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ISOCEDRENE DERIVATIVES AND OTHER SESQUITERPENES FROM *MOSCHARIA PINNATIFIDA*

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Key Word Index—*Moscharia pinnatifida*; Compositae; sesquiterpenes; isocedrenes; guaianes; cyperenes; nerolidol derivatives.

Abstract—From the aerial parts of *Moscharia pinnatifida* nine further α-isocedrene, two guaiane, three cyperene and two nerolidol derivatives were isolated. The structures were elucidated by high field NMR studies. Chemotaxonomic aspects are discussed.

INTRODUCTION

The two species of the genus *Moscharia* are both annuals and are distributed in Central Chile. The genus is placed in the tribe Mutisieae, subtribe Nassauviine [1]. So far only the roots of *Moscharia pinnatifida* Ruiz. et Pav. have been investigated chemically affording only the widespread tridecapentaynene [2]. We have now studied the aerial parts.

RESULTS AND DISCUSSION

The extract of the aerial parts afforded squalene, lupeol and taraxasterol as well as a very complex mixture of sesquiterpenes which finally gave nine further representatives of the rare α-isocedrenes (**1**–**9**), two guaiane derivatives (**10** and **11**), three substituted cyperenes (**12**–**14**) and two nerolidol derivatives (**15** and **16**).

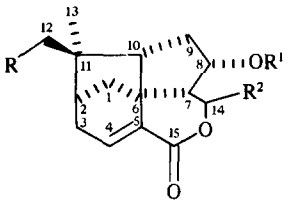
The molecular formula of **2** was $C_{19}H_{24}O_6$. The presence of two acetate groups in the molecule was deduced from the loss of two molecules of acetic acid in the mass spectrometer, and the presence of two singlets at δ2.06 and 2.07 in the ^{1}H NMR spectrum (Table 1). In deuteriobenzene all the ^{1}H NMR signals could be assigned by spin decoupling. As H-1 showed a W-coupling with H-10 the whole sequence could be established starting with the pair of doublets at δ3.65 and 3.92 (H-14). The remaining signals (H-12 and H-13) could only be assigned as shown in Table 1. All data were very similar to those of 14-hydroxy-α-isocedren-15-oic acid-14,15-lactone [**3**]. The presence of two acetoxy groups, however, caused the expected changes in the spectrum of **2**. The stereochemistry of **2** was established by NOE difference spectroscopy. Clear NOEs were observed between H-13 and H-1β, H-2, H-12 and H-9α, between H-9α and H-7, between H-1α and H-3α, between H-10 and H-8, H-12 and H-12′ and between H-8β and H-14β. These results agreed with the previously proposed stereochemistry for this new type of sesquiterpene lactone [3]. The ^{13}C NMR spectrum (see Experimental) was in good agreement with the structure.

The ^{1}H NMR spectrum of **1** (Table 1) was in part similar to that of **2** However, the methyl acetoxy signal was replaced by a methyl singlet and the H-8 signal was shifted upfield. The couplings observed indicated identical stereochemistry at all chiral centres.

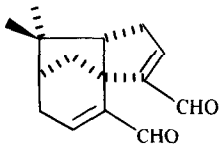
The spectra of **3**–**6** showed that each of these compounds differed from **2** in the nature of one ester group. As the H-12 signals were not altered, 12-acetoxy derivatives were assumed in all cases. The spectra of **7** and **8** (Table 1) indicated that there was no oxygen function at C-12 while a broadened low-field signal at δ5.62 showed a small coupling with H-7 and was due to H-14. Inspection of a model and the downfield shift of the H-7 signal showed that a 14α-hydroxy group was present while the threefold doublets at δ5.02 and 5.04 respectively indicated that these lactones were also 8α-acyloxy derivatives.

The molecular formula of **9** was $C_{15}H_{18}O_2$ and the ^{1}H NMR spectrum (Table 1) indicated the presence of a dialdehyde. The low field triplets at δ6.62 and 6.53 (in deuteriochloroform) could only be assigned to olefinic protons in β-positions to carbonyl groups. The remaining ^{1}H NMR signals were close to those of a corresponding dialdehyde from *Jungia malvaefolia* [4] which represents the corresponding 7,8-dihydro derivative of **9**. Accordingly, in the ^{1}H NMR spectrum of the α-isocedren-14,15-dial the second low field triplet (δ6.62) was missing. As in similar cases, the *E*-configuration of the conjugated aldehydes followed from the chemical shifts of the aldehyde protons. The ^{1}H NMR signals of **9** showed nearly the same couplings as those of **1**–**6**; however, several signals were shifted downfield due to the second carbonyl group and the additional double bond.

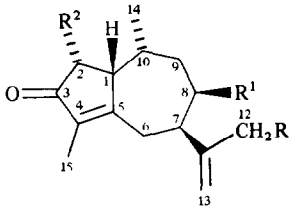
The structure of **10** was easily deduced from the ^{1}H NMR spectrum (Table 2) which was very close to that of the corresponding known acetate [5]. Though the configuration at C-1 and C-10 could be inferred from biogenetic considerations [5], we established the stereochemistry by NOE difference spectroscopy. Clear NOEs were observed between H-14 and H-2α, between H-1 and H-2β and H-6β as well as between H-1 and H-10. The ^{1}H NMR spectral data of **11** (Table 2) showed that again a guaiadienone was present. However, the broadened singlet at δ4.63 (H-12) was replaced by a methyl singlet at δ1.78 while the pair of double doublets for H-2 were replaced by a doublet at δ3.87 indicating a 2-hydroxy group. As H-14 and not H-1 was shifted downfield a 2α-



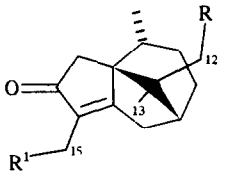
	1	2	3	4	5	6	7	8
R	H	OAc	OAc	OAc	OAc	OAc	H	H
R^1	H	Ac	iBu	Sen	Ang	iVal	Sen	iVal
R^2	H	H	H	H	H	H	OH	OH



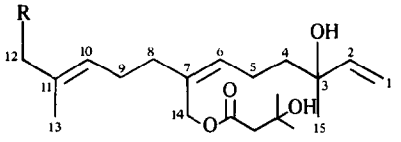
9



	10	**11**
R	$OCOCH_2C(OH)Me_2$	H
R^1	H	OiVal
R^2	H	OH



	12	**13**	**14**
R	H	OAc	$OCOCH_2C(OH)Me_2$
R^1	$OCOCH_2C(OH)Me_2$	OAc	OAc



15 R = H
16 R = OAc

orientation of the hydroxyl group was proposed. The threefold doublet at δ5.26 was due to H-8 as followed from spin decoupling. Accordingly, the isovaleryloxy group was at C-8. The configuration followed from the couplings observed.

The ^{1}H NMR spectra of **12**–**14** (Table 2) indicated that cyperen-3-one derivatives were present. Thus the spectra were similar to that of the corresponding 12-acetate [5]. The nature of the ester group in **12** followed from the ^{1}H NMR signals and from the fragment in the mass spectrum $[M-RCO_2H]^+$. Its position was easily deduced from the absence of the olefinic methyl signal in the spectrum of **12** which was replaced by a pair of doublets around δ4.80. Similarly, in the spectrum of **13** a broadened singlet at δ4.80 indicated that one of the two acetoxy groups was at C-15 while the second could only be placed at C-12. The spectrum of **14** (Table 2) indicated that one of the acetoxy groups was replaced by a 3-hydroxyisovaleryloxy residue. The relative positions of the two ester groups were deduced from the mass spectrum which showed, after loss of the C_5-acid, a strong fragment due to loss of an acetoxy radical obviously leading to an allylic ion and thus showing that the acetoxy group was at C-15.

The ^{1}H NMR spectra of **15** and **16** (see Experimental) indicated clearly that we were dealing with nerolidol derivatives. The position of the ester group in **15** followed from spin decoupling as irradiation of the olefinic broadened triplet at δ5.08 sharpened the signals of both olefinic methyl signals. Similar irradiation of the broadened triplet at δ5,44 (H-10) sharpened the H-12 and H-13 signals in the spectrum of **16**. The chemical shift of the olefinic methyl at C-11 indicated the *E*-configuration for the Δ^{10} double bond as the *Z*-configuration showed a methyl singlet at δ1.74 [6].

The chemistry of the genus *Moscharia* agrees well with the placement of this genus in the subtribe Nassauviinae the members of which have already yielded some 30α-isocedrene derivatives [3, 4, 7–9]. This type of sesquiterpene has not been reported from any other group. Cyperenes may also be typical. They are present in *Pleocarpus* [5], *Jungia* [3] and *Perezia* [10]. In the latter genus, however, bisabolene derivatives like perezone are

Table 1. ^{1}H NMR spectral data of compounds **1–9** (400 MHz, $CDCl_3$, TMS as internal standard)

H	1	2†	2 (C_6D_6)	7‡	9 (C_6D_6)
1α	1.90 *d* (*br*)	1.90 *d* (*br*)	1.31 *d* (*br*)	*	2.08 *dd*
1β	2.08 *dd*	*	1.58 *dd*	*	1 51 *dd*
2	*	*	1.65 *t*	*	1 58 *m*
3α	2.46 *ddd*	2.50 *ddd*	1.93 *ddd*	2.54 *ddd*	} 2.00 *m*
3β	2.54 *ddd*	2.43 *ddd*	2.03 *ddd*	2.45 *ddd*	
4	6.80 *t* (*br*)	6.84 *t* (*br*)	6.77 *t* (*br*)	6.80 *t* (*br*)	5.76 *dt*
7	*	*	1.60 *ddd*	2.28 *dd*	—
8	4 23 *ddd*	5.06 *ddd*	5.08 *ddd*	5.02 *ddd*	5 95 *t* (*br*)
9α	*	1.54 *m*	1 24 *ddd*	1.52 *ddd*	2.04 *ddd*
9β	*	*	1 79 *ddd*	2 12 *ddd*	2 08 *dd* (*br*)
10	*	*	1.50 *ddd*	*	2 30 *ddd*
12	} 1.10 *s*	3 97 *d*	3.79 *d*	} 1.08 *s*	} 0.79 *s*
12′		3.90 *d*	3.66 *d*		
13	1.06 *s*	1.05 *s*	0.76 *s*	1.02 *s*	0 74 *s*
14α	4.24 *d*	4.21 *m*	3.65 *dd*	} 5 62	} 9 78 *s*
14β	4.40 *d*		3.92 *dd*		
15	—	—	—	—	9.23 *s* (*br*)
OAc	—	2.06 *s*	1.72 *s*	—	—
		2.07 *s*	1.73 *s*		

*Overlapped multiplets.

†Compounds **3–6** all signals identical in the range of ±0.01 ppm except H-8 in **4** 5.08 *ddd*, in **5** 5.11 *ddd* and OiBu: 2.36 *qq*, 1.17 *d*; OSen (**4** and **7**): 5.65 *qq*, 2.18 *d*, 1.90 *d*; OAng: 6.11 *qq*, 1.99 *dq*, 1.89 *dq*, OiVal (**6** and **8**): 2 19 *d*, 2 10 *m*, 0.94 *d*

‡Compound **8** identical signals except H-14 5.60 *d* (*br*).

J (Hz): 1α, 1β = 12; 1α, 2 = 1α, 10 = 1; 1β, 2 = 2, 3α = 4; 2, 3β ~ 1; 3α, 3β = 21, 3α, 4 = 3; 3β, 4 = 4; 7, 8 = 6; 7, 14α = 4; 7, 14β = 3; 8, 9α = 13; 8, 9β = 7.5; 9α, 9β = 12.5; 9α, 10 = 10; 9β, 10 = 7.5; 12, 12′ = 11.5; 14α, 14β = 12 (compound **1**: 7, 14α = 3; 7, 14β = 1.5; compounds **7** and **8**: 7, 14 = 2; compound **9**: 4, 15 = 0.5, 8, 9α = 8, 9β = 2 7; 9α, 10 = 9β, 10 = 9).

more widespread [10–13]. They are also present in *Jungia* [3, 13] and *Acourtia* [14] which are also placed in this subtribe. As the guaia-4,11-dien-3-ones of type **10** are almost certainly the direct precursors of the corresponding cyperen-3-ones [4], the occurrence of these guaianes in *Pleocarpus* [5] and *Jungia* [3] should be mentioned. Nothing is known about the chemistry of the other genera placed in the subtribe Nassauviinae. Most of them are small genera and, as all genera present mainly in South America, some have migrated to Central America and to the South of the United States.

The subtribe Nassauviinae is the most natural in the tribe Mutisiinae and is also morphologically quite uniform [1]. From a taxonomic viewpoint some unspecialized *Trixis* are proposed to be the basic group in the subtribe. The occurrence of isocedrenolides like **1–8** in this genus [7, 9] may be an indication that these compounds are specialized sesquiterpenes. Their biogenesis developed very early and may be restricted to this group. The proposed grouping of the subtribe [15] does not agree very well with the chemistry. However, to get a clear picture, representatives of the so far uninvestigated genera need to be studied. The chemistry of the three other subtribes clearly differs though some more rare types of compounds show relationships in the whole tribe. In particular the 5-methyl coumarins are typical. They are present in *Perezia* [16] and *Jungia* [17] and also in genera belonging to the subtribe Mutisiinae [13, 17–19], while the most primitive subtribe Gochnatiinae [1] elaborates several types of more common sesquiterpene lactones indicating relationships to the Cynareae or the Heliantheae from which the Mutisieae may have been derived [1].

EXPERIMENTAL

The air dried plant material (270 g, grown in the Botanical Garden Berlin-Dahlem, voucher 1700/84) was extracted with MeOH–Et_2O–petrol (1:1:1) and the extract obtained was separated in the usual fashion [20]. The CC (silica gel) fractions were as follows: 1 (Et_2O–petrol, 1:4), 2 (Et_2O) and 3 (Et_2O–MeOH, 9:1). TLC (silica gel, PF 254) of fraction 1 (Et_2O–petrol, 1:4) gave 15 mg squalene, 200 mg lupeol and 150 mg taraxasterol. These compounds were identical with authentic samples (TLC, 400 MHz ^{1}H NMR). TLC of the second fraction (Et_2O–C_6H_6–CH_2Cl_2, 1:1:1) gave a mixture (2/1, R_f 0.70), 1 mg **3** (R_f 0.68), 8 mg **2** (R_f 0.65), 2.7 mg **9** (R_f 0.60), a mixture (2/5, R_f 0.55), 2 mg **14** (R_f 0.50) and a mixture (2/7, R_f 0.40). HPLC (RP 8, MeOH–H_2O, 7:3, 100 bar, flow rate, 3 ml/min) of 2/1 afforded 0.5 mg **13** (R_t 3.0 min), 1 mg **4** (R_t 6.5 min), 1 mg **5** (R_t 6 7 min) and 1.5 mg **6** (R_t 6.9 min). TLC of 2/5 (Et_2O–C_6H_6–CH_2Cl_2, 1:4:4) gave 1 mg **12** (R_f 0.58), 2 2 mg **10**

Table 2. ^{1}H NMR spectral data of **10–14** (400 MHz, $CDCl_3$, TMS as internal standard)

H	10	11	12	13†
1	3.01 *s (br)**	2.85 *s (br)**	—	—
2α	2.04 *dd*	—	2.55 *d*	2.20 *s (br)*
2β	2.38 *dd*	3.87 *d*	2.47 *d*	
6α	2.80 *d (br)*	2.70 *m*	2.83 *dd*	2.88 *dd (br)*
6β	2.40 *dd*		2.46 *dd (br)*	2.46 *dd (br)*
7	2.05 *m*	1.98 *m*	2.20 *m*	2.19 *m*
8α	1.90 *m*	5.26 *ddd*	1.65 *m*	1.65 *m*
8β	1.50 *m*	—	1.10 *m*	1.10 *m*
9α	1.32 *m*	1.78 *m*	1.90 *m*	1.90 *m*
9β	1.13 *m*	1.30 *m*	1.45 *m*	1.46 *m*
10	2.15 *dddq*	2.65 *dddq*	2.20 *m*	2.17 *ddq*
12	4.63 *s (br)*	1.78 *s (br)*	0.73 *s*	4.48 *d*
12′				4.19 *d*
13	5.13 *s (br)*	4.89 *s (br)*	1.10 *s*	0.85 *s*
13′	5.04 *s (br)*	4.75 *s (br)*		
14	0.95 *d*	1.10 *d*	0.60 *d*	0.62 *d*
15	1.70 *d*	1.73 *s (br)*	4.82 *d*	4.80 *s (br)*
15′			4.78 *d*	
OAc	—	—	—	2.07 *s* (6H)
OCOR	2.53 *s* (2H)	2.20 *d*	2.50 *s* (2H)	—
	1.28 *s* (6H)	2.10 *m*	1.28 *s* (6H)	
		0.94 *d*		
		0.93 *d*		

*Half width ~ 12 Hz.

†Compound **14** signals identical except 2.25 *d* and 2.19 *d* (H-2), 4.85 *d* and 4.80 *d* (H-15), 2.51 *s* and 1.28 *s* (OCOR).

J (Hz): Compounds **10** and **11**: 1, 2α = 3; 1, 2β = 5; 1, 15 = 1, 10 ~ 2; 2α, 2β = 17; 6α, 6β = 12; 6β, 7 = 7, 8β = 11; 8α, 8β = 13.5; 8β, 9α = 11; 8β, 9β = 3; 9α, 10 ~ 1; 9β, 10 = 10; 10, 14 = 7 (compound **11**: 1, 2α = 1, 2β = 3.5; 7, 8α = 2; 7, 8α, 9α = 3; 8α, 9β = 2); compounds **12–14**: 6α, 6β = 19; 6α, 7 = 6.5; 10, 14 = 6.5; 15, 15′ = 13.5 (compound **12**: 2α, 2β = 16; 12, 12′ = 11, compound **14**: 2α, 2β = 17; 12, 12′ = 11)

(R_f 0.55), 1 mg **7** (R_f 0.53), 1 mg **8** (R_f 0.52) and 3.8 mg **11** (R_f 0.51). TLC of 2/7 (Et_2O–C_6H_6–CH_2Cl_2, 1:4:4) gave 1.5 mg **15** (R_f 0.40) and 1.6 mg **16** (R_f 0.35). The last CC fraction gave by TLC (Et_2O) 1.2 mg **1** (R_f 0.45). The purity of the compounds was monitored by TLC in different solvent mixtures and by 400 MHz ^{1}H NMR.

8α,14-*Dihydroxy-α-isocedren-15-oic acid-14,15-lactone* (**1**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1730, 1620 (conjugated lactone); MS *m/z* (rel. int.): 248.141 $[M]^+$ (100) (calc. for $C_{15}H_{20}O_3$: 248.141), 230 $[M-H_2O]^+$ (11), 202 $[230-CO]^+$ (3), 187 $[202-Me]^+$ (8).

8α,12-*Diacetoxy-14-hydroxy-α-isocedren-15-oic acid-14,15-lactone* (**2**) Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}. 1740 (OAc, lactone), 1640 (C=C); MS *m/z* (rel int.): 348.157 $[M]^+$ (6) (calc. for $C_{19}H_{24}O_6$: 348.157), 306 $[M-$ketene$]^+$ (4), 288 $[M-HOAc]^+$ (0.8), 228 $[288-HOAc]^+$ (4), 61 (100); ^{13}C NMR ($CDCl_3$) (C-1–C-15): 39.4 *t*, 45.8 *d**, 31.0 *t**, 138.3 *d*, 136.4 *s*, 49.6 *s*, 57.1 *d*, 76.8 *d*, 32.7 *t**, 45.2 *d**, 46.6 *s*, 70.9 *t*, 22.2 *q*, 64.6 *t*, 164.2 *s*, $OCOCH_3$: 169.8 *s*, 169.5 *s*, 20.5 *q*, 20.3 *q* (*may be interchangeable); $[\alpha]_D$ = +54 ($CHCl_3$; *c* = 0.77).

12-*Acetoxy-8α-isobutyryloxy-14-hydroxy-α-isocedren-15-oic acid-14,15-lactone* (**3**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R, lactone); MS *m/z* (rel. int.): 376.189 $[M]^+$ (30) (calc. for $C_{21}H_{28}O_6$: 376.189), 334 $[M-$ketene$]^+$ (20), 316 $[M-HOAc]^+$ (3), 228 $[316-RCO_2H]^+$ (18), 213 $[228-Me]^+$ (5), 71 $[C_3H_7CO]^+$ (58), 43 (100); $[\alpha]_D$ = +83 ($CHCl_3$; *c* = 0.1)

12-*Acetoxy-8α-senecioyloxy-14-hydroxy-α-isocedren-15-oic acid-14,15-lactone* (**4**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (OAc, lactone), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 388.189 $[M]^+$ (44) (calc. for $C_{22}H_{28}O_6$: 388.189), 346 $[M-$ketene$]^+$ (20), 328 $[M-HOAc]^+$ (2), 228 $[328-RCO_2H]^+$ (18), 213 $[228-Me]^+$ (4), 83 $[C_4H_7CO]^+$ (100).

12-*Acetoxy-8α-angeloyloxy-14-hydroxy-α-isocedren-15-oic acid-14,15-lactone* (**5**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (OAc, lactone), 1720 (C=CCO_2R); MS *m/z* (rel int.): 388.189 $[M]^+$ (40) (calc. for $C_{22}H_{28}O_6$: 388.189), 328 $[M-HOAc]^+$ (3), 228 $[328-RCO_2H]^+$ (21), 83 $[C_4H_7CO]^+$ (100).

12-*Acetoxy-8α-isovaleryloxy-14-hydroxy-α-isocedren-15-oic acid-14,15-lactone* (**6**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R, lactone); MS *m/z* (rel. int.): 390.204 $[M]^+$ (24) (calc. for $C_{22}H_{30}O_6$: 390.204), 348 $[M-$ketene$]^+$ (10), 330 $[M-HOAc]^+$ (6), 228 $[330-RCO_2H]^+$ (26), 200 $[228-CO]^+$ (26), 185 $[200-Me]^+$ (8), 85 $[C_4H_9CO]^+$ (24), 55 (100).

8α-*Senecioyloxy-14-hydroxy-α-isocedren-15-oic acid-14,15-lactone* (**7**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}. 3600 (OH), 1740 (γ-lactone), 1720 (C=CCO_2R); MS *m/z* (rel int.): 346.178 $[M]^+$ (1.7) (calc. for $C_{20}H_{26}O_5$: 346.178), 328 $[M-H_2O]^+$ (6), 246 $[M-RCO_2H]^+$ (21), 83 $[C_4H_7CO]^+$ (100).

8α-*Isovaleryloxy-14-hydroxy-α-isocedren-15-oic acid-14,15-lactone* (**8**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CO_2R, lactone); MS *m/z* (rel. int.): 348.194 $[M]^+$ (1.5) (calc for $C_{20}H_{28}O_5$: 348.194), 330 $[M-H_2O]^+$ (3), 246 $[M-RCO_2H]^+$ (21), 218 $[246-CO]^+$ (28), 85 $[C_4H_9CO]^+$ (28), 57 $[85-CO]^+$ (100)

7,8-*Dehydro-α-isocedren-14,15-dial* (**9**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2750, 1690, 1630 (C=CCHO); MS *m/z* (rel. int.): 230.131 $[M]^+$ (32) (calc. for $C_{15}H_{18}O_2$: 230.131), 202 $[M-CO]^+$ (100), 187 $[202-Me]^+$ (33), 159 $[187-CO]^+$ (32), 144 $[159-Me]^+$ (20), 129 (20), 107 (92); $[\alpha]_D$ = +66 ($CHCl_3$, *c* = 0.27).

12-[3-*Hydroxyisovaleryloxy*]-*guaia-4,11-diene-3-one* (**10**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CO_2R), 1705 (C=CCO); MS *m/z* (rel. int.): 334.214 $[M]^+$ (8) (calc. for $C_{20}H_{30}O_4$: 334.214), 316 $[M-H_2O]^+$ (2), 276 $[M-Me_2CO]^+$ (10), 216 $[M-RCO_2H]^+$ (4), 105 (34), 61 (100); $[\alpha]_D$ = −23 ($CHCl_3$; *c* = 0.22)

2α-*Hydroxy-8β-isovaleryloxy-guaia-4,11-diene-3-one* (**11**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}. 3600 (OH), 1730 (CO_2R), 1715 (C=CCO); MS *m/z* (rel. int.): 334.214 $[M]^+$ (8) (calc for $C_{20}H_{30}O_4$: 334.214), 232 $[M-RCO_2H]^+$ (46), 214 $[232-H_2O]^+$ (20), 199 $[214-Me]^+$ (8), 171 $[199-CO]^+$ (7), 85 $[C_4H_9CO]^+$ (44), 57 $[85-CO]^+$ (100); $[\alpha]_D$ = +57 ($CHCl_3$; *c* = 0.38)

15-[3-*Hydroxyisovaleryloxy*]-*cyperen-3-one* (**12**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CO_2R), 1710 (C=CCO); MS *m/z* (rel. int.): 334.214 $[M]^+$ (10) (calc. for $C_{20}H_{30}O_4$: 334.214), 216 $[M-RCO_2H]^+$ (100).

12,15-*Diacetoxycyperen-3-one* (**13**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1235 (OAc), 1710 (C=CCO); MS *m/z* (rel. int.): 334.178 $[M]^+$ (20) (calc. for $C_{19}H_{26}O_5$: 334.178), 292 $[M-$ketene$]^+$ (20), 275 $[M-OAc]^+$ (6), 274 $[M-HOAc]^+$ (14), 215 $[274-OAc]^+$ (20), 214 $[274-HOAc]^+$ (100), 199 $[214-Me]^+$ (20), 171 $[199-CO]^+$ (20).

15-*Acetoxy-12-[3-hydroxyisovaleryloxy]-cyperen-3-one* (**14**) Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CO_2R), 1715 (C=CCO); MS *m/z* (rel. int.): 392.220 $[M]^+$ (22) (calc. for $C_{22}H_{32}O_6$: 392.220), 377 $[M-Me]^+$ (18), 274 $[M-RCO_2H]^+$ (34), 215 $[274-OAc]^+$ (63), 214 $[274-HOAc]^+$ (100), 199 $[214-Me]^+$ (22), 171 $[199-CO]^+$ (20); $[\alpha]_D$ = +18 ($CHCl_3$; *c* = 0.2).

14-[3-*Hydroxyisovaleryloxy*]-*nerolidol* (**15**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1730 (CO_2R); MS *m/z* (rel. int.) 220.182 $[M-RCO_2H]^+$ (12) (calc. for $C_{15}H_{24}O$: 220.182), 202 $[220-H_2O]^+$ (10), 187 $[202-Me]^+$ (12), 69 $[C_5H_9]^+$ (100); ^1H NMR ($CDCl_3$): 5.25 (*dd*, H-1t), 5.08 (*dd*, H-1c), 5 93 (*dd*, H-2), 2.2–2 0 (*m*, H-5, H-8, H-9), 5.46 (*t* (*br*), H-6), 5.08 (*t* (*br*), H-10) 1 75 (*s* (*br*), H-12), 1 62 (*s* (*br*), H-13), 4 66 (*s* (*br*), H-14), 1 30 (*s*, H-15), 2.52 and 1 30 (each *s*, OCOR); [*J* (Hz): 1c, 1t = 1.5; 1c, 2 = 11; 1t, 2 = 17; 5, 6 = 9, 10 = 7]

12-*Acetoxy*-14-[3-*hydroxyisovaleryloxy*]-*nerolidol* (**16**) Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CO_2R); MS *m/z* (rel. int) 278.188 $[M-RCO_2H]^+$ (4) (calc for $C_{17}H_{26}O_3$ 278.188), 218 $[278-HOAc]^+$ (15), 203 $[218-Me]^+$ (14), 185 $[203-H_2O]^+$ (10), 83 $[C_4H_7CO]^+$ (75), 55 $[83-CO]^+$ (100); ^1H NMR ($CDCl_3$): 5.23 (*dd*, H-1t), 5.07 (*dd*, H-1c), 5 92 (*dd*, H-2), 2.2–2 0 (*m*, H-5, H-8, H-9), 5.46 (*t* (*br*), H-6), 5 44 (*t* (*br*), H-10), 4 45 (*s* (*br*), H-12), 1.64 (*s* (*br*), H-13), 4 66 (*s* (*br*), H-14), 1 30 (*s*, H-15), 2 52 and 1.30 (each *s*, OCOR), 2 08 (*s*, OAc); [*J* (Hz) 1t, 1c = 1 5; 1c, 2 = 11; 1t, 2 = 17, 5, 6 = 9, 10 = 7]; $[\alpha]_D$ = +14 ($CHCl_3$, *c* = 0 16).

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