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TYPES OF SESQUITERPENES FROM *ARTEMISIA DOUGLASIANA**

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Key Word Index—*Artemisia douglasiana*; Compositae; sesquiterpenes; longipinene derivatives; nerolidol derivatives; new type of sesquiterpene lactone; acetylenic spiroketal enol ethers; lavendulol-2-methylbutyrate.

Abstract—*Artemisia douglasiana* afforded, in addition to known compounds, two new C_{14}-acetylenes, five longipinene derivatives, three nerolidol derivatives, a lactone and a ketone with a new carbon skeleton and lavendulol-2-methylbutyrate. The structures were elucidated by spectroscopic methods and some chemical transformations. The configurations of several oxo longipinene-7, 9-di- and 7, 8, 9-triesters isolated previously were corrected. The biogenesis of the new lactones is discussed briefly.

INTRODUCTION

Many species of the large genus *Artemisia* (tribe Anthemideae) have been investigated chemically and numerous types of compounds have been isolated. In addition to acetylenes [1], many species contain sequiterpene lactones [2], mainly eudesmanolides, but coumarins are also widespread. We now have investigated the constituents of *Artemisia douglasiana* Bess. in Hook. The results will be discussed in this paper.

RESULTS AND DISCUSSION

The roots of *A. douglasiana* afforded **2** [1] and **10** [3–5] as well as two further spiroketal enol ethers, the acetate **3** and the corresponding *iso*-valerate **4**. The structures of **3** and **4** followed from the ^{1}H NMR spectra (Table 1). The axial orientation of the 2-acyloxy group in both compounds was deduced from the couplings $J_{1,2}$, while the stereochemistry of the 8, 9-double bond followed from the chemical shift of H-9. The configuration at C-6 and C-7 cannot be assigned, but the absolute configuration at C-5 for this type of spiro ketal has been established by X-ray analysis and CD measurements (unpublished results).

The aerial parts gave germacrene D, caryophyllene, γ-humulene, dehydromatricarianal (**1**) [1], **10** and vulgarone A (**22**) [3, 4] as well as the nerolidol derivatives **5–7**, lavendulol-2-methylbutyrate (**8**), the ketone **9**, the longipinene derivatives **11**, **12**, **14**, **17** and **25** and the hydroperoxide **26** [6]. The structures of **5–7** followed from the ^{1}H NMR spectra (Table 2) and the mass spectra. Spin decoupling allowed the assignment of H-1, H-2, H-4–H-6 and H-14 in all three compounds, while the position of the keto group followed from the chemical shift of H-6. The presence of a C-9 methylene group in **5** could be deduced from the chemical shift of the broadened doublet at δ 3.36; accordingly the structure of **5** was settled. The ^{1}H NMR spectra of **6** and **7** differed only slightly. A signal at δ 8.64 in **7** indicated the presence of a hydroperoxide. Reaction with triphenylphosphine

Table 1. ^{1}H NMR spectral data of compounds **3** and **4** (400 MHz, $CDCl_3$, TMS as int. standard)

	3	**4**
H-1α	4.01 *dd*	4.02 *dd*
H-1β	3.85 *ddd*	3.85 *ddd*
H-2α	4.90 *br s*	4.92 *br s*
H-6	3.90 *d*	3.90 *d*
H-7	4.33 *d*	4.33 *d*
H-9	5.20 *br s*	5.21 *br s*
H-14	2.00 *d*	2.01 *d*
OCOR	2.14 *s*	2.27 *d*
		2.10 *m*
		1.00 *d*

J(Hz): 1α, 1β = 13; 1α, 2α = 2; 1β, 2 = 1β, 3β = 1.5; 6, 7 = 3; 9, 14 = 1; O*i*Val: 2′, 3′ = 3′, 4′ = 3′, 5′ = 7.

*Part 449 in the series "Naturally Occurring Terpene Derivatives". For Part 448 see Bohlmann, F., Gupta, R. K., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 2117.

Table 2. ^{1}H NMR spectral data compounds **5**–**7** and **9** (400 MHz, $CDCl_3$, TMS as int. standard)

	5	**6**	**7**	**9**
H-1*c*	5.11 *dd*	5.11 *dd*	5.11 *dd*	4.96 *dd*
H-1*t*	5.25 *dd*	5.25 *dd*	5.24 *dd*	5.16 *dd*
H-2	5.94 *dd*	5.93 *dd*	5.92 *dd*	5.85 *dd*
H-4	1.70*	1.70*	1.71*	1.76 *m*
H-5	2.28†	2.31†	2.32†	1.87 *m*
H-6	6.63 *tq*	6.68 *tq*	6.68 *tq*	4.30 *t*
H-9	3.36 *br d*	6.87 *s*	6.80 *d*	6.84 *d*
H-10	5.29 *tqq*		6.72 *d*	5.92 *d*
H-12	1.63 *br s*	1.38 *s*	1.40 *s*	1.45 *s* (6H)
H-13	1.74 *d*		1.39 *s*	1.44 *s*
H-14	1.78 *d*	1.84 *br s*	1.80 *br s*	
H-15	1.34 *s*	1.33 *s*	1.33 *s*	1.30 *s*

*ABXY system.

†ABX_2 system.

J(Hz): 1*c*, 2 = 10; 1*t*, 2 = 17; 1*c*, 1*t* = 1.5; compound **5**: 4, 5 = 5, 6 = 7; 6, 14 = 10, 12 = 10, 13 ~ 1; 9, 10 = 7; compound **6**: 5, 6 = 7; 6, 14 = 1; compound **7**: 5, 6 = 7; 6, 14 = 1; 9, 10 = 15 (OOH 8.64 *br s*); compound **9**: 5, 6 = 7; 8, 9 = 10.

transformed **7** to **6**. Whereas in the spectrum of **6** the olefinic signals of H-9 and H-10 had coalesced into a singlet, in the spectrum of **7** a pair of doublets was visible, whose coupling indicated a *trans*-double bond. As the remaining signals were close to those of **5**, the structures of **6** and **7** could be deduced. Obviously **5** was the precursor of **6** and **7**. The structure of **8** was deduced from the ^{1}H NMR spectral data (see Experimental), which were close to those of known esters. The ^{1}H NMR spectrum of **9** (Table 2) indicated the presence of a conjugated ketone with a vinylic end group and a secondary ether function. H-6 was coupled with a 2-proton multiplet at δ 1.87 which in turn was coupled with a 2-proton multiplet at δ 1.76. Four methyl singlets around δ 1.45 indicated that all methyls were on oxygen bearing carbons. The mass spectrum did not show a molecular ion, but two strong fragments at *m/z* 140 ($C_8H_{12}O_2$) and *m/z* 111 ($C_7H_{11}O$) were in good agreement with the proposed structure. The first fragment was undoubtedly due to a McLafferty fragmentation, while the second was formed by splitting of the 6, 7-bond leading to an oxonium cation. **9** could be formed via the 6, 7-epoxide of the 9, 10-*cis*-isomer of **6**. The stereochemistry at C-3, C-6 and C-7 could not be determined. We have named **9** artedouglasiaoxide.

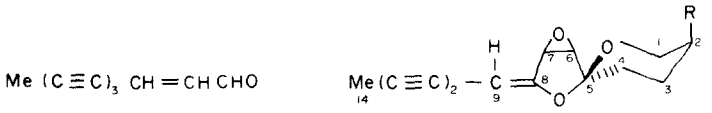
In addition to the main constituent **10**, several derivatives were present in minute amounts, which could not be separated. Acetylation led to a mixture of acetates, from which only **20** could be separated, while oxidation gave the ketones **13** and **16** as well as the aldehyde **21**, which could be separated. The structure of **17** clearly followed from the ^{1}H NMR spectra of **17**, **20** and **21** (Table 3), which in part were close to that of **10**. The position of the oxygen function followed from the downfield shift of the signal of the olefinic proton and from the replacement of the olefinic methyl signals by a pair of lowfield doublets. Sodium borohydride reduction of **13** gave a mixture of **11** and **12**, while reduction of **16**, where the position of the keto group followed from the presence of a *W*-coupling $J_{5,7}$, gave a mixture of **14** and **15**. In the spectra of **11** and **12**, H-4 and H-11 were clearly differentiated by Eu(fod)$_3$-induced shifts, which further showed that the hydroxyl groups were at C-7 and consequently those of **14** and **15** at C-9. In the ^{1}H NMR spectra of the C-9 alcohols the differences in the chemical shift of H-4 and H-11 could be explained best if **15** had a 9β-hydroxy group, which would deshield H-4, while a 9α-hydroxy group in **14** would deshield H-11, as in the spectra of the 7, 8, 9-trisubstituted ketones [7]. The epimers **11** and **12** showed the same values of $J_{7,8}$ as did **14** and **15** for $J_{8,9}$. This indicates that for each epimeric pair the conformations of the seven-membered ring must be different, which posed a problem in determining the stereochemistry at C-7 and C-9 respectively. One of the epimers (**11**) was identical with 7-hydroxy-1-oxo-α-longipinene [6], for which an α-orientation of the hydroxyl at C-7 had been proposed earlier [6]. However, the configuration of these substances has to be changed (see below). An analogous 7, 8, 9-triol-diangelate, whose configuration has been established by X-ray analysis [Joseph-Nathan, P., personal communication], has a 7β-angeloyloxy group. Several additional longipinene derivatives have been isolated from Compositae [6–10]. The ^{1}H NMR spectra of all these compounds showed differences in the chemical shifts of H-4 and H-11. Inspection of models in the two quasi-chair conformations showed that in one conformation when the 7-hydroxyl is β and equatorial, H-7 and H-11 were close together. This may be the cause of the upfield shift of H-11 in **11** as compared with the shift of H-11 in **12** with a 7α-hydroxy group, whose conformation is changed to avoid a strong interaction of H-11 with the hydroxyl group, or with the shift of H-11 in **10**. This seems to be the only possible explanation for the differences in chemical shifts of H-11. Thus the proposed stereochemistry of

Table 3. ^{1}H NMR spectral data of compounds **11–21** (400 MHz, $CDCl_3$, TMS as int. standard)

	11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
H-2	5.75 *q*	5.76 *q*	5.81 *q*	5.79 *q*	5.77 *q*	5.80 *q*	6.00 *br s*	5.76 *q*	5.76 *q*	5.91 *t*	6.55 *t*
H-4	2.74 *br d*	2.49 *br d*	2.60 *br d*	2.54 *br d*	2.80 *br d*	3.15 *br d*	2.58 *br d*	2.80 *br d*	2.58 *br d*	2.60 *br d*	3.32 *br d*
H-5	2.22 *br s*		2.30 *br s*	2.20 *br s*		2.37 *br s*	2.19 *br s*	2.19 *br s*		2.19 *br s*	2.06 *br s*
H-7	3.55 *dd*		2.79 *ddd* 2.77 *ddd*	*	*	2.72 *ddd* 2.63 *ddd*		4.71 *br s*	4.78 *br d*		
H-8		*					*	*	*	*	*
H-9	*	*	1.93 *ddd* 1.89 *ddd*	3.82 *dd*	3.86 *dd*	1.69 *m* —	*	*	*	*	*
H-11	2.69 *br d*	2.95 *dd*	2.90 *br d*	2.99 *br d*	2.80 *br s*	2.79 *br d*	2.82 *br d*	2.68 *br d*	2.98 *br d*	2.83 *dd*	2.95 *br d*
H-12	0.96 *s*	1.04 *s*	1.14 *s*	1.10 *s*	1.12 *s*	1.14 *s*	0.96 *s*	1.00 *s*	0.98 *s*	0.96 *s*	0.97 *s*
H-13	0.95 *s*	1.00 *s*	1.08 *s*	0.97 *s*	0.93 *s*	1.04 *s*	0.94 *s*	0.96 *s*	0.96 *s*	0.94 *s*	0.87 *s*
H-14	0.95 *s*	0.91 *s*	1.03 *s*	0.86 *s*	0.88 *s*	0.99 *s*	0.87 *s*	0.88 *s*	0.91 *s*	0.86 *s*	0.87 *s*
H-15	2.03 *d*	2.03 *d*	2.06 *d*	2.02 *d*	2.05 *d*	2.06 *d*	4.37 *dd* 4.28 *dd*	2.02 *d*		4.77 *dd* 4.69 *dd*	9.84 *s*
OAc	—	—	—	—	—	—	—	2.19 *s*	2.08 *s*	2.13 *s*	—

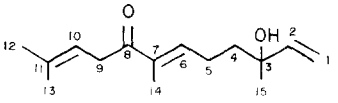
*Overlapped multiplets.

J(Hz): 2, 15 = 4, 5 = 1.5; 4, 11 = 6.5; compounds **11**, **12**, **18** and **19**: 7, 8 = 10; compounds **14** and **15**: 8, 9 = 3; compound **13**: 8, 8′ = 12; 9, 9′ ~ 15; 8, 9 ~ 5,5; compound **16**: 5, 7 ~ 1; 7, 8 = 5; 7, 8′ = 7; 7′, 8 = 4.5; 7′, 8′ = 7; 8, 8′ = 12.5; compounds **17** and **20**: 2, 15 = 1.5; 15, 15′ = 16.



1

2 R = H
3 R = OAc
4 R = O*i*Val



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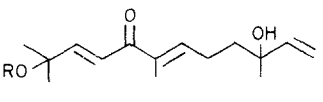
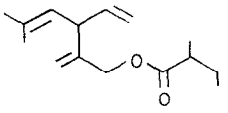


6 R = H
7 R = OH



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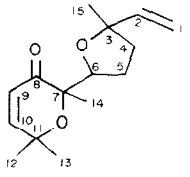

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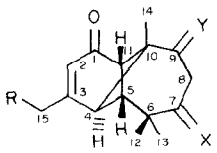
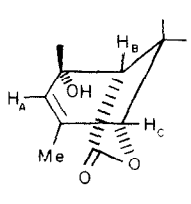


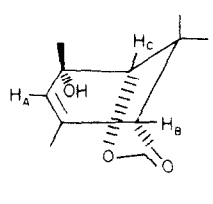
	10	11	12	13	14	15	16	17	18	19	20	21
R	H	H	H	H	H	H	H	OH	H	H	OAc	CHO
X	H_2	β-OH,H	α-OH,H	=O	H_2	H_2	H_2	H_2	β-OAc,H	α-OAc,H	H_2	H_2
Y	H_2	H_2	H_2	H_2	α-OH,H	β-OH,H	=O	H_2	H_2	H_2	H_2	H_2

the alcohols **11**, **12**, **14** and **15** was most likely. NOE experiments further supported these assignments. Irradiation of H-7 caused NOE of H-11 with **11** and of H-4 with **12**. As a result of these assignments and the results of the X-ray analysis of 9α-acetoxy-7β, 8α-diangeloyloxy-2,3-dihydrolongipinan-1-one [Joseph-Nathan, P., personal communication], the stereochemistries of several other longipinene derivatives have to be corrected. The 7,9-diesters previously ascribed structures of type **27** [5, 8–10] should be changed to **28**, the di- and triesters previously thought to be of type **29** [7] to **30** and those of type **31** [8] to **32**.

The structure of the lactone **25**, which we have named artedouglasiolide, followed from the molecular formula and the spectral data. The IR spectrum indicated the presence of a hydroxy-γ-lactone and the ^{1}H NMR spectrum (Table 4) was in part similar to that of **22**. Again four methyl signals were visible, one of them being that of an olefinic proton. The latter was further coupled with two narrowly split signals at δ 4.11 and 2.71, which were also coupled to each other. Most likely all three were *W*-couplings. As no further lowfield signal was visible the hydroxyl group was tertiary. Partial structures **A** or **B** agreed with these data:

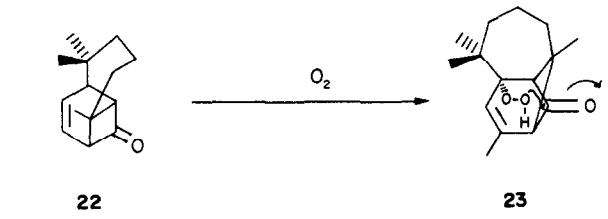


A

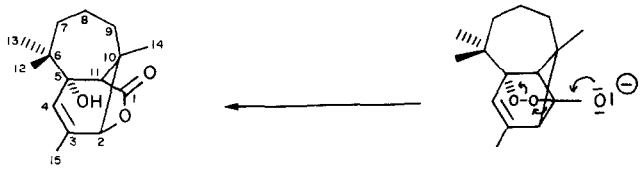


B

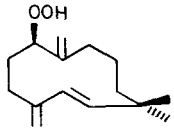
The Eu(fod)$_3$-induced shifts favoured partial structure **A**, as the signal at 2.71 (H_B) showed the largest shift, an observation which could not be explained by **B**. The remaining ^{1}H NMR signals were overlapping multiplets of three CH_2 groups. **25**, therefore, was the



22 23



25 24



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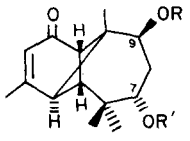
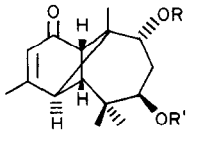


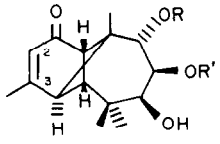
R Sen, Ang, H, Ang, Sen, Meacr, Tigl, Ang
R' H, H, Ang, Ang, Sen, Meacr, Tigl, Meacr

27

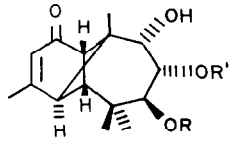


R Meacr, Ang, Tigl, Ang, Tigl, Tigl, Sen, Meacr, Epang
R' Ang, Tigl, Ang, Sen, Sen, Meacr, Meacr, Sen, Ang

28



29
31 2.3 α-H



R Ang, Ang, Ang, Ang
R' Ang, *i*-Val, MeBu, Ang (β)

30
32 2.3 β-H

Table 4. ^{1}H NMR spectral data of compound **25** ($CDCl_3$, TMS as int. standard)

	^{1}H NMR	Δ		^{13}C NMR		
H-2	4.11 *dd*	0.69	C-1	177.7 *s*	C-9	34.7 *s*
H-4	5.68 *ddq*	1.36	C-2	85.6 *d*	C-10	40.1 *s*
H-7–H-9	1.2–1.6 *m*		C-3	138.9 *s*	C-11	54.9 *d*
H-11	2.71 *dd*	2.12	C-4	126.9 *d*	C-12	27.2 *q*
H-12	1.03 *s*	0.58	C-5	73.1 *s*	C-13	25.6 *q*
H-13	1.22 *s*	0.46	C-6	48.2 *s*	C-14	22.2 *q**
H-14	1.03 *s*	0.94	C-7	41.6 *t*	C-15	21.6 *q**
H-15	1.89 *d*	0.41	C-8	20.0 *t*		

*May be interchangeable.
J(Hz): 2, 4 = 2, 11 = 2, 15 = 4, 11 ~ 1.

most likely structure, if it belonged to a compound related to the main constituents. **25** could have been formed from **22** via the hydroperoxide **23**, which by nucleophilic attack of the peroxide group on the carbonyl carbon would lead through **24** to the lactone **25**. The ^{13}C NMR spectrum also was in agreement with the proposed structure as was the fragmentation pattern of the mass spectrum. The base peak, *m/z* 122 ($C_8H_{10}O$), could be formed by splitting the bonds 6, 7 and 9, 10 followed by loss of carbon dioxide leading to a xylenol ion. From *Artemisia douglasiana* depending on the season different eudesmanolides and guaianolides have been isolated previously [11, 12]. These lactones were not detected in the present collection.

EXPERIMENTAL

The air-dried plant material, collected in California (voucher RMK 8414, deposited in the U.S. National Herbarium, Washington) was extracted with Et_2O–petrol (1 : 2), and the resulting extracts were separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing their ^1H NMR spectra with those of authentic material. The roots (20 g) afforded 2 mg **2**, 2 mg **3** (Et_2O–petrol, 1 : 3), 3.3 mg **4** (same solvent) and 2 mg **10**, while the aerial parts (550 mg) gave germacrene D, 25 mg γ-humulene, 25 mg caryophyllene, 4.7 mg **1**, 46 mg **5** (Et_2O–petrol, 1 : 1), 7 mg **6** (Et_2O), 16 mg **7** (Et_2O), 4 mg **8** (Et_2O–petrol, 1 : 10), 2.5 mg **9** (Et_2O–petrol, 1 : 1), 1.5 g **10**, 2 mg **11**, 8 mg **12**, 4 mg **14**, 1 mg **15**, 40 mg **17** [the last five compounds (Et_2O) not separated], 5 mg **25** (Et_2O) and 2 mg **26**. 20 mg of the mixture of **11**, **12**, **14**, **15** and **17** on heating with 0.1 ml Ac_2O for 1 hr at 70° afforded a mixture of acetates, from which **20** could be separated. Further, 20 mg of the mixture on oxidation with pyridine chlorochromate in CH_2Cl_2 gave 4 mg **13**, 2 mg **16** and 10 mg **21**, which could be separated by TLC (Et_2O–petrol, 1 : 1).

The acetate **3** was a colourless gum, UV $\lambda_{max}^{Et_2O}$ nm: 292, 277, 264; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2140 (C≡C), 1745, 1250 (OAc), 1655 (C=C–OR); MS *m/z* (rel. int.): 288.110 $[M]^+$ (21) ($C_{16}H_{16}O_5$), 228 $[M-HOAc]^+$ (3), 124 $[C_7H_8O_2]^+$ (100); $[\alpha]_D = -12.6$ ($CHCl_3$; *c* 0.2).

Isovalerate **4**. Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2140 (C≡C), 1735 (CO_2R), 1655 (C=COR); MS *m/z* (rel. int.): 330.147 $[M]^+$ (18) ($C_{19}H_{22}O_5$), 228 $[M-RCO_2H]^+$ (6), 124 $[C_7H_8O_2]^+$ (100), 85 $[C_4H_9CO]^+$ (30), 57 $[85-CO]^+$ (88);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546\ nm}{-16.5 \quad -21.3 \quad -23.7} (CHCl_3;\ c\ 0.33).$$

8-Oxo-nerolidol (**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1690, 1650 (C=CC=C); MS *m/z* (rel. int.): 236.178 $[M]^+$ (1) ($C_{15}H_{24}O_2$), 218 $[M-H_2O]^+$ (2), 167 $[M-C_5H_9]^+$ (31), 149 $[167-H_2O]^+$ (20), 139 $[167-CO]^+$ (10), 121 $[139-H_2O]^+$ (48), 111 (74), 93 $[121-C_2H_4]^+$ (100), 81 (42), 69 (54), 55 (77).

11-Hydroxy-8-oxo-9, 10-dehydro-10, 11-dihydronerolidol (**6**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1665 (C=CCOC=C); MS *m/z* (rel. int.): 234.162 $[M-H_2O]^+$ (4) ($C_{15}H_{22}O_2$), 167 $[M-Me_2C(OH)CH=CH_2^+$ (38), 149 $[167-H_2O]^+$ (100), 113 $[Me_2C(OH)CH=CHCO]^+$ (54), 95 $[113-H_2O]^+$ (50), 71 $[HO=C(Me)CH=CH_2]^+$ (78);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-27.1 \quad -27.6 \quad -24.0 \quad -31.4} (CHCl_3;\ c\ 0.21).$$

11-Perhydroxy-8-oxo-9, 10-dehydro-10, 11-dihydronerolidol (**7**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3080, 995, 930 (CH=CH_2), 1660 (C=CCOC=C); MS *m/z* (rel. int.): 268 $[M]^+$ (0.2), 250.157 $[M-H_2O]^+$ (1) ($C_{15}H_{22}O_3$), 235 $[250-Me]^+$ (6), 217 $[250-O_2H]^+$ (7), 149 (42), 71 (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{-20.9 \quad -22.3 \quad -26.6 \quad -52.8} (CHCl_3;\ c\ 0.48).$$

To 5 mg **7** in 0.5 ml $CDCl_3$ 20 mg triphenylphosphine were added. After 5 min the ^1H NMR spectrum was identical with that of **6**.

Lavendulol-(2-methylbutyrate) (**8**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745 (CO_2R), 920 (CH=CH_2); MS *m/z* (rel. int.): 236.178 $[M]^+$ (0.5) ($C_{15}H_{24}O_2$), 134 $[M-RCO_2H]^+$ (24), 119 $[134-Me]^+$ (100), 85 $[C_4H_6CO]^+$ (12), 57 $[85-CO]^+$ (76);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{+22.6 \quad +24.2 \quad +26.9 \quad +51.5} (CHCl_3;\ c\ 0.4).$$

Artedouglasiaoxide (**9**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1685 (C=CCO), 3080, 925 (CH=CH_2); MS *m/z* (rel. int.): 140 $[C_8H_{12}O_2]^+$ (100), 125 $[140-Me]^+$ (95), 111 $[C_7H_{11}O]^+$ (28), 93 $[111-H_2O]^+$ (58), 81 $[111-CH_2O]^+$ (38), 67 $[C_5H_7]^+$ (48).

7α- and β-Hydroxy-α-longipinen-1-one (**11** *and* **12**). Colourless gum, not obtained free from **14**, **15** and **17**. Oxidation afforded **13**, colourless gum, ^1H NMR see Table 3. $NaBH_4$ reduction in MeOH at 0° afforded a mixture of **11** and **12** (1 : 1), which could not be separated; colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1685, 1620 (C=CC=O); MS *m/z* (rel. int.): 234.167 $[M]^+$ (6) ($C_{15}H_{22}O_2$), 217 $[M-OH]^+$ (4), 216 $[M-H_2O]^+$ (3), 200 $[217-OH]^+$ (38), 185 $[200-Me]^+$ (21), 83 $[C_4H_7CO]^+$ (87), 55 $[83-CO]^+$ (100); CI (iso-butane): 235 $[M+1]^+$ (100), 217 $[235-H_2O]^+$ (12).

9α- and β-Hydroxy-α-longipinen-1-one (**14** *and* **15**). Colourless gum, obtained as a mixture, which could not be separated, oxidation afforded **16**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1695 (CO, C=CC=O); MS *m/z* (rel. int.): 232.146 $[M]^+$ (43) ($C_{15}H_{20}O_2$), 217 $[M-Me]^+$ (7), 199 $[217-H_2O]^+$ (9), 189 $[217-CO]^+$ (20), 55 (100). $NaBH_4$ reduction of **16** afforded a mixture of **14** and **15**, which again could not be separated; colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1685 (C=CCO); MS *m/z* (rel. int.): 234.167 $[M]^+$ (5) ($C_{15}H_{22}O_2$), 217 $[M-OH]^+$ (5), 216 $[M-H_2O]^+$ (4), 83 $[C_4H_7CO]^+$ (82), 55 $[83-CO]^+$ (100).

15-Hydroxy-α-longipinen-1-one (**17**). Colourless gum, not free from **11**, **12**, **14** and **15**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1685 (C=CC=O); acetylation (Ac_2O, 70°) afforded **20**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1230 (OAc), 1685, 1620 (C=CC=O); MS *m/z* (rel. int.): 276.173 $[M]^+$ (32) ($C_{17}H_{28}O_3$), 234 $[M-ketene]^+$ (48), 216 $[M-HOAc]^+$ (63), 201 $[216-Me]^+$ (67), 173 $[201-CO]^+$ (70), 145 $[173-CO]^+$ (65), 55 (100). Oxidation of **17** (pyridine chlorochromate) gave **21**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1695 (C=CC=O); MS *m/z* (rel. int.): 232.146 $[M]^+$ (33) ($C_{15}H_{20}O_2$), 217 $[232-Me]^+$ (12), 204 $[M-CO]^+$ (27), 203 $[M-CHO]^+$ (26), 189 $[204-Me]^+$ (52), 161 $[189-CO]^+$ (52), 55 (100).

Artedouglasiolide (**25**). Colourless crystals, mp 100°, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1780 (γ-lactone); MS *m/z* (rel. int.): 250.157 $[M]^+$ (16) ($C_{15}H_{22}O_3$), 235 $[M-Me]^+$ (6), 232 $[M-H_2O]^+$ (12), 17 $[232-Me]^+$ (4), 204 $[232-CO]^+$ (7), 167 (35), (47), 124 (58), 123 (87), 122 (100) ($C_8H_{10}O$), 109 (70);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{+9.2 \quad +12.8 \quad +13.5 \quad +33.5} (CHCl_3;\ c\ 0.14).$$

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