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AN UNUSUAL DIMERIC SESQUITERPENE AND OTHER CONSTITUENTS FROM CHILEAN *BACCHARIS* SPECIES

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Key Word Index—*Baccharis santelicis*; *B. petiolata*; Compositae; diterpenes; labdanes; clerodanes; phenolics, dimeric sesquiterpene.

Abstract—The aerial parts of *B. santelicis* afforded several known furoclerodanes and phenolics. In addition to known compounds an unusual dimeric sesquiterpene and five labdane derivatives were isolated from *B. petiolata*. The structures were elucidated by high field NMR techniques and a few chemical transformations.

INTRODUCTION

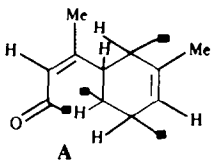
From the large genus *Baccharis* (Compositae, tribe Astereae, subtribe Baccharidinae) nearly 100 species have been studied chemically. The most widespread compounds are furoclerodanes, but labdanes, kauranes and several aromatic compounds have also been reported. We have studied now two species from Chile.

RESULTS AND DISCUSSION

From the extract of the aerial parts of *B. santelicis* Phil. we identified germacrene D, bicyclogermacrene, spathulenol, the *ent*-clerodanes **1** [1], **2** [2], **3** [3], **4** [4] and **5** [5], the phenolics **8** [6] and **9** [7] as well as the chromene derivative **7** [6] and its precursor **6**, a compound already isolated from a *Helichrysum* species [8]. As only 60 MHz ^{1}H NMR data are reported [8] for **6** we have added the 400 MHz data in the Experimental.

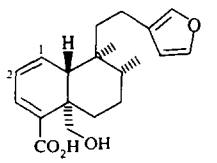
The aerial parts of *B. petiolata* DC. have been studied previously. In addition to bisabolol, several flavones and a triterpene [9, 10], a labdane was reported from a collection in Argentina [10]. We have reinvestigated material from Chile. In addition to the flavanoids **20, 21** and sakuranetin and the bisprenylcoumaric acid **10** [4], the labdane derivatives **12** [11], **13, 14, 16, 17** and **19** as well as the dimeric sesquiterpene **11** were isolated.

At first glance the ^{1}H NMR spectrum of **11** (Table 1) looks like that of a mixture of sesquiterpenes. However, the molecular formula was $C_{30}H_{44}O_4$. The presence of a fragment *m/z* 234 and the ^{1}H NMR spectrum indicated that it may be a dimeric sesquiterpene which itself could be a bisabolene derivative as the NMR data clearly showed the signals of the corresponding side chains. Spin decoupling of the remaining signals led to the sequence **A**:

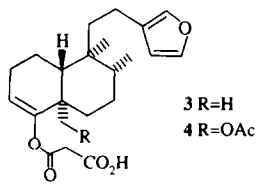


A

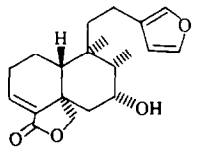
The ^{13}C NMR spectrum indicated the presence of two tertiary alcohols and two keto groups—one conjugated and one unconjugated (δ78.7, 78.3, 201.6 and 214.7, respectively). If the partial structure **A** had to be combined with these groups and the mentioned side chains, the most likely possibility is a bicyclo-[2,2,2]-octenone derivative, a system which could be formed by a 4+2-cycloaddition of the bisabolene derivative **12** with itself. Inspection of the possible structures of such additions



1 **2** 1.2H



3 R=H
4 R=OAc



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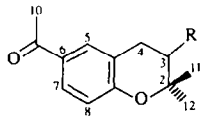
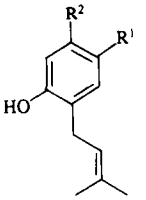
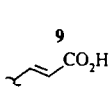


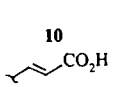
6 R=OH **6Ac** R=OAc **7** R=H, Δ^3



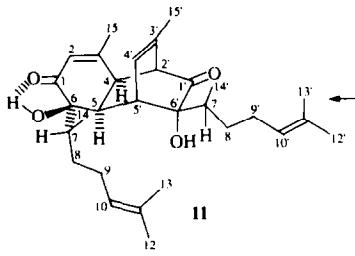
8 R^1 Ac, R^2 H



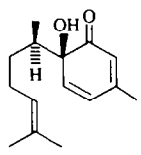
9 H



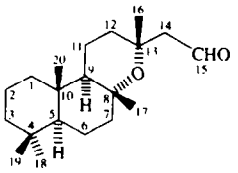
10 prenyl



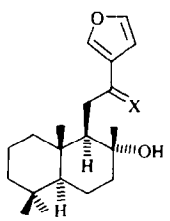
11



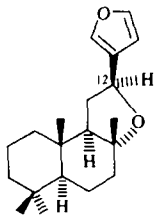
11a



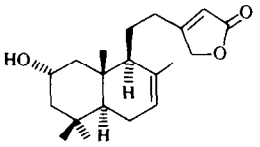
12 13 13*epi*



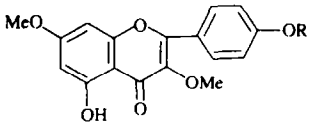
14 X=O 15 X=αOH,H 16 X=βOH,H



17 18 12*epi*



19



20 R=Me
21 R=H

shows that there are 64 possibilities as a result of *endo*-or *exo*-addition, of the regiospecifity and of the configurations at C-6 and C-7. These problems could be solved by extensive studies of the NOEs (Table 2). The regiospecifity followed from the effect between H-14′ and H-5′ as the latter showed an NOE with H-5. The *exo*-addition was deduced from the effects of OH-6′ with H-5′ and H-5 as well as of H-2 with H-15′. Furthermore, the absence of effects between H-4′ and H-5 as well as between H-4 and H-15′ requires an *exo*-addition. Clear NOEs of H-14 with H-2 and H-5 as well as H-5 with H-7 support the proposed configuration at C-7 while the NOE of H-14′ with H-5′ and H-5′ with H-8′ led to the stereochemistry at C-7′. The NOEs of the hydroxy protons were determined with a very short time for the formation of the effects as usual times led to a complete exchange between the two hydroxy protons. The effect of OH-6′ with H-5′ and H-5 indicated the α-position of the hydroxy group at C-6′, while the NOE of OH-6 with H-5′ and H-4′ requires a β-orientation of this group. This was further supported by the sharp signal at δ3.81 which indicates a hydrogen bond with the C-1 carbonyl as also followed from the IR band. Thus all data show that the dimer **11** is formed by a regiospecific *exo*-4 + 2-cycloaddition of the quinol **11a** with itself. The absolute configuration followed from the observed negative Cotton effect at 306 nm. As in bicyclo-[2,2,2]-oct-5-en-2-one [12] the orientation of the β,γ-unsaturated ketone determines the sign of the Cotton effect. The weak positive effect of the conjugated keto group at 342 nm also supports the proposed absolute configuration if the helicity rule was used. Thus, the precursor **11a** must have the given configuration which agrees with that deduced for bisabolone [13]. Bisabolone may be a precursor of **11a** which presumably formed by oxidation of the corresponding phenol (1-hydroxy-α-curcumene [14]). With the simple quinol, 2-acetoxy-2-methyl-cyclohexa-3,5-dien-1-one no cyclo-addition was observed [15]. Therefore, compound **11** is not an artifact. The unusual exo-addition is favoured by steric effects as can be visualized from models. We have named compound **11** bacchopetiolone.

The structure of **19** was deduced from its ^{1}H NMR spectrum which was identical with that of the saponification product of the corresponding succinate [16]. As in the previous case, the absolute configuration followed from the Cotton effect of the corresponding ketone, the identical sign of optical rotation also showed that lactone **19** has the labdane configuration which is probably valid for the other compounds (**12**–**17**), especially as the signs are always positive as in manoyloxide.

Table 1. ^{1}H NMR and ^{13}C NMR spectral data of compound **11** (400 and 100.6 MHz, δ-values)

H	$CDCl_3$	C_6D_6	H	$CDCl_3$	C_6D_6	C	13_C	C	
2	5.98 *dq*	5.80 *dq*	2′	3.16 *dd*	3.05 *dd*	1	201.6	1′	214.7
4	3.02 *br dd*	2.93 *br dd*	4′	5.80 *ddq*	5.77 *ddq*	2	125.3	2′	57.2
5	3.28 *br dd*	3.62 *br dd*	5′	3.35 *dd*	3.71 *dd*	3	155.7	3′	135.4
7	1.28 *m*	1.43 *m*	7′	1.60 *m*	1.72 *m*	4	47.4	4′	126.6
8_1	1.35 *m*	2.14 *m*	$8'_1$	1.75 *m*	1.48 *m*	5	37.3	5′	41.4
8_2	1.12 *m*	1.48 *m*	$8'_2$	1.12 *m*	1.25 *m*	6	78.7[a]	6′	78.3[a]
9_1	2.02 *m*	2.14 *m*	$9'_1$	2.02 *m*	1.95 *m*	7	41.8	7′	37.0
9_2	1.84 *m*	2.07 *m*	$9'_2$	1.75 *m*	1.86 *m*	8	30.6	8′	30.0
10	5.08 *br t*	5.22 *br t*	10′	5.01 *br t*	5.11 *br t*	9	26.1	9′	25.6
12	1.66 *br s*	1.71 *br s*	12′	1.66 *br s*	1.69 *br s*	10	124.4	10′	124.1
13	1.56 *br s*	1.57 *br s*	13′	1.56 *br s*	1.55 *br s*	11	131.7	11′	131.8
14	0.60 *d*	0.76 *d*	14′	0.86 *d*	0.97 *d*	12	25.6	12′	25.6
15	1.96 *d*	1.31 *d*	15′	1.61 *d*	1.32 *d*	13	17.6	13′	17.6
OH	3.81 *s*	4.25 *br s*	OH′	2.27 *s*	2.25 *br s*	14	13.8	14′	12.6
						15	22.0	15′	21.2

J Hz: 2,4 = 2,15 = 2′,15′ = 2′,4′ ~ 1.5; 4,5 = 8; 5,5′ = 2; 7,14 = 7′,14′ = 9,10 = 9,10′ = 4′,5′ = 7.

[a]Assigned by 2D-techniques.

[a]May be interchangeable.

Table 2. NOEs of compound **11**

H irradiated	NOE (%)
14	H-2 (3), 9 (3), 5 (2), 4 (1), 7 (3)
14′	H-5′ (3), 9′ (4)
15	H-4 (5), 2 (10), 9 (3)
15′	H-2′ (10), 4′ (6), 2 (4)
4	H-15 (6), 2′ (6)
2′	H-15 (6), 15′ (4), 4 (6)
5	H-7 (3), 9 (3), 5′ (3)
5′	H-14′ (3), 8′ (4), 5 (4)
6-OH	H-5′ (4), 4′ (2), 14 (3)
6′-OH	H-5′ (4), 5 (3), 14′ (10)
4′	H-5′ (5), 15′ (4), 7 (4)
2	H-15 (10), 7 (2), 14 (2), 15′ (3)

The ^{1}H NMR spectrum of **13** (Table 3) was very similar to that of **12**. Shift differences were observed especially for the signals of H-14, H-15 and H-16, indicating the presence of a 13-epimeric aldehyde. This and the configuration of the other chiral centres was confirmed by the observed NOEs between H-17, H-20 (8%), H-15 (3%) and H-14 (6%), between H-20 and H-17 (8%) and between H-16 and H-15 (4%). Furthermore, the ^{13}C NMR spectrum (Table 4) showed the characteristic differences in the chemical shift of C-16 (**12**: 13-methyl axial δ28.5, **13**: 13-methyl equatorial δ31.3).

The ^{1}H NMR spectrum of **14** (Table 3) showed that a furolabdane with a 12-keto group was present, from the chemical shift of H-16 and the pair of double doublets at δ2.86 and 2.80. Comparison of the chemical shift of H-17 with that of **12** and **13** indicated the axial orientation. The ^{13}C NMR spectrum (Table 4) also supports the structure.

The ^{1}H NMR spectrum of **16** (Table 3) showed a broadened double doublet at δ4.98 which was coupled with H-14 and H-16 indicating a hydroxy group at C-12. The chemical shift of H-17 required a second hydroxy group at C-8. Again the chemical shift of H-17 required an axial methyl group. The configuration at C-12 could not be deduced directly from the spectral data. By transformation of **16** to **17** (see below) the stereochemistry could be determined. Alanat-reduction of **14** gave the two epimeric alcohols **15** and **16**, the latter being identical with the naturally occurring diol.

The ^{1}H NMR spectrum of **17** (Table 3) was in part similar to that of **16**. However, several signals were shifted and the couplings of H-12 also differed. As the molecular formula was $C_{20}H_{30}O_2$ the presence of the corresponding ether derived from **16** is very likely. Indeed, brief acid treatment of **16** gave an ether, its ^{1}H NMR spectrum being identical with that of **17**. Acid treatment of **15** gave the ether **18**, its ^{1}H NMR spectrum differed clearly from that of **17**. The couplings of H-12 also differed from those of **17**; the real values were visible only in deuteriobenzene but in deuteriochloroform the H-11 signals were not first order. The configuration of C-12 in compound **17** followed from the NOE of H-12 with H-9 (3%) while H-17 gave no effect with H-12, but with H-20 (3%), H-11 (4%)

Table 3. ^{1}H NMR spectral data of compounds **13–18** (400 MHz, $CDCl_3$, δ-values)

H	**13** (C_6D_6)	**14**	**15*** (C_6D_6)	**16**	**17**	**18**
5	0.80 *dd*	1.05 *dd*	0.78 *dd*	1.10 *dd*	1.00 *dd*	1.01 *dd*
6α	1.53 *br d*	1.70 *dq*	1.53 *br d*	1.65 *br d*	1.78 *br d*	1.78 *br d*
6β	1.10 *m*	1.30 *dq*	1.06 *dq*	1.24 *m*	1.31 *dq*	1.32 *dq*
7α	1.47 *m*	1.48 *dt*	1.55 *m*	1.55 *dt*	1.45 *m*	1.45 *m*
7β	1.82 *m*	1.96 *dt*	1.67 *dt*	1.42 *m*	1.99 *dt*	1.99 *dt*
9	1.09 *dd*	2.13 *t*	1.45 *t*	1.38 *m*	+	+
11	+	2.86 *dd*	1.81 *dt*	1.92 *ddd*	2.09 *ddd*	2.15 *ddd*
11′	+	2.80 *dd*	1.72 *dt*	1.85 *ddd*	1.78 *m*	1.78 *m*
12	+	—	4.62 *dd*	4.98 *dd*	4.93 *dd*	5.06 *dd*
14	2.60 *br dd* 2.05 *br dd*	6.78 *br d*	6.42 *br s*	6.37 *br s*	6.38 *t*	6.33 *br s*
15	9.87 *t*	7.43 *t*	7.20 *t*	7.37 *t*	7.36 *d*	7.35 *t*
16	1.25 *s*	8.10 *br s*	7.49 *br s*	7.38 *br s*		7.36 *br s*
17	1.12 *br s*	1.15 *s*	0.99 *s*	1.24 *s*	1.16 *s*	1.19 *s*
18	0.85 *s*	0.88 *s*	0.88 *s*	0.86 *s*	0.89 *s*	0.89 *s*
19	0.79 *s*	0.86 *s*	0.78 *s*	0.79 *s*	0.84 *s*	0.84 *s*
20	0.65 *s*	0.80 *s*	0.63 *s*	0.78 *s*	0.87 *s*	0.87 *s*

+ Overlapped multiplets.

*$CDCl_3$: H-11 1.76 *m*, H-12 4.52 *t* (J = 6 Hz).

J Hz: Compound **13**: 5,6α = 2; 5,6β = 6α,6β = 12; 9,11 = 2.5; 9,11′ = 12; 14,14′ = 15; 14,15 = 2.5; compound **14**: 5,6α = 2; 5,6β = 6α,6β = 6β,7α = 12; 6α,7α = 6α,7β = 6β,7β = 3; 7α,7β = 12; 9,11 = 9,11′ = 5; 11,11′ = 17; 14,15 = 14,16 = 1.5; compound **15**: 5,6α = 2; 5,6β = 6α,6β = 12, 6α,7α = 6α,7β = 6β,7β = 3; 7α,7β = 13; 9,11 = 9,11′ = 4; 11,11′ = 11,12 = 10; 11′,12 = 2; 14,15 = 14,16 = 1.5; compound **16**: 5,6α = 2; 5,6β = 6α,6β = 12; 6α,7α = 6α,7α = 6β,7β = 3; 7α,7β = 13; 9,11 = 11,12 ~ 5; 9,11′ ~ 10; 11,11′ = 15; 11′,12 = 7; 14,15 = 15,16 = 1.3; compound **17**: 5,6α = 2.5; 5,6β − 6α,6β = 6β,7α = 12; 6α,7α = 6α,7β = 6β,7β = 3; 7α,7β = 12; 9,11 = 5; 11,11′ = 12; 11,12 = 7; 12′,12 = 9; 14,15 = 14,16 = 1.3; compound **18**: see **17**, except 11,12 = 9; 11′,12 = 2.

Table 4. ^{13}C NMR spectral data of compounds **12**–**14** and **17** ($CDCl_3$, 100.6 MHz, δ-values)

C	12	13	14	17
1	39.1	39.2	36.3	40.0
2	18.5	18.5	18.3	18.3
3	42.1	42.1	39.4	40.3
4	33.1	33.3	33.2	33.0
5	56.4	56.4	55.9	57.0
6	19.8	19.9	20.6	20.8
7	42.8	43.2	41.7	42.4
8	75.5	75.8	73.0	81.0
9	58.2	57.3	55.8	61.1
10	36.9	36.9	38.6	36.3
11	15.3	15.2	44.6	30.5
12	37.3	38.2	196.2	72.5
13	72.6	71.8	127.7	129.3
14	57.2	53.7	108.9	109.0
15	204.1	203.8	144.0	138.7
16	28.5	31.3	147.0	143.0
17	24.6	24.8	23.3	24.5
18	33.3	33.3	33.3	33.4
19	21.2	21.2	21.4	21.0
20	15.7	15.7	15.7	15.5

and H-14 (2%) indicating the axial orientation of H-17. Accordingly, the stereochemistry of **17** was established and therefore also that of **16** (see above).

Comparison of the chemistry of these two *Baccharis* species shows that both have the typical prenylated coumaric acids (**9** and **10**, respectively). However, in one species clerodanes and in the other labdanes were present, again indicating that there are chemically different groups in the large genus *Baccharis*. Further studies may show whether a correlation with morphological features is possible.

EXPERIMENTAL

The air-dried aerial parts of *B. santelicis* (457 g, collected near Putre, Region de Tarapaca, Chile, in May 1989, voucher Niemeyer 8958, deposited in the Herbarium of the University of Chile, Santiago) was extracted with MeOH–Et_2O–petrol (1:1:1). The extract was separated as reported previously [17] to yield 30 mg germacrene D, 30 mg bicyclogermacrene, 100 mg spathulenol, 700 mg **1**, 60 mg **2**, 230 mg **3**, 30 mg **4**, 40 mg **5**, 200 mg **7**, 6 g **8**, 2 g **9** and 200 mg **6**. Compound **6** was an oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH), 1690, 1620 (PhCO); MS *m/z* (rel. int.): 220.110 $[M]^+$ (100) (calc. for $C_{13}H_{16}O_3$: 220.110), 205 (14), 203 (14), 187 (26), 162 (18), 150 (54), 149 (50); ^1H NMR ($CDCl_3$): δ 3.87 (*br q*, H-3), 3.11 and 2.83 (*br dd*, H-4), 7.74 (*br s*, H-5), 7.75 (*br d*, H-7), 6.86 (*d*, H-8), 2.54 (*s*, H-10), 1.39 (*s*, H-11), 1.35 (*s*, H-12), 1.80 (*br d*, OH) (*J* [Hz] s. **6** Ac). Acetylation of **6** (Ac_2O, 2 hr, 70°) gave **6**Ac; crystals, mp 125° (lit. [8] 121–122°); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1245 (OAc), 1685, 1610 (PhCO); MS *m/z* (rel. int.): 262.121 $[M]^+$ (12) (calc. for $C_{15}H_{18}O_4$: 262.121), 202 (26), 187 (100), 159 (7), 150 (21), 149 (16); ^1H NMR ($CDCl_3$): δ 5.06 (*t*, H-3), 3.17 and 2.85 (*br dd*, H-4), 7.72 (*br d*, H-5), 7.76 (*dd*, H-7), 6.88 (*d*, H-8), 2.54 (*s*, H-10), 1.37 (*s*, H-11), 1.34 (*s*, H-12); *J* [Hz]: 3,4 = 3,4′ = 5; 4,4′ = 17; 5,7 = 2.

The extract of the aerial parts (358 g) of *B. petiolata* (collected in Valle de Lluta, Region de Tarapaca, Chile, voucher Niemeyer 89119, deposited in the Herbarium of the University of Chile, Santiago) was separated by CC into 4 frs. Fr. 1 gave by TLC (Et_2O–petrol, 1:9) 20 mg **17** (R_f 0.50) and 20 mg **12** (R_f 0.20). Fr. 2 gave 200 mg crystallin **20** and the mother liquor by HPLC (MeOH–H_2O, 9:1) 25 mg **11** (R_t 4.7 min), 15 mg **13** (R_t 9.7 min) and 5 mg **12** (R_t 11.0 min). Fr. 3 was sepd into acidic parts by shaking with $NaHCO_3$-soln (Fr. 3/1) and Na_2CO_3 soln (Fr. 3/2) and the neutral part (Fr. 3/3). Fr. 3/1 gave 1.7 g **10** and fr. 3/2 1 g **10**, 500 mg **21** and 500 mg sakuranetin. Fr. 3/3 gave by HPLC (MeOH–H_2O, 4:1) 200 mg **14** (R_t 11.5 min) and 200 mg **16** (R_t 12.3 min). Fr. 4 gave by HPLC (MeOH–H_2O, 17:3) 300 mg **19** (R_f 7.2 min). Known compounds were identified by their 400 MHz ^1H NMR spectra and comparison with those of authentic samples.

Bacchopetiolone (**11**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3560, 3460 (OH, H-bond), 1720 (CO), 1685 (C=CC=O); MS *m/z* (rel. int.): 468.324 $[M]^+$ (4) (calc. for $C_{30}H_{44}O_4$: 468.324), 450 $[M-H_2O]^+$ (1.5), 422 $[450-CO]^+$ (1.5), 234 $[C_{15}H_{22}O_2]^+$ (10), 199 (28), 152 (16), 151 (20), 135 (14), 124 (28), 95 (18), 69 $[C_5H_9]^+$ (100); $[\alpha]_D^{24}$ −125° ($CHCl_3$; *c* 2.17); CD (MeOH): $\Delta\varepsilon_{342}$ +0.2, $\Delta\varepsilon_{306}$ −4.6.

15-*Oxo*-14,15-*dihydro*-13-epi-*manoyloxide* (**13**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2740, 1725 (CHO); MS *m/z* (rel. int.): 306.256 $[M]^+$ (7) (calc. for $C_{20}H_{34}O_3$: 306.256), 291 $[M-Me]^+$ (86), 273 $[291-H_2O]^+$ (15), 245 $[273-CO]^+$ (85), 199 (52), 191 (100), 137 (87), 123 (72), 109 (74), 95 (77), 81 (85), 69 (92); $[\alpha]_D^{24}$ +34° ($CHCl_3$; *c* 0.93).

8α-*Hydroxy*-15,16-*epoxy*-*labda*-13(16),14-*dien*-12-*one* (**14**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3590 (OH), 1680, 890 (furan ketone); MS *m/z* (rel. int.): 318.219 $[M]^+$ (74) (calc. for $C_{20}H_{30}O_3$: 318.219), 300 $[M-H_2O]^+$ (44), 285 $[300-Me]^+$ (10), 195 (34), 190 (46), 177 (82), 175 (50), 137 (60), 123 (85), 109 (58), 95 $[C_5H_3O_2]^+$ (100), 81 (68), 69 (82); $[\alpha]_D^{24}$ +20° ($CHCl_3$; *c* 0.49). To 20 mg **14** in 3 ml Et_2O was added 20 mg $LiAlH_4$. After 5 min at room temp. NH_4Cl soln was added. Usual work-up and TLC (Et_2O–petrol, 1:1) gave 7 mg **15** (R_f 0.43) and 7 mg **16** (R_f 0.37) identical with the natural product (^1H NMR spectrum). Compound **15**: MS *m/z* (rel. int.): 302.224 $[M-H_2O]^+$ (52) (calc. for $C_{20}H_{30}O_2$: 302.224), 287 (48), 206 (80), 123 (100), 95 (75), 82 (88), 69 (92).

Compound **15** (5 mg) in 10 ml Et_2O was shaken for 5 min with 5 ml 1 M H_2SO_4. TLC (Et_2O–petrol, 1:1) gave 4 mg **18** (R_f 0.85); MS *m/z* (rel. int.): 302.224 $[M]^+$ (58) (calc. for $C_{20}H_{30}O_2$: 302.224), 287 (82), 206 (95), 191 (68), 150 (58), 137 (76), 125 (89), 123 (100), 95 (90), 82 (91), 81 (91), 69 (88).

8α,12-*Dihydroxy*-15,16-*epoxy*-12S-*labda*-13(16),14-*diene* (**16**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 880 (furan); MS *m/z* (rel. int.): 302.224 $[M-H_2O]^+$ (28) (calc. for $C_{20}H_{30}O_2$: 302.224), 287 $[302-Me]^+$ (25), 206 (24), 192 (72), 177 (100), 137 (52), 123 (85), 110 (88), 95 (90), 81 (86), 69 (94); $[\alpha]_D^{24}$ +14° ($CHCl_3$; *c* 0.83). compound **16** (5 mg) in 10 ml Et_2O was shaken for 5 min with 5 ml 1 M H_2SO_4. TLC (Et_2O–petrol, 1:1) gave 4 mg **17** (R_f 0.85), identical with the natural compound.

8α,12S,15,16-*Bis*-*epoxy*-*labda*-13(16),14-*diene* (**17**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 890 (furan); MS *m/z* (rel. int.): 302.224 $[M]^+$ (22) (calc. for $C_{20}H_{30}O_2$: 302.224), 287 $[M-Me]^+$ (100), 206 (51), 137 (33), 123 (54), 109 (43), 95 (48), 82 (48), 81 (53), 69 (64); $[\alpha]_D^{24}$ −9° ($CHCl_3$; *c* 0.86).

2α-*Hydroxy*-*labda*-7,13-*dien*-15,16-*olide* (**19**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1790, 1760, 1645 (butenolide); MS *m/z* (rel. int.): 318 $[M]^+$ (1), 303 $[M-Me]^+$ (1.5), 300.209 $[M-H_2O]^+$ (4) (calc. for $C_{20}H_{28}O_2$: 300.209), 285 $[300-Me]^+$ (3), 221 (8), 220 (8), 122 (100), 107 (46), 98 (52), 81 (31), 69 (24); $[\alpha]_D^{24}$ +28° ($CHCl_3$; *c* 0.42).

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REFERENCES

1. Warning, U., Bohlmann, F., Sanchez, H., del Rio, E. S. and Dominguez, X. A. (1986) *Rev. Latinoam. Quim.* **17**, 199.
2. Bohlmann, F. and Grenz, M. (1972) *Chem. Ber.* **105**, 3123.
3. Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1979) *Phytochemistry* **18**, 1993.
4. Zdero, C., Bohlmann, F., King, R. M. and Robinson, H. (1986) *Phytochemistry* **25**, 2841.
5. Tonn, C. E. and Giordano, O. S. (1980) *An. Asoc. Quim. Argent.* **68**, 237.
6. Bohlmann, F. and Grenz, M. (1970) *Chem. Ber.* **103**, 90.
7. Bohlmann, F. and Jakupovic, J. (1979) *Phytochemistry* **18**, 1189.
8. de Quesada, G. T., Rodriguez, B. and Valverde, S. (1972) *Phytochemistry* **11**, 446.
9. Faini, C. L. F. and Castillo, M. (1990) *Phytochemistry* **29**, 324.
10. Gianello, J. C., Pestchanker, M. J., Tonn, C. E., Guo, M. and Giordano, O. S. (1990) *Phytochemistry* **29**, 656.
11. Bohlmann, F., Banerjee, S., Jakupovic, J., Grenz, M., Misra, L. N., Schmeda-Hirschmann, G., King, R. M. and Robinson, H. (1985) *Phytochemistry* **24**, 511.
12. Kirk, D. N. (1986) *Tetrahedron* **42**, 811.
13. Müller, T. (1981) Diss. Univ. Dortmund.
14. Bohlmann, F. and Lonitz, M. (1978) *Chem. Ber.* **111**, 843.
15. Wessely, F. and Sinwel, F. (1950) *Monatsh.* **81**, 1067.
16. Jakupovic, J., Schuster, A., Ganzer, U., Bohlmann, F. and Boldt, P. E. (1990) *Phytochemistry* **29**, 2217.
17. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1984) *Phytochemistry* **23**, 1979.