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A TETRACYCLIC SESQUITERPENE, FURTHER ISOCEDRENE AND GUAIENE DERIVATIVES FROM *JUNGIA STUEBELII**

FERDINAND BOHLMANN, CHRISTA ZDERO, ROBERT M KING† and HAROLD ROBINSON†

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany, †Smithsonian Institution, Department of Botany, Stop No 166, Washington, DC 20560, U S A

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Key Word Index—*Jungia stuebelii*, Compositae, sesquiterpenes, isocedrene derivatives, guaiene derivatives, pseudoguaiane derivative, jungistuebene derivative, new carbon skeleton, norsesquiterpene

Abstract—The aerial parts of *Jungia stuebelii* afforded, in addition to known compounds, two guaiene derivatives, a pseudoguaiane derivative, nine isocedrene derivatives, one being a norsesquiterpene and a keto acetate with a new carbon skeleton, most likely derived from a guaiene derivative. The structures were elucidated by high field NMR spectroscopy and by some chemical transformations The chemotaxonomic relevance of the constituents is discussed briefly

INTRODUCTION

The genus *Jungia* (tribe Mutisieae) is placed in the subtribe *Nassauviinae* [1] So far the chemistry of this genus showed interesting chemotaxonomic aspects as several rare types of compounds, especially isocedrene derivatives and perezone-like compounds, were isolated [2, 3] which showed close relationships to related genera placed in the same subtribe [3–13] We now have studied the constituents of *Jungia stuebelii* (Hieron) Cuatr The results are discussed in this paper

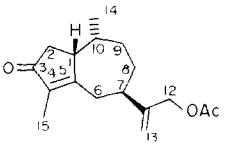
RESULTS AND DISCUSSION

The aerial parts of *J stuebelii* afforded the widespread tridecapentainene, α-farnesene, the patchoulene derivatives **3** and **4** [8] and the perezone derivatives **17** [2] and **18** [2], as well as several new compounds which were difficult to separate Finally, two guaiene (**1** and **2**), one pseudoguaiane (**15**) and nine isocedrene derivatives (**6**–**13**) and a ketone with a new carbon skeleton (**5**) were isolated. The structure of **1** was deduced from the molecular formula and the ^{1}H NMR spectrum (Table 1) which was close to that of the corresponding 12-desacetoxy compound [8] The presence of a 12-acetoxy group followed from the typical ^{1}H NMR signals for an acetoxyisopropenyl side chain [4.62 *br s* (2 H), 5.04 *br s* and 5.13 *br s*, 2 11 *s* (3 H)] The stereochemistry at C-7 followed from the coupling $J_{6\beta\ 7\alpha}$, while that at C-1 and C-10 could not be assigned with certainty A *cis*-position of H-1 and H-10 followed from the coupling $J_{1\ 10}$. A 1β-H may be more likely from biogenetic considerations as a corresponding 6β-hydroxy derivative was isolated from a closely related species [8] The ^{1}H NMR spectrum of **2**, molecular formula $C_{15}H_{22}O_2$, showed signals of an isopropenyl side chain, a tertiary and a secondary methyl group while the presence of a hydroxy ketone was indicated by the IR spectrum. Two doublets at δ 2 45 and 2 30 (J = 17 5 Hz) required a methylene group α to a keto group with a neighbouring quarternary carbon Spin decoupling allowed the assignment of H-6–H-8 The chemical shifts of H-6 required an allylic position and the IR spectrum (1715 cm^{-1}) favoured a conjugated five-membered ring ketone The hydroxyl had to be placed at C-1 to explain the fact that H-2 had no neighbouring protons In agreement with this proposal was the absence of the homoallylic coupling $J_{1\ 15}$ present in the spectrum of the related ketone, **1** The only alternative structure would be a 4-hydroxyguaia-1(5),11-dien-3-one. However, the chemical shifts of H-2 and H-6 would not agree with such an arrangement of the double bond Furthermore, the H-15 signal should be at higher fields. The stereochemistry at C-1 was deduced from the small Eu(fod)$_3$-induced shift of H-14 which would be much larger if a *cis*-orientated hydroxyl was present. Furthermore, a 1α-hydroxyl should induce a downfield shift of H-7

The structure of **5** followed from the ^{1}H NMR spectral data (Table 1) which in part were close to those of **4** However, as already deduced from the molecular formula, **5** had two hydrogens less than **4**. The ^{1}H NMR spectrum of **5** displayed only two methyl signals, one being olefinic The presence of an acetoxy methylene group was indicated by a singlet at δ 2 09 and a pair of doublets at 4 08 and 4 00. A further pair of doublets at δ 2 32 and 2 07 obviously were the signals of a methylene group α to a keto group as followed from the geminal coupling As the signals at δ 2 54 and 2 80 also showed a 17 Hz geminal coupling a similar situation as in **4** was very likely. The H-14 methyl doublet, however, was replaced by a singlet in the spectrum of **5** while in place of a H-13 singlet a further pair of doublets at δ 2.12 and 1.90 were present The geminal coupling of 9 5 Hz is typical for a cyclobutane derivative. Spin decoupling allowed a clear assignment of the signals of H-6–H-8 and H-15

A *W*-coupling between H-7 and H-13 supported the proposed arrangement of the cyclobutane ring Inspection of a model showed that the stereochemistry directly followed from the presence of the ring junction if, as usual

*Part 474 in the series "Naturally Occurring Terpene Derivatives" For Part 473 see Bohlmann, F, Castro, V. and Jakupovic, J. (1983) *Phytochemistry* **22**, 1223



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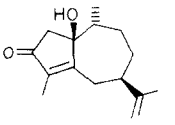

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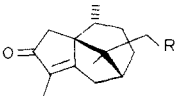
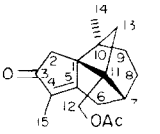


3 R = H
4 R = OAc



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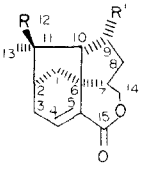
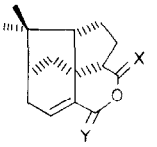
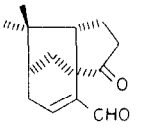


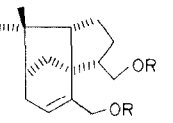
	6	6a	7	7a	8
R	CO_2H	CO_2Me	Me	Me	Me
R'	H	H	OH	OAc	H



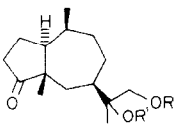
	9	10	11
X	H,β-OH	=O	H,OH
Y	=O	H_2	H_2



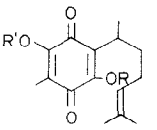
12



13 R = Ac
14 R = H



15 R = Ac, R' = H
16 R = R' = Ac



17 R = H, R' = iVal
18 R = iVal, R' = H

in the guaiane series, there was an α-proton at C-7 The model further explained the downfield shift of H-7 which was influenced by the deshielding effect of the 12-acetoxy group This new type of sesquiterpene we have named jungistuebane Compound **5**, therefore, is 12-acetoxy-jungistueb-4-en-3-one, which most likely was formed in the plant by formal two-plus-two addition of the 1,10-dehydro compound of **1**. The absolute configuration of **1**–**5** has not been determined. Biogenetic considerations may support the proposed since in the Compositae sesquiterpenes usually have a 7α-H

The structures of the isomers **8** and **10**, which could be separated only with difficulty, followed from the molecular formula, $C_{15}H_{20}O_2$, and the ^{1}H NMR spectra (Table 2). The presence of isomeric lactones was already obvious form the result of the alanate reduction which in both cases afforded the diol, **14**, which on acetylation gave the diacetate, **13**, identical with the natural compound (see below) Accordingly, **8** and **10** only differed in the position of the lactone carbonyl In the spectrum of **8**, the lowfield triplet at δ 6 88 clearly showed that the carbonyl group was at C-15 and, therefore, **10** had a carbonyl group at C-14 Spin decoupling allowed the assignment of all signals in the spectrum of **10** although those of H-8α and H-10 were unresolved multiplets Also, in the spectrum of **8** most signals could be assigned by spin decoupling The spectrum of the latter was in part close to that of the corresponding aldehyde present in *Jungia malvaefolia* [3] Accordingly, **8** and **10** were further derivatives of iso-α-cedrene

The ^{1}H NMR spectrum of **9** (Table 2) was close to that of **8** However, in addition to small shift differences the pair of double doublets at δ 4 19 and 4 08 were replaced by a low field double doublet at 5.49 in the spectrum of **9** Deuterium oxide exchange changed this signal to a doublet while a doublet at δ 3 70 disappeared Spin decoupling showed that the double doublet at δ 5 49 was coupled with a three-fold doublet at 2 14 and with the hydroxyl doublet at 3 70

The ^{1}H NMR spectrum (Table 3) and the molecular formula of **11** indicated that most likely a hemiacetal was present A double doublet at δ 4 52 was coupled with a doublet at 2 59, which disappeared on deuterium oxide exchange, and with a multiplet at 1 79 Most of the remaining signals were close to those of **10** However, due to the absence of the lactone carbonyl at C-14 the signals of H-15 were shifted upfield Spin decoupling starting with the latter signals allowed the assignment of H-1–H-4 All data agreed nicely with the structure **11** Only the configuration at C-14 could not be assigned

The ^{1}H NMR spectrum of **6a** (Table 3) clearly showed that again an iso-α-cedrene derivative was present. Obviously, one of the methyl groups of **8** was replaced by a carbomethoxy group Accordingly, most of the signals

Table 1 ^{1}H NMR spectral data of **1**, **2**, **5**, **15** and **16** (400 MHz, $CDCl_3$, TMS as int standard)

	1	2	5	15	16*
H-1	3 01 *m*	—	—	—	2 22 *ddd*
H-2α	2 42 *dd*	2 45 *d*	2 32 *d*	—	1 78 *ddd*
H-2β	2 04 *dd*	2 30 *d*	2 07 *d*	—	1 92 *ddd*
H-6α	2 82 *br d*	2 66 *br d*	2 54 *br d*	—	2 33 *dd*
H-6β	2 43 *dd*	2 43 *dd*	2 80 *br dd*	—	1 30 *dd*
H-7α	2 04 *m*	1 96 *m*	2 58 *br dd*	—	2 55 *dddd*
H-8α	1 93 *br d*	1 89 *m*	1 59 *m*	—	1 60 *m*
H-8β	1 53 *dddd*	1 49 *m*	1 99 *m*	—	1 68 *m*
H-9	1 38 *br d*		1 52 *m*	—	1 60 *m*
H-9′	1 17 *m*	1 05 *m*	1 33 *m*	—	1 52 *m*
H-10	2 17 *dddq*	1 96 *m*	—	—	2 01 *m*
H-12	4 62 *br s*	1 79 *br s*	4 08 *d*	4 07 *d*	4 38 *s*
H-12′			4 00 *d*	3 95 *d*	
H-13	5 13 *br s*	4 78 *br s*	2 12 *br d*	1 13 *s*	1 38 *s*
H-13′	5 04 *br s*	4 76 *dq*	1 90 *d*		
H-14	1 01 *d*	1 12 *d*	1 20 *s*	1 03 *d*	1 05 *d*
H-15	1 73 *d*	1 70 *s*	1 71 *d*	1 03 *s*	1 04 *s*
OAc	2 11 *s*	—	2 09 *s*	2 11 *s*	2 08 *s*
					2 03 *s*

*H-3 2 44 *br dd*, H-3′ 2 15 *ddd*

J (Hz) Compound **1** 1, 2α = 5, 1, 15 = 2, 1, 10 ~ 2, 2α, 2β = 17, 1, 2β = 3, 6α, 6β = 12, 6β, 7 = 11, 7, 8β = 11, 8α, 8β = 13 5, 8β, 9α = 11, 8β, 9β = 3, 9α, 10 ~ 1, 9β, 10 = 10, 14 ~ 7, compound **2** 2α, 2β = 17 5, 6α, 6β = 12, 6β, 7 = 11, 7, 13′ = 12, 13 = 1, 10, 14 = 7, compound **5** 2α, 2β = 18, 6α, 6β = 17, 6β, 7 = 7, 8β = 6, 6β, 15 = 1 5, 6β, 8β = 7, 9β = 7, 13 = 1, 12, 12′ = 11, 13, 13′ = 9 5, compound **16** 1, 2α = 1, 10 = 6, 1, 2β = 12, 2α, 2β = 13, 2α, 3′ = 8 5, 2β, 3 = 9, 2β, 3′ = 9, 3, 3′ = 19, 6α, 6β = 14, 6α, 7 = 2, 6β, 7 = 12, 7, 8α ~ 3, 7, 8β ~ 10, 10, 14 = 7 (compound **15** 12, 12′ = 11 5)

were close to those of **8** A pronounced downfield shift of the signal of H-2 and H-10 allowed the assignment of the stereochemistry at C-11 The downfield shift of H-13 further supported the position of the ester group. Hence, the structure of the natural compound was **6**.

The ^{1}H NMR spectral data of **7a**, obtained by acetylation but also present in one of the crude polar fractions (Table 3), were also close to those of **8** An additional lowfield broadened double doublet at δ 5 29 and a singlet at 2.08 (3H) indicated the presence of an acetoxy derivative of **8**. By spin decoupling the position of this group could be established. Inspection of a model showed that the acetoxy group most likely was α-orientated as $J_{9,10}$ was only 4 Hz.

The molecular formula of **12** indicated that a norsesquiterpene was present The nature of the oxygen functions followed from the IR spectrum while the ^{1}H NMR spectral data (Table 3) showed that an iso-α-cedrene derivative was present with an aldehyde carbonyl at C-15 as followed from the double doublet at δ 6 67, obviously the signal of a proton β to an aldehyde carbonyl This proton was coupled with an allylic signal at δ 2 55 Spin decoupling allowed the assignment of all signals and also showed that the keto group was at C-7. Thus, the structure of the keto aldehyde, **12**, was established

The structure of **13** also followed from the ^{1}H NMR spectrum (Table 3) and from the partial synthesis via the diol **14** which was obtained by reduction of **8** (see above).

The spectral data of **15**, which was transformed to the diacetate **16** (Table 1), showed some similarities to those for damsinic acid [14]. The relative position of the acetoxy group in **15** followed from the shift differences of H-13 in the spectra of **15** and **16** Spin decoupling allowed the assignment of the signals of H-1–H-3, H-6, H-7 and H-10 The latter, however, was an unresolved multiplet Accordingly, the stereochemistry at C-10 could not be established with certainty Inspection of a model showed that the couplings of H-1 would agree with the proposed stereochemistry.

The constituents of this *Jungia* species again showed that iso-α-cedrene derivatives are characteristic for the subtribe Nassauviinae Guaiane derivatives of type **1** and related patchoulene derivatives similar to **4** may be useful markers as they were also isolated from *Pleocarphus* [8] and *Perezia* species [13], especially as it is likely that iso-α-cedrenes are derived from patchoulene derivatives [3] The formation of **5** is a further example of the variations starting with guaiane derivatives Furthermore, from a *Trixis* species [6] an unusual sesquiterpene derived from a guaiane derivative was isolated. Also typical may be perezone-like compounds, such as **17**, which also were present in *Perezia* [9–13] and *Acourtia* species [7] The subtribe Naussauviinae also was found to be morphologically quite uniform, being the most natural in the tribe Mutisieae [1]

EXPERIMENTAL

The air-dried aerial parts (160 g), collected in Peru (voucher RMK 9048, deposited in the US National Herbarium, Washington), were extracted with Et_2O–petrol (1 2) and the extract obtained was separated first by CC (Si gel) and further by

Table 2 ^{1}H NMR spectral data of **8**–**11** (400 MHz, $CDCl_3$, TMS as int standard)

	8	**9**	**10**	**11**
H-1α	1 65 *br d*	1 81 *dd*	1 76 *br d*	1 62 *dd*
H-1β	1 92 *dd*	2 00 *dd*	2 11 *br dd*	1 91 *dd*
H-2	1 95 *m*	1 97 *br dd*	1 95 *br dt*	1 64 *m*
H-3α	2 55 *br dd*	2 54 *br dd*	2 29 *br dt*	2 26 *br d*
H-3β	2 42 *ddd*	2 44 *ddd*		2 17 *br d*
H-4	6 88 *dd*	6 81 *dd*	5 34 *ddd*	5 14 *br s*
H-7	1 61 *m*	2 14 *ddd*	2 71 *dd*	1 79 *m*
H-8β	2 11 *m*	2 05 *m*	2 39 *ddddd*	2 05 *m*
H-8α	1 65 *m*	1 70 *m*	1 88 *m*	
H-9α			1 65 *dddd*	1 9 1 7 *m*
H-9β	1 51 *m*	1 44 *dddd*	1 45 *dddd*	
H-10	1 95 *m*	2 05 *m*	1 91 *m*	1 64 *m*
H-12	1 09 *s*	1 08 *s*	1 09 *s*	1 09 *s*
H-13	1 02 *s*	1 02 *s*	1 02 *s*	1 02 *s*
H-14	4 19 *dd*	5 49 *dd*		4 52 *dd*
H-14′	4 08 *dd*			
H-15	–	–	4 79 *dddd*	4 29 *br d*
H-15′		–	4 54 *dddd*	4 22 *ddd*
OH		3 70 *d*	–	2 59 *d*

J (Hz) Compound **8** 1α, 1β = 11, 1β, 2 = 5, 2, 3α ~ 1, 2, 3β = 4 3α, 4 = 3β, 4 = 3 5, 3α 3β = 20 5, 7, 14 = 4, 7 14′ = 5 5, 14 14′ = 11 5, compound **9** 1α 1β = 11, 1α, 2 = 1, 1β, 2 = 4 5 2, 3α ~ 1 2, 3β = 4, 3α, 3β ~ 21, 3α, 4 = 3β, 4 = 3 5, 7, 8 = 7, 7, 8′ = 10, 7 14 = 1 5, 8α, 9β ~ 11, 8β, 9β ~ 5, 9α, 9β ~ 13, 9β, 10 ~ 11, 14, OH = 4, compound **10** 1α 1β = 11, 1α, 2 ~ 1, 1β, 2 = 6, 2, 3 = 3, 4 ~ 3, 3, 15 = 4 15 ~ 2 3, 15′ = 4, 15′ ~ 0 5 7 8β = 7, 7, 8α = 10, 8α, 8β = 14, 8β 9α ~ 2, 8β 9β ~ 5, 8α, 9β ~ 11, 8α 9α ~ 11 9α, 9β ~ 13, 9α 10 ~ 7, 9β, 10 ~ 11 15 15′ = 13, compound **11** 1α, 1β = 10 5, 1α, 2 ~ 1 1β, 2 = 5, 2, 3α ~ 1, 2, 3β = 3α, 4 = 3β, 4 = 3β, 15 ~ 2 5 3α, 3β = 18, 7, 14 = 7, 14, OH = 5 5, 15 15′ = 14

Table 3 ^{1}H NMR spectral data of **6a**, **7a** and **12**–**14** (400 MHz $CDCl_3$, TMS as int standard)

	6a	**7a** ($CDCl_3$)	**7a** (C_6D_6)	**12**	**13***	**14**†
H-1α	1 72 *dd*	1 89 *dd*	1 49 *dd*	1 69 *dd*	1 96 *dd*	1 99 *dd*
H-1β	1 97 *dd*	2 26 *dd*	1 93 *dd*	2 13 *dd*	1 82 *dd*	1 88 *m*
H-2	2 36 *br dd*	2 08 *m*	1 70 *m*	2 05 *m*	1 88 *m*	
H-3α	2 27 *br dd*	2 52 *br dd*	2 08 *br ddd*	2 55 *br s*	2 20 *br s*	2 23 *br s*
H-3β	2 53 *ddd*	2 45 *ddd*	1 98 *ddd*			
H-4	6 83 *dd*	6 84 *dd*	6 83 *dd*	6 67 *dd*	5 39 *br s*	5 45 *br dd*
H-7	2 15 *ddd*	2 05 *m*	1 70 *m*	–	2 15 *m*	2 10 *m*
H-8α	1 54 *m*	2 05 *m*		2 51 *dd*	2 03 *m*	1 9 1 5 *m*
H-8β	1 77 *m*	2 11 *m*		2 77 *dd*	1 57 *m*	
H-9α	1 81 *m*	–	–	1 77 *m*		
H-9β	2 01 *ddd*	5 29 *br dd*	5 09 *br dd*	1 92 *m*		
H-10	3 25 *br dd*	2 27 *br d*	1 76 *br d*	2 34 *dd*	2 03 *m*	
H-12	–	1 14 *s*	0 97 *s*	1 11 *s*	1 06 *s*	1 08 *s*
H-13	1 35 *s*		0 85 *s*	1 10 *s*	0 97 *s*	1 00 *s*
H-14	4 22 *dd*	4 30 *dd*	3 69 *dd*		4 23 *dd*	3 85 *dd*
H-14′	4 12 *dd*	4 17 *dd*	3 59 *br d*	–	4 12 *dd*	3 78 *dd*
OAc		2 08 *s*	1 70 *s*	–	2 08, 2 03 *s*	
OMe	3 71 *s*		–		–	–

*H-15 4 55 *ddd*, 4 51 *ddd*

†H-15 4 14 *ddd*, 4 09 *ddd*

J (Hz) Compound **6a** 1α, 1β = 11, 1α, 2 ~ 1, 1β, 2 = 4, 2, 3α ~ 1, 2, 3β = 5, 3α, 3β = 21, 3α, 4 = 3β, 4 = 3 5, 7, 8α ~ 6, 7, 8β ~ 10, 7, 14 = 4 5, 7, 14′ = 6, 8β, 10 ~ 1, 9α, 10 = 9β, 10 = 8 5, compound **7a** 1α, 1β = 11, 1α, 2 ~ 1, 1β, 2 = 4 5, 2, 3α ~ 1, 2, 3β = 4, 3α, 3β = 21 3α, 4 = 3β, 4 = 3 3, 7, 8α = 6 5, 7, 8β = 11, 7, 14 = 3 7, 14′ = 1, 8β, 9 = 9 10 = 4, 8β, 10 ~ 1, compound **12** 1α, 1β = 11, 1α, 2 = 1 5, 1β, 2 = 4, 3, 4 = 3 5 8α, 8β = 17, 8α 9 = 7, 8β, 9α = 13, 8β 9β = 8 5, 9α, 10 = 10 9β, 10 = 7 compounds **13** and **14** 1α, 1β = 11, 1α, 2 ~ 1, 1β, 2 = 5 3 15 ~ 2, 7, 14 = 9 7 14 = 7 5, 14, 14′ = 11 15 15′ = 12 5

repeated TLC (Si gel) Known compounds were identified by comparing the ^{1}H NMR spectra with those of authentic material The petrol fraction afforded 2 mg tridecapentaimene and 30 mg α-farnesene, the fractions obtained with Et_2O–petrol (1 1) gave 3 mg **1**, 2 mg **2**, 2 mg **3**, 10 mg **4**, 2 mg **5**, 10 mg **8**, 2 mg **9**, 8 mg **10**, 2 mg **11**, 2 mg **12**, 4 mg **13**, 4 mg **17** and 3 mg **18** (these compounds were separated by TLC, Et_2O–petrol, 3 1, then several times 1 1 and finally HPLC, reversed phase, MeOH–H_2O, 3 1) The CC fractions obtained with Et_2O and Et_2O–MeOH (20 1) could not be separated directly Only 2 mg crude **7a** and 2 mg **15** were obtained by HPLC (MeOH–H_2O, 3 1) After treatment of the mixture with CH_2N_2 in Et_2O and acetylation (Ac_2O, $CHCl_3$, 4-pyrrolidinopyridine, 60°), TLC (Et_2O–petrol, 3 1, several times) and HPLC (reversed phase, MeOH–H_2O, 3 1) afforded 5 mg **6a**, 4 mg **7a** and 8 mg **16** Most likely the original concns of the sesquiterpenes were higher as the tedious separations must have caused loss of material

12-*Acetoxy*-10β*H*-*guaia*-4,11-*dien*-3-*one* (**1**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1745, 1235 (OAc), 1710, 1640 (C=CC=O), MS *m/z* (rel int) 276 173 [M]$^+$ (77) ($C_{17}H_{24}O_3$), 217 [M − OAc]$^+$ (100), 216 [M − HOAc]$^+$ (78), 201 [216 − Me]$^+$ (46), 173 [201 − CO]$^+$ (56),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-36 \quad -36 \quad -42 \quad -80} (CHCl_3,\ c\ 0.28)$$

1β-*Hydroxy*-10β*H*-*guaia*-4,11-*dien*-3-*one* (**2**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1715, 1650 (C=CC=O), MS *m/z* (rel int) 234 162 [M]$^+$ (26) ($C_{15}H_{22}O_2$), 216 [M − H_2O]$^+$ (10), 206 [M − CO]$^+$ (7), 201 [216 − Me]$^+$ (8), 173 [201 − CO]$^+$ (17), 69 [C_5H_9]$^+$ (100),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-29 \quad -31 \quad -38 \quad -112} (CHCl_3, c\ 0.14)$$

12-*Acetoxyjungistueb*-4-*en*-3-*one* (**5**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1740, 1240 (OAc), 1710, 1660 (C=CC=O), MS *m/z* (rel int). 274 157 [M]$^+$ (4) ($C_{17}H_{22}O_3$), 214 [M − HOAc]$^+$ (14), 199 [214 − Me]$^+$ (4), 93 [C_7H_9]$^+$ (100),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+10 \quad +16 \quad +15 \quad +9} (CHCl_3,\ c\ 0.15)$$

14-*Hydroxy*-*iso*-α-*cedren*-12,15-*dioic acid*-14,15-*lactone* (**6**) Only isolated as its methyl ester, **6a**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1730 (CO_2R, δ-lactone), 1635 (C=C), MS *m/z* (rel int) 276 136 [M]$^+$ (100) ($C_{16}H_{20}O_4$), 244 [M − MeOH]$^+$ (13), 216 [M − HCO_2Me]$^+$ (33), 198 [216 − H_2O]$^+$ (32),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+11 \quad +13 \quad +15 \quad +40} (CHCl_3,\ c\ 0.48)$$

9α,14-*Dihydroxy*-*iso*-α-*cedren*-15-*oic acid*-14,15-*lactone* (**7**) Only isolated as its acetate, **7a**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1735 (OAc, δ-lactone), 1635 (C=C), MS *m/z* (rel int) 290 152 [M]$^+$ (57) ($C_{17}H_{22}O_4$), 248 [M − ketene]$^+$ (8), 230 [M − HOAc]$^+$ (58), 215 [230 − Me]$^+$ (17), 204 [248 − CO_2]$^+$ (30), 148 (100),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+95 \quad +100 \quad +118 \quad +231} (CHCl_3,\ c\ 0.25)$$

14-*Hydroxy*-*iso*-α-*cedren*-15-*oic acid*-14,15-*lactone* (**8**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1720 (δ-lactone), 1640 (C=C), MS *m/z* (rel int) 232 146 [M]$^+$ (100) ($C_{15}H_{20}O_2$), 217 [M − Me]$^+$ (12), 189 [217 − CO]$^+$ (17), 162 (44), 161 (40), 150 (56), 105 (56), 91 (62),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+86 \quad +91 \quad +104 \quad +199} (CHCl_3,\ c\ 0.62)$$

To 2 mg **8** in 2 ml Et_2O, 10 mg $LiAlH_4$ and after 5 min dilute H_2SO_4 were added TLC (Et_2O) afforded 1 5 mg **14** which on acetylation (Ac_2O, 30 min, 70°) gave **13**, identical with the natural compound

14,14-*Dihydroxy*-*iso*-α-*cedren*-15-*oic acid*-14,15-*lactone* (**9**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3580 (OH), 1730 (δ-lactone), 1630 (C=C), MS *m/z* (rel int) 248 131 [M]$^+$ (9) ($C_{15}H_{20}O_3$), 230 [M − H_2O]$^+$ (10), 202 [230 − CO]$^+$ (17), 187 [202 − Me]$^+$ (7), 55 (100),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+70 \quad +76 \quad +88 \quad +172} (CHCl_3,\ c\ 0.1)$$

15-*Hydroxy*-*iso*-α-*cedren*-14-*oic acid*-15,14-*lactone* (**10**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1740 (δ-lactone), MS *m/z* (rel int) 232 146 [M]$^+$ (100) ($C_{15}H_{20}O_2$), 217 [M − Me]$^+$ (11), 204 [M − CO]$^+$ (42), 189 [204 − Me]$^+$ (21), 175 (41), 150 (95), 105 (63), 91 (70),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+60 \quad +63 \quad +72 \quad +133} (CHCl_3,\ c\ 0.45)$$

To 2 mg **10** in 2 ml Et_2O, 10 mg $LiAlH_4$ and after 5 min dilute H_2SO_4 were added TLC (Et_2O) afforded 1 5 mg **14**, identical with the diol obtained from **8** 1 5 mg **14** in 2 ml Et_2O was stirred for 1 hr with 25 mg MnO_2 TLC (Et_2O–petrol, 1 1) gave 1 mg **8**, identical with the natural compound.

14-*Hydroxy*-14,15-*oxido*-*iso*-α-*cedrene* (**11**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), MS *m/z* (rel int) 234 162 [M]$^+$ (28) ($C_{15}H_{22}O_2$), 216 [M − H_2O]$^+$ (19), 188 [216 − CO]$^+$ (22), 145 (100), 91 (41);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+33 \quad +46 \quad +47 \quad +79} (CHCl_3,\ c\ 0.1)$$

7-*Oxo*-14-*nor*-*iso*-α-*cedren*-15-*al* (**12**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1745 (C=O), 2730, 1690, 1640 (C=CCHO), MS *m/z* (rel int) 218 131 [M]$^+$ (100) ($C_{14}H_{18}O_2$), 203 [M − Me]$^+$ (6), 190 [M − H_2O]$^+$ (31), 175 [190 − Me]$^+$ (34), 147 [175 − CO]$^+$ (64),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546\ 436 \quad 365\,nm}{+25 \quad +24 \quad +23 \quad +9 \quad -360} (CHCl_3,\ c\ 0.16)$$

14,15-*Diacetoxy*-*iso*-α-*cedrene* (**13**) Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1745, 1240 (OAc), MS *m/z* (rel int) 320 195 [M]$^+$ (2 5) ($C_{19}H_{28}O_4$), 278 [M − ketene]$^+$ (3), 260 [M − HOAc]$^+$ (5), 218 [278 − HOAc]$^+$ (100), 200 [260 − HOAc]$^+$ (17),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+52 \quad +55 \quad +63 \quad +115} (CHCl_3,\ c\ 0.38)$$

12-*Acetoxy*-11-*hydroxypseudoguaian*-4-*one* (**15**) Purified as its diacetate, **16**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1745, 1235 (OAc), MS *m/z* (rel int) 278 188 [M − HOAc]$^+$ (5) ($C_{17}H_{26}O_3$), 218 [278 − HOAc]$^+$ (12), 97 (100),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+70 \quad +74 \quad +85 \quad +168} (CHCl_3,\ c\ 0.71)$$

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