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LABDANE DERIVATIVES AND OTHER CONSTITUENTS FROM *WAITZIA ACUMINATA*

J. JAKUPOVIC, A. SCHUSTER, F. BOHLMANN, R. M. KING* and L. HAEGI†

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, F.R.G.; *Smithsonian Institution, Dept. of Botany, Washington DC 20560, U.S.A.; †Botanic Gardens Adelaide, North Terrace, Adelaide, South Australia 5000, Australia

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Key Word Index—*Waitzia acuminata*; Compositae; diterpenes; labdane derivatives; *nor*-labdane, sesquiterpenes.

Abstract—The aerial parts of *Waitzia acuminata* afforded in addition to known compounds 14 new labdane derivatives, one being a *nor* compound, and a new type of a sesquiterpene derived from spathulenol. Structures and stereochemistry were elucidated by high field NMR spectroscopy. Chemotaxonomic aspects are discussed briefly.

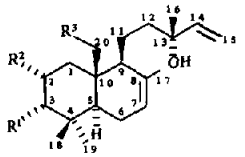
INTRODUCTION

In continuation of our investigations of Australian representatives of the tribe *Inuleae*, we have studied the constituents of a *Waitzia* species which is placed in the *Schoenia* group of the subtribe Gnaphaliinae [1]. So far little is known about the chemistry of this group. The results are presented in this paper.

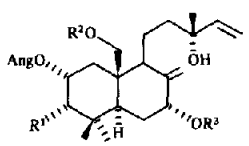
RESULTS AND DISCUSSION

The extract of the aerial parts of *W. acuminata* Steetz. afforded the known labdane derivatives **1** [2] and **2** [2] as well as the new ones **3**–**16**. Furthermore, in addition to the sesquiterpenes caryophyllenepoxide, ledol, anhydrooplopanone and spathulenol, a ketone (**18**), derived from the latter, and 3,6,7,8,4′-pentamethoxy-5-hydroxyflavone [3] were isolated.

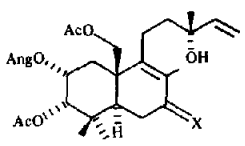
The structure of the diol **3** followed from the ^{1}H NMR spectrum (Table 1) which indicated that **3** differed from **1**



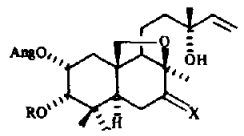
	1	1a	2	3	3a	4	5
R^1	H	H	OH	OH	O	OH	OH
R^2	OH	O	OH	H	H	OAng	OAng
R^3	H	H	H	H	H	OAc	OMeBu



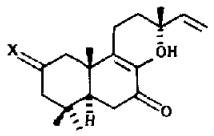
	6	7	8	9	9Ac
R^1	H	OH	OH	OAc	OAc
R^2	Ac	Ac	MeBu	Ac	Ac
R^3	H	H	H	H	Ac



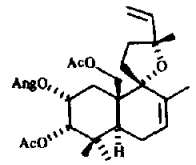
	10	10a
X	αOH,H	O



	11	11Ac	12	12a
R	H	Ac	Ac	Ac
X	αOH,H	αOAc,H	αOH,H	O



	13	14
X	αOH,H	O



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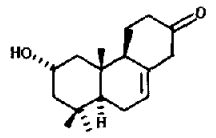
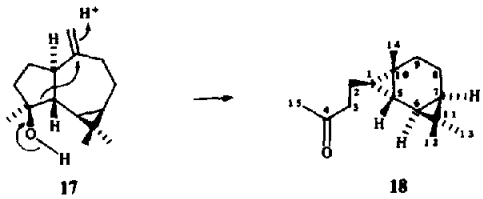


16



17 18

only by the position of the hydroxy group. Thus the H-2 signal of **1** was replaced by a narrowly split triplet at δ3.44. Irradiation of H-18 (δ0.93 *s*) and H-19 (δ0.89 *s*) gave NOE's with H-3 while H-20 (δ0.77 *s*) gave no effect. Accordingly, an axial hydroxy group was at C-3 and not at C-1.

To establish the absolute configuration of the diterpenes we have transformed the main constituent (**1**) to the corresponding ketone (**1a**). The observed positive Cotton-effect required the presence of labdanes. Similar oxidation of **3** gave the ketone **3a** which showed, as expected, a negative Cotton-effect. The ^{1}H NMR data of **1a** and **3a** are given in Table 1.

Table 1. ^{1}H NMR data of compounds **1a**, **3**, **3a**, **13**, **14** and **16** ($CDCl_3$, 400 MHz, δ-values)

H	1a	3	3a	13	14	16*
1α	2.15 *br d*	†	1.46 *ddd*	1.29 *dd*	2.50 *br d*	1.29 *dd*
1β	2.50 *dd*	†	2.15 *ddd*	2.29 *br dd*	2.65 *dd*	2.20 *ddd*
2α	—	1.90 *m*	2.25 *ddd*	—	—	—
2β	—	1.60 *m*	2.71 *ddd*	4.01 *dddd*	—	3.86 *dddd*
3α	2.36 *br d*	—	—	1.19 *dd*	2.38 *br d*	1.13 *dd*
3β	2.09 *dd*	3.44 *t*	—	1.85 *ddd*	2.26 *m*	1.76 *ddd*
5	1.75 *dd*	†	†	1.66 *dd*	2.26 *m*	†
6α	2.10 *m*	1.93 *m*	1.91 *br d*	2.51 *dd*	2.62 *dd*	†
6β	1.93 *m*		2.08 *m*	2.33 *dd*	2.42 *dd*	†
7	5.41 *br s*	5.38 *br s*	5.41 *br s*	—	—	5.42 *br s*
9	1.87 *br s*	†	1.62 *m*	—	—	†
14	5.88 *dd*	5.91 *dd*	5.91 *dd*	5.93 *dd*	5.91 *dd*	—
15*t*	5.20 *dd*	5.21 *dd*	5.21 *dd*	5.27 *br d*	5.27 *br d*	—
15*c*	5.06 *dd*	5.06 *dd*	5.07 *dd*	5.14 *br d*	5.14 *br d*	
16	1.27 *s*	1.28 *s*	1.29 *s*	1.34 *s*	1.33 *s*	2.15 *s*
17	1.69 *br s*	1.66 *br s*	1.68 *br s*	1.74 *s*	1.78 *s*	1.66 *br s*
18	1.03 *s*	0.93 *s*	1.09 *s*	1.11 *s*	1.08 *s*	0.91 *s*
19	0.89 *s*	0.89 *s*	1.05 *s*	0.96 *s*	1.08 *s*	0.91 *s*
20	0.78 *s*	0.77 *s*	0.99 *s*	0.95 *s*	0.97 *s*	0.81 *s*

*H-12 2.65 *ddd* and 2.44 *ddd*.

†Overlapping multiplets.

J [Hz]: 14,15c = 10.5; 14, 15t = 17.5; 15c, 15t = 1.5; compound **1a**: 1α, 1β = 3α, 3β = 5, 6β = 12.5; 1β,3β = 2.5; 5,6α = 5; compound **3**: 2α,3 = 2β,3 = 3; compound **3a**: 1α,1β = 13.5; 1α,2β = 2α,2β = 14.5; 1α,2β = 5; 1β,2α = 1β,2β = 4; 6α,6β = 17; compounds **13** and **16**: 1α,1β = 3α,3β = 12.5; 1α,2 = 2,3α = 11.5; 1β,2 = 2,3β = 4; 1β,3β = 1.5; compound **13**: 5,6α = 4; 5,6β = 14.5; 6α,6β = 18; compound **14**: 1α,1β = 3α,3β = 12; 1β,3β = 2; 5,6α = 3.5; 5,6β = 11; 6α,6β = 17.5; compound **16**: 11,12 = 5; 11,12′ = 10; 11′,12 = 11; 11′,12′ = 6; 12,12′ = 17.

The structures of **4** and **5** also followed from the ^{1}H NMR spectra (Table 2). The H-20 methyl singlet in the spectra of **1**–**3** were replaced by pairs of doublets around δ4.0 and in addition to the typical signals of angelates those of an acetate and a 2-methylbutyrate residue, respectively, were visible. Accordingly, acyloxy groups were at C-20 and as followed from the chemical shifts, at C-2. Though the relative position of the ester groups could not be determined with certainty the proposed one is most likely as (i) the chemical shift of H-2 is nearly the same in both compounds and (ii) in the mass spectrum elimination of methyl acetate and 2-methylbutyrate, respectively, was observed. This is probably restricted to 20-acyloxy derivatives.

Inspection of the ^{1}H NMR spectrum of **7** (Table 3) indicated that again acyloxy groups were at C-2 and C-3. An additional low field signal at δ4.41 and broadened singlets at δ4.74 and 5.15 showed, together with the absence of the olefinic methyl signal of **4**, that a 7-hydroxy $\Delta^{8(17)}$ derivative of **4** was present. The configuration at C-7 followed from the observed coupling. The NOE's [H-19 with H-2 (6%), H-3 (4%) and H-20 (5%), H-18 with H-3 (4%), H-5 (6%) and H-6β (6%)] supported the proposed stereochemistry and allowed the assignment of the methyl signals.

The ^{1}H NMR spectrum of **8** (Table 3) indicated that it differed from **7** by the replacement of the acetoxy by a 2-methylbutyryloxy group while in that of **6** (Table 3) the low field H-3 signal was replaced by a multiplet at δ1.85 and a double doublet at δ1.38 as followed from spin decoupling. Accordingly, compound **6** was the 3-desoxy derivative of **7**. In the spectrum of **9** the H-3 signal was shifted to low field (δ5.08 *d*) and a further acetate singlet was visible. Thus this compound was the 3-O-acetate of **7**. Acetylation gave the triacetate **9Ac** where the H-7 signal was shifted downfield (δ5.45 *dd*).

The ^{1}H NMR spectra of **10** (Table 2) was in part similar to that of **9**. However, the exomethylene proton signals (H-17) were replaced by an olefinic methyl signal (δ1.78 s) and the H-7 signal was now a broadened doublet. All data indicated that **10** was the Δ^8 isomer of **9**. Oxidation gave the ketone **10a**, the ^{1}H NMR spectrum (Table 2) of which further supported the structure.

The ^{1}H NMR spectrum of **11** and its acetate **11Ac** (Table 2) again indicated that an oxygen function was present at C-20. However, the chemical shifts of the observed doublets showed that no acyloxy groups were present. Furthermore, an additional methyl singlet at δ1.26 in the spectrum of **11**, which was shifted upfield in the acetate **11Ac**, most likely was due to H-17. Therefore, the best explanation was an 8,20-epoxy derivative, which biogenetically may be formed by addition of the 20-hydroxy group to the double bond at C-8. The couplings of H-2, H-3 and H-7 indicated the same stereochemistry as in **7** and **10**. Furthermore, the configurations were established by the observed NOE's which corresponded to those of **7**. An effect of H-20 with H-1β indicated that again the oxygen functions were at C-2 and C-3 while an

Table 2. ^{1}H NMR data of compounds **4**, **5**, **10**, **10a**, **11**, **11Ac**, **12**, **12a** and **15** ($CDCl_3$, 400 MHz, δ-values)

H	4	5	10	10a	11	11Ac	12	12a	15
1α	1.60 *dd*	1.62 *dd*	*	*	2.12 *dd*	2.00 *dd*	2.01 *dd*	2.05 *dd*	2.18 *dd*
1β	2.23 *dd*	2.23 *dd*	*	2.29 *m*	1.72 *dd*	1.80 *dd*	1.78 *dd*	1.88 *dd*	1.72 *dd*
2	5.32 *ddd*	5.29 *ddd*	5.35 *ddd*	5.38 *ddd*	5.01 *ddd*	5.00 *ddd*	5.00 *ddd*	5.08 *ddd*	5.36 *ddd*
3	3.65 *d*	3.57 *d*	5.11 *d*	5.16 *d*	3.54 *d*	5.05 *d*	5.04 *d*	5.12 *d*	5.03 *d*
5	*	*	*	2.29 *m*	1.98 *dd*	1.70 *dd*	1.95 *m*	1.87 *dd*	2.40 *dd*
6α	1.85–	1.85–	*	2.39 *dd*	1.28 *m*	1.65 *dd*	*	2.33 *dd*	2.09 *m*
6β	2.0 *m*	2.0 *m*	*	2.61 *dd*	1.91 *ddd*	1.91 *ddd*	1.95 *m*	2.77 *dd*	1.92 *m*
7	5.42 *br s*	5.43 *br s*	4.02 *br d*	– –	3.65 *dd*	4.76 *br d*	3.68 *m*	– –	5.61 *br s*
9	*	*	—	—	1.85 *dd*	1.82 *dd*	1.91 *m*	*	–
14	5.89 *dd*	5.89 *dd*	5.93 *dd*	5.94 *dd*	5.89 *dd*	5.91 *dd*	5.91 *dd*	5.89 *dd*	6.05 *dd*
15*t*	5.20 *dd*	5.18 *dd*	5.23 *dd*	5.27 *dd*	5.21 *dd*	5.23 *br d*	5.22 *dd*	5.23 *br d*	5.18 *dd*
15*c*	5.06 *dd*	5.05 *dd*	5.09 *br d*	5.13 *br d*	5.07 *dd*	5.10 *br d*	5.08 *dd*	5.11 *br d*	4.94 *dd*
16	1.28 *s*	1.28 *s*	1.31 *s*	1.35 *s*	1.28 *s*	1.32 *s*	1.31 *s*	1.31 *s*	1.39 *s*
17	1.68 *br s*	1.69 *br s*	1.78 *s*	1.81 *s*	1.26 *s*	1.18 *s*	1.28 *s*	1.29 *s*	1.83 *br s*
18	1.03 *s*	1.02 *s*	1.09 *s*	1.18 *s*	1.03 *s*	1.09 *s*	1.09 *s*	1.18 *s*	0.92 *s*
19	1.01 *s*	1.02 *s*	0.95 *s*	0.92 *s*	1.00 *s*	0.86 *s*	0.89 *s*	0.89 *s*	1.09 *s*
20	4.30 *br d*	4.35 *br d*	4.36 *d*	4.46 *br d*	3.99 *d*	4.13 *d*	4.21 *d*	4.39 *d*	4.20 *d*
20′	4.01 *d*	3.97 *d*	4.15 *d*	4.30 *d*	3.54 *d*	3.58 *d*	3.56 *d*	3.81 *d*	3.96 *br d*
OAng	6.09 *qq*	6.07 *qq*	6.07 *qq*	6.11 *qq*	6.11 *qq*	6.08 *qq*	6.08 *qq*	6.11 *qq*	6.04 *qq*
	2.00 *dq*	1.98 *dq*	1.97 *dq*	1.98 *dq*	1.99 *dq*	1.97 *dq*	1.97 *dq*	1.97 *dq*	1.95 *dq*
	1.91 *dq*	1.90 *dq*	1.82 *dq*	1.83 *dq*	1.90 *dq*	1.81 *dq*	1.81 *dq*	1.81 *dq*	1.82 *dq*
OAc	2.13 *s*	2.45 *tq*	2.10 *s*	2.10 *s*		2.14 *s*	2.12 *s*	2.11 *s*	2.15 *s*
(OR)		1.16 *d*	2.05 *s*	1.97 *s*		2.10 *s*			2.09 *s*
		0.89 *t*							

*Overlapping multiplets.

J [Hz]: 1α,1β = 1α,2 = 12.5; 1β,2 = 4; 2,3 = 2.5; 14,15t = 17.5; 14,15c = 10.5; 15c,15t = 1; compounds **4**, **5**, **10**, **10a** and **15**: 20,20′ = 12; compound **10**: 6,7 = 2; compound **10a**: 5,6α = 5; 5,6β = 14.5; 6α, 6β = 18; compounds **11**, **11Ac**, **12** and **12a**: 20,20′ = 8; compounds **11** and **11Ac**: 5,6α = 4; 5,6β = 6α,6β = 14; 6α,7 = 1; 6β,7 = 3; 9,11 = 2.5; 9,11′ = 9; compound **12a**: 5,6α = 5.5; 5,6β = 6α,6β = 14; compound **15**: 5,6α = 6; 5,6β = 12.5.

NOE of H-16 with H-14 and H-15*t* allowed the differentiation of the signals of H-16 and H-17.

The ^{1}H NMR data of **12** (Table 2) were close to those of **11** but as in the case of **9** the H-3 signal was shifted downfield indicating that the 3-hydroxy group of **11** was acetylated. Oxidation of **12** gave the ketone **12a**. Its ^{1}H NMR data (Table 2) also supported the structure. As expected several signals were shifted downfield. The observed negative Cotton-effect again agreed with the presence of a labdane.

The ^{1}H NMR spectrum of **13** (Table 1) was in part similar to that of **10a**. However, the signals of ester residues were missing and the triplet of triplets at δ4.01 indicated that only one oxygen function was at C-2 in ring A. The couplings required a 2α-orientation. The spectral data of **14** (Table 1) differed from those of **13** by the absence of the H-2 signal and the downfield shift of those for H-1 and H-3 requiring a 2-keto group. As the remaining signals showed only small differences to those of **13** the structure was settled.

The ^{1}H NMR spectrum of **15** (Table 2) was partly similar to that of **4**. However, in addition to a second acetate methyl singlet and the downfield shift of H-3, the chemical shifts of the signals of the side chain (H-14, H-15 and H-16) differed slightly. The ^{13}C NMR spectrum (Table 4) indicated the presence of an additional oxygen-bearing carbon which replaced the C-9 doublet. Accordingly, a 9,13-ether ring was present. A clear NOE between H-16 and H-17 allowed the assignment of the configuration at C-13 which is probably the same in all compounds. Further NOE's were observed between H-17, H-7, H-11 and H-20′, between H-19, H-20, H-6β, H-3 and H-2, as well as between H-18, H-3, H-6α and H-5. These effects also allowed the assignment of the methyl singlets.

The molecular formula ($C_{18}H_{30}O_2$) and the ^{1}H NMR spectrum of **16** (Table 1) indicated the presence of a *nor*-labdane. The singlet at δ2.14 and the three-fold doublets at δ2.65 and 2.44 required the presence of the end group CH_2Ac. As the remaining signals corresponded to those of **1**, all data agreed with the structure **16** which was supported by the observed fragment at *m/z* 220 (McLafferty, loss of acetone).

The ^{1}H and ^{13}C NMR spectrum of **18** (see Experimental) required the presence of a sesquiterpene ketone with two cyclopropane rings. Careful spin decoupling showed that one of these rings was linked with a CH_2CH_2Ac side chain and that the cyclopropane rings were vicinal as followed from the fact that both H-5 and H-6 were only broadened doublets indicating *trans* orientation of these protons and absence of neighbouring methylene groups. Furthermore, three methyl singlets were visible. These data agreed with the structure **18**. The stereochemistry was determined by the observed NOE's. In particular the effects between H-1 and H-9α, between H-5, H-12 and H-14, as well as between H-13, H-6 and H-7 required the *trans* orientation of the cyclopropane rings. The carbon skeleton of **18** seems to be new. We have named ketone **18** waitziacuminone. Most likely it is

Table 3. ^{1}H NMR data of compounds **6–9** and **9Ac** ($CDCl_3$, 400 MHz, δ-values)

H	6	7	8	9	9Ac
1α	1.12 *dd*	1.68 *dd*	1.70 *dd*	*	*
1β	2.53 *ddd*	2.17 *dd*	2.17 *dd*	2.22 *m*	2.24 *dd*
2	5.06 *dddd*	5.28 *ddd*	5.25 *ddd*	5.29 *ddd*	5.29 *ddd*
3	1.85 *m* 1.38 *dd*	3.57 *d*	3.59 *d*	5.08 *d*	5.08 *d*
5	*	2.35 *dd*	2.35 *dd*	2.22 *m*	2.04 *dd*
6α	*	1.79 *ddd*	1.75 *ddd*	*	*
6β	*	1.59 *ddd*	1.60 *m*	*	*
7	4.43 *dd*	4.41 *dd*	4.43 *dd*	4.44 *dd*	5.45 *dd*
9	2.33 *br d*	2.38 *br d*	2.38 *br d*	2.40 *br d*	2.21 *br d*
14	5.88 *dd*	5.88 *dd*	5.88 *dd*	5.89 *dd*	5.88 *dd*
15*t*	5.22 *dd*	5.22 *dd*	5.21 *dd*	5.23 *dd*	5.22 *dd*
15*c*	5.06 *dd*	5.07 *dd*	5.06 *dd*	5.08 *dd*	5.08 *dd*
16	1.27 *s*	1.27 *s*	1.28 *s*	1.28 *s*	1.28 *s*
17	5.15 *br s*	5.15 *br s*	5.15 *br s*	5.17 *br s*	5.30 *br s*
17′	4.74 *br s*	4.74 *br s*	4.76 *br s*	4.76 *br s*	4.87 *br s*
18	0.98 *s*	1.05 *s*	1.05 *s*	1.02 *s*	1.02 *s*
19	0.93 *s*	0.94 *s*	0.97 *s*	0.91 *s*	0.86 *s*
20	4.18 *br d*	4.21 *br d*	4.31 *br d*	4.19 *d*	4.21 *br d*
20′	4.01 *d*	3.99 *d*	3.92 *d*	4.03 *d*	4.03 *d*
OAng	6.05 *qq*	6.10 *qq*	6.09 *qq*	6.08 *qq*	6.09 *qq*
	1.98 *dq*	2.00 *dq*	2.00 *dq*	1.98 *dq*	1.98 *dq*
	1.89 *dq*	1.91 *dq*	1.91 *dq*	1.82 *dq*	1.82 *dq*
OAc	2.06 *s*	2.08 *s*	2.41 *tq*	2.12 *s*	2.14 *s*
			1.16 *d*	2.07 *s*	2.07 *s*
			0.89 *t*		2.07 *s*

*Overlapping multiplets.

J[Hz]: 14,15c = 10.5; 14,15t = 17.5; 15c,15t = 1; 20,20′ = 12; compound **6**: 1α,1β = 1α,2 = 2,3α = 12.5; 1β,2 = 2,3β = 4; 1β,3β = 2; 6α,7 = 6β,7 = 3; 9,11 = 11; compounds **7**, **8**, **9** and **9Ac**: 1α,1β = 1α,2 = 12.5; 1β,2 = 4; 2,3 = 2.5; 5,6α = 6α,7 = 6β,7 = 3; 5,6β = 6α,6β = 14; 9,11 = 11.

Table 4. ^{13}C NMR data of compounds **1a**, **3**, **4**, **7**, **11** and **15** ($CDCl_3$, 67.9 MHz)

C	1a	3	4	7	11	15
1	53.9 *t*	31.1 *t*	31.2 *t*	30.8 *t*	29.8 *t*	27.2 *t*
2	211.6 *s*	25.2 *t*	70.6 *d*	70.5 *d*	71.1 *d*	68.7 *d*
3	56.4 *t*	76.1 *d*	76.9 *d*	76.4 *d*	76.5 *d*	77.0 *d*
4	39.2 *s*	37.2 *s*	38.1 *s*	38.1 *s*	38.7 *s*	37.8 *s*
5	55.2 *d*	43.7 *d*	42.9 *d*	40.7 *d*	40.5 *d*	36.7 *d*
6	24.1 *d*	23.4 *t*	22.7 *t*	29.9 *t*	28.8 *t*	28.8 *t*
7	122.0 *d*	122.1 *d*	122.7 *d*	73.3 *d*	74.9 *d*	127.0 *d*
8	135.2 *s*	135.4 *s*	135.1 *s*	148.2 *s*	84.9 *s*	135.6 *s*
9	49.9 *d*	54.7 *d*	54.7 *d*	50.6 *d*	52.0 *d*	89.7 *s*
10	43.3 *s*	36.6 *s*	41.1 *s*	43.8 *s*	49.2 *s*	45.5 *s*
11	21.4 *t*	21.2 *t*	21.7 *t*	19.0 *t*	18.3 *t*	23.0 *t*
12	44.5 *t*	44.8 *t*	44.6 *t*	40.8 *t*	42.1 *t*	37.2 *t*
13	73.5 *s*	73.6 *s*	73.6 *s*	73.6 *s*	73.6 *s*	83.7 *s*
14	144.7 *d*	144.9 *d*	144.8 *d*	144.9 *d*	144.6 *d*	144.6 *d*
15	112.2 *t*	111.8 *t*	112.0 *t*	111.9 *t*	112.1 *t*	111.0 *t*
16	32.6 *q*	27.9 *q*	28.0 *q*	28.7 *q*	28.2 *q*	29.3 *q*
17	14.4 *q*	13.5 *q*	21.2 *q*	111.8 *t*	20.6 *q*	20.6 *q*
18	24.1 *q*	27.8 *q*	27.8 *q*	28.7 *q*	27.4 *q*	27.1 *q*
19	22.6 *q*	22.2 *q*	22.0 *q*	21.5 *q*	21.7 *q*	21.2 *q*
20	22.0 *q*	22.1 *q*	62.8 *t*	62.1 *t*	72.6 *t*	63.8 *t*
OAng			166.8 *s*	166.8 *s*	167.1 *s*	166.9 *s*
			128.0 *s*	127.9 *s*	127.7 *s*	127.9 *s*
			137.8 *d*	138.3 *d*	138.5 *d*	137.9 *d*
			15.9 *q*	15.9 *q*	15.9 *q*	15.7 *q*
			20.7 *q*	20.7 *q*	20.7 *q*	20.7 *q*
OAc			171.2 *s*	171.1 *s*		171.3 *s*
			21.1 *q*	21.1 *q*		170.3 *s*
						20.9 *q*
						20.7 *q*

formed by a proton catalysed rearrangement of spathulenol (see Scheme). Therefore the same absolute configuration was proposed.

The chemistry of this species is related to that of several Australian *Helichrysum* species [4] which differs clearly from that of the South African species. This supports the proposal that parts of the Australian *Helichrysum* species should be placed in the *Schoenia* group [1]. However, the chemistry of the Australian *Helipterum* species [5] is not related to that of *Waitzia* and *Helichrysum*. Therefore, the proposed relationship of parts of the Australian *Helipterums* to this group is not supported by the chemistry. Further investigations of related genera are necessary to obtain a clear picture.

EXPERIMENTAL

The air-dried plant material was extd with Et_2O–MeOH–petrol (1:1:1). The extract of 1200 g aerial parts (voucher RMK 9622, collected 33°14′ S, 140°39′ E in S Australia) gave by CC five fractions [1: petrol; 2: petrol–Et_2O (3:1); 3: petrol–Et_2O (1:1); 4: Et_2O and 5: Et_2O–MeOH (9:1)]. Fraction 1 gave nothing of interest and fraction 2 by TLC 30 mg caryophyllenepoxide, 30 mg spathulenol (**17**), 15 mg ledol and a mixture of 10 mg anhydrooplopanone and 10 mg **18** which could not be separated even on $AgNO_3$-impregnated TLC plates. The isolation of 10 mg pure **18** was achieved only after the mixture had been epoxidized with *m*-chloroperbenzoic acid [TLC, petrol–Et_2O (9:1), R_f 0.35]. Fractions 3–5 were combined and separated again by CC with CH_2Cl_2–Et_2O mixtures. Further purification by TLC and/or HPLC (RP 8, flow rate 3 ml/min) gave 50 mg **20** [TLC, petrol–Et_2O (1:1), R_f 0.39] as well as the diterpenes **1**–**16**: 500 mg **1**, 10 mg **2**, 10 mg **3**, 100 mg **4**, 3 mg **5**, 5 mg **6**, 20 mg **7**, 10 mg **8**, 25 mg **9**, 5 mg **10**, 25 mg **11**, 25 mg **12**, 5 mg **13**, 3 mg **14**, 5 mg **15** and 3 mg **16**. The conditions for final separation of new compounds are given in Table 5. Compounds **1**, **3**, **10** and **12** were transformed to the corresponding ketones by stirring the carbinols with pyridine dichromate in CH_2Cl_2.

Table 5. IR and MS data including R_f (R_t) values of new diterpenes and some of their reaction products

	$\nu_{max}^{CHCl_3}$ cm^{-1}		*M/z*
1a*	3450, 1720, 935	$C_{20}H_{32}O_2$ R_f 0.54	304 (0.2), 286.230 (3) (calc. for $C_{20}H_{30}O$: 286.230), 271 (2), 218 (100), 162 (32)
3	3400, 930	$C_{20}H_{34}O_2$ R_t 18.3 min	306 (0.1), 288.246 (1.5) (calc. for $C_{20}H_{32}O$: 288.245), 220 (100), 202 (10), 187 (14)
3a*	3380, 1710, 935	$C_{20}H_{32}O_2$ R_f 0.73	304 (0.3), 286.230 (5) (calc. for $C_{20}H_{30}O$: 286.230), 218 (100), 203 (31)
4	3360, 1735, 1710	$C_{27}H_{42}O_6$ R_f 0.34	402.277 (1) (calc. for $C_{25}H_{38}O_4$: 402.277), 388 [M −MeOAc]$^+$ (1), 303 (6), 216 (26), 203 (37), 83 (100), 55 (64)
5	3360, 1730	$C_{30}H_{48}O_6$ R_f 0.79	402.277 (1.3) (calc. for $C_{25}H_{38}O_4$: 402.277), 388 [M −MeOCOR]$^+$ (6), 303 (8), 216 (36), 203 (25), 85 (20), 83 (100)
6	3400, 1740, 1710	$C_{27}H_{42}O_6$ R_f 0.12	462 (0.1), 444.288 (3) (calc. for $C_{27}H_{40}O_5$: 444.288), 384 (2), 344 (3), 284 (12), 83 (100)
7	3400, 1735, 1710	$C_{27}H_{42}O_7$ R_t4 min	478 (0.3), 460.283 (0.5) (calc. for $C_{27}H_{40}O_6$: 460.282), 400 (1), 300 (4), 83 (100)
8	3400, 1730, 1720	$C_{30}H_{48}O_7$ R_t 9.1 min	520 (0.1), 502.329 (1) (calc. for $C_{30}H_{46}O_6$: 502.329), 400 (1), 300 (5), 83 (100), 57 (85)
9	3400, 1740, 1710	$C_{29}H_{44}O_8$ R_t 4.4 min	502.294 (1) (calc. for $C_{29}H_{42}O_7$: 502.293), 442 (1), 343 (2), 83 (100), 55 (40)
10a	3400, 1750, 1715, 1665	$C_{29}H_{42}O_8$ R_f 0.29	518 (0.2), 500.278 (1.5) (calc. for $C_{29}H_{40}O_7$: 500.277), 458 (0.5), 358 (2), 83 (100), 55 (44)
11	3400, 1710	$C_{25}H_{40}O_6$ R_t 4.8 min	436.283 (3) (calc. for $C_{25}H_{40}O_6$: 436.282), 418 (1), 336 (2), 305 (48), 83 (100), 55 (36)
11Ac	3400, 1750, 1710	$C_{29}H_{44}O_8$ R_f 0.4	520 (8), 460 (7), 442 (3), 305 (15), 205 (18), 166 (30), 95 (90), 83 (100)
12	3400, 1720	$C_{27}H_{42}O_7$ R_t 4 min	478.294 (3) (calc. for $C_{27}H_{42}O_7$: 478.293), 418 (3), 319 (4), 305 (10), 83 (100), 55 (60)
12a*	3500, 1750, 1725	$C_{27}H_{40}O_7$ R_f 0.48	476.277 (2) (calc. for $C_{27}H_{40}O_7$: 476.277), 416 (1), 317 (3), 305 (18), 83 (100)
13$^+$	3400, 1700, 1655	$C_{20}H_{32}O_3$ R_t 4.5 min	320.235 (5) (calc. for $C_{20}H_{32}O_3$: 320.235), 302 (6), 287 (10), 203 (45), 135 (56), 55 (100)
14	3400, 1710, 1660	$C_{20}H_{30}O_3$ R_f 0.18	318.220 (10) (calc. for $C_{20}H_{30}O_3$: 318.220), 300 (8), 55 (100)
15	1750, 1720	$C_{29}H_{42}O_7$ R_f 0.58	502.293 (0.2), 442 (0.1), 343 (0.1), 164 (100); CI: 503 [M + 1] (25), 164 (100)
16	3400, 1720	$C_{18}H_{30}O_2$ R_t 12.3 min	278.225 (9) (calc. for $C_{18}H_{30}O_2$: 278.225), 260 (12), 220 (34), 95 (100)

HPLC, MeOH–H_2O (7:3). TLC, Et_2O–petrol (3:1) except for compound **4** (Et_2O–petrol, 1:1, three developments) and compound **6** (CH_2Cl_2–Et_2O, 9:1).

*CD, **1a**: $\Delta\varepsilon_{296} = +1.42$; $\Delta\varepsilon_{305}$ 1.29; $\Delta\varepsilon_{316} = +0.67$; **3a**: $\Delta\varepsilon_{289} = -2.4$; $\Delta\varepsilon_{297} = -2.4$; **12a**: $\Delta\varepsilon_{305} = -2.78$.

Acetylation of compound **11** was achieved with Ac_2O in the presence of DMAP in $CHCl_3$.

Waitziacuminone (**18**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720 (C=O); MS *m/z* (rel. int.): 220.184 $[M]^+$ (3) (calcd for $C_{15}H_{24}O$: 220.184), 205 $[M-Me]^+$ (5), 177 $[M-C_3H_7]^+$ (7), 162 $[M-Me_2CO$, McLafferty$]^+$ (36), 147 $[162-Me]^+$ (35), 119 (55), 93 (100); ^1H NMR ($CDCl_3$): δ0.26 (*ddd*, H-1), 1.67 (*m*, H-2), 1.52 (*m*, H-2'), 2.53 (*t*, H-3), 0.01 (*br d*, H-5), 0.49 (*br d*, H-6), 0.53 (*ddd*, H-7), 1.60 and 0.90 (*m*, H-8), 1.55 and 0.77 (*m*, H-9), 0.92 (*s*, H-12), 1.00 (*s*, H-13), 0.88 (*s*, H-14), 2.16 (*s*, H-15); *J* [Hz]: 1,2 = 6.5; 1,2' = 8; 1,5 = 5; 2,3 = 7.5; 6,7 = 8.5; 7,8 = 8.5; 7,8' = 5.5; 8,9' = 4; 8',9' = 12; 9,9' = 13; ^{13}C NMR (C_6D_6, C-1–C-15): 32.2, 24.3, 43.7, 206.3, 21.8, 20.9, 22.7, 16.7, 33.2, 18.6, 19.8, 28.3, 16.2, 19.3, 29.4 (a few signals may be interchangeable).

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