *dd*	3.14 *dd*	3.55 *t*	3.58 *t*	3.89 *dd*	1.90 *t* 1.59 *ddd*
2α	1.92 *m*	2.02 *m*	4.04 *br s*	4.05 *br s*	4.08 *ddd*	2.44 *dddd*	2.03 *m*	1.87 *dddd*	2.05 *m*	2.05 *m*	2.34 *dddd*	4.14 *tt*
2β	1.27 *m*	1.87 *m*				1.89 *m*	1.60 *br d*	1.44 *dddd*	1.57 *m*	1.60 *m*	1.88 *m*	
3α	1.18 *m*	1.17 *m*	×	1.36 *br d*	1.50 *ddd*	3.46 *ddd*	1.26 *m*	1.12 *dddd*	1.29 *br d*	1.30 *m*	1.34 *br d*	2.05 *dt*
3β	1.92 *m*	1.48 *dddd*	×	1.53 *m*	1.60 *ddd*		1.57 *m*	1.59 *dddd*	1.60 *m*	1.60 *m*	1.70 *dddd*	1.84 *dddd*
4	1.70 *ddq*	1.99 *m*	1.56 *m*	1.77 *m*	2.02 *ddq*	1.58 *m*	1.74 *ddq*	1.69 *m*	1.67 *m*	1.74 *ddq*	1.76 *m*	2.17 *br dq*
6α	2.20 *dd*	1.77 *dd*	2.27 *dd*	1.95 *br d*	1.75 *dd*	1.89 *m*	2.00 *m*	1.81 *dd*	1.60 *m*	1.87 *dd*	2.02 *dd*	6.83 *d*
6β	1.83 *dd*	0.95 *t*	1.83 *dd*	1.71 *m*	0.98 *t*	1.73 *dd*		1.59 *br d*		1.62 *dd*	1.99 *d*	
7	3.33 *ddddd*	2.68 *ddd*	3.36 *ddddd*	2.90 *br tt*	2.65 *dddd*	2.37 *m*	3.27 *dddd*	2.84 *dddd*	2.93 *ddddd*	2.34 *br ddd*	3.29 *dddd*	5.99 *br d*
8	4.87 *ddd*	4.72 *ddd*	4.90 *ddd*	4.77 *ddd*	4.71 *ddd*	4.78 *ddd*	5.04 *ddd*	4.86 *ddd*	4.71 *ddd*	4.92 *ddd*	4.99 *ddd*	—
9α	1.64 *dd*	1.83 *dd*	1.75 *dd*	1.71 *dd*	1.98 *dd*	1.65 *dd*	1.97 *m*	1.94 *dd*	1.80 *dd*	1.91 *dd*	2.05 *dd*	2.96 *br d*
9β	2.01 *dd*	2.17 *dd*	2.05 *dd*	2.20 *dd*	2.20 *dd*	2.15 *dd*		1.71 *dd*	2.73 *dd*	2.19 *dd*	2.17 *dd*	2.00 *br d*
11	—	2.82 *dq*	—	2.71 *dq*	2.83 *dq*	2.68 *dq*	—	—	2.77 *dq*	2.75 *dq*	—	—
13	6.37 *d*	1.16 *d*	6.40 *d*	1.29 *d*	1.14 *s*	1.28 *d*	6.34 *d*	6.30 *d*	1.19 *d*	1.25 *d*	6.37 *d*	—
13′	5.65 *d*		5.67 *d*				5.62 *d*	5.09 *d*			5.63 *d*	—
14	0.93 *s*	0.97 *s*	0.91 *s*	1.04 *s*	0.89 *s*	1.10 *s*	1.01 *s*	0.97 *s*	1.05 *s*	1.18 *s*	1.12 *s*	1.17 *s*
15	0.78 *d*	0.79 *d*	0.83 *d*	0.79 *d*	0.80 *d*	0.93 *d*	0.87 *d*	0.78 *d*	0.83 *d*	0.83 *d*	0.90 *d*	1.14 *d*

× obscured.

J [Hz]: 4,15 = 7, 6α,6β = 9α,9β = 14; compound **10**: 1,2 = 4; 3α,4 = 4; 3β,4 = 7; 6α,7 = 1.5, 6β,7 = 7.5; 7,8 = 7; 7,13 = 3.5; 7,13′ = 3; 8,9α = 6.5, 8,9β = 10.5, compound **12**: 1,2 = 4; 6α,7 = 1.5; 6β,7 = 7.5; 7,8 = 8; 7,13 = 4; 7,13′ = 3.5, 8,9α = 7; 8,9β = 10; compound **13**: 1,2 = 4; 3α,3β = 15; 6α,7 = 6β,7 = 7,8 ~ 7; 7,11 = 13; 8,9α = 7; 8′,9β = 11, compound **14**: 1,2 = 2,3α = 3; 2,3β = 8; 3α,4 = 6; 3β,4 = 11; 6α,7 = 4.5, 6β,7 = 14; 7,8 = 6, 7,13 = 7, 8,9α = 9; 8,9β = 6.5; compound **15**. 1,2α = 4, 2α,2β = 15; 2α,3 = 2β,3 = 8; 3,4 = 10; 6β,7 = 7,8 = 7; 7,11 = 13, 8,9α = 6; 8,9β = 11; compounds **16** and **19**: 1,2α = 1,2β = 2.5; 2α,2β = 13; 3α,4 = 3; 2α,3α = 2β,3α = 2β,3β ~ 2, 2α,3β = 12; 3α,3β = 3β,4 = 12; 6α,7 = 7.5; 6β,7 = 1; 7,8 = 7.5; 7,13 = 4, 7,13′ = 3.5; 8,9α = 10; 8,9β = 6; compound **24**: 1α,1β = 1α,2 = 3,3α = 12; 1β,2 = 2,3β = 5; 3α,4 = 6, 3β,4 = 1.5, 4,15 = 7; 6,7 = 10; 9α,9β = 16.5.

Table 3. ^{1}H NMR spectral data of compounds **20**–**23**, **25**, **30** and **30**Ac (400 MHz, $CDCl_3$, δ-values)

H	**20**	**21**	**22***	**23** (C_6D_6)†	**25**	**30** (C_6D_6)‡	**30**Ac§
1	5.91 *br s*	5.55 *ddd*	2.92 *d*	2.40 *d*	4.31 *ddd*	1.05 *m*	1.68 *ddd*
2α	—	5.75 *ddd*	3.37 *dd*	1.67 *m*	2.19 *ddd*	1.33 *m*	1.49 *dddd*
2β	—			1.34 *m*	1.49 *m*	0.96 *m*	1.77 *m*
3α	2.35 *d*	2.07 *m*	2.01 *br dd*	0.84 *m*	1.65 *m*	1.10 *m*	2.09 *m*
3β	2.41 *dd*	1.74 *dddd*	1.50 *ddd*	1.67 *m*		1.66 *m*	1.38 *m*
4	2.24 *m*	2.03 *m*	1.62 *m*	1.67 *m*	1.49 *m*	3.32 *t*	4.80 *t*
6α	1.90 *dd*	2.05 *dd*	1.95 *dd*	1.76 *br d*	1.77 *ddd*	1.79 *dd*	2.17 *dd*
6β	1.68 *dd*	1.96 *br d*	1.81 *br d*	2.56 *d*	2.02 *ddd*	1.01 *dd*	1.34 *dd*
7	2.98 *ddddd*	3.29 *dddd*	3.29 *dddd*	—	2.44 *ddd* 2.36 *ddd*	2.16 *ddddd*	2.80 *ddddd*
8	4.62 *ddd*	5.04 *ddd*	5.09 *ddd*	4.64 *br dd*	—	3.69 *ddd*	4.22 *ddd*
9α	2.59 *ddd*	2.16 *dd*	2.30 *dd*	1.49 *dd*	6.18 *d*	0.90 *q*	1.33 *q*
9β	2.88 *dd*	1.63 *dd*	1.67 *ddd*	1.64 *dd*		2.03 *dt*	2.36 *dt*
13	6.30 *d*	6.34 *d*	6.34 *d*	4.20 *br dd*	—	6.16 *d*	6.14 *d*
13′	5.67 *d*	5.61 *d*	5.60 *d*	4.13 *br dd*	—	4.97 *d*	5.41 *d*
14	1.09 *s*	0.74 *s*	0.70 *s*	0.42 *s*	1.11 *s*	0.55 *s*	0.95 *s*
15	0.96 *d*	0.93 *d*	0.82 *d*	0.50 *d*	0.93 *d*	0.62 *d*	0.96 *d*

*OH 2.84 *d* †OH 2.01 *t* ‡H-10 1.18 *m* §H-10 1.80 *m*.

J [Hz]. Compound **20**: 1,9α = 1.5, 3α,3β = 17, 3β,4 = 5.5, 4,15 = 7, 6α,6β = 15; 6α,7 = 4.5; 6β,7 = 13, 7,8 = 8,9β = 7.5, 7,13 = 1.8; 7,13′ = 1.5; 8,9α = 9; compound **21**. 1,2 = 10, 1,3α = 1,3β = 2; 2,3α = 2, 2,3β = 4, 3α,3β = 13, 3β,4 = 10, 4,15 = 7, 6α,6β = 14; 6α,7 = 6, 7,8 = 9; 7,13 = 3.5, 7,13′ = 3; 8,9α = 7; 8,9β = 10, 9α,9β = 13; compound **22** 1,2 = 4; 2,3β = 2.5, 3α,3β = 15, 3α,4 = 4.5; 3β,4 = 12; 4,15 = 7; 6α,6β = 14; 6α,7 = 7; 7,8 = 9; 7,13 = 3.5, 7,13′ = 3; 8,9α = 7; 8,9β = 10; 9β,OH = 1.5, 9α,9β = 13, compound **23**: 1,2α = 4, 4,15 = 7, 6α,6β = 13; 6α,13 = 8,13 ~ 1, 8,9α = 7, 8,9β = 11, 9α,9β = 13, compound **25**. 1,2α = 6, 1,2β = 12; 1,9 = 1.5; 4,15 = 7, 6α,6β = 6α,7β = 14, 6α,7α = 5, 6β,7α = 6β,7β = 4.5, 7α,7β = 16, compounds **30** and **30**Ac 3α,4 = 3β,4 = 9; 6α,6β = 14, 6α,7 = 6, 6β,7 = 12, 7,8 = 9, 7,13 = 3.5, 7,13′ = 3, 8,9α = 9α,9β = 9α,10 = 12, 8,9β = 9β,10 = 3.5, 10,14 = 7 (compound **30**Ac. 1,2α = 8, 1,2β = 1,10 ~ 10, 2α,2β = 2α,3β ~ 12, 2α,3α = 4.5)

EXPERIMENTAL

The air-dried aerial parts (700 g, voucher 88/48, deposited in the SWA Herbarium at Windhoek, collected near Okahandja in March 1988) were extracted and worked-up as reported previously [20]. The extract was first separated by CC into six fractions. Fraction 1 gave by TLC 50 mg selina-4,11-diene and fraction 2 100 mg geranyl isobutyrate. TLC of fraction 3 (Et_2O–petrol, 1:3) gave 60 mg **32** and 60 mg **33**. HPLC (MeOH–H_2O, 4:1, always RP 8, *ca* 100 bar, flow rate 12 ml/min) of fraction 4 gave 450 mg **10** (R_t 26 min) and 30 mg **11** (R_t 30 min). Medium pressure chromatography (MPC) of fraction 5 (silica gel ϕ 30–60 μ, Et_2O–petrol, 1:3 with increasing amounts of Et_2O) gave 45 fractions which were combined after monitoring by TLC into five fractions (5/1–5/5). Fraction 5/1 contained 100 mg **10**, fraction 5/2 10 mg **11**, fraction 5/4 100 mg **31** and 5/5 60 mg **30**. Fraction 5/3 was separated by HPLC (MeOH–H_2O, 4:1) affording 12 mg **22** (R_t 11 min), 10 mg **21** (R_t 16 min) and a mixture (R_t 33 min) which gave by TLC (Et_2O–petrol, 3:1) 5 mg **34** (R_f 0.70) and 3 mg **19** (R_f 0.65). Fraction 6 was also separated again by MPC (Et_2O–petrol, 1:3 with increasing amounts of Et_2O and finally Et_2O–MeOH, 9:1). The fractions obtained were combined into nine fractions (6/1–6/9). Fraction 6/1 gave 4 mg **27** and fraction 6/6 550 mg **5**. HPLC of fraction 6/2 (MeOH–H_2O, 13:7) gave 15 mg **26** (R_t 3.6 min) and 60 mg **30** (R_t 5.1 min). HPLC of 6/3 (MeOH–H_2O, 13:7) afforded 10 mg **20** (R_t 1.8 min), 8 mg **23** (R_t 23 min) and 5 mg **25** (R_t 26 min). TLC of fraction 6/4 gave 15 mg **1** and 15 mg **16**. HPLC of 6/5 (MeOH–H_2O, 13:7) gave 6 mg **7** (R_t 42 min), 20 mg **16** (R_t 49 min), 2 mg **18** (R_t 6.0 min) and 12 mg **2** (R_t 7.0 min). HPLC of 6/7 (MeOH–H_2O, 3:2) gave 30 mg **9** (R_t 45 min), 2 mg **12** (R_t 28 min) and 2 mg **3** (R_t 59 min). HPLC of 6/8 (MeOH–H_2O, 3:2) afforded 4 mg **8** (R_t 24 min), 15 mg **14** (R_t 32 min) and three mixtures (6/8/1–6/8/3). Fraction 6/8/1 gave by TLC ($CHCl_3$–C_6H_6–Et_2O–MeOH, 30:30:30:1) 2 mg **15** (R_f 0.45) and 8 mg vomifoliol (R_f 0.20). Fraction 6/8/2 gave by TLC (same solvent) 3 mg **28** (R_f 0.58) and 2 mg **13** (R_f 0.42). TLC of 6/8/3 (Et_2O–MeOH, 30:1) gave a mixture of **4** and **6**. After acetylation HPLC (MeOH–H_2O, 13:7) gave 5 mg **4**Ac (R_t 66 min) and 10 mg **6**Ac (R_t 69 min). HPLC of 6/9 (MeOH–H_2O, 1:1) gave 10 mg **24** (R_t 23 min). Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

3α-Hydroxy-11βH-eudesm-4-en-12,8β-olide (**2**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3580 (OH), 1760 (γ-lactone), MS *m/z* (rel. int.) 250.157 $[M]^+$ (47) (calc for $C_{15}H_{22}O_3$ 250.157), 235 (56), 232 (40), 161 (35), 143 (100), 119 (74), 105 (68), 91 (59), $[\alpha]_D^{24}$ +145° ($CHCl_3$, *c* 0.12).

3α-Hydroxy-11αH-eudesm-4-en-12,8β-olide (**3**). Colourless crystals, mp 123°; IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3580 (OH), 1765 (γ-lactone), MS *m/z* (rel int.) 250.157 $[M]^+$ (58) (calc for $C_{15}H_{22}O_3$, 250.157), 235 (64), 231 (25), 217 (12), 189 (20), 161 (37), 143 (100), 124 (57), 119 (71), 105 (70), $[\alpha]_D^{24}$ +99° ($CHCl_3$, *c* 0.54).

2α-Hydroxy-eudesm-3,11(13)-dien-12,8β-olide (**4**). Colourless gum, not free from **3**. Acetylation (Ac_2O, 70°) gave **4**Ac, colourless crystals, mp 153°, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1770 (γ-lactone), 1735, 1240 (OAc), MS *m/z* (rel int.) 290.152 $[M]^+$ (0.6) (calc for $C_{17}H_{22}O_4$, 290.152), 230 (36), 215 (23), 143 (94), 119 (100), 105 (63), 91 (60); $[\alpha]_D^{24}$ +71° ($CHCl_3$, *c* 0.27).

2α-Hydroxy-11α,13-dihydroalantolactone (**6**). Colourless crystals, mp 147°, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3580 (OH), 1760 (γ-lactone), MS *m/z* (rel int.) 250 $[M]^+$ (1), 232.146 $[M-H_2O]^+$ (100) (calc for $C_{15}H_{20}O_2$ 232.146), 217 (20), 159 (28), 143 (53), 119 (42), 105 (25). Acetylation gave **6**Ac (Ac_2O, 70°) colourless crystals, mp 175°,

IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1740, 1250 (OAc); MS *m/z* (rel. int.) 232.146 $[M-HOAc]^+$ (76) (calc. for $C_{15}H_{20}O_2$: 232.146), 217 (21), 159 (37), 143 (200), 119 (48), 105 (32)

2α-*Hydroxy*-11β,13-*dihydroalantolactone* (**7**). Colourless crystals, mp 134°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590 (OH), 1760 (γ-lactone); MS *m/z* (rel. int.): 250.157 $[M]^+$ (0.6) (calc. for $C_{15}H_{22}O_3$: 250.157), 232 (84), 217 (19), 159 (33), 143 (100), 119 (65), 105 (34), 91 (34); $[\alpha]_D^{24°}$ +9° ($CHCl_3$; *c* 0.18).

2α,11α-*Dihydroxy*-11,13-*dihydroalantolactone* (**8**). Colourless crystals, mp 186°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1765 (γ-lactone); MS *m/z* (rel. int): 266 152 $[M]^+$ (0.5) (calc. for $C_{15}H_{22}O_4$: 266.152), 248 (5), 160 (100), 145 (61), 119 (54), 105 (29), $[\alpha]_D^{24°}$ −26° ($CHCl_3$, *c* 0.16).

1β,10β-*Epoxyeremophil*-11(13)-*en*-12,8β-*olide* (**10**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone); MS *m/z* (rel. int.) 248.141 $[M]^+$ (9) (calc for $C_{15}H_{20}O_3$: 248.141), 233 (12), 220 (12), 204 (8), 179 (31), 161 (37), 145 (32), 138 (57), 121 (51), 119 (44), 93 (72), 67 (77), 55 (100); $[\alpha]_D^{24°}$ −17° ($CHCl_3$; *c* 3.68). Reaction of **10** with dil H_2SO_4 in dioxane afforded **16**, identical with the natural product.

1β,10β-*Epoxy*-11α*H*-*eremophilan*-12,8β-*olide* (**11**). Colourless crystals, mp 98°, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1780 (γ-lactone); MS *m/z* (rel. int.). 250.157 $[M]^+$ (16) (calc. for $C_{15}H_{22}O_3$: 250.157), 235 (14), 182 (36), 181 (72), 133 (82), 119 (100), 93 (72), 91 (54).

2α-*Hydroxy*-1β,10β-*epoxyeremophil*-11(13)-*en*-12,8β-*olide* (**12**) Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.). 264.136 $[M]^+$ (1) (calc. for $C_{15}H_{20}O_4$: 264.136), 246 (6), 208 (7), 181 (41), 119 (36), 84 (100).

2α-*Hydroxy*-1β,10β-*epoxy*-11β*H*-*eremophilan*-12,8β-*olide* (**13**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}. 3560 (OH), 1765 (γ-lactone); MS *m/z* (rel. int.) 266.152 $[M]^+$ (0.5) (calc. for $C_{15}H_{22}O_4$: 266.152), 183 (37), 153 (66), 84 (100).

2α-*Hydroxy*-1β,10β-*epoxy*-11α*H*-*eremophilan*-12,8β-*olide* (**14**). Colourless crystals, mp 145°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3560 (OH), 1770 (γ-lactone); MS *m/z* (rel. int): 266.152 $[M]^+$ (1) (calc for $C_{15}H_{22}O_4$: 266 152), 183 (12), 125 (37), 112 (100); $[\alpha]_D^{24°}$ −74° ($CHCl_3$, *c* 0.4).

3α-*Hydroxy*-1β,10β-*epoxy*-11β*H*-*eremophilan*-12,8β-*olide* (**15**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1760 (γ-lactone); MS *m/z* (rel. int.) 266 152 $[M]^+$ (4) (calc. for $C_{15}H_{22}O_4$: 266.152); 251 (1), 248 (3), 233 (3), 181 (21), 121 (50), 111 (57), 55 (100).

1β,10α-*Dihydroxyeremophil*-11(13)-*en*-12,8β-*olide* (**16**) Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.) 266.152 $[M]^+$ (12) (calc for $C_{15}H_{22}O_4$: 266 152), 248 (10), 230 (20), 192 (21), 180 (66), 143 (32), 84 (100), 69 (53); $[\alpha]_D^{24°}$ +43° ($CHCl_3$; *c* 1.14): $NaBH_4$ reduction gave **17**, colourless crystals, mp 190°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3585 (OH), 1760 (γ-lactone); MS *m/z* (rel. int.): 268 168 $[M]^+$ (4) (calc. for $C_{15}H_{24}O_4$: 268.168), 250 (6), 232 (12), 217 (5), 182 $[M-MeCHCH_2CH_2CHOH]^+$ (92), 109 $[C_7H_9O]^+$ (100).

1β,10α-*Dihydroxy*-11β*H*-*eremophilan*-12,8β-*olide* (**18**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1760 (γ-lactone); MS *m/z* (rel. int): 268 168 $[M]^+$ (4) (calc. for $C_{15}H_{24}O_4$: 268.168), 250 (4), 232 (4), 182 (46), 129 (50), 109 (68), 84 (100).

10α-*Chloro*-1β-*hydroxyeremophil*-11(13)-*en*-12,8β-*olide* (**19**) Colourless crystals, mp 203°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}. 3580 (OH), 1760 (γ-lactone); MS *m/z* (rel. int.): 284.118 $[M]^+$ (2) (calc for $C_{15}H_{21}O_3Cl$ 284.118), 266 $[M-H_2O]^+$ (1.5), 249 $[M-Cl]^+$ (3), 231 $[249-H_2O]^+$ (5), 180 (100), 135 (21), 84 (48); $[\alpha]_D^{24°}$ +41° ($CHCl_3$; *c* 0.46). Reaction of **10** in $CHCl_3$ with HCl at room temp. gave quantitatively the lactone **19**.

2-*Oxo*-*eremophila*-1(10),11(13)-*dien*-12,8β-*olide* (**20**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1675 (C=CC=O); MS *m/z* (rel. int.) 246.126 $[M]^+$ (16) (calc. for $C_{15}H_{18}O_3$: 246.126), 204 (26), 192 (30), 177 (52), 176 (70), 134 (50), 121 (74), 119 (83), 105 (100), 93 (96), 79 (91), 67 (64); CD (MeCN) $\Delta\varepsilon_{290}$ + 1.92.

10α-*Hydroxyeremophila*-1,11(13)-*dien*-12,8β-*olide* (**21**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1775 (γ-lactone); MS *m/z* (rel int.). 248.141 $[M]^+$ (calc. for $C_{15}H_{20}O_3$: 248.141), 233 $[M-Me]^+$ (16), 230 $[M-H_2O]^+$ (14), 215 $[230-Me]^+$ (84), 204 $[M-CO_2]^+$ (82), 69 (100).

10α-*Hydroxy*-1α,2α-*epoxyeremophil*-11(13)-*en*-12,8β-*olide* (**22**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1} 3530 (OH), 1775 (γ-lactone), MS *m/z* (rel int.). 264.136 $[M]^+$ (6) (calc for $C_{15}H_{20}O_4$. 264.136), 246 $[M-H_2O]^+$ (8), 193 (88), 165 (40), 137 (54), 95 (81), 69 (100).

13-*Hydroxy*-1β,10β-*epoxyeremophil*-7(11)-*en*-12,8β-*olide* (**23**) Colourless crystals, mp 129°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1775, 1755 (γ-lactone), MS *m/z* (rel. int): 264.136 $[M]^+$ (9) (calc for $C_{15}H_{20}O_4$: 264.136), 249 $[M-Me]^+$ (5), 246 $[M-H_2O]^+$ (12), 126 $[C_6H_6O_3]^+$ (68), 95 $[126-CH_2OH]^+$ (100); $[\alpha]_D^{24°}$ −75° ($CHCl_3$; *c* 0.20).

2α,10β-*Dihydroxyondetianone* (**24**). Colourless crystals, mp 148°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1675 (C=CC=O); MS *m/z* (rel. int.): 210.126 $[M]^+$ (1) (calc for $C_{12}H_{18}O_3$: 210.126), 192 (18), 177 (8), 124 (49), 112 (100), 110 (56), 96 (57), 82 (72), 67 (54), 55 (47), $[\alpha]_D^{24°}$ +27° ($CHCl_3$, *c* 0.23)

1α-*Hydroxyisoondetianone* (**25**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400 (OH), 1680 (C=CC=O); MS *m/z* (rel. int): 194 131 $[M]^+$ (84) (calc. for $C_{12}H_{18}O_2$: 194.131), 179 $[M-Me]^+$ (38), 176 $[M-H_2O]^+$ (11), 137 (74), 119 (64), 109 (100), 95 (96); $[\alpha]_D^{24°}$ +140° ($CHCl_3$, *c* 0.27)

1β,10β-*Epoxyeremophil*-11(13)-*en*-12-*oic acid* (**27**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}. 3500–2500, 1690, 1620 (C=CCO_2H); MS *m/z* (rel. int): 250 157 $[M]^+$ (12) (calc. for $C_{15}H_{22}O_3$. 250 157), 235 $[M-Me]^+$ (14), 191 (16), 152 (37), 147 (42), 121 (56), 105 (81), 91 (84), 77 (82), 55 (100); ^{1}H NMR ($CDCl_3$): δ 2 94 (*d*, H-1, *J* = 4 Hz), 1 97 and 1.71 (*m*, H-2), 1.32 and 1.17 (*m*, H-3), 1.70 (*m*, H-4), 1.82 (*dd*, H-6, *J* = 15, 5 Hz), 1.73 (*dd*, H-6′, *J* = 15, 6.5 Hz), 3.02 (*dt*, H-7, *J* = 6, 6 Hz), 1.97 and 1 89 (*m*, H-8), 2.36 (*m*, H-9), 1 09 (*dt*, H-9′, *J* = 14, 6 Hz), 6.30 and 5.74 (*br s*, H-13), 0.94 (*s*, H-14), 0.68 (*d*, H-15, *J* = 7 Hz).

2-*Desoxy*-4-epi-*pulchellin* (**30**) Colourless crystals, mp 135°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 250.157 $[M]^+$ (22) (calc. for $C_{15}H_{22}O_3$: 250.157), 232 $[M-H_2O]^+$ (28), 217 $[232-Me]^+$ (14), 149 (32), 136 (38), 121 (40), 109 (51), 108 (100), 81 (76); $[\alpha]_D^{24°}$ +43° ($CHCl_3$, *c* 0.59). Acetylation (Ac_2O, 1 hr, 70°) afforded **30**Ac, colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1} 1775 (γ-lactone), 1740, 1250 (OAc); MS *m/z* (rel. int.): 292.167 $[M]^+$ (1.3) (calc. for $C_{17}H_{24}O_4$: 292.167), 232 $[M-HOAc]^+$ (24), 217 $[232-Me]^+$ (9), 108 (100).

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