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HIGHLY OXYGENATED SESQUITERPENES FROM *POLYACHYRUS SPHAEROCEPHALUS* AND FURTHER CONSTITUENTS FROM CHILEAN MUTISIEAE

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Key Word Index—*Polyachyrus sphaerocephalus*, *P. fuscus*, *Mutisia* spp., *Leuceria* spp., *Nassauvia* spp., *Chaetanthera* spp.; Compositae; sesquiterpenes; 5-methylcoumarines; isocedrene derivative; bisabolene derivatives.

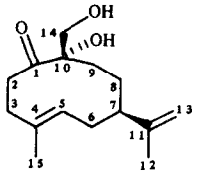
Abstract—The aerial parts of *Polyachyrus sphaerocephalus* gave seven new eudesmane derivatives and a germacra-diendiol while a reinvestigation of *P. fuscus* afforded a new caryophyllene, two nerolidolglycosides, a curcumene and two bisabolene derivatives. *Chaetanthera euphrasioides* gave a clerodane and *Ch. chilensis* two thiophene acetylenes while several other species only gave known compounds. The structures were elucidated by high field NMR techniques. Chemotaxonomic aspects are discussed briefly.

INTRODUCTION

The genus *Polyachyrus* (tribe Mutisieae) is placed in the subtribe Nassauviinae [1]. They are distributed over the west slopes of the Andes. Of the seven known species, only one has been studied chemically [2]. We have now studied *P. spaerocephalus* D. Don., reinvestigated *P. fuscus* as well as several other species all belonging to the tribe *Mutisieae*.

RESULTS AND DISCUSSION

The aerial parts of *P. sphaerocephalus* gave 12-acetoxy-tremetone [3], the germacrene derivative **1** and the eudesmanes **2–8**. The structure of **1** followed from the ^1H and ^{13}C NMR data (Table 1). Spin decoupling allowed the assignment of all signals and the resulting sequence led to proposed structure. The stereochemistry could be deduced from the observed NOEs. Thus effects were



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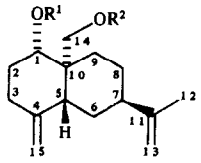
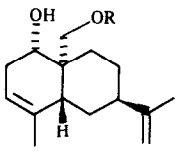
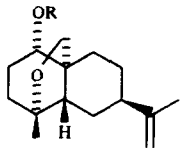


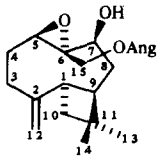
	2	**3**	**4**
R^1	H	H	Ac
R^2	H	Ac	H



	5	**6**
R	H	Ac



	7	**8**
R	H	Ac



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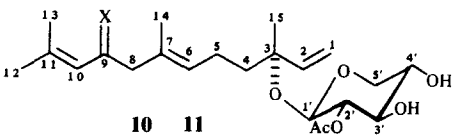
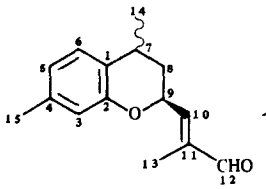


	10	**11**
X	H,OH	O



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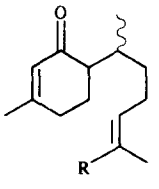
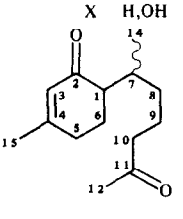
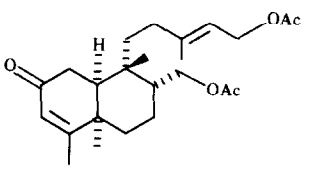


	13	**14**	**15**
R	CH_2OH	CHO	CO_2Me



16 **17**
Δ^{9E}



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observed for H-15 with H-14′ (3%) but not with H-5, H-7 with H-5 (3%), H-9ax with H-14′ (4%), H-2ax with H-5 (4%), H-5 with H-9ax (4%) and H-6β with H-14′ (3%). Furthermore these effects and the coupling constants indicate a conformation with both H-14 and H-15 below the plane.

The ^{1}H NMR data of **2–4** (Table 2) indicated that we were dealing with eudesmane derivatives which only differed in the nature of the oxygen function. While **2** is a diol, compounds, **3** and **4** are the isomeric monoacetates of **2**. Spin decoupling showed that the latter is a 1,14-dihydroxy-eudesmane. The observed couplings of H-7 require an axial orientation of the isopropenyl group. This and the configurations at C-5 was established by a NOE between H-5, H-1 (4%) and H-12 (3%). Inspection of models shows that the presence of a *W*-coupling between H-1 and H-14 require the proposed *trans*-decalin configuration which agree with that of similar eudesmane derivatives isolated from *P. fuscus* [2]. The ^{13}C NMR data (Experimental) support the structure. The chemical shifts of H-1 and H-14 in the spectra of the isomeric acetates **3** and **4** clearly indicate the position of the acetoxy groups.

The ^{1}H NMR spectra of **5** and **6** (Table 2) were in part very similar to those of **2** and **3**. However, the exo-methylene proton signals were replaced by those of an olefinic proton and a methyl group. Accordingly, the presence of the corresponding 3-eudesmane derivatives was very likely. This was supported by spin decoupling which led to corresponding sequences.

Table 1. ^{1}H and ^{13}C NMR data of compound **1** ($CDCl_3$, δ-values)

H		C	
2	3.23 *ddd*	1	214.3 *s*
2′	2.27 *ddd*	2	36.1 *t*
3	2.45 *ddd*	3	32.7 *t*[a]
3′	2.39 *br dd*	4	137.3 *s*
5	5.34 *ddq*	5	124.8 *d*
6	2.14 *m*	6	24.7 *t*
6′	2.09 *m*	7	45.8 *d*
7	2.02 *m*	8	32.1 *t*[a]
8	1.37 *ddd*	9	32.5 *t*[a]
8′	0.64 *ddd*	10	83.4 *s*
9	1.80 *ddd*	11	150.2 *s*
9′	1.60 *br dd*	12	108.7 *t*
12	4.65 *dq*	13	19.8 *q*[a]
12′	4.61 *dq*	14	67.1 *t*
13	1.67 *br s*	15	19.7 *q*[a]
14	3.80 *br d*		
14′	3.56 *d*		
15	1.71 *br s*		
OH	4.19 *br s*		

[a]May be interchangeable.

J [Hz]: 2,2′ = 15; 2,3 = 12; 2,3′ = 6; 2′,3 = 5; 3,3′ = 8,8′ = 9,9′ = 14; 8,9 = 8,9′ = 8′,9 ~ 10; 12,12′ = 12,13 = 12′,13 ~ 1.5; 14,14′ = 11.5.

Table 2. ^{1}H NMR spectral data of compounds **2–8** ($CDCl_3$, 400 MHz, δ-values)

H	2*	3	4	5†	6	7	8
1	3.56 *br dd*	3.46 *m*	4.85 *br dd*	3.70 *br dd*	3.60 *br dd*	3.49 *m*	4.69 *ddd*
2α	1.95 *m*	+	+	2.25 *m*	2.03 *m*	+	+
2β	1.84 *m*	+	+	2.44 *m*	2.47 *m*	+	+
3α	2.35 *ddd*	2.36 *ddd*	2.37 *ddd*	5.30 *br s*	5.32 *br s*	+	+
3β	2.13 *br ddd*	2.15 *br ddd*	2.20 *br ddd*			+	+
5	1.95 *br d*	1.95 *br d*	1.91 *br d*	2.14 *br d*	2.22 *br d*	+	+
6α	1.57 *ddd*	+	+	1.30 *ddd*	1.39 *m*	+	+
6β	1.86 *m*	+	+	1.99 *br d*	2.02 *br d*	+	+
7	2.44 *br s*	2.45 *br s*	2.46 *br s*	2.42 *br s*	2.42 *br s*	2.41 *br s*	2.40 *br s*
8α	1.75 *ddd*	+	+	1.97 *m*	1.96 *m*	+	+
8β	1.94 *m*	+	+	1.84 *dddd*	1.78 *dddd*	+	+
9α	2.28 *ddd*	+	+	2.28 *ddd*	2.02 *br d*	+	+
9β	1.29 *br ddd*	+	+	1.31 *br ddd*	1.39 *m*	+	+
12	4.93 *ddq*	4.94 *br s*	4.93 *br s*	4.94 *ddq*	4.94 *br s*	4.92 *br s*	4.92 *br s*
12′	4.81 *br s*	4.81 *br s*	4.78 *br s*	4.86 *br s*	4.85 *br s*	4.80 *br s*	4.77 *br s*
13	1.72 *br s*	1.73 *br s*	1.72 *br s*	1.74 *br s*	1.74 *br s*	1.74 *br s*	1.72 *br s*
14	3.81 *br d*	4.48 *br d*	3.90 *br d*	3.99 *br dd*	4.65 *br d*	3.86 *d*	3.92 *d*
14′	3.87 *br d*	4.15 *br d*	3.72 *br d*	3.95 *br dd*	4.19 *br d*	3.80 *br d*	3.87 *br d*
15	4.81 *ddd*	4.78 *ddd*	4.77 *ddd*	1.57 *br s*	1.59 *br s*	1.15 *s*	1.16 *s*
15′	4.74 *ddd*	4.55 *ddd*	4.56 *ddd*				
OAc	—	2.07 *s*	2.06 *s*		2.07 *s*	—	2.02 *s*

+ Overlapped multiplets.

*OH 3.01 *br s*, 3.36 *br s*.

†OH 2.75 *d*, 2.48 *t*.

J [Hz]: Compounds **2–4**: 1,2α = 11; 1,2β = 4.5; 2α,3α = 5; 2α,3β = 13; 2β,3α = 2; 2β,3β = 5; 3α,3β = 13; 3,15 = 3′,15 = 5.15 = 1.5; 5,6α = 6α,6β = 13; 6α,7 = 5; 7,8β = 4; 8α,8β = 8β,9α = 14; 8α,9α = 3; 7,12 = 12,13 = 12,12′ ~ 1; 14,14′ = 12; compounds **5** and **6**: 1,2α = 10; 1,2β = 6; 1, OH = 6; 5,6α = 6α,6β = 13; 6α,7 = 5; 7,8β = 4; 8α,8β = 8β,9α = 13; 7,12 = 12,13 = 12,12′ ~ 1; 14,14′ = 12; compounds **7** and **8**: 14,14′ = 9.

The molecular formula of **7** ($C_{15}H_{24}O_2$) is identical with those of **2** and **5**. In the ^{1}H NMR spectrum of compound **7** (Table 2) only olefinic signals for H-12 were visible, thus an ether ring is proposed. In agreement with this assumption, the ^{1}H NMR spectrum showed a sharp methyl singlet for H-15 and changed vicinal couplings of H-14. The downfield shift of H-1 in the spectrum of **8** (Table 2) indicated that we were dealing with the 1-*O*-acetate of **7**.

A reinvestigation of *P. fuscus* Meyen et Walp. gave desoxyperezone, the bisabolene derivatives **12**, **13** [4], **14** [4], **15** [5], **16** and **17**, the caryophyllene derivative **9** and the nerolidolglycosides **10** and **11**.

The ^{1}H NMR spectrum of **10** (Table 3) was similar to that of nerolidol. However, the H-10 signal showed only one vicinal coupling with a three-fold doublet at δ4.42. Thus, a 9-hydroxy derivative was present. Furthermore, the typical signals of a xylopyranoside were observed with an acetate group at C-2 as followed from the downfield shift of the corresponding proton. The relative position of the oxygen function followed from the NOE's between H-2 and H-1′ (4%) and between H-15 and H-1′ (5%). Furthermore, a strong mass spectral fragment *m/z* 85 supported a free 9-hydroxy group. The NMR data are close to those of the 9-desoxy derivative [6]. The configuration at C-9 could not be determined.

The spectral data of **11** (Table 3) clearly showed that we were dealing with the corresponding 9-keto derivative. Accordingly, the signals of H-10 and H-8 as well as those of H-12 and H-13 were shifted downfield. This was further supported by the ^{13}C NMR spectrum (Table 3).

The structure of **9** followed from its ^{1}H NMR spectrum (Table 4) which was in part close to that of caryophyllene-poxide. The presence of a hydroxy angeloyloxy derivative could be deduced from the ^{1}H NMR spectrum. Spin decoupling indicated that the hydroxy group was at C-7. The angeloyloxy group had to be placed at C-15 as the methyl signal of caryophyllenepoxide (*s*, δ1.20) was replaced by a pair of doublets at δ4.09 and 4.60. The configuration at C-7 followed from the NOE between H-7, H-5α (7%) and H-8α (5%).

The ^{1}H NMR spectrum of **12** (Table 5) indicated the presence of a trisubstituted benzene derivative. Spin decoupling led to a sequence which only agreed with the structure **12**. The relative position of the aldehyde group followed from the chemical shifts of H-10 and H-12.

The ^{1}H NMR spectra of **16** and **17** (Table 5) were in part close to that of bisabol-1-one. The nature of the changed side chain followed from the ^{1}H NMR data. Thus **16** and **17** were *nor*-sesquiterpenes. The configuration at C-7 in **12**–**17** was not established.

Table 3. ^{1}H and ^{13}C NMR spectral data of compounds **10** and **11** ($CDCl_3$, 400 and 100.6 MHz, δ-values)

H	10	11	C	10	11
1c	5.26 *dd*	5.27 *dd*	1	116.1	116.1
1t	5.21 *dd*	5.20 *dd*	2	141.5	141.5
2	5.77 *dd*	5.77 *dd*	3	80.5	80.6
4	1.59 *m*	1.61 *m*	4	41.6	41.4
5	2.03 *m*	2.02 *m*	5	22.4	22.8
6	5.20 *br t*	5.22 *br t*	6	128.1	128.8
8	2.12 *br d*	3.02 *br s*	7	131.2	130.0
9	4.42 *ddd*	—	8	48.0	55.2
10	5.15 *br d*	6.09 *br s*	9	66.0	199.5
12	1.72 *d*	1.88 *d*	10	127.4	122.9
13	1.68 *d*	2.13 *d*	11	134.9	155.9
14	1.63 *br s*	1.69 *br s*	12	25.7	27.7
15	1.36 *s*	1.36 *s*	13	18.2	20.7
1′	4.63 *d*	4.64 *d*	14	16.1	16.3
2′	4.72 *dd*	4.71 *dd*	15	22.9	22.8
3′	3.61 *dd*	3.62 *dd*	1′	116.1	116.2
4′	3.69 *ddd*	3.70 *ddd*	2′	70.0	70.0
$5'_1$	4.08 *dd*	4.08 *dd*	3′	73.1	72.0
$5'_2$	3.33 *dd*	3.33 *dd*	4′	73.9	73.7
OAc	2.13 *s*	2.13 *s*	5′	63.8	63.7
			OAc	170.5	170.4
				21.0	21.0

J [Hz]: 1c,1t = 1; 1c,2 = 11; 1t,2 = 17.5; 5,6 = 7; 10,12 = 10,13 ~ 1.5; 1′,2′ = 5.5; 2′,3′ = 7; 3′,4′ = 7.5; 4′,$5'_2$ = 4.5; 4′,$5'_2$ = 7.5; $5'_1$,$5'_2$ = 12 (compound **10**: 8,9 = 9,10 ~ 8).

Table 4. ^{1}H NMR spectral data of compound **9** ($CDCl_3$, 400 MHz, δ-values)

H		H	
1	2.70 *br ddd*	12	4.90 *br s*
3α	2.32 *m*	12′	5.05 *br s*
3β	2.17 *m*	13	1.01 *s*
4α	2.32 *m*	14	1.04 *s*
4β	1.46 *m*	15	4.09 *d*
5α	3.01 *dd*	15′	4.60 *d*
7α	3.26 *m*	OAng	6.11 *qq*
8α	1.92 *m*		2.01 *dq*
8β	1.66 *m*		1.92 *dq*
9	1.68 *m*	OH	2.52 *d*
10	1.71 *dd*		
10′	1.60 *dd*		

J [Hz]: 1,9 = 1,10 = 8.5; 1,10′ = 11; 4α,5 = 4.5; 4β,5 = 10,10′ = 11; 15,15′ = 13; OAng: 3,4 = 7; 3,5 = 4,5 = 1.5.

Table 5. ^{1}H NMR spectral data of compounds **12**, **16** and **17** (400 MHz, $CDCl_3$, δ-values)

H	12	16	17
1	—	2.15 *m*	2.15 *m*
3	6.67 *br s*	5.85 *ddq*	5.87 *ddq*
5	6.74 *br s*	2.30 *m*	2.30 *m*
6	7.04 *d*	1.93 *m* 1.77 *m*	1.93 *m*
7	2.99 *tq*	2.30 *m*	2.52 *m*
8	2.05 *m*	1.50 *m*	2.15 *m*
8′	1.77 *ddd*		
9	5.09 *ddd*	1.70 *m*	6.75 *dt*
10	6.61 *dq*	2.43 *t*	6.07 *dt*
12	9.47 *s*	2.13 *s*	2,24 *s*
13	1.83 *br s*	—	—
14	1.38 *d*	0.80 *d*	0.84 *d*
15	2.29 *br s*	1.92 *br s*	1.93 *br s*

J [Hz]: Compound **12**: 5,6 = 8; 7,14 = 7; 7,8 = 7,8′ ~ 3; 8,8′ = 13; 8′,9 = 2.5; 9,10 = 7.5; 10,13 = 1.5; compounds **16** and **17**: 1,3 = 2,15 = 1.5 (compound **16**: 9,10 = 7; compound **17**: 8,9 = 7; 8,10 = 1.5; 9,10 = 16).

Table 6. ^{1}H NMR spectral data of compounds **30** and **31** (400 MHz, $CDCl_3$, δ-values)

H	30	31*	
1	4.06	4.10	*ddd*
1′	3.19	3.30	*dd*
2	3.74	4.81	*tt*
3	2.17	2.18	*m*
3′, 4	1.48	1.57	*m*
4′	1.84	1.86	*m*
5	3.87	3.91	*m*
6	6.17	6.18	*dd*
7	5.93	5.93	*dd*
11	7.18	7.18	*dd*
12	6.97	6.97	*dd*
13	7.24	7.24	*dd*

*OSen 5.64 *qq*, 2.16 *d*, 1.86 *d* (*J* [Hz]: 2,4 = 2,5 = 1.5). *J* [Hz]: 1,1′ = 11; 1,2 = 2,3 = 5; 1,3 = 2; 1′,2 = 2,3′ = 10; 5,6 = 5; 5,7 = 1.5; 6,7 = 16; 11,12 = 3.5; 11,13 = 1; 12,13 = 5.

The aerial parts of *Chaetanthera euphrasioides* (DC.) Meyen gave the diterpene **18**. The structure followed from its ^{1}H NMR spectrum (Experimental) which showed that a clerodane derivative with acetoxy groups at C-15 and C-17 was probably present. All signals could be assigned by spin decoupling. The chemical shifts of H-3, H-18 and H-1 require a 2-keto group. The stereochemistry was determined by the NOEs between H-19 and H-10 (5%), between H-17 and H-10 (2%), between H-20 and H-8 (7%) and between H-15 and H-16 (5%). The absolute configuration was not determined.

The aerial parts of *Ch. chilensis* (DC.) var. *tenuifolia* (Gill. ex D. Don) Cabr. gave amyrin, oleanolic acid and the thiophene derivatives **30** and **31**.

The structure of **30** followed from its ^{1}H NMR spectrum (Table 5). The signals at δ 6.97, 7.18 and 7.24 indicate the presence of a monosubstituted thiophene while the UV maxima at 308 and 292 nm require a conjugation with an ynene group. Spin decoupling supported this assumption and showed further that a tetrahydropyrane moiety was present. The stereochemistry followed from the couplings of H-2, H-5 and H-6. The ^{1}H NMR data of **31** (Table 5) only differed from those of **30** by the downfield shift of the H-2 signal and the presence of the typical senecioate signals. So far similar acetylenic compounds have not been reported. The hydroxy epoxide **29** is probably the precursor of these thiophenes. We have named compound **30** chaetantherol, its absolute configuration was not determined.

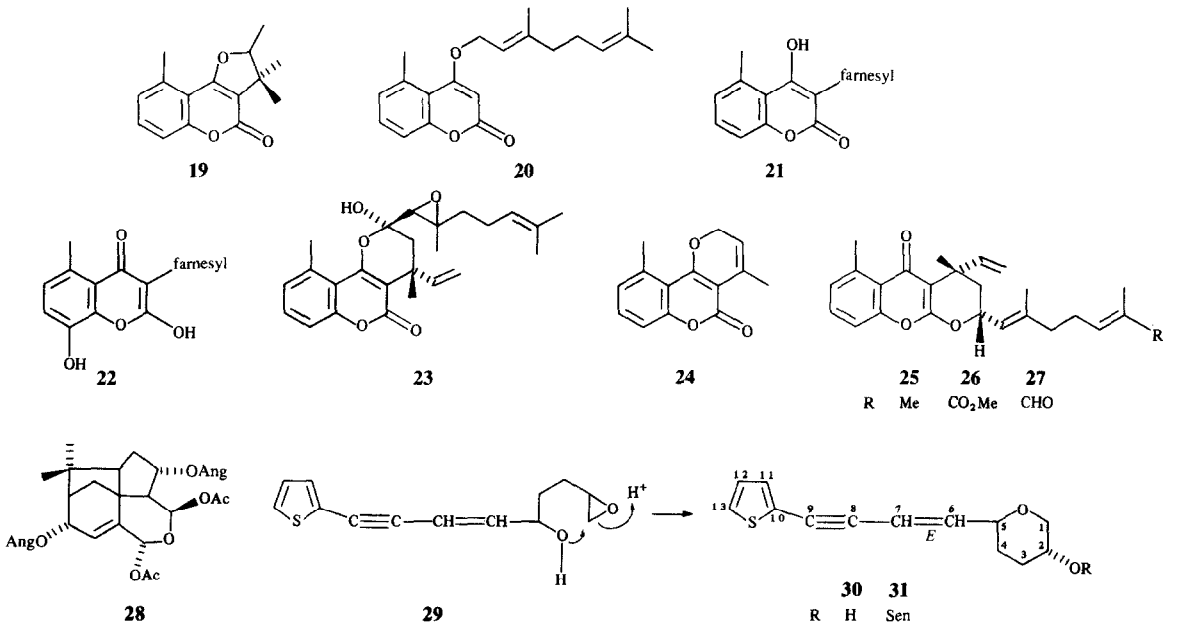
The thiophenes **30** and **31** were also isolated from the aerial parts of *Chaetanthera chilensis* (DC.) var. *argentea* (Phil.) Cabr. while *Ch. lycopodioides* (Remy) Cabr. and *Ch. ciliata* R. et P. only gave triterpenes. The chemistry of the genus *Chaetanthera* is not homogeneous. The isolation of a clerodane is remarkable as diterpenes are so far not reported from the whole tribe.

The aerial parts of *Mutisia subulata* (R. et P.) fma. *rosmarinifolia* (P. et E.) Cabr. gave lupeol, taraxasterol, β-amyrin and the characteristic 5-methylcoumarins **19** [7] and **20** [8]. From *M. oligondon* P. et E. the 5-methylcoumarin **21** [9] and the corresponding chromone **22** [9] were isolated, while *M. decurrens* Cav. var. *decurrens* only gave lupeol and lupeylacetate.

Leuceria millefolia Dusen et Skottsb. gave the isocedrene derivative **28** [10] while five other species gave no characteristic compounds.

Nassauvia digitata Wedd gave the 5-methylcoumarins **22** [9] and **23** [11]. This type of characteristic compounds were also present in *Nassauvia aculeata* (Less.) P. et E. var. *aculeata*. In addition to the coumarin **24** [11] the chromones **25** [12], **26** [12] and **27** [11] were isolated.

The new results on the chemistry of the tribe *Mutisieae* again show that very special natural products are characteristic for the tribe. However, as reported previously, it is often found that several species of a certain genus do not accumulate these typical compounds and only widespread triterpenes can be detected. In the case of *Poly-*



19 20 21 22 23 24 25 26 27 28 29 30 31

Table 7. Compounds isolated from the investigated species

Species (vouchers and locations)	Aerial parts	Isolated compounds
Polyachyrus sphaerocephalus (Niemeyer 8977, region de Tarapaca, Chile, May 1989)	268 g	24 mg acetoxytremetone, 65 mg **1**, 40 mg **2**, 60 mg **3**, 60 mg **4**, 40 mg **5**, 45 mg **6**, 15 mg **7**, 15 mg **8**
P. fuscus (Rodriguez 191, region de Concepcion, Chile, March 1987)	1000 g	330 mg **9**, 600 mg **10**, 600 mg **11**, 70 mg **12**, 20 mg **13**, 150 mg **14**, 300 mg **15**, 50 mg **16**, 500 mg **17**, 150 mg desoxyperezone, 800 mg lupeol, 280 mg taraxasterol
Chaetanthera euphrasioides (Niemeyer 8909, region de Liberator Bernardo O'Higgins, Chile, February 1989)	126 g	5 mg **18**, 12 mg *p*-hydroxybenzaldehyde
Ch. lycopodioides (Niemeyer 8802, region Metropolitana, Chile, December 1988)	80 g	10 mg sitosterol
Ch. chilensis var. *tenuifolia* (Bittner 1917, Laguna la Invernada, Chile, March 1987)	60 g	11 mg **30**, 6 mg **31**, 20 mg amyrin, 20 mg oleanolic acid
Ch. chilensis var. *argentea* (Bittner 1888, Pangal del Laja, Chile, March 1987)	30 g	8 mg **30**, 6 mg **31**
Ch. ciliata (Bittner 1890, Cabrero, Chile, March 1987)	11 g	triterpenes
Leuceria glacialis (Poepp. ex Less.) Reiche (Niemeyer 8934, region del Maule, Chile, February 1989)	330 g	50 mg lupeol, 50 mg taraxasterol
L. bridgesii H. et A. (Niemeyer 8808, region Metropolitana, Chile, December 1989)	610 g	85 mg lupeol, 85 mg taraxasterol
L. gayana (Remy) Reiche (Niemeyer 8902, region Liberator Bernardo O'Higgins, Chile, February 1987)	308 g	130 mg lupeol, 180 mg of its acetate, 50 mg taraxasteryl acetate
L. rosea Poepp. ex Less. (Niemeyer 8903, region Liberator Bernardo O'Higgins, Chile, February 1989)	297 g	100 mg lupeol, 100 mg taraxasterol, 5 mg each of its acetates
L. millefolia (Niemeyer 8920, region del Maule, Chile, February 1989)	83 g	400 mg **28**
L. lithospermifolia (Less.) Reiche (Niemeyer 8941, region del Bio Bio, Chile, February 1989)	725 g	100 mg lupeol, 130 mg of its acetate, 100 mg taraxasterol, 130 mg of its acetate
Mutisia subulata (Niemeyer 8901, region Liberator Bernardo O'Higgins, Chile, February 1989)	366 g	55 mg lupeol, 50 mg taraxasterol, 20 mg amyrin, 35 mg **19**, 100 mg **21**
M. decurrens (Niemeyer 8937, region del Maule, Chile, February 1989)	690 g	10 mg, lupeol, 15 mg of its acetate
M. oligodon (Niemeyer 8940, region del Bio Bio, Chile, February 1989)	557 g	500 mg **21**, 1100 mg **22**, 60 mg arbutin
Nassauvia aculeata (Niemeyer 8936, region del Maule, Chile, February 1989)	625 g	100 mg lupeol, 10 mg spathulenol, 200 mg **25**, 100 mg **26**, 900 mg **27**, 50 mg umbelliferon
N. digitata (Rodriguez 1915, region de Nuble, Chile, June 1989)	88 g	100 mg **21**, 50 mg **23**

achyrus fuscus, it was interesting to see that this species produces different compounds in two collections, perhaps duc to the locality or the time of collection.

EXPERIMENTAL

The air-dried aerial parts were extracted with MeOH–Et_2O–petrol (1:1:1). The defatted extracts (MeOH, −20°) were separated as reported previously [13]. The isolated compounds are presented in Table 7. Final purification of new compounds are given along with the spectral data (HP1 = MeOH–H_2O, 7:3, HP2 = MeOH–H_2O, 3:1, HP3 = MeOH–H_2O, 13:7). Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

10α,14-*Dihydroxygermacra*-4,11(13)-*dien*-1-*one* (**1**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1720 (C=O); MS *m/z* (rel. int.): 252.173 $[M]^+$ (3) (calc. for $C_{15}H_{24}O_3$: 252.173), 234 $[M-H_2O]^+$ (8), 221 $[M-CH_2OH]^+$ (10), 121 (74), 107 (83), 93 (85), 83 (100); HP1: R_t 14.7 min.

1α,14-*Dihydroxy*-5,10-*bisepieudesma*-4(15),11(13)-*diene* (**2**). Oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH); MS *m/z* (rel. int.): 218.167 $[M-H_2O]^+$ (64) (calc. for $C_{15}H_{22}O$: 218.167), 205 $[M-CH_2OH]^+$ (58), 187 $[205-H_2O]^+$ (90), 145 (96), 131 (100), 105 (77), 91 (82); ^{13}C NMR ($CDCl_3$, C-1–C-15): 81.1, 31.9, 34.1, 147.9, 40.6, 25.3, 38.0, 22.6, 26.3, 42.2, 146.4, 111.0, 22.4, 60.1, 106.8; HP1: R_t 17.6 min.

14-*Acetoxy*-1α-*hydroxy*-5,10-*bis*-epi-*eudesma*-4(15),11(13)-*diene* (**3**). Oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1745 (OAc); MS *m/z* (rel. int.): 278.188 $[M]^+$ (1.3) (calc. for $C_{17}H_{26}O_3$: 278.188), 218 $[M-HOAc]^+$ (20), 193 (100), 177 (51), 151 (73), 109 (43); TLC (Et_2O–petrol, 1:4, ×2) R_f 0.5.

1α-*Acetoxy*-14-*hydroxy*-5,10-*bis*-epi-*eudesma*-4(15),11(13)-*diene* (**4**). Oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (OAc); MS *m/z* (rel. int.): 278.188 $[M]^+$ (0.8) (calc. for $C_{17}H_{26}O_3$: 278.188), 218 $[M-HOAc]^+$ (23), 58 (100); TLC (Et_2O–petrol, 3:7, ×2) R_f 0.65.

1α,14-*Dihydroxy*-5,10-*bis*-epi-*eudesma*-3,11(13)-*diene* (**5**). Oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 218.167 $[M-H_2O]^+$ (13) (calc. for $C_{15}H_{22}O$: 218.167), 200 $[218-H_2O]^+$ (12), 187 $[218-CH_2OH]^+$ (72), 145 (82), 131 (100), 105 (66), 91 (65); HP1: R_t 18.9 min.

14-*Acetoxy*-1α-*hydroxy*-5,10-*bis*-epi-*eudesma*-3,11(13)-*diene* (**6**). Oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1745 (OAc); MS *m/z* (rel. int.): 278.188 $[M]^+$ (1.3) (calc. for $C_{17}H_{26}O_3$: 278.188), 209 (33), 193 (100), 177 (53), 151 (76), 109 (42); HP1: R_t 29.1 min.

4α,14-*Epoxy*-1α-*hydroxy*-5,10-*bis*-epi-*eudesma*-11(13)-*ene* (**7**). Oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 218 $[M-H_2O]^+$ (6), 176 (23), 105 (44), 91 (52), 659 (64), 57 (100); TLC (Et_2O–petrol, 3:7, ×2) R_f 0.20.

1α-*Acetoxy*-4α,14-*epoxy*-5,10-*bis*-epi-*eudesma*-11(13)-*ene* (**8**). Oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1750 (OAc); MS *m/z* (rel. int.): 218 $[M-HOAc]^+$ (2), 193 (100), 177 (45), 109 (45); TLC (Et_2O–petrol, 3:7) R_f 0.50.

15-*Angeloyloxy*-7β-*hydroxycaryophyllenepoxide* (**9**). Oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1730 (C=CCO_2R); MS *m/z* (rel. int.): 334 $[M]^+$ (0.3), 234 $[M-AngOH]^+$ (2.3), 151 (17), 83 $[RCO]^+$ (100); TLC (Et_2O–petrol, 3:1) R_f 0.65.

9-*Hydroxy*-3-O-(2-O-acetyl-β-D-*xylopyranosyl*)-*nerolidol* (**10**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1750 (OAc); CIMS *m/z* (rel. int.): 395 $[M+1-H_2O]^+$ (2.5), 361 $[M+1-$ketene$]^+$ (1), 221 $[M-$sugar part$]^+$ (17), 203 $[221-H_2O]^+$ (100), 175 (26), 135 (45); HP2: R_t 8.0 min.

9-*Oxo*-3-O-(2-O-*acetyl*-β-D-*xylopyranosyl*)-*nerolidol* (**11**) Gum; CIMS *m/z* (rel. int.): 411 $[M+1]^+$ (1.3), 395 $[M+1-H_2O]^+$ (0.4), 219 $[M-$sugar part$]^+$ (100); HP2: R_t 8.0 min.

2,9-*Epoxycurcumen*-12-*al* (**12**). Oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2740, 1715 (C=CCHO); MS *m/z* (rel. int.): 230.131 $[M]^+$ (26) (calc. for $C_{15}H_{18}O_2$: 230.131), 215 $[M-Mc]^+$ (4), 135 (100), 134 (54), 95 (40), 91 (31); TLC (Et_2O–petrol, 1:9) R_f 0.22.

2,11-*Dioxo*-13-nor-*bisabol*-3-*ene* (**16**). Oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1700 (C=CC=O); MS *m/z* (rel. int.): 222.162 $[M]^+$ (3) (calc. for $C_{14}H_{22}O_2$: 222.162), 137 $[M-C_5H_9O]^+$ (24), 110 $[M-C_7H_{12}O$, McLafferty$]^+$ (100), 95 (26), 82 (44), HP3: R_t 8.1 min.

2,11-*Dioxo*-13-nor-*bisabol*-3,9E-*diene* (**17**). Oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1700 (C=CC=O); MS *m/z* (rel. int.): 220.146 $[M]^+$ (12) (calc. for $C_{14}H_{22}O_2$: 220.146), 110 $[M-C_7H_{12}O$, McLafferty$]^+$ (100), HP3: R_t 9.5 min.

15,17-*Diacetoxy*-2-*oxo*-*cis*-*cleroda*-3,13*E*-*diene* (**18**). Gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (OAc), 1680 (C=CC=O); MS *m/z* (rel. int.): 282 $[M-2\times HOAc]^+$ (7), 243 (60), 229 (62), 214 (73), 200 (72), 197 (100), 183 (82), 157 (67), 101 (92), 69 (96); ^{1}H NMR ($CDCl_3$): 2.59 (*dd*, H-1), 2.72 (*dd*, H-1β), 5.89 (*br s*, H-3), 1.60 and 1.90 (*m*, H-6), 1.46 and 1.60 (*m*, H-7), 1.80 (*m*, H-8), 1.87 (*dd*, H-10), 1.13 and 1.73 (*m*, H-11), 1.96 and 2.04 (*m*, H-12), 5.34 (*tq*, H-14), 4.57 (*d*, H-15), 1.70 (*br s*, H-16), 4.19 (*m*, H-17), 1.97 (*d*, H-18), 1.27 (*s*, H-19), 0.89 (*s*, H-20), 2.06 (*s*, OAc, 6H); *J* [Hz]: 1,10 = 3.5; 1β,10 = 6.5; 1,1β = 18; 3,18 = 14,16 = 1.5; 14,15 = 7.

Chaetantherol (**30**). Oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1600, 950 (tr CH=CH); UV (Et_2O): 308, 292 nm; MS *m/z* (rel. int.): 234.071 $[M]^+$ (63) (calc. for $C_{13}H_{14}O_2S$: 234.071), 189 (21), 149 (63), 134 (68), 111 (72), 97 (82), 83 (86), 71 (88), 55 (100); TLC (Et_2O–petrol, 1:1) R_f 0.45.

Chaetanterolsenecioate (**31**). Oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2230 (C≡C), 1720, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 316.113 $[M]^+$ (6) (calc. for $C_{18}H_{20}O_3S$: 316.113), 216 $[M-RCO_2H]^+$ (12), 198 (24), 176 (22), 149 (24), 83 $[RCO]^+$ (100); TLC (Et_2O–petrol, 1:6) R_f 0.55.

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