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TYPES OF SESQUITERPENES FROM *ARTEMISIA FILIFOLIA**

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Key Word Index—*Artemisia filifolia*; Compositae; sesquiterpenes; longipinane derivative; longibornane derivative; seco-longibornane derivatives; himachalene derivative.

Abstract—The roots of *Artemisia filifolia* afforded in addition to known compounds an oxo-longipinane, a longibornan endoperoxide, two seco-longibornane derivatives and a himachalene derivative. The structures of the new sesquiterpenes were elucidated by several chemical transformations and by NMR spectroscopic investigations. Possible biogenetic pathways are discussed briefly.

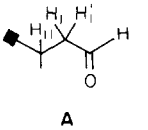
INTRODUCTION

Many species of the large genus *Artemisia* (Compositae, tribe Anthemideae) have been studied chemically. In addition to sesquiterpene lactones [1] different types of acetylenic compounds [2] are widespread. So far, however, the overall picture is not very uniform. We have now investigated *Artemisia filifolia*.

RESULTS AND DISCUSSION

The roots of *Artemisia filifolia* afforded caryophyllene, germacrene *D*, γ-humulene, cadinene, dehydromatricaria ester, longipinene and a mixture of two sesquiterpenes, molecular formula $C_{15}H_{24}O$ which were separated by TLC. The IR spectra showed that one compound was an aldehyde while the second was a ketone. The latter on reduction with lithium alanate afforded two epimeric alcohols. The ^{1}H NMR spectra (Table 1) led to the structures **4**–**6**. In the spectrum of **4** three methyl singlets and one methyl doublet could be recognized. The doublet was coupled with a broadened quartet at δ 2.44, its chemical shift indicated a proton α to a keto group (H-3). This proton showed a small coupling with a double doublet (H-4) which, however, was visible only in deuteriobenzene. As the corresponding proton showed a coupling with a three-fold doublet at δ 1.79 (C_6D_6), which itself was coupled with a pair of double doublets at 2.61 and 2.32, the presence of a longipinane derivative was very likely, especially as the relatively large coupling of 7 Hz between H-4 and H-11 was observed which is a typical *W*-coupling in such compounds [3]. Furthermore, the broadened singlet at δ 1.04 (C_6D_6) (H-5) was characteristic and the chemical shifts of the remaining signals were close to those of longipinene. The spectra of the epimeric alcohols **5** and **6** further supported the proposed structure. Compound **5**, which was the main product, had a 2α-hydroxyl group as was shown by the couplings $J_{1\alpha,\,2\beta}$ and $J_{2\beta,\,3\alpha}$. Accordingly, **6** was the epimeric 2β-hydroxy derivative. As $J_{1\beta,\,2\alpha}$ was 9 Hz compound **6** had the second possible chair conformation with the hydroxyl group being equatorial while the 3-methyl group now became axial.

The ^{1}H NMR spectrum (Table 1) of the aldehyde showed that in addition to the aldehyde group there were three tertiary methyls and one olefinic methyl, indicating that most probably an unusual carbon skeleton was present. The molecular formula suggested that it could be a bicyclic compound with one double bond. This was confirmed by the ^{13}C NMR spectrum (see Experimental) which clearly showed that no additional double bond was present. From the ^{1}H NMR spectrum and spin decoupling sequence **A** could be deduced.



A

An olefinic proton (δ 4.97, H-4) was coupled with the olefinic methyl as well as with the broadened double doublet (H-11). The latter coupling was a *W*-coupling. A broadened singlet at δ 1.69 (H-5) was sharpened on irradiation of the multiplet at δ 1.30 (C_6D_6). The Eu(fod)$_3$ induced shifts indicated a relative central position of the aldehyde group as all signals showed clear shifts. All data, therefore, agreed with structure **8**, which also was supported by the chemical shifts in the ^{13}C NMR spectrum and biogenetic considerations. Most likely **4** was formed from longipinene via the corresponding epoxide which after protonation could be rearranged to **4**. The precursor of **8** most likely was the ion **7**, an oxidation product of the longibornane ion **3** (see Scheme 1). The new carbon skeleton of **8** without an oxygen function we have named 2,3-seco-longibornane. Compound **8**, therefore, is 2,3-seco-longiborn-3-en-2-al.

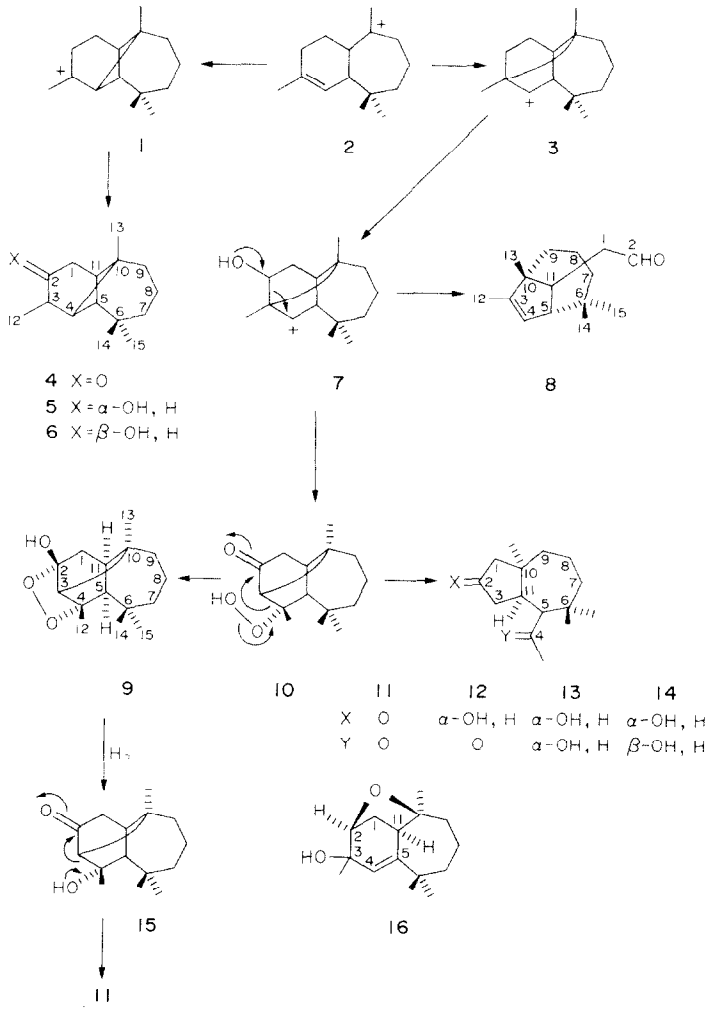
The more polar fractions afforded three additional sesquiterpenes, the diketone **11** as well as the endoperoxide **9** and the alcohol **16**. The structures followed from the spectroscopic data and from several chemical trans-

* Part 466 in the series "Naturally Occurring Terpene Derivatives". For Part 465 see, Bohlmann, F., Ahmed, M., Jakupovic, J., King, R. M. and Robinson, H. (1983) *Phytochemistry* **22**, 191.

Table 1. ^{1}H NMR spectral data of compounds **4**–**6** and **8** (400 MHz, $CDCl_3$, TMS as internal standard)

	4	**4**(C_6D_6)	**5**	**6**	**8**	Δ	$CDCl_3$/C_6D_6
H-1α	2.70 *br dd*	2.61 *br dd*	2.55 *ddd*	1.70 *m*	2.22 *ddd*	0.6	2.14 *ddd*
H-1β	2.50 *br dd*	2.32 *br dd*	1.86 *ddd*	2.58 *ddd*	2.34 *ddd*	0.7	2.03 *ddd*
H-2	—	—	4.42 *ddd*	4.06 *ddd*	9.71 *dd*	0.9	9.48 *dd*
H-3	2.44 *br q*	2.25 *br q*	2.50 *ddq*	1.97 *m*	—	—	—
H-4	2.18 *m*	1.93 *dd*	1.95 *m*	1.95 *dd*	4.97 *br s*	0.33	4.83 *br s*
H-5	1.30 *br s*	1.04 *br s*	1.09 *br s*	1.21 *br s*	1.69 *br s*	0.61	1.58 *br s*
H-7–H-9	1.63, 1.43 *m*	1.5 *m*	1.53, 1.40 1.32 *m*	1.50–1.30 *m*	1.6–1.3 *m*	0.4	1.3 *m*
H-11	2.18 *m*	1.79 *ddd*	1.95 *m*	1.89 *ddd*	2.40 *br dd*	0.6	2.21 *br dd*
H-12	1.24 *d*	1.30 *d*	1.07 *d*	1.13 *d*	1.76 *d*	0.32	1.66 *d*
H-13	0.87 *d*	0.74 *s*	1.02 *s*	0.86 *s*	0.94 *s*	0.38	0.85 *s*
H-14	0.94 *s*	0.84 *s*	0.84 *s*	0.84 *s* (6H)	0.92 *s*	0.33	0.83 *s*
H-15	0.95 *s*	0.87 *s*	0.83 *s*		0.91 *s*	0.42	0.78 *s*

J (Hz): Compound **4**: 1α, 1β = 18; 1α, 3 = 1α, 5 ~ 0.5; 1α, 11 = 3; 1β, 11 = 2.5; 3,4 = 1.5; 3,12 = 7; 4,11 = 7; compound **5**: 1α, 1β = 14; 2α, 2β = 9.5; 1α, 11 = 3; 1β, 2β = 4; 1β, 11 = 1.5; 2β, 3α = 9.5; 3α, 4 ~ 2; 3α, 12 = 8; compound **6**: 1α, 1β = 14; 1α, 2α = 4; 1β, 2α = 9; 1β, 11 = 3; 2α, 3α = 4; 3, 12 = 7; 4, 11 ~ 6; compound **8**: 1, 1′ = 15; 1, 2 = 1.5; 1′, 2 = 3.5; 1, 11 = 4.5; 1′, 11 = 9.5; 4, 12 = 1.



Scheme 1.

formations. The molecular formula of **9** was $C_{15}H_{24}O_3$. The fragmentation pattern in the mass spectrum did not allow a clear assignment of the nature of the oxygen functions, while an IR band at 3580 cm^{-1} showed that a hydroxy group was present. But again no further indications of additional oxygen groups could be deduced from the IR. The ^1H NMR spectrum (Table 2) only displayed signals above δ 2.5 indicating that this compound had no olefinic protons and also no protons on an oxygen bearing carbon. Accordingly, the hydroxy group was tertiary and the remaining oxygens were part of ether bridges. The molecular formula required the presence of four rings and the ^{13}C NMR spectrum (see Experimental) showed that most likely only two oxygen bearing carbons were present (δ 115.2 *s* and 95.5 *s*). The couplings of two further lowfield doublets (72.8 *d* and 67.1 *d*) were not in agreement with the presence of an epoxide. Therefore, an endoperoxide was proposed. Catalytic hydrogenation afforded a hydroxy ketone (**15**) which was transformed readily to the diketone **11**, identical with the natural compound, thus indicating that **9** and **11** had at least in part the same carbon skeleton. The formation of **11** could be explained only as the result of a retro-aldol reaction (see Scheme 1) while the isolation of the primary product with a tertiary hydroxyl and a keto group agreed with the presence of an endoperoxide. Alanate reduction of **9** gave a mixture of products, two of them being identical with the diols **13** and **14**, obtained by alanate reduction of the diketone **11**. Again this supported an endoperoxide as the isolation of **13** and **14** most likely was an indication that they were formed through an alcoholate of **15** again by a retro-aldol reaction. Therefore, the structure elucidation of **11** would also lead to the structure of the endoperoxide.

The ^1H NMR spectrum of **11** (Table 3) showed that a

Table 2. ^1H NMR spectral data of compounds **9**, **15** and **16** (400 MHz, TMS as internal standard)

	9($CDCl_3$)	**9**(C_6D_6)	**15**($CDCl_3$)	**16**($CDCl_3$)	**16**(C_6D_6)
H-1α	1.75 *d*	1.91 *d*	1.96 *d*	1.82 *br d*	1.82 *br d*
H-1β	2.23 *dd*	2.29 *dd*	2.40 *dd*	2.10 *ddd*	1.92 *ddd*
H-2	—	—	—	3.94 *dd*	4.08 *dd*
H-3	1.86 *s*	2.00 *s*	2.07 *br d*	—	—
H-4	—	—	—	5.26 *br d*	5.25 *br d*
H-5	2.08 *d*	2.03 *d*	1.69 *br s*	—	—
H-7–H-9	1.56, 1.39 *m*	1.52, 1.35 *m*	1.91, 1.72, 1.65, 1.58, 1.41 *m*	1.8–1.3 *m*	1.77 *br dd* (J = 14, 8 Hz); 1.51 *br dd* (J = 13, 12 Hz); 1.35 *m*
H-11	2.22 *dd*	1.96 *dd*	2.52 *dd*	2.63 *br d*	2.37 *br d*
H-12	1.10 *s*	1.08 *s*	1.13 *s*	1.32 *s*	1.42 *s*
H-13	1.03 *s*	1.00 *s*	1.04 *s*	1.24 *s*	1.15 *d*
H-14	0.98 *s*	0.83 *s*	0.96 *s*	1.12 *s*	1.05 *s*
H-15	1.67 *s*	1.63 *s*	1.79 *s*	1.07 *s*	0.93 *s*

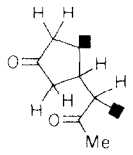
J (Hz): Compound **9**: 1α, 1β = 13; 1β, 11 = 4; 5, 11 = 2; compound **15**: 1α, 1β = 18.5; 1β, 11 = 6; 3, 11 = 2; compound **16**: 1α, 1β = 12; 1β, 2 = 6; 1β, 11 = 5; 2, 4 = 2; 9β, 12 = 1.

Table 3. ^1H NMR spectral data of compounds **11**–**14** (400 MHz, $CDCl_3$, TMS as internal standard)

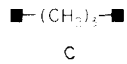
	11	**12**	**13**	**14**
H-1	2.04 *br d*	2.09 *br dd*	1.70 *dd*	1.69 *dd*
H-1′	1.87 *d*	1.33 *br dd*	1.33 *m*	1.4 *m*
H-2	—	4.27 *dddd*	4.36 *dddd*	4.38 *dddd*
H-3	2.74 *dd*	2.39 *ddd*	2.34 *ddd*	2.51 *ddd*
H-3′	2.32 *dd*	1.7 *m*	1.94 *ddd*	1.94 *ddd*
H-4	2.84 *d*	2.78 *d*	4.08 *dq*	4.20 *dq*
H-5	—	—	1.67 *m*	1.6–1.3 *m*
H-7–H-9	1.68, 1.48, 1.35 *m*	1.7–1.3 *m*	1.7–1.3 *m*	
H-11	2.07 *ddd*	1.72 *ddd*	1.64 *br dd*	1.61 *br dd*
H-12	1.03 *s*	1.00 *s*	1.01 *s*	0.99 *s*
H-13	0.95 *s*	0.98 *s*	0.94 *s*	0.91 *s*
H-14	0.82 *s*	0.98 *s*	0.84 *s*	0.88 *s*
H-15	2.12 *s*	2.20 *s*	1.20 *d*	1.14 *d*

J (Hz): Compound **11**: 1,1′ = 19; 3, 3′ = 20; 3, 11 = 9; 3′, 11 = 8.5; 4, 11 = 2; compound **12**: 1, 1′ = 13.5; 1, 2 = 1′, 2 = 2, 3 = 2, 3′ ~ 7; 3, 3′ = 13.5; 3, 11 = 7; 4, 11 = 3; compounds **13**/**14**: 1, 1′ = 14; 1, 2 = 8; 1′, 2 = 2.5; 2, 3 = 2, 3′ ~ 7; 3, 3′ = 14; 3, 11 = 7; 3′, 11 = 14; 4, 5 = 2.5; 5, 15 = 7 (**14**: 4, 5 = 1).

methyl ketone was present while a second keto group followed from a pair of double doublets and a pair of doublets. From the IR spectrum the presence of a cyclopentanone derivative was likely (1740 cm^{-1}). In agreement with this, spin decoupling led to the sequences **B** and **C**, though the signals of the latter were overlapped multiplets.



B



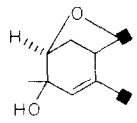
C

As three tertiary methyls were also present a combination of these sequences led to **11**. As followed from a model, the coupling $J_{3,4}$ required a *cis*-orientation of the corresponding protons, which obviously was necessary to form the aldol **15**. The ^1H NMR spectrum of the latter (Table 2) further supported the proposed structures of **11** and **15**. The couplings observed agreed well with the angles shown by a model. While H-1 and H-3 should show a *W*-coupling, the angles H-1′–H-11 and H-5–H-11 were nearly 90°.

Boranate reduction of **11** gave the hydroxy ketone, **12**. Most likely the second carbonyl group was hydrogen bonded and, therefore, was reduced only by alanate which afforded the C-4 epimeric diols **13** and **14**. The ^1H NMR spectra of **12**–**14** (Table 3) supported the proposed structures. The stereochemistry of **13** and **14** at C-4 followed from the differences in the coupling $J_{4,5}$. Most likely only the epimer **14** was hydrogen bonded which led to an angle of nearly 90° between H-4 and H-5. In the epimer **13** steric hindrance may prevent a hydrogen bridge as followed from inspection of models.

If the ^1H NMR spectra of **9** and **15** were compared, an obvious similarity could be observed. In particular, the spin systems were identical, though due to the additional ring in **9**, small changes of the angles led to differences in the couplings. The observed shift differences agreed with the absence of a carbonyl group in **9**. The stereochemistry of **9** clearly followed from a model which showed that an α-peroxide bridge must be present. Compound **9** was formed by oxidation of the longibornane intermediate **7** which also was proposed as the precursor of **8**. The proposed intermediate **10** could be also the direct precursor of **11** (see Scheme 1), which is a 3,4-seco-derivative of longibornane.

The structure of **16**, molecular formula $C_{15}H_{24}O_2$, followed from the spectroscopic data. The ^1H NMR spectrum (Table 2) displayed signals of four tertiary methyl groups and two lowfield signals, a broadened doublet at δ 5.26 (J = 2 Hz) and a double doublet at 3.94 (J = 6, 2 Hz). Furthermore, a broadened doublet at δ 2.63 (J = 5 Hz), a three-fold doublet at 2.10 (J = 12, 6, 5 Hz) and a broadened doublet at 1.82 (J = 12 Hz) were present. Spin decoupling showed that most likely all these signals had to be assigned to a polysubstituted cyclohexene ring. Irradiation at δ 2.10 collapsed the doublet at 1.82 to a singlet, the double doublet at 3.94 to a doublet (J = 2 Hz) and the doublet at 2.63 to a singlet. Irradiation of the latter sharpened the broadened doublet at δ 5.26, which also was coupled with the signals at 3.94. These results agree with sequence **D**.



D

Inspection of a model showed that *W*-couplings should be present between H-2 and H-4, H-4 and H-11, as well as between H-9 and H-12. Also the absence of couplings between H-1α, H-2 and H-11 could be explained by the observed angles which were nearly 90°. Though the remaining signals were overlapped multiplets (6H) the proposed structure **16** was likely. The ^{13}C NMR signals also agreed with this proposal. The stereochemistry at C-3, however, could not be determined. A change of the functionality at C-2 and C-3 could be excluded as no acetylation or oxidation could be achieved. This alcohol could be formed from an oxidation product of **2**. Further investigations of *Artemisia* species may show whether the new types of sesquiterpenes are of chemotaxonomic importance. So far only *A. douglasiana* afforded longipinene derivatives [4].

From the aerial parts of *Artemisia filifolia* some rare monoterpenes, a eudesmanolide and a flavone were isolated [5]. Most likely this species does not belong to the subgenus *Dracunculus* as already proposed from morphological aspects [6]. The subgenus *Dracunculus* can be characterized by the occurrence of dehydrofalcarinone and related compounds, and aromatic acetylenes [7].

EXPERIMENTAL

The air-dried roots of *Artemisia filifolia* Torr. (216 g) (voucher AR-1003, deposited in the Herbarium of the Botanical Institute, University of Vienna, Austria) were extracted with Et_2O–petrol (1:2) and the resulting extract was separated by CC (Si gel) and further by repeated TLC (Si gel). The petrol fractions afforded 15 mg caryophyllene, 4 mg germacrene D, 6 mg γ-humulene, 10 mg cadinene and 30 mg longipinene.

The fractions obtained with Et_2O–petrol (1:10 and 1:3) gave 1 mg dehydromatricaria ester, 60 mg **4** and 45 mg **8** (TLC; Et_2O–petrol, 1:10) while the most polar fractions gave 35 mg **9** (Et_2O–petrol, 1:1), 25 mg **11** (Et_2O–petrol, 1:1) and 3 mg **16** (Et_2O–petrol, 3:1, and HPLC, reversed phase, MeOH–H_2O, 3:1). Known compounds were identified by comparing the high field ^1H NMR spectra with those of authentic compounds.

Longipinan-2-one (**4**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1710 (C=O); MS *m/z* (rel. int.): 220.18 $[M]^+$ (5) ($C_{15}H_{24}O$), 205 $[M - Me]^+$ (4), 177 $[205 - CO]^+$ (8), 149 (42), 124 (93), 109 (90), 95 (77), 82 (89), 81 (100), 69 (60), 67 (72), 55 (88).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ nm}{+19 \quad +20 \quad +23 \quad +46} \quad (CHCl_3;\ c\ 1.34).$$

To 15 mg **4** in 2 ml Et_2O, 20 mg $LiAlH_4$ and after 5 min dilute H_2SO_4 were added. TLC (Et_2O–petrol, 1:3) afforded 10 mg **5** and 2 mg **6**. Compound **5**: colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH); MS *m/z* (rel. int.): 222.198 $[M]^+$ (1) ($C_{15}H_{26}O$), 207 $[M - Me]^+$ (4), 204 $[M - H_2O]^+$ (10), 189 $[204 - Me]^+$ (13), 175 $[204 - CHO]^+$ (7), 161 $[204 - C_3H_7]^+$ (17), 124 (57), 109 (100), 95 (61), 82 (56), 81 (60), 69 (64), 67 (48), 55 (82).

Compound **6**: colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH); MS *m/z* (rel. int.): 222.198 $[M]^+$ (1) ($C_{15}H_{26}O$), 204 $[M - H_2O]^+$ (12), 161 $[204 - C_3H_7]^+$ (20), 109 (100).

2,3-*Seco-longiborn-3-en-2-al* (**8**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2740, 1725 (CHO); MS *m/z* (rel. int.): 220.183 $[M]^+$ (13)

($C_{15}H_{24}O$), 205 $[M-Me]^+$ (28), 191 $[M-CHO]^+$ (24), 177 $[205-CO]^+$ (17), 161 (25), 124 (30), 121 (35), 107 (100), 94 (60); ^{13}C NMR ($CDCl_3$): (C-1–C-15) 47.0 *t*, 203.5 *d*, 141.7 *s*, 134.4 *d*, 64.6 *d*, 36.3 *s*, 44.0 *t*, 21.1 *t*, 41.7 *t*, 49.1 *s*, 45.3 *d*, 18.9 *q*, 28.8 *q*, 23.6 *q*, 32.6 *q*.

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{+89 \quad +94 \quad +109 \quad +215} \ (CHCl_3;\ c\ 4.21).$$

2β-Hydroxylongibornane-2α,4α-endoperoxide (**9**). Colourless crystals, mp 142° (petrol), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3580 (OH), 1480, 1460, 1310, 1155; MS *m/z* (rel. int.): 252.173 $[M]^+$ (5) ($C_{15}H_{24}O_3$), 237 $[M-Me]^+$ (6), 236 $[M-O]^+$ (3), 234 $[M-H_2O]^+$ (3), 221 $[236-Me]^+$ (10), 219 $[234-Me]^+$ (6), 109 (58), 95 (62), 83 (68), 55 (100); CI (*iso*-butane): 253 $[M+1]^+$ (34), 237 (100), 236 (45), 235 (71), 221 (35); ^{13}C NMR ($CDCl_3$): (C-1–C-15) 45.2 *t*, 115.2 *s*, 72.8 *d*, 95.5 *s*, 67.1 *d*, 34.7 *s*, 40.1 *t*, 22.0 *t*, 35.3 *t*, 50.4 *s*, 44.3 *d*, 31.2 *q*, 23.8 *q*, 20.3 *q*, 32.6 *q*.

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{-68 \quad -70 \quad -80 \quad -143} \ (CHCl_3;\ c\ 1.48).$$

Compound **9** (10 mg) and 10 mg $LiAlH_4$ in 1 ml THF were heated for 15 min at 60°. After addition of Et_2O and dilute H_2SO_4 TLC (Et_2O) afforded in addition to unidentified compounds 3 mg **13** and 3 mg **14** (^1H NMR spectra see Table 3). Compound **9** (10 mg) in 3 ml Et_2O was hydrogenated in the presence of Pd–$BaSO_4$ (5%). TLC (Et_2O–petrol, 1 : 1) afforded 6 mg **11** (identical with the natural diketone) and 2 mg **15** (^1H NMR spectra see Table 2).

2,4-Dioxo-3,4-seco-longibornane (**11**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (cyclopentanone), 1710 (C=O); MS *m/z* (rel. int.): 236.178 $[M]^+$ (27) ($C_{15}H_{24}O_2$), 221 $[M-Me]^+$ (14), 203 $[221-H_2O]^+$ (3), 193 $[221-CO]^+$ (38), 165 (10), 152 (60), 137 (57), 109 (80), 95 (100), 81 (84), 69 (77), 55 (93).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{+22 \quad +23 \quad +27 \quad +58} (CHCl_3;\ c\ 2.67).$$

To 7 mg **11** in 1 ml MeOH 10 mg $NaBH_4$ and after 5 min dilute H_2SO_4 were added. TLC (Et_2O–petrol, 1 : 1) gave 5 mg **12**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH), 1720 (C=O); MS *m/z* (rel. int.): 238.193 $[M]^+$ (1) ($C_{15}H_{26}O_2$), 220 $[M-H_2O]^+$ (33), 205 $[220-Me]^+$ (18), 202 $[220-H_2O]^+$ (7), 177 $[205-CO]^+$ (92), 95 (100), 81 (87), 69 (73), 55 (74).

Compound **12** (5 mg) in 2 ml Et_2O was reduced with 10 mg $LiAlH_4$ (5 min, 20°). TLC (Et_2O) afforded 2 mg **13** and 2 mg **14**. Compound **13**: colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH); MS *m/z* (rel. int.): 222.198 $[M-H_2O]^+$ (2) ($C_{15}H_{26}O$), 204 $[222-H_2O]^+$ (2), 177 $[222-CH(OH)Me]^+$ (47), 84 $[C_6H_{12}]^+$ (100). Compound **14**: colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3640 (OH); MS *m/z* (rel. int.): (CI, *iso*-butane): 241 $[M+1]^+$ (1), 223 $[241-H_2O]^+$ (24), 205 $[223-H_2O]^+$ (100).

3-Hydroxy-2,10-oxido-himachal-4-ene (**16**). Colourless crystals, mp 133° (petrol); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH); MS *m/z* (rel. int.): 236.178 $[M]^+$ (19) ($C_{15}H_{24}O_2$), 221 $[M-Me]^+$ (32), 218 $[M-H_2O]^+$ (6), 203 $[221-H_2O]^+$ (6), 192 $[M-C_2H_4O]^+$ (100), 177 $[192-Me]^+$ (78); ^{13}C NMR ($CDCl_3$): 150.1 *s*, 122.6 *d*, 85.4 *s*, 82.1 *d*, 71.4 *s*, 45.1 *s*, 42.7 *d*, 40.1 *t*, 37.4 *t*, 31.9 *t*, 28.1 *q*, 27.1 *q*, 26.2 *q*, 25.0 *q*, 20.8 *t*.

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{+119 \quad +131 \quad +143 \quad +254} \ (CHCl_3;\ c\ 0.07).$$

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