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ENT-CLERODANES AND OTHER CONSTITUENTS FROM BOLIVIAN *BACCHARIS* SPECIES

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Key Word Index—*Baccharis* species; Compositae; diterpenes; *ent*-clerodanes; *ent*-labdanes; sesquiterpenes; guaiane, eudesmane, cadinane, bisabolane and germacrane derivatives.

Abstract—Investigation of seven Bolivian *Baccharis* species afforded in addition to known compounds 17 *ent*-clerodane, 10 *ent*-labdane, two bisabolene, a germacrane, a cadinane, a guaiane and a *p*-coumaric acid derivative. In one case the *ent*-labdane was linked with a bisabolene derivative via a malonate group. The structures were elucidated mainly by high field NMR techniques.

INTRODUCTION

From the large American genus *Baccharis* many of the 400 species already have been studied chemically. Recently, we have studied several representatives from Argentina [1]. We now have investigated some species from Bolivia and the results are discussed in this paper.

RESULTS AND DISCUSSION

Baccharis boliviensis (Wedd.) Cuatr. (previously *Heterothalamus boliviensis* Wedd.) is widely distributed from Peru across Bolivia to Chile and Argentina [2]. The extract of the aerial parts afforded in addition to known compounds (see Experimental) the *ent*-clerodane derivatives **1**–**9** and **14**–**20** as well as the *ent*-labdanes **10**–**13**, the sesquiterpenes **21**–**23** [3] and the prenylated coumaric acids **24** [4] and **25** [5].

The structure of the acid **1**, which we have named bacchabolivic acid, followed from its ^{1}H NMR spectrum (Table 1) which is very similar to that of the corresponding aldehyde from *B. hutchisonii* [6] and also to that of the acid where the furan moiety was replaced by a 15-acetoxy-16-hydroxy side chain [1]. However, in the case of the acid **1** and its Me ester **1a** all signals could be assigned by spin decoupling provided the ^{1}H NMR spectrum in deuteriobenzene was used. The ^{13}C spectrum further established the structure (see Experimental).

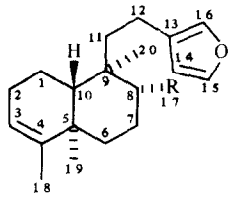
The ^{1}H NMR spectra of **3**Ac and **3a**Ac, obtained by acetylation of the natural product (Table 2), clearly showed that derivatives of **1** were present. In agreement with the molecular formula of **3**Ac ($C_{31}H_{42}O_{10}$) a triacetate of a C_5-sugar derivative was very likely. Inspection of the ^{1}H NMR data showed that the acid was esterified with the 1′-*O*-position of a xylopyranoside as followed from the vicinal couplings of the sugar moiety where all signals could be assigned by spin decoupling. Furthermore the values agreed well with those of other xylopyranosides from *Baccharis* species [1]. In the spectrum of the diacetate **3a**Ac (Table 2) the position of the free hydroxy group could be readily assigned by spin decoupling. Due to the missing 2-*O*-acetyl group the chemical shifts H-1′–H-3′ differed from those of **3**Ac.

The ^{1}H NMR spectrum of **2a**, obtained by esterification of the natural product (Table 1), agreed with the presence of a succinate of an *ent*-clerodane. This was supported by the mass spectrum which showed in addition to the required molecular formula ($C_{25}H_{36}O_5$) elimination of methyl succinate. The ^{1}H NMR spectrum was in part close to that of **1**. However, the H-8 double doublet was replaced by an upfield shifted multiplet at δ 1.75. Irradiation of the latter collapsed a pair of double doublets at δ 4.28 and 3.84 to doublets. Accordingly, an oxygen function was at C-17. The observed couplings of H-8 indicated the configuration at C-8. Similar diterpene succinates have been reported from other *Baccharis* species [1, 7].

The ^{1}H NMR spectra of **4** and of the corresponding acetate **4**Ac (Table 1) showed that again a furanoclerodane was present as in addition to the furan signals two methyl singlets and two methyl doublets were visible. Spin decoupling indicated that in the spectrum of **4**Ac the methyl doublet at δ 0.93 was coupled with a broadened quartet at δ 2.30 which itself showed a *W*-coupling with the angular methyl group at C-5. Further spin decouplings allowed the assignment of H-2, H-1 and H-10. Accordingly, the acetoxy group was at C-2. The configuration followed from the couplings of H-2.

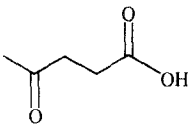
The ^{1}H NMR spectra of **5** and its acetate **5**Ac (Table 1) indicated the presence of a furanoclerodane with vicinal oxygen functions at C-2–C-4. The configuration at C-2 and C-3 followed from the couplings while the complete stereochemistry was determined by NOE difference spectroscopy. Clear effects were observed between H-20 and H-11, between H-17, H-1α and H-11, between H-19, H-18 and H-1α, between H-3, H-2 and H-18 as well as between H-2, H-3 and H-10 (the first signal is always the irradiated one).

The ^{1}H NMR spectrum of **6** (Table 1) was in part close to that of **5**. However, the chemical shifts of H-2 and especially H-3 differed clearly. An epoxide was indicated by a broadened singlet at δ 3.07 which showed a small

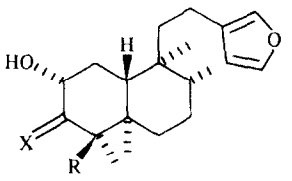


1 R = CO_2H

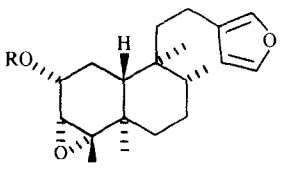
2 R = CH_2O



3 R = CO_2A^*

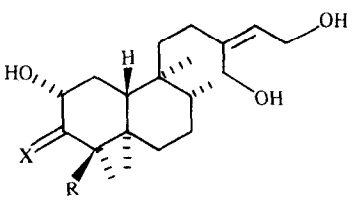


	4	**5**
R	H	OH
X	O	αOH,H

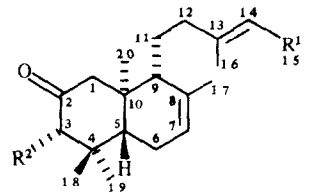


6 R = H

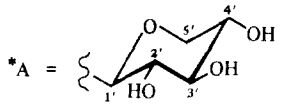
7 R = Me



	8	**9**
R	OH	H
X	αOH,H	O



	10	**11**	**12**	**13**
R^1	CH_2OH	CHO	CHO	CHO
R^2	OH	H	OH	OH
				C-13Z



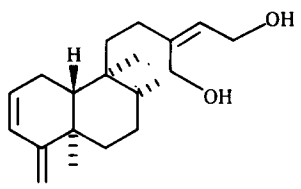
coupling with H-2 and a *W*-coupling with H-1β. The resulting stereochemistry was supported by the observed NOE's between H-2, H-3 and H-10, between H-18 and H-3 as well as between H-19 and H-1α. The ^{1}H NMR data of **7** (Table 1) indicated that this diterpene was the 2-*O*-Me ether of **6**. Accordingly, the H-2 signal was now shifted somewhat up field and more sharp. Furthermore a methoxy singlet at δ 3.46 was visible.

The ^{1}H NMR spectra of **8**Ac and **8a**Ac (Table 3) showed that in the natural pentahydroxy derivative the configurations at C-2–C-4 were the same as in compound **5**. Most likely the triol **5** is biogenetically formed by hydrolysis of the epoxide **6** from the less hindered β-side.

The ^{1}H NMR spectrum of **8b**Ac (Table 3) indicated that now a 4,15,16-triacetate of **8** was present. Accordingly, the H-18 signal was shifted downfield while the H-2 signal was shifted up field if compared with the shift in the spectrum of **8**Ac. The tetraacetate of **8** has been prepared from the pentahydroxy derivative isolated from a *Goyazianthus* species [8].

The ^{1}H NMR spectrum of the triacetate **9**Ac (Table 3) was in part close to those of **8**Ac and **4**. Thus, the natural product was the triol **9** which most probably is the precursor of **4**. The positive Cotton-effect of **9**Ac agreed with the presence of *ent*-clerodanes. Therefore, we propose, as in all *Baccharis* species, *ent*-clerodanes for the new compounds.

The ^{1}H NMR spectra of **10**–**13** (Table 4) clearly showed that we were dealing with labdane derivatives, only differing in the side chain, as three methyl singlets and two olefinic methyl signals were visible which excluded the presence of clerodanes. The spectrum of **10** and its acetate **10**Ac (Table 4) showed a narrowly split doublet at δ 3.96 which collapsed to a singlet on irradiation of the Me singlet at δ 0.78 (H-19). Accordingly, a 3α-hydroxy group was present. The absence of further couplings of H-3 and the chemical shift of a pair of doublets at δ 2.64 and 2.21 required a 2-keto group. A negative Cotton-effect indicated the presence of an *ent*-labdane. Therefore, most likely the others also had this absolute configuration. The ^{1}H NMR spectra of **12** and **13** (Table 4) indicated that we were dealing with the corresponding isomeric aldehydes differing in the configuration of the 13,14-double bond. Accordingly, the signals of H-1, H-3 and H-18–H-20 were



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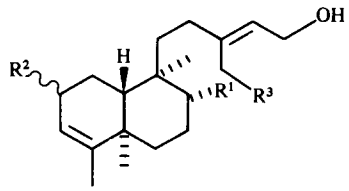
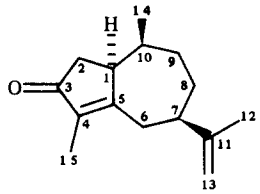


	15	**16**	**17**	**18**	**19**	**20**
R^1	Me	Me	CH_2OH	CO_2H	CH_2OA^*	Me
R^2	αOH	βOMe	H	H	H	H
R^3	H	OH	OH	OH	OH	OA^*

3α,4α epoxide



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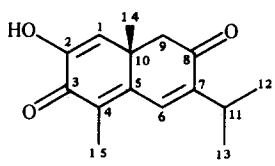

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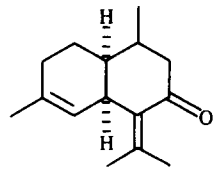

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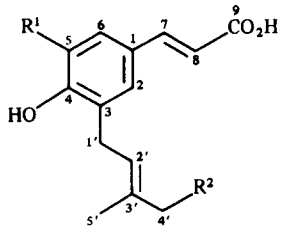
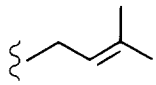


24 $R^1 = R^2 = H$

25 R^1 =  , $R^2 = H$

26 $R^1 = H$, $R^2 = OH$

nearly identical in all three compounds. The spectrum of **11** indicated that this aldehyde was the 3-desoxy derivative of **12**.

The ^{1}H NMR data of **14**Ac (Table 3) showed two methyl singlets, one methyl doublet, two acetoxy methylene signals and a pair of exomethylene proton signals. Thus, a clerodane with an exomethylene group at C-4 was very likely. Spin decoupling showed that a 2,3-double bond was also present. All data therefore agreed with the proposed structure. It cannot be excluded that **14**Ac was formed during acetylation of 2α,15,16-trihydroxy-*ent*-cleroda-3,14*E*-diene which was not isolated. Compound **15**Ac, however, was the acetate of the corresponding epoxide. The structure of the latter again followed from the ^{1}H NMR spectrum (Table 3) which was in part similar to that of **6**, only the signals of the side chain being different. The configuration at C-3 again followed from the observed *W*-coupling of H-3 with H-1β. Obviously, the stereochemistry was the same as that in the epoxide reported from a *Goyazianthus* species [8]. The configuration therefore has to be revised from 3β,4β- to 3α,4α-epoxide.

The spectral data of **16**Ac (Table 3) showed that the diacetate of 2β-methoxy-15,16-dihydroxy-*ent*-cleroda-3,13*E*-diene was present. Accordingly, the spectrum was in part close to that of similar clerodanes. The configuration at C-2 followed from the observed small couplings typical for a 2β-configuration with a quasi axial hydrogen [9].

The ^{1}H NMR spectrum of **17**Ac (Table 3) showed that a 15,16,17-triacetoxy clerodane derivative must be present. Accordingly, the spectrum was in part similar to that of **2a**; the signals for the side chain were obviously different. The couplings of H-8 indicated identical configuration at this centre. Accordingly, the data were close to those of the corresponding 16-desoxy compounds [10]. The spectrum of **19**Ac (Table 2) also was related to that of **17**Ac. The spectrum of **19**Ac (Table 2) also was related to that of **17**Ac. However, the chemical shifts of H-17 were different and the typical signal of an acetylated β-xylopyranoside was present. Accordingly, the natural compound was the β-xylopyranoside of **19**.

The ^{1}H NMR spectrum of **18**Ac (Table 3) was in part very similar to that of **1**. However, again the signals of the side chain indicated the absence of the furan moiety which was replaced by the 15,16-oxygenated side, most likely the precursor of **1**.

The spectral data of **20**Ac (Table 2) showed that again an acetylated β-xylopyranoside was present. Inspection of the chemical shifts of H-15 and H-16 clearly showed that the sugar was linked with the 16-hydroxy group. Therefore, the H-17 signal was now a methyl doublet at δ 0.79. The configuration of the 13,14-double bond in the diterpenes **8**–**10** and **14**–**20** followed from the chemical shifts of H-14–H-16 and from the NOE's.

The ^{1}H NMR spectrum of **21** (see Experimental) was in part close to that of a guaianone from a *Pleocarpus* species [11]. However, small differences in the chemical

Table 1. ^{1}H NMR spectral data of **1**, **1a**, **2a**, **4**, **4**Ac, **5**, **6** and **7** (400 MHz, $CDCl_3$, δ-values)

H	1†	1a	2a‡	4§	4Ac§	5	6	7
1α	1.49 *m*	1.47 *m*	1.45 *m*	+	1.83 *m*	1.51 *m*	1.49 *m*	1.50 *m*
1β	1.61 *m*	1.61 *m*		+	2.12 *m*			
2α	2.10 *m*	2.09 *m*	2.08 *br d*	—	—	—	—	—
2β	2.00 *m*	2.01 *m*	2.00 *m*	4.09 *br dd*	5.14 *br dd*	4.03 *ddd*	3.90 *br dd*	3.56 *ddd*
3	5.22 *br s*	5.21 *br s*	5.21 *br s*	—	—	3.57 *d*	3.07 *br s*	3.11 *br s*
6α	1.82 *dt*	1.80 *dt*	1.71 *dt*			1.60 *m*		
6β	1.19 *dt*	1.18 *dt*	1.18 *dt*		1.55–1.73 *m*	1.40 *m*	1.65–1.45 *m*	1.65–1.45 *m*
7α	1.99 *dq*	2.01 *dq*	+	1.55–1.80 *m*				
7β	1.73 *m*	1.65 *dq*	+			1.5–1.70 *m*		
8	2.58 *dd*	2.58 *dd*	1.75 *m*		1.63 *m*			
10	1.49 *m*	1.47 *m*	1.45 *m*		1.83 *m*	1.85 *dd*	0.98 *br d*	1.00 *br d*
11	1.78 *m*	1.75 *dt*	1.75 *m*	1.65 *m*	1.63 *m*	1.65 *m*	1.60 *m*	1.60 *m*
11′	1.63 *m*	1.39 *ddd*	1.60 *m*	1.45 *m*	1.45 *m*	1.51 *m*	1.49 *m*	1.50 *m*
12	2.53 *dt*	2.52 *dt*	2.38 *dt*	2.45 *m*	2.44 *m*	2.35 *dt*	2.29 *dt*	2.32 *dt*
12′	2.26 *dt*	2.24 *dt*	2.28 *dt*	2.33 *m*	2.35 *m*	2.25 *dt*	2.09 *dt*	2.13 *dt*
14	6.28 *br s*	6.26 *br s*	6.28 *br s*	6.28 *br s*	6.29 *br s*	6.27 *br s*	6.23 *br s*	6.25 *br s*
15	7.33 *t*	7.34 *t*	7.34 *t*	7.36 *t*	7.36 *t*	7.34 *t*	7.34 *t*	7.35 *t*
16	7.21 *br s*	7.20 *br s*	7.21 *br s*	7.23 *br s*	7.24 *br s*	7.20 *br s*	7.19 *br s*	7.20 *br s*
17	—	—	4.28 *dd*	0.86 *d*	0.87 *d*	0.81 *d*	0.80 *d*	0.81 *d*
			3.84 *dd*					
18	1.60 *q*	1.60 *q*	1.60 *q*	0.97 *d*	0.93 *d*	1.30 *s*	1.21 *s*	1.22 *s*
19	1.07 *s*	0.96 *s*	1.02 *s*	0.76 *s*	0.77 *s*	1.10 *s*	1.06 *s*	1.07 *s*
20	0.95 *s*	0.80 *s*	0.80 *s*	0.72 *s*	0.74 *s*	0.75 *s*	0.67 *s*	0.88 *s*
OMe (OAc)	—	3.66 *s*	3.69 *s*	—	2.17 *s*	—	—	3.46 *s*

*Obscured multiplets; †in C_6D_6: H-1α 1.34 *dddd*, H-1β 1.46 *br dd*, H-7β 1.60 *dq*, H-10 1.39 *br d*; ‡H-2′,3′ 2.61 *br s*, H-1α 1.35 *dddd*, H-1β 1.50 *br dd*, H-10 1.43 *d*; §H-4 2.30 *br q*.

J [Hz]: 14, 15 = 15, 16 = 1.5; 11, 11′ = 11, 12 = 11′, 12′ = 12, 12′ = 13; 11, 12′ = 11′, 12 = 4.5; compounds **1**, **1a** and **2a**: 6α, 6β = 6β, 7α = 13; 6α, 7α = 6α, 7β = 6β, 7β ~ 3; (compounds **1** and **1a**: 7α, 8 = 12; 7β, 8 = 3; compound **2a**: 8, 17 = 3.5; 8, 17′ = 8; 17, 17′ = 11); compounds **4** and **4**Ac: 1α, 2 = 11; 1β, 2 = 7; 8, 17 = 7; compound **5**: 1α, 2 = 10; 1β, 2 = 4; 1α, 10 = 10; 1β, 10 = 3; 2, 3 = 3.5; compounds **6** and **7**: 1α, 2 = 11; 1β, 2 = 5; 1β, 3 = 1.5; 1α, 10 = 11.

shifts and couplings indicated a different stereochemistry. All signals could be assigned by spin decoupling and the stereochemistry was determined from the observed NOE's. Clear effects were observed between H-7 and H-1, between H-9α, H-10, H-7 and H-1 as well as between H-10 and H-1, between H-9α, H-10, H-7 and H-1 as well as between H-10 and H-1. Thus, H-1, H-7 and H-10 were all on the same side. Therefore, the stereochemistry also differed from that of a synthetic ketone [12]. The ^{13}C NMR data supported the structure.

The ^{1}H NMR spectrum of **22** (see Experimental) showed only a few signals. In agreement with the molecular formula ($C_{15}H_{18}O_3$) a highly unsaturated sesquiterpene was present. In addition to four methyl signals only a pair of doublets at δ 2.65 and 2.41, the coupling partner of the two methyl doublets, and three low field singlets were visible. One of the latter disappeared after deuterium exchange. All data best agreed with an eudesmane derivative with keto groups at C-3 and C-8. The position of the enolic hydroxy group followed indirectly from the observed NOE between H-14 and H-1. Thus, this compound was an eudesm-4,6-diene-2,3,8-trione where the 2-keto group was present completely in the enol form. The CD-curve showed a negative Cotton-effect at 378 nm and positive ones at 329 and 266 nm. A definite assignment of the absolute configuration therefore is difficult. However, the proposed one is most likely as most eudesmanes have this configuration.

The aerial parts of *B. obtusifolia* HBK gave baccharis oxide, *epi*-friedelinol, the prenylated coumaric acid derivatives **24** and **25**, the flavonol rhamnocitrin [13] and the *ent*-clerodanes **27** [14], **28** [15] and **29** [16] as clearly followed from the detailed analysis of the ^{1}H NMR spectra which are presented in Table 5 as no complete sets of data are available especially for **27** where one signal must be wrong (7.58 *t*, *J* = 5 Hz?).

The aerial parts of *B. dracunculifolia* DC gave in addition to known compounds rhamnocitrin [13], the *p*-coumaric acid derivatives **24** [4] and **25** [5] and a further derivative which turned out to be **26**. The ^{1}H NMR spectrum (see Experimental) was close to that of the corresponding prenyl derivative [17]. Therefore, again an *E*-configurated double bond was proposed.

The aerial parts of *B. trimera* (Less.) DC has been investigated previously [18]. A reinvestigation afforded in addition to eupatorin, isolated previously [18], the malonates **30** and **31**, which were purified as their Me esters. The latter clerodane already had been prepared by acid catalysed methanolysis of a dimer [1]. The ^{1}H NMR spectrum of **30a** indicated that this clerodane also was a 18-hydroxymalonate. However, the signals of the side chain were replaced by those of a 15,16-diacetoxy deriva-

Table 2. ^{1}H NMR spectral data of 3Ac, **3a**Ac, **19**Ac and **20**Ac (400 MHz, $CDCl_3$, δ-values)

H	3Ac	3aAc	19Ac*	20Ac
3	5.21 *br s*	5.21 *br s*	5.17 *br s*	5.18 *br s*
6α	1.81 *dt*	1.82 *dt*	+	+
6β	1.17 *dt*	1.19 *dt*	+	+
7α	2.00 *m*	2.03 *m*	+	+
7β	1.75 *m*	1.73 *m*	+	+
8	2.59 *dd*	2.63 *dd*	+	1.41 *m*
10	1.47 *m*	1.47 *m*	+	1.32 *br d*
12	2.46 *dt*	2.54 *dt*	2.00 *m*	2.00 *m*
12′	2.27 *dt*	2.28 *dt*		
14	6.28 *br s*	6.30 *br s*	5.52 *br t*	5.51 *br t*
15	7.34 *t*	7.36 *t*	4.65 *br d*	4.62 *dd*, 4.58 *dd*
16	7.21 *br s*	7.24 *br s*	4.61 *br s*	4.25 *br d*, 4.17 *br d*
17	—	—	3.54 *m*	0.79 *d*
18	1.59 *br s*	1.60 *br s*	1.55 *br s*	1.57 *br s*
19	1.07 *s*	1.07 *s*	0.98 *s*	0.98 *s*
20	0.95 *s*	0.95 *s*	0.73 *s*	0.79 *s*
1′	5.77 *d*	5.57 *d*	4.45 *d*	4.46 *d*
2′	5.00 *dd*	3.50 *br t*	4.88 *dd*	4.90 *dd*
3′	5.20 *t*	5.05 *t*	5.13 *t*	5.14 *t*
4′	4.96 *ddd*	4.94 *ddd*	4.91 *ddd*	4.93 *ddd*
$5'_1$	4.12 *dd*	4.08 *dd*	4.09 *dd*	4.11 *dd*
$5'_2$	3.50 *dd*	3.45 *dd*	3.35 *dd*	3.36 *dd*
OAc	2.06 *s*	2.10 *s*	2.05 *s*	2.05 *s*
	2.03 *s*	2.05 *s*	2.04 *s*	2.06 *s* (6H)
	1.92 *s*		2.03 *s*	2.02 *s*
			2.02 *s*	
			2.01 *s*	

*C_6D_6: H-8 1.70 *m*, H-17 3.66 *dd*, H-17′ 3.55 *dd*.

†Overlapped multiplets.

J [Hz]: 6α,6β = 6β,7α = 13; 6α,7α = 6β,7β = 3; 7α,8 = 12; 7β,8 = 4.5; 1′,2′ = 7; 2′,3′ = 3′,4′ = 8.5; 4′,$5'_1$ = 5; 4′,$5'_2$ = 8.5; $5'_1$,$5'_2$ = 12; compounds 3Ac and **3a**Ac: 11,12 = 12,12′ = 11′,12′ = 13; 11,12 = 11′,12 = 5; 14,15 = 15,16 = 1; compounds **19**Ac and **20**Ac: 14,15 = 7; (compound **19**Ac: 8,17 = 10; 8,17′ = 5; 17,17′ = 10; compound **20**Ac: 8,17 = 6; 15,15′ = 16,16′ = 12).

tive. The corresponding signals could be assigned in a mixture of $CDCl_3$ and C_6D_6. Furthermore spin decoupling showed that a broadened narrowly split quartet was due to the presence of an axial hydroxy group at C-7. The configuration at C-13 could not be determined. The 15,16-lactones reported previously [18] were not isolated. However, **30** and **31** are closely related to these lactones.

The aerial part of *B. sternbergiana* Steud. (male plant) gave in addition to **24** and lachnophyllum lactone [19] the *ent*-labdanes **32**–**35**. The main compound was the diol **32**. The ^{1}H NMR spectrum and that of the corresponding diacetate indicated that this compound was the 3-*epi* derivative of a diol which has already been prepared by alanate reduction of the 2β-angeloyloxy-*ent*-labda-7,13-dien-15-oic acid [20]. The changed configuration at C-2 clearly followed from the small vicinal couplings. The assignment of the signals in ring A followed the observed NOE's (irradiation of H-20 gave effects with H-1α, H-6α, H-11; of H-19 with H-3α and H-6α; of H-18 with H-3α, H-3β, H-5 and H-6β). PCC oxidation afforded the keto aldehyde **11**. Accordingly, the configuration of the Δ^{13} bond also was established. The ^{1}H NMR spectral data of the acetate of **35** (Table 4) showed that we were dealing with the corresponding 2-keto derivatives. The position of the keto group followed from the observed *W*-coupling of H-1α and H-3α which both only showed geminal couplings. The signals were in part assigned by the NOE's. Clear effects were observed between H-20 and H-1α, between H-19, H-20 and H-3α, between H-18, H-5, H-3α and H-3β as well as between H-15 and H-16. The latter effect also established the configuration of the Δ^{13} bond. The observed negative Cotton-effect of **35**Ac again supported the presence of *ent*-labdanes as here surely the octant rule was valid. The ^{1}H NMR spectrum of **33** clearly showed that the 15-*O*-acetate of **32** was present. Accordingly, the H-15 signal was shifted downfield. The last diterpene **34** was isolated as its triacetate. In deuteriobenzene all important signals could be assigned. The shift differences of H-18 and H-19 in the spectra of **32**Ac and **34**Ac showed that the additional oxygen function was at C-3. The couplings already indicated that a 2α,3α-diacetoxy derivative was present. Accordingly, no downfield shift of H-5 was visible which always has been observed if an axial oxygen function at C-3 is present. Furthermore the configuration was established by a NOE between H-1β and H-3β. A second collection of this species which was a female plant, gave somewhat different diterpenes (see Experimental).

The aerial parts of *B. latifolia* (R. et P.) Pers. afforded the *ent*-labdane **36** which has been isolated previously from a *Stevia* species [21]. Furthermore two derivatives of the latter were present in minute amounts, the methyl malonate **37** and the unusual sesquiterpene ester of the malonate **38**. In addition to the cinnamic acid derivative **25** several sesquiterpenes were isolated, bacchascandone (**42**) [22], the isomer **43**, the hydroxygermacradiene **44** [23] and the bisabolene derivatives **39**, **40** [24] and **41**.

The structure of the diol **39** followed from the ^{1}H and ^{13}C NMR data (see Experimental) which were in part close to those of related compounds like **40**. The changed situation at C-3 clearly followed from the ^{1}H NMR data of **39** and of the corresponding acetate. The olefinic proton and aldehyde signals are missing and a doublet at δ 3.45 and 3.88, respectively, indicated the presence of the corresponding tetrahydro derivative. The couplings of H-3 and H-6 showed that a cyclohexane derivative with two equatorial residues must be present. The relative configuration at C-7 could not be determined. The ^{1}H NMR data of **41**Ac (see Experimental) indicated that a closely related bisabolene derivative was present. The broadened triplet at δ 5.13 and the exomethylene signals showed that the natural product was a compound formed by allylic oxidation of **39**. The spectral data of **43** (see Experimental) clearly showed that we were dealing with an isomer of **42**. In addition to a pair of exomethylene proton signals the chemical shift of a pair of doublets at δ 3.32 and 2.97 indicated a methylene group which must be placed between two sp^2 carbons.

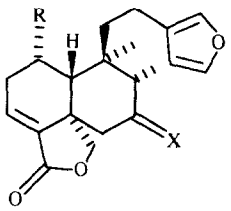
The structure of **37** could be easily deduced from the molecular formula ($C_{24}H_{40}O_5$) and its ^{1}H NMR spectrum (see Experimental) which was very similar to that of the diacetate of **36** [21]. However, one acetate signal was replaced by singlets at δ 3.38 and 3.75 while the H-2 signal was slightly shifted down field. These data required a Me malonate residue at C-2.

Table 3. ^{1}H NMR spectral data of **8**Ac, **8a**Ac, **8b**Ac, **9**Ac and **14**Ac–**18**Ac 400 MHz, $CD3l_3$, δ-values)

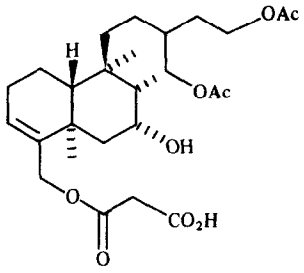
H	8Ac	8aAc	8bAc	9Ac†	14Ac(C_6D_6)	15Ac	16Ac	17Ac	18Ac‡
1α	1.65 *q*	1.66 *q*	1.64 *m*	1.82 *q*	1.98 *br dd*	1.45 *m*	1.50 *m*	1.44 *m*	1.44 *m*
1β	1.56 *m*	1.57 *m*		2.15 *m*					1.65 *m*
2	5.13 *ddd*	5.21 *ddd*	5.37 *ddd*	5.15 *br dd*	5.73 *br dt*	5.01 *br dd*	3.59 *br t*	2.05 *m*	2.00 *m*
3	3.66 *d*	5.05 *d*	5.06 *d*	—	6.16 *dt*	3.05 *br s*	5.38 *br d*	5.20 *br s*	5.17 *br s*
10	1.84 *dd*	1.91 *dd*	*	1.74 *br d*	1.55 *br t*	0.96 *br d*	1.82 *br d*	*	1.37 *br d*
12	2.00 *br t*	2.00 *br t*	2.00 *m*	2.02 *m*	1.85 *m*	2.00 *m*	2.03 *m*	1.98 *m*	1.95 *m*
14	5.59 *br t*	5.55 *br t*	5.63 *br t*	5.59 *br t*	5.50 *br t*	5.57 *br t*	5.56 *br t*	5.57 *br t*	5.55 *br t*
15	4.63 *br d*	4.63 *br d*	4.66 *br d*	4.66 *br d*	4.70 *br d*	4.63 *br d*	4.65 *br d*	4.65 *br d*	4.62 *br d*
16	4.62 *br s*	4.61 *br s*	4.65 *br s*	4.65 *br s*	4.64 d 4.60 d	4.60 *br s*	4.62 *br s*	4.64 *br s*	4.61 *br s*
17	0.77 *d*	0.78 *d*	0.79 *d*	0.84 *d*	0.78 *d*	0.76 *d*	0.80 *d*	4.20 *dd* 3.79 *dd*	—
18	1.26 *s*	1.11 *s*	1.66 *s*	0.92 *d*	4.92 *br s* 4.80 *br s*	1.18 *s*	1.64 *br s*	1.59 *br s*	1.55 *br s*
19	1.08 *s*	1.05 *s*	1.21 *s*	0.75 *s*	1.10 *s*	1.04 *s*	0.95 *s*	1.01 *s*	1.02 *s*
20	0.71 *s*	0.73 *s*	0.73 *s*	0.73 *s*	0.73 *s*	0.64 *s*	0.73 *s*	0.80 *s*	0.90 *s*
OAc	2.06 *s*	2.09 *s*	2.08 *s*	2.15 *s*	1.71 *s*	2.06 *s*	2.06 *s*	2.06 *s*	2.02 (2×)*s*
	2.05 *s*	2.04 *s*	2.06 *s*	2.06 *s*	1.70 *s*	2.03 *s*	2.05 *s*	2.06 *s*	
	2.04 *s*	2.03 *s*	2.05 *s*	2.05 *s*				2.05 *s*	
		1.95 *s*	2.04 *s*						

*Overlapped multiplets; †H-4 2.29 *br q*, H-8 1.56 *m*; ‡H-8 2.44 *dd*; OMe 3.33 *s*.

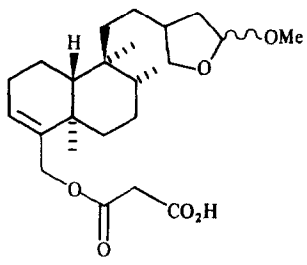
J[Hz]: Compounds **8**Ac, **8a**Ac, **8b**Ac and **9**Ac: 1α,1β = 1α,2β = 1α,10 = 12; 1β,2 = 4.5; 1β,10 = 2; 2,3 = 3.5; 8,17 = 7; 11,12 = 8; **14**,15 = 7; (compound **9**Ac: 1β,2 = 6.5; 1β,10 = 1; 4,18 = 7); compound **14**Ac: 1α,2 = 1β,2 ~ 4; 1α,10 = 1β,10 = 8; 1α,3 = 1β,3 = 1.5; 2,3 = 9.5; 8,17 = 14,15 = 7; 16,16′ = 12; compounds **15**Ac–**18**Ac: 1α,10 ~ 12; 8,17 = 14,15 = 7; (compound **15**Ac: 1α,2 = 10; 1β,2 = 5; 1β,10 = 1.5; 2,3 ~ 1; compound **16**Ac: 1α,2 = 3; 2,3 = 4; compound **17**Ac; 8,17 = 3.5; 8,17′ = 8; 17,17′ = 11; compound **18**Ac: 7α,8 = 12.5; 7β,8 = 3.5).



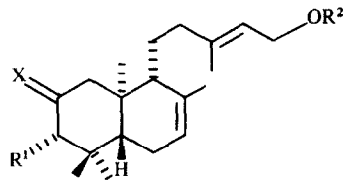
	27	28	29
R	OH	H	H
X	H_2	O	αOH,H



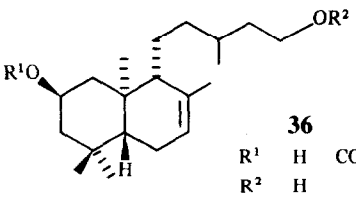
30



31



	32	33	34	35
R^1	H	H	OH	H
R^2	H	Ac	H	H
X	αOH,H	αOH,H	αOH,H	O



	36	37	38
R^1	H	$COCH_2CO_2Me$	$—COCH_2CO_2$
R^2	H	H	H

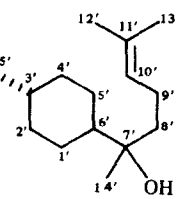


Table 4. ^{1}H NMR spectral data of **10**, **10Ac**, **11**–**13**, **32**, **32**Ac, **33**, **34**Ac and **35**Ac (400 MHz, $CDCl_3$, δ-values)

H	**10***	**10Ac**†	**11**	**12**	**13**	**32**	**32Ac**	**33**	**34Ac**(C_6D_6)‡	**35Ac**
1α	2.64 *d*	2.64 *d*	2.13 *m*	2.65 *d*	2.65 *d*	1.98 *m*	2,13 *dt*	1.98 *m*	1.96 *dd*	2.56 *dd*
1β	2.20 *br d*	2.21 *br d*	2.37 *br d*	2.20 *br d*	2.23 *br d*	1.32 *dd*	1.22 *dd*	1.29 *dd*	1.06 *dd*	2.13 *d*
2	—	—	—	—	—	4.20 *dq*	5.13 *dq*	4.20 *dq*	5.65 *q*	—
3α	—	—	2.45 *br d*	—	—	1.45 *dd*	1.76 *dt*	1.62 *m*	4.76 *d*	2.10 *dd*
3β	3.95 *br s*	3.96 *d*	2.13 *m*	3.96 *br s*	3.97 *br s*	1.64 *ddd*	1.38 *dd*	1.43 *dd*		2.47 *d*
5	1.85 *dd*	1.86 *dd*	1.78 *dd*	1.86 *dd*	1.87 *dd*	1.29 *dd*	1.29 *m*	1.23 dd	1.23 dd	1.77 dd
6α	1.99 *br dd*	2.00 *br dd*	2.15 *m*	2.00 *m*	1.95 *m*		1.95 *m*	1.98 *m*	1.96 *m*	1.94 *m*
6β	2.11 *br d*	2.13 *br d*			2.16 *br d*		2.02 *m*			2.05 *m*
7	5.44 *br s*	5.45 *br s*	5.47 *br s*	5.49 *br s*	5.50 *br s*	5.42 *br s*	5.42 *br s*	5.42 *br s*	5.43 *br s*	5.44 *br s*
12	2.25 *ddd*	2.27 *ddd*	2.15 *m*	2.46 *ddd*	2.75 *ddd*	2.23 *ddd*	2.22 *ddd*	2.25 *ddd*	2.13 *ddd*	2.36 *ddd*
12′	1.95 *m*	1.95 *m*		2.14 *m*	2.57 ddd	1.98 *m*	1.94 *m*	1.98 *m*	1.96 *m*	1.95 *m*
14	5.40 *br t*	5.34 *br t*	5.87 *br d*	5.88 *br d*	5.91 *br d*	5.42 *br t*	5.32 *br t*	5.34 *br t*	5.50 *br t*	5.33 *br t*
15	4.15 *br d*	4.58 *br d*	9.98 *d*	9.99 *d*	9.92 *d*	4.15 *br d*	4.56 *br d*	4.58 *br d*	4.60 *br d*	4.57 *br d*
16	1.67 *br s*	1.71 *br s*	2.18 *d*	2.18 *d*	1.99 *d*	1.70 *br s*	1.69 *br s*	1.71 *br s*	1.57 *br s*	1.70 *br s*
17	1.73 *br s*	1.73 *br s*	1.73 *br s*	1.73 *br s*	1.77 *br s*		1.67 *br s*	1.68 *br s*	1.68 *br s*	1.72 *br s*
18	1.13 *s*	1.14 *s*	1.05 *s*	1.14 *s*	1.15 *s*	0.88 *s*	0.86 *s*	0.87 *s*	1.20 *s*	1.04 *s*
19	0.72 *s*	0.73 *s*	0.91 *s*	0.72 *s*	0.73 *s*	1.11 *s*	1.03 *s*	1.11 *s*	1.02 *s*	0.90 *s*
20	0.77 *s*	0.78 *s*	0.80 *s*	0.78 *s*	0.78 *s*	1.00 *s*	2.04 *s*	0.91 *s*	0.88 *s*	0.78 *s*
OAc							2.01 *s*	2.05 *s*	1.86 *s*	2.05 *s*
									1.73 *s*	
									1.77 *s*	

*H-9 1.95 *m*, H-11 1.44 and 1.37 *m*, OH 3.41 *br s*; †OAc 2.05 *s*; ‡in $CDCl_3$: H-18 1.12 *s*, H-19 0.97 *s*, H-20 0.88 *s*;

J[Hz]: 5, 6α = 11; 5, 6β = 4.5; 6α, 6β = 18; 11, 12 = 12, 12′ = 13; 11′, 12 = 5; compounds **10**, **10**Ac, **12**–**13**: 1α, 1β = 13; 3, 19 = 1; (compounds **10** and **10**Ac: 14, 15 = 7; compounds **12** and **13**: 14, 15 = 7.5); compound **11**: 1α, 1β = 3α, 3β = 13; 14, 15 = 8; compounds **32**–**35**Ac: 5, 6α = 11; 5, 6β = 5; 11, 12 = 12, 12′ = 13; 11′, 12 = 5; 14, 15 = 7; compounds **32**, **32**Ac and **33**: 1α, 1β = 3α, 3β = 14; 1α, 3α = 1α, 2 = 2, 3α = 1β, 2 = 2, 3β ~ 2.5; compounds **34**Ac: 1α, 1β = 15; 1α, 2 = 1β, 2 = 2, 3 = 3; compounds **35**Ac: 1α, 1β = 12.5; 3α, 3β = 12; 1α, 3α = 2; 5, 6α = 11; 5, 6β = 4.

Table 5. ^{1}H NMR spectral data of **27–29** (400 MHz, $CDCl_3$, δ-values)

H	27	28†	29
1	4.43 *br t*	1.87 *br d* 1.24 *ddd*	1.74 *br d* 1.19 *ddd*
2	2.49 *dt*	2.50 *dddd*	*
2′	2.42 *ddd*	2.28 *dddd*	*
3	6.57 *dd*	6.87 *dd*	6.73 *dd*
7	1.96 *dt*		4.13 *br d*
7′	1.67 *m*	—	—
8	1.67 *m*	2.68 *q*	1.66 *m*
10	1.79 *br s*	2.45 *br d*	*
12	2.42 *dt*	2.45 *m*	2.18 *m*
12′	2.11 *dt*	2.30 *m*	
14	6.28 *br s*	6.28 *br s*	6.27 *br s*
15	7.36 *t*	7.38 *t*	7.37 *t*
16	7.22 *br s*	7.25 *br s*	7.23 *br s*
17	0.86 *d*	1.03 *d*	1.0 *d*
18	—	—	—
19	4.62 *dd* 4.33 *d*	3.93 *dd* 4.02 *d*	3.93 *dd* 5.30 *d*
20	0.88 *s*	0.65 *s*	0.88 *s*

*Overlapped multiplets; †H-6 2.72 *d*, H-6′ 2.37 *br d*.

J [Hz]: 6β,19 = 2; 8,17 = 7; 14,15 = 15,16 = 1.5; 19,19′ = 7.5; compound **27**: 1,2 = 1,2′ ~ 2.5; 2,3 = 2.5; 2′,3 = 6; 2,2′ = 18; 6,7 = 7,8 = 3; 7,7′ = 13; 11,12 = 11′,12′ = 12,12′ = 13; 11,12′ = 11′,12 = 5; compounds **28** and **29**: 1,1′ = 1′,2 = 1′,10 = 12; 1′,2′ = 3.5; 2,3 = 2.5; 2′,3 = 7; (compound **28**: 6,6′ = 13; compound **29**: 7,8 = 4).

Compound **38** only could be isolated as its acetate (**38**Ac). In the mass spectrum the highest peak agreed with $C_{40}H_{64}O_6$. As, however, peaks for $[M-OAc]^+$ and $[M-C_8H_{14}O]^+$ (side chain at C-6′) were also visible the highest peak already was a fragment formed by loss of water. The ^{1}H NMR spectrum (see Experimental) was nearly an addition of the spectra of **39**Ac and the 15-*O*-acetate of **36** [21]. However, one acetate signal was replaced by a two proton singlet at δ 3.37. Furthermore, now the H-15′ displayed a pair of double doublets due to the chiral ester group at C-15′. Compound **38**, which we have named bacchalatifolin, is a very unusual one. However, similar esters with two diterpene units have been reported previously [25].

The aerial parts of *B. peruviana* Cuatr. afforded a mixture mono- and diMe ethers of luteolin, the dimeric clerodane malonate **45** [1] and the corresponding succinate **46** [1].

The overall picture of Bolivian *Baccharis* species shows again that an accumulation of diterpenes, especially of *ent*-clerodanes is characteristic. However, the frequent occurrence of prenylated *p*-coumaric acids should also be mentioned. All the other constituents are more sporadic. A clear correlation of the chemistry with the proposed sectional classification is only possible in part.

As shown previously [1] representatives of the sections Alatae (*B. trimera*), Cuneifoliae (*B. obtusifolia*) and Inoolucratae (*B. peruvianae*) gave *ent*-clerodanes. They are now isolated from section Heterothalamus (*B. boliviensis*). In a species from the section Molinae (*B. latifolia*) these diterpenes are replaced by *ent*-labdanes which are also isolated from *B. sternbergiana* (sect. Oblongifoliae), while *B. dracunculifolia* (sect. Racemosae) gave no diterpenes but large amounts of prenylated coumaric acids, which, however, seem to be widespread in the whole genus as they were isolated from all species except *B. trimera* and *B. peruviana*.

EXPERIMENTAL

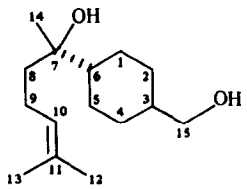
Air-dried aerial parts were collected in February 1987 in Bolivia; vouchers are deposited in the US National Herbarium, Washington and in the Herbarium Nacionale de Bolivia. They were extracted and worked-up as reported previously [26].

The extract of 620 g of *B. boliviensis* (voucher Solomon 16348), was sepd into five crude CC fractions. The first one gave by TLC 50 mg germacrene D. Fraction 2 was extd with K_2CO_3 soln. The acidic part gave 800 mg crystalline **1** while the neutral fraction afforded by TLC (Et_2O–petrol, 1:9) 20 mg friedelin and 30 mg **23**. CC fraction 3 was a complex mixt. of acids which was sepd after esterification with CH_2N_2 by flash chromatography (silica gel, ϕ 30–60 μm, Et_2O–petrol, 1:9, Et_2O) affording 200 mg **1a**, 280 mg **25a**, 1 g **2a** and three mixts (3/4–3/6). HPLC (MeOH–H_2O, 17:3, RP 8, *ca* 100 bar) of fraction 3/4 gave 20 mg **22** (R_t 0.8 min), 10 mg **24a**, 20 mg **25a**, 5 mg **7** (R_t 4.8 min), 20 mg Meoleanolate and again a mixt (R_t 3.3 min). After acetylation (Ac_2O, 3 hr, 70°) and TLC (Et_2O–petrol, 1:1) 5 mg **4**Ac (R_f 0.65) and 5 mg **21** (R_f 0.52) were obtained. TLC of fraction 3/5 (Et_2O–petrol, 3:1) gave 200 mg **15** (R_f 0.50) (purified by HPLC, R_t 5.2 min), 200 mg **10** (R_f 0.35) and a mixt. which afforded by TLC (Et_2O–petrol, 3:1), 1.5 mg **11** (R_f 0.65), 2 mg **13** (R_f 0.57) and 2 mg **12** (R_f 0.46). TLC of 3/6 (Et_2O–petrol, 3:1) gave 6 mg **6** (purified by HPLC (MeOH–H_2O, 17:3, R_t 5.2 min) and 5 mg **10**Ac (purified by HPLC, MeOH–H_2O, 17:3, R_t 6.9 min). CC fraction 4 was first extracted with K_2CO_3 soln. The acid part gave 200 mg **2** while the neutral fraction afforded by TLC (Et_2O–petrol, 3:1) 500 mg **10** and 40 mg **5**. The most polar CC fraction showed no acetate singlets in the ^{1}H NMR spectrum. As the mixt. could not be sepd it was acetylated (Ac_2O, $CHCl_3$, DMAP, 3 hr. 70°). Flash chromatography gave five fractions (5/1–5/5) (Et_2O–petrol, 1:3, Et_2O–MeOH, 9:1). Fraction 5/1 gave by TLC (Et_2O–petrol, 1:3) 20 mg **14**Ac (R_f 0.65). Fraction 5/2 gave by HPLC 30 mg **10**Ac (R_t 2.3 min), 5 mg **17**Ac (purified by TLC, Et_2O–petrol, 1:1, R_f 0.60) and a mixt. (R_t 4.4 min) which gave by TLC (Et_2O–petrol, 1:1, 2×) 5 mg **16**Ac (R_f 0.65) and 10 mg **3**Ac (R_f 0.45). Fraction 5/3 gave by HPLC 10 mg **9**Ac (R_t 1.7 min), 120 mg **15**Ac (R_t 2.2 min), 160 mg **18**Ac (R_t 2.6 min), 120 mg **3**Ac (R_t 4.9 min) and 20 mg **20**Ac (R_t 6.6 min). HPLC of fraction 5/4 afforded 40 mg **5**Ac (R_f 1.8 min), 10 mg **8b**Ac (R_t 2.1 min), 3 mg **8a**Ac (R_t 2.7 min) and 40 mg **19**Ac (R_t 3.9 min). Fraction 5/5 gave by HPLC 20 mg **8b**Ac (R_t 1.2 min).

The extract of 1100 g of aerial parts of *B. obtusifolia* (voucher Solomon 16314), gave after CC and TLC (see above) 60 mg *epi*-friedelinol, 400 mg baccharisoxide, 2 g **24**, 4.5 g **25a**, 200 mg rhamnocitrin, 1.0 g **27**, 1.9 g **28** and 200 mg **29**.

The extract of 380 g of aerial parts of *B. dracunculifolia* (voucher RMK 9644) gave by CC and TLC (see above) 100 mg germacrene D, 10 mg bicyclogermacrene, 100 mg oleanolic acid, 100 mg rhamnoctirin, 50 mg 4β-hydroxygermacra-1(10),5*E*-diene, 1 g **24**, 300 mg **25** and 50 mg **26**; colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 1700, 1630, 1600 (PhC=CCO$_2$R); MS *m/z* (rel. int.): 244.110 $[M-H_2O]^+$ (59) (calc. for $C_{15}H_{16}O_3$: 244.110), 229 $[244-Me]^+$ (100), 197 $[229-MeOH]^+$ (24); ^{1}H NMR ($CDCl_3$): δ 7.29 (*m*, H-1, H-6), 6.77 (*d*, H-5), 7.61 (*d*, H-7), 6.27 (*d*, H-8), 3.40 (*d*, H-1′), 5.60 (*br t*, H-2′), 4.08 (*br s*, H-4′), 1.81 (*br s*, H-5′) (*J* [Hz]: 5, 6 = 8.5; 7, 8 = 16; 1′, 2′ = 7).

The extract of 850 g of aerial parts of *B. trimera* (voucher RMK 9642) on standing in Et_2O at −20° gave 6 g crystalline



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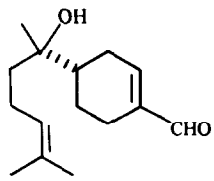
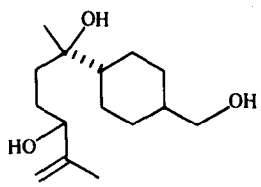


40



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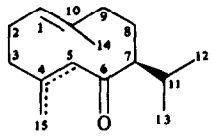
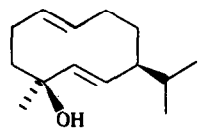


42 Δ^4
43 $\Delta^{4(15)}$



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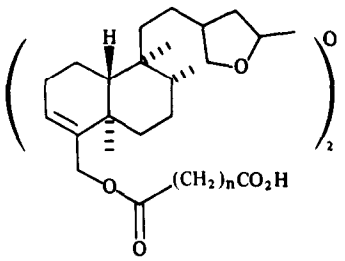

45 n = 1
46 n = 2

1a, **2a**, **24a**, **25a**, **29a**-**31a** are the Me esters; **3**Ac, **4**Ac, **5**Ac, **9**Ac, **14**Ac, **15**Ac-**20**Ac, **32**Ac, **34**Ac, **35**Ac and **36**Ac are the peracetylated compounds, **3a**Ac is the 3',4'-diacetate, **8**Ac the 1,15,16-triacetate, **8a**Ac the 15,16-diacetate, **8b**Ac the 4,15,16-triacetate, **10**Ac the 15-acetate, **38**Ac the 2-acetate, **39**Ac the 15-acetate and **41**Ac the 10,15-diacetate.

eupatorin. The mother liquor was sepd by CC affording 50 mg germacrene D and a polar fraction (Et_2O and Et_2O–MeOH, 9:1) which gave after esterification with CH_2N_2 by medium pressure chromatography 800 mg **30a** and 1.5 g **31a**.

The extract of 320 g aerial parts of *B. sternbergiana* (male plant) (voucher Solomon 16349) was sepd by CC affording two polar fractions (1 and 2). TLC of fraction 1 (Et_2O–petrol, 1:1) gave 20 mg **24** and 40 mg **33** (R_f 0.50). Fraction 2 contained mainly **32** but could not be purified as such. As no acetate singlets were visible in the ^1H NMR the mixt was acetylated (Ac_2O, 1.5 hr, 70°). TLC (Et_2O–petrol, 1:3) gave 1 g **32**Ac (R_f 0.65) and a mixt. which gave by HPLC (MeOH–H_2O, 9:1) 10 mg lachnophyllum lactone (R_t 1.5 min), 10 mg **35**Ac (R_t 3.7 min) and 30 mg **34**Ac (R_t 5.2 min. The ext of 310 g aerial parts of the same species (female plants) (voucher Solomon 16350) was sepd by CC. The most polar fraction gave 1.5 g **32**, and 10% of the less polar one gave by HPLC 20 mg **33**, 60 mg **25** and 10 mg lachnophyllum lactone.

The extract of 685 g aerial parts of *B. latifolia* (voucher Solomon 16316) afforded after CC four fractions (1: Et_2O–petrol, 1:9; 2: Et_2O–petrol, 1:1; 3: Et_2O and 4: Et_2O–MeOH, 9:1). TLC of one-tenth of fraction 1 (Et_2O–petrol, 1:19) gave 20 mg **43** (R_f 0.65) and 200 mg **42** (R_f 0.55). Fraction 2 contained 300 mg **44**. Fraction 3 was further sepd by medium pressure CC affording 1 g **25** and 800 mg **40**. TLC of fraction 4 (Et_2O, one-tenth) gave 80 mg **39** (R_f 0.70), 170 mg **36** (R_f 0.55) and a mixt. which showed no acetate signals in the ^1H NMR. Acetylation of the remaining part of fraction 4 (Ac_2O, 1 hr, 70°)

gave a crude mixt. which gave by CC with Et_2O–petrol, 1:3, 1.4 g **36**Ac, with Et_2O–petrol, 1:1, 700 mg **39**Ac and with Et_2O a mixt. which gave by HPLC (MeOH–H_2O, 9:1) 10 mg **37** (R_t 4.4 min) and a mixt. (R_t 1.1 min) which gave by TLC (Et_2O–petrol, 3:1) 10 mg **38**Ac (R_f 0.75) and 30 mg **41**Ac (R_f 0.50).

The ext of 680 g aerial parts of *B. peruviana* (voucher Solomon 16259) gave by CC and TLC 3 g of a mixt. of luteolin mono- and diMe ether, 1 g **45** and 1 g **46** which were isolated as their Me esters.

Bacchabolivic acid (**1**). Colourless crystals, mp 147°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400–2500, 1700 (CO_2H); 880 (β-furan); MS *m/z* (rel. int.): 316.204 $[M]^+$ (8) (calc. for $C_{20}H_{28}O_3$: 316.204), 301 $[M-Me]^+$ (2.5), 218 (40), 161 (51), 95 $[CH_2CH_2C_4H_3O]^+$ (100), 81 $[C_5H_5O]^+$ (87); ^{13}C NMR ($CDCl_3$, C-1–C-20: δ 17.9, 26.6, 120.8, 145.1, 38.6, 35.4, 21.7, 49.1, 37.7, 49.1, 40.7, 18.5, 125.3, 111.2, 138.8, 143.1, 181.5, 17.9, 19.8, 19.9; $[\alpha]_D^{24}$ −66 ($CHCl_3$; *c* 0.73). Addition of CH_2N_2 in Et_2O afforded the Me ester **1a**; colourless crystals, mp 92.5°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735 (CO_2R), 880 (β-furan); MS *m/z* (rel. int.): 330.219 $[M]^+$ (31) (calc. for $C_{21}H_{30}O_3$: 330.219), 315 (7), 283 (315 − MeOH]$^+$ (8), 255 (283 − CO]$^+$ (11), 235 $[M-C_6H_7O]^+$ (27), 175 [235 − $HCO_2Me]^+$ (32), 95 (100), 81 (44); $[\alpha]_D^{24}$ −79 ($CHCl_3$, *c* 1.31).

17-*Succinoyloxy*-ent-*cleroda*-3,13(16),14-*trien*-15,16-*oxide* (**2**). Purified as its Me ester **2a**; colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R), 880 (β-furan); MS *m/z* (rel. int.): 416.257 $[M]^+$ (59) (calc. for $C_{25}H_{36}O_5$: 416.257), 401 (3), 284 $[M-RCO_2H]^+$ (12), 269 [284 − Me]$^+$ (3), 218 (7), 204 (6), 203 (6), 189 (15), 161 (16), 115 $[RCO]^+$ (50), 107 $[C_8H_{11}]^+$ (100) 95 (25), 81 (44); $[\alpha]_D^{24}$ −48 ($CHCl_3$; *c* 2.18).

1′-O-*Bacchabolivyl xylopyranoside* (**3**). Purified as its triacetate **3**Ac (Ac_2O, DMAP, $CHCl_3$, 2 hr, 70°); colourless crystals, mp 121°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1250, 1230 (OAc); MS *m/z* (rel. int.): 574.278 (0.06) (calc. for $C_{31}H_{42}O_{10}$: 574.278), 514 (0.2), 454 (0.4), 394 (0.2), 259 $[C_5H_6O(OAc)_3]^+$ (52), 199 [259 − HOAc]$^+$ (46), 157 [199 − ketene]$^+$ (100), 139 [199 − HOAc]$^+$ (96), 97 [157 − HOAc]$^+$ (92), 81 $[C_5H_5O]^+$ (46); $[\alpha]_D^{24}$ −65 ($CHCl_3$; *c* 0.74). In addition to **3**Ac *ca* 15% of the diacetate **3a**Ac was obtained, colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH), 1750, 1235 (OAc), 880 (β-furan); MS *m/z* (rel. int.): 532.262 $[M]^+$ (0.3) (calc. for $C_{29}H_{40}O_9$: 532.262), 514 $[M-H_2O]^+$ (1), 499 [514 − Me]$^+$ (1); 454 [514 − HOAc]$^+$ (1.2), 394 [544 − HOAc]$^+$ (0.7), 217 $[C_5H_6O(OH)(OAc)_2]^+$ (41), 157 [217 − HOAc]$^+$ (39), 97 [157 − HOAc]$^+$ (100), 81 (33).

2α-*Hydroxy*-3-*oxo*-4β*H*-ent-*cleroda*-13(16),14-*diene*-15,16-*oxide* (**4**). Colourless gum, which was converted to the acetate **4**Ac; colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1250 (OAc), 1740 (C=O) 885 (β-furan); MS *m/z* (rel. int.): 360.230 $[M]^+$ (9) (calc. for $C_{22}H_{32}O_4$: 360.230), 318 [M − ketene]$^+$ (8), 206 (21), 205 (14), 95 $[CH_2CH_2C_4H_3O]^+$ (100); 81 (51); $[\alpha]_D^{24}$ +56 ($CHCl_3$; *c* 0.18).

2α,3α,4β-*Trihydroxy*-ent-*cleroda*-13(16),14-*diene*-15,16-*oxide* (**5**). Colourless crystals, mp 155°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH), 890 (β-furan); MS *m/z* (rel. int.): 336.230 $[M]^+$ (2.5) (calc. for $C_{20}H_{32}O_4$: 336.230), 318 $[M-H_2O]^+$ (3), 303 [318 − Me]$^+$ (3), 285 $[303-H_2O]^+$ (1), 275 $[303-CO]^+$ (2), 257 $[275-H_2O]^+$ (2), 223 $[318-C_6H_7O]^+$ (74), 205 $[223-H_2O]^+$ (22), 123 (64), 96 (78), 81 (100); $[\alpha]_D^{24}$ +15 ($CHCl_3$; *c* 0.43). Acetylation (see above) afforded **5Ac**; colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1750, 1250 (OAc), 880 (β-furan); MS *m/z* (rel. int.): 378.241 $[M]^+$ (8) (calc. for $C_{22}H_{34}O_5$: 378.241), 360 $[M-H_2O]^+$ (2), 300 [360 − HOAc]$^+$ (4), 265 $[360-C_6H_7O]^+$ (72), 205 [265 − HOAc]$^+$ (86), 187 $[205-H_2O]^+$ (44), 123 (86), 81 (100).

2α-*Hydroxy*-3α,4α-*epoxy*-ent-*cleroda*-13(16),14-*diene*-15,16-*oxide* (**6**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 890 (β-furan); MS *m/z* (rel. int.): 318.219 $[M]^+$ (8) (calc. for $C_{20}H_{30}O_3$: 318.219), 303 (5), 223 $[M-C_6H_7O]^+$ (21), 205 $[223-H_2O]^+$ (9), 123 (52), 95 (61), 81 (100); $[\alpha]_D^{24}$ +8 ($CHCl_3$; *c* 5.65).

2α-*Methoxy*-3α,4α-*epoxy*-ent-*cleroda*-13(16),15-*diene*-15,16-*oxide* (**7**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 880 (β-furan); MS *m/z* (rel. int.): 332.235 $[M]^+$ (8) (calc. for $C_{21}H_{32}O_3$: 332.235), 317 [M − Me]$^+$ (6), 300 [M − MeOH]$^+$ (6), 285 [300 − Me]$^+$ (4.5), 237 $[M-C_6H_7O]^+$ (10), 123 (46), 95 (72), 81 (100).

2α,3α,4β,15,16-*Pentahydroxy*-ent-*cleroda*-13E-*ene* (**8**). This compound was acetylated (see above) and afforded the diacetate **8**Ac; colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1745, 1240 (OAc); MS *m/z* (rel. int.): 422.267 $[M-HOAc]^+$ (1.5) (calc. for $C_{24}H_{38}O_6$: 422.267), 362 [422 − HOAc]$^+$ (65), 302 [362 − HOAc]$^+$ (12), 205 (46), 123 (100), and the triacetate **8a** Ac; colourless gum; MS *m/z* (rel. int.): 464.277 $[M-HOAc]^+$ (1) (calc. for $C_{26}H_{40}O_7$: 422.277), 404 [464 − HOAc]$^+$ (2.5), 344 [404 − HOAc]$^+$ (3), 302 [344 − ketene]$^+$ (10), 205 (63), 107 (60), 55 (100).

2α,15,16-*Trihydroxy*-3-*oxo*-ent-*cleroda*-13E-*ene* (**9**). Isolated as its triacetate **9**Ac; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1235 (OAc), 1740 (C=O); MS *m/z* (rel. int.): 464 $[M]^+$ (0.5), 411 [M − ketene]$^+$ (4), 404.256 $[M-HOAc]^+$ (5) (calc. for $C_{24}H_{36}O_5$: 404.256), 362 [422 − HOAc]$^+$ (28), 320 [362 − ketene]$^+$ (42), 302 [362 − HOAc]$^+$ (15), 205 (100), 177 (22), 135 (40), 109 (55), 95 (97); $[\alpha]_D^{24}$ +32 ($CHCl_3$; *c* 0.31); CD (MeCN): $\Delta\varepsilon_{285}$ +0.54.

3α,15-*Dihydroxy*-ent-*labda*-7,13E-*dien*-2-*one* (**10**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3615 (OH), 1725 (C=O); MS *m/z* (rel. int.): 320.235 $[M]^+$ (0.3) (calc. for $C_{20}H_{32}O_3$: 320.235), 303 [M − OH]$^+$ (0.8), 302 $[M-H_2O]^+$ (0.3), 234 [M − $C_5H_{10}O$, McLafferty]$^+$ (100), 161 (76), 81 (54). Acetylation (see above) afforded **10Ac**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3480 (OH, hydrogen bonded), 1740, 1240 (OAc), 1715 (C=O); MS *m/z* (rel. int.): 362.246 $[M]^+$ (1) (calc. for $C_{22}H_{34}O_4$: 362 .246), 302 [M − HOAc]$^+$ (2.5), 234 [M − C_5H_9OAc, McLafferty]$^+$ (100), 161 (48), 81 (32); CD (MeCN); $\Delta\varepsilon_{292}$ −0.065.

2,15-*Dioxo*-ent-*labda*-7,13E-*diene* (**11**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2740, 1690 (C=CCHO), 1735 (C=O); MS *m/z* (rel. int.): 302.225 $[M]^+$ (1) (calc. for $C_{20}H_{30}O_2$: 302.225), 287 [M − Me]$^+$ (3), 218 [M − C_5H_8O, McLafferty]$^+$ (82), 119 (57), 81 (100). $[\alpha]_D^{24}$ −6 ($CHCl_3$; *c* 0.2).

3α-*Hydroxy*-2,15-*dioxo*-ent-*labda*-7,13E-*diene* (**12**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH, hydrogen bonded), 2750, 1700 (C=CCHO), 1730 (C=O); MS *m/z* (rel. int.): 318.219 $[M]^+$ (2) (calc. for $C_{20}H_{30}O_3$: 318.219), 303 [M − Me]$^+$ (3), 234 [M − $C_5H_8O]^+$ (96), 161 (58), 81 (100).

3α-*Hydroxy*-2,15-*dioxo*-ent-*labda*-7,13Z-*diene* (**13**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH, hydrogen bonded), 2745, 1700 (C=CCHO), 1730 (C=C); MS *m/z* (rel. int.): 318.219 $[M]^+$ (2) (calc. for $C_{20}H_{30}O_3$: 318.219). 303 (1.5), 235 $[M-C_5H_7O]^+$ (78), 234 (28), 161 (56), 119 (74), 84 (100), 81 (96).

15,16-*Dihydroxy*-ent-*labda*-2,4(18),13E-*triene* (**14**). Isolated as its diacetate **14**Ac; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750, 1240 (OAc), 1640, 1600, 895 (C=CH_2); MS *m/z* (rel. int.) 328.240 [M − HOAc]$^+$ (3.5) (calc. for $C_{22}H_{32}O_2$: 328.240), 268 [328 − HOAc]$^+$ (25), 253 (268 − Me]$^+$ (28), 187 [M − side chain]$^+$ (79), 159 (64), 119 (100), 105 (94), 95 (76), 81 (56); $[\alpha]_D^{24}$ +15 ($CHCl_3$; *c* 1.29).

15,16-*Dihydroxy*-2β-*methoxy*-ent-*cleroda*-3,13E-*diene* (**16**). Isolated as its diacetate **16**Ac; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1235 (OAc); MS *m/z* (rel. int.): 420.288 $[M]^+$ (2) (calc. for $C_{25}H_{40}O_5$: 420.288), 360 $[M-HOAc]^+$ (4), 345 [360 − Me]$^+$ (2.5), 328 [360 − MeOH]$^+$ (2.5), 301 [360 − OAc]$^+$ (7), 285 [345 − HOAc]$^+$ (8), 253 [285 − MeOH]$^+$ (6), 189 (25), 123 (76), 98 (100).

15,16,17-*Trihydroxy*-ent-*cleroda*-3,13E-*diene* (**17**). Isolated as its triacetate **17**Ac; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1235 (OAc); MS *m/z* (rel. int.): 448 $[M]^+$ (0.1), 433.259 $[M-Me]^+$ (1) (calc. for $C_{25}H_{27}O_6$: 433.259), 373 [433 − HOAc]$^+$ (21), 313 [373

$-HOAc]^+$ (6), 253 $[313-HOAc]^+$ (24), 187 $[C_{14}H_{19}]^+$ (100), 107 (72).

16-*Hydroxybacchasalicylic acid* (**18**). Isolated as its diacetate **18Ac**; colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3400–2600, 1710 (CO_2H), 1745, 1240 (OAc); MS *m/z* (rel. int.): 420.251 $[M]^+$ (4) (calc. for $C_{24}H_{36}O_6$: 420.251), 360 $[M-HOAc]^+$ (6), 205 (61), 187 $[C_{14}H_{19}]^+$ (100), 95 (76).

15,16,17-*Trihydroxy*-ent-*cleroda*-3,15E-*diene*-17-O-*β*-*xylopyranoside* (**19**). Isolated as its pentaacetate **19Ac**; colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1755, 1740, 1245, 1230 (OAc); MS *m/z* (rel. int.): 664 $[M]^+$ (0.05), 604.325 $[M-HOAc]^+$ (0.5) (calc. for $C_{33}H_{48}O_{10}$: 604.325), 589 $[604-Me]^+$ (1), 544 $[604-HOAc]^+$ (1), 259 $[C_5H_6(OAc)_3]^+$ (66), 199 $[259-HOAc]^+$ (50), 157 $[199-ketene]^+$ (100), 139 $[199-HOAc]^+$ (8), 97 $[139-ketene]^+$ (85), 95 (60); $[\alpha]_D^{24^\circ}$ −50 ($CHCl_3$; *c* 3.41).

15,16,17-*Trihydroxy*-ent-*cleroda*-3,13E-*diene*-16-O-*β*-*xylopyranoside* (**20**). Isolated as its tetraacetate **20Ac**; colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1745, 1250, 1230 (OAc); MS *m/z* (rel. int.): 606 $[M]^+$ (0.1), 546.319 $[M-HOAc]^+$ (5) (calc. for $C_{31}H_{46}O_8$: 546.319), 486 $[546-HOAc]^+$ (0.4), 426 $[486-HOAc]^+$ (0.6), 331 $[M-$sugar moiety$]^+$ (4.5), 259 $[C_5H_6(OAc)_3]^+$ (100), 199 (82), 189 $[C_{14}H_{21}]^+$ (51), 157 (97), 139 (97), 97 (84), 95 (72); $[\alpha]_D^{24^\circ}$ −48 ($CHCl_3$; *c* 0.55).

1α,7α,10αH-*Guaia*-4,11(13)-*dien*-3-*one* (**21**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1710, 1650 (C=CC=O); MS *m/z* (rel. int.): 218.167 $[M]^+$ (100) (calc. for $C_{15}H_{22}O$: 218.167), 203 $[M-Me]^+$ (28), 190 $[M-CO]^+$ (14), 175 $[190-Me]^+$ (34), 161 $[203-C_6H_6]^+$ (56), 109 (92), 91 (56), 55 (70); ^1H NMR (400 MHz, $CDCl_3$): δ 3.13 (*dddq*, H-1), 2.04 (*ddd*, H-2α), 2.58 (*ddd*, H-2β), 2.77 (*br d*, H-6α), 2.95 (*br dd*, H-6β), 2.32 (*br dd*, H-7), 1.58 (*m*, H-8), 1.75 and 1.84 (*m*, H-9), 2.11 (*dddq*, H-10), 1.77 (*br s*, H-12), 4.75 and 4.70 (*br s*, H-13), 0.65 (*d*, H-14), 1.66 (*br s*, H-15) (*J* [Hz]: 1, 2α = 2α, 6β = 1, 15 = 2β, 6α = 7, 13 = 12, 13′ = 1; 1, 2β = 7; 2α, 2β = 18; 6α, 6β = 19; 6β, 7 = 7, 8β = 10); ^{13}C NMR ($CDCl_3$, C-1–C-15); δ 44.6, 38.0, 208.2, 137.7, 175.2, 35.4, 46.0, 31.4, 36.8, 41.4, 150.3, 20.2, 109.0, 12.1, 8.0 (some signals may be interchangeable); $[\alpha]_D^{24^\circ}$ +63 ($CHCl_3$; *c* 0.23).

2-*Hydroxyeudesm*-1, 4, 6-*triene*-3, 8-*dione* (**22**). Colourless crystals, mp 96°; UV (Et_2O) λ_{max} 298 nm; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3440 (OH, hydrogen bonded), 1690, 1640 (C=CC=O); MS *m/z* (rel. int.): 246.126 $[M]^+$ (100) (calc. for $C_{15}H_{18}O_3$: 246.126), 231 $[M-Me]^+$ (16), 218 $[M-CO]^+$ (34), 203 $[218-Me]^+$ (97), 175 $[203-CO]^+$ (77); ^1H NMR (400 MHz, $CDCl_3$): δ 6.09 (*s*, H-1), 7.32 (*br s*, H-6), 2.65 (*d*, H-9), 2.41 (*br d*, H-9′), 3.06 (*br qq*, H-11), 1.17 (*d*, H-12), 1.12 (*d*, H-13), 1.30 (*d*, H-14), 2.15 (*s*, H-15), 6.46 (*s*, OH) (*J* [Hz]: 6, 11 = 9′, 14 = 1; 9, 9′ = 15; 11, 12 = 11, 13 = 7); $[\alpha]_D^{24^\circ}$ +123 ($CHCl_3$; *c* 0.49); CD (MeCN): $\Delta\varepsilon_{378}$ −2.1; $\Delta\varepsilon_{329}$ +8.1; $\Delta\varepsilon_{266}$ +2.46.

15, 16-*Diacetoxy*-7α-*hydroxy*-18-*malonyloxy*-ent-*cleroda*-3-*ene* (**30**). Colourless gum, which was purified as its Me ester **30a**; colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1750, 1240 (OAc), 1750 (CO_2R); MS *m/z* (rel. int.): 406.272 $[M-HOAc,$ ketene$]^+$ (2) (calc. for $C_{24}H_{38}O_5$: 406.272), 389 $[M-HOAc, OAc]^+$ (7), 388 $[M-2\times HOAc]^+$ (3), 373 $[388-Me]^+$ (4), 314 $[388-MeCO_2Me,$ McLafferty$]^+$ (5.5), 205 $[C_{14}H_{21}O]^+$ (64), 187 $[C_{14}H_{19}]^+$ (100); CIMS *m/z* (rel. int.): 407 $[M+1-HOAc,$ ketene$]^+$ (4.5), 389 $[M+1-2\times HOAc]^+$ (100); ^1H NMR ($CDCl_3/C_6D_6$): δ 2.05 (*br d*, H-2), 1.93 (*br dd*, H-2′), 5.54 (*br dd*, H-3), 1.87 (*dd*, H-6α), 1.32 (*dd*, H-6β), 3.78 (*br q*, H-7), 1.32 (*m*, H-8), 3.97 (*t*, H-15), 3.89 and 3.85 (*dd*, H-16), 0.83 (*d*, H-17), 4.50 (*br s*, H-18), 1.23 (*s*, H-19), 0.89 (*s*, H-20), 1.82 and 1.85 (OAc), 3.51 and 3.19 (*s*, $COCH_2CO_2Me$); (*J* [Hz]: 1, 2′ = 10; 2, 2′ = 18; 6α, 6β = 13; 6α, 7 = 2.5; 6β, 7 = 7, 8 ~ 3; 8, 17 = 14, 15 = 7; 13, 16 = 2; 13, 16′ = 6; 16, 16′ = 11).

2α, 15-*Dihydroxy*-ent-*labda*-7, 13E-*diene* (**32**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH); MS *m/z* (rel. int.): 306 $[M]^+$ (0.2), 288.245 $[M-H_2O]^+$ (0.5) (calc. for $C_{20}H_{32}O$: 288.245), 220 $[M-C_5H_{10}O]^+$ (98), 205 $[220-Me]^+$ (10), 202 $[220-H_2O]^+$ (9), 135 (52), 81 $[C_6H_9]^+$ (100); $[\alpha]_D^{24^\circ}$ −5 ($CHCl_3$; *c* 0.8).

Acetylation gave the diacetate **32Ac**. Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1250 (OAc): MS *m/z* (rel. int.): 348 $[M-$ketene$]^+$ (0.2), 330.177 $[M-HOAc]^+$ (0.6) (calc. for $C_{22}H_{34}O_2$: 330.177), 262 $[M-$side chain$]^+$ (82), 202 $[262-HOAc]^+$ (69), 187 (38), 81 $[C_6H_9]^+$ (100); ^{13}C NMR ($CDCl_3$, C-1–C-20): δ 41.8, 70.7, 43.6, 32.2, 54.9, 23.5, 122.5, 134.8, 49.5, 36.0, 25.3, 41.2, 142.4, 118.5, 61.3, 16.6, 23.5, 33.8, 21.2, 15.0; OAc: 21.0, 21.2, 171.1, 170.5. **32** (10 mg) in 3 ml $CHCl_3$ was stirred for 2 hr with 20 mg PCC and 10 mg $NaHCO_3$. TLC (Et_2O–petrol, 1:1) afforded 6 mg **11**, identical with the natural product (see above).

2α, 15-*Dihydroxy*-ent-*labda*-7, 13E-*diene*-15-O-*acetate* (**33**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740, 1235 (OAc); MS *m/z* (rel. int.): 348 $[M]^+$ (0.15), 288.245 $[M-HOAc]^+$ (1) (calc. for $C_{20}H_{32}O$: 288.245), 273 $[288-Me]^+$ (1.2), 220 $[288-C_5H_8]^+$ (92), 81 $[C_6H_9]^+$ (100) $[\alpha]_D^{24^\circ}$ −9.5 ($CHCl_3$; *c* 2.13).

2α, 3α, 15-*Trihydroxy*-ent-*labda*-7, 13E-*diene* (**34**). Isolated as its triacetate **34Ac**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1245; MS *m/z* (rel. int.): 448 $[M]^+$ (0.2), 388.261 $[M-HOAc]^+$ (1.6) (calc. for $C_{24}H_{36}O_4$: 388.261), 320 $[388-C_5H_8]^+$ (100), 260 $[320-HOAc]^+$ (21), 218 $[260-$ketene$]^+$ (36), 203 $[218-Me]^+$ (17), 200 $[218-H_2O]^+$ (32), 185 $[200-Me]^+$ (36), 81 $[C_6H_9]^+$ (84); $[\alpha]_D^{24^\circ}$ −42 ($CHCl_3$; *c* 2.18).

15-*Hydroxy*-ent-*labda*-7, 13E-*dien*-2-*one* (**35**). Isolated as its acetate **35Ac**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1240 (OAc), 1715 (CO); MS *m/z* (rel. int.): 346.251 $[M]^+$ (1.5) (calc. for $C_{22}H_{34}O_3$: 346.251), 286 $[M-HOAc]^+$ (2), 218 $[C_{15}H_{22}O]^+$ (100), 81 $[C_6H_9]^+$ (42); CD (MeCN): $\Delta\varepsilon_{296}$ −0.6.

2β, 15-*Dihydroxy*-ent-7-*labdene*-2-O-*methylmalonate* (**37**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH), 1755, 1740 ($OCOCH_2CO_2Me$); MS *m/z* (rel. int.): 408.288 $[M]^+$ (0.5) (calc. for $C_{24}H_{40}O_5$: 408.288), 390 (0.4), 377 (3.7), 290 (42), 275 (19), 206 (46), 189 (82), 119 (100), 107 (72); ^1H NMR ($CDCl_3$): δ 1.04 (*t*, H-1β), 2.16 (*ddd*, H-1α), 5.05 (*tt*, H-2), 1.19 (*m*, H-3β), 1.79 (*dd*, H-3α), 1.85 (*br d*, H-6α), 1.98 (*br d*, H-6β), 5.39 (*br s*, H-7), 1.54 (*m*, H-13), 3.68 (*m*, H-15), 0.90 (*d*, H-16), 1.67 (*br s*, H-17), 0.95 (*s*, H-18), 0.91 (*s*, H-19), 0.82 (*s*, H-20), 3.38 and 3.75 (*s*, CH_2CO_2Me); (*J* [Hz]: 1α, 1β = 1β, 2 = 3α, 3β = 12; 1α, 2 = 3α, 2 = 3.5; 6α, 6β = 17; 13, 16 = 7); $[\alpha]_D^{24^\circ}$ −13 ($CHCl_3$; *c* 0.93).

Bacchalatifolin acetate (**38Ac**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1740 (CO_2R); MS *m/z* (rel. int.): 640.470 $[M-H_2O]^+$ (0.7) (calc. for $C_{40}H_{64}O_6$: 640.470), 532 $[M-Me_2C{=}CHCH_2CH_2COMe]^+$ (1.7), 333 (100), 189 (58), 109 (64); ^1H NMR ($CDCl_3$: δ 5.06 (*tt*, H-2), 5.39 (*br s*, H-7), 4.09 (*m*, H-15), 0.92 (*d*, H-16), 1.67 (*br s*, H-17), 0.97 (*s*, H-18), 0.92 (*s*, H-19), 0.84 (*s*, H-20), 2.05 (*s*, OAc), 3.37 (*s*, $OCOCH_2CO_2$), 1.48 (*dd*, H-8′) 2.04 (*m*, H-9′), 5.12 (*br t*, H-10′), 1.69 (*br s*, H-12′), 1.62 (*br s*, H-13′), 1.10 (*s*, H-14′), 3.99 and 3.95 (*dd*, H-15′); (*J* [Hz]: 1α, 2α = 2α, 3α = 3.5; 1β, 2α = 2α, 3β = 12; 13, 16 = 6; 3′, 15′ = 6; 8′, 9′ = 7 and 10; 9′, 10′ = 7; 15′, 15₂· = 10); $[\alpha]_D^{24^\circ}$ −6 ($CHCl_3$; *c* 0.94).

7,15-*Dihydroxybisabol*-10-*ene* (**39**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620, 3430 (OH); MS *m/z* (rel. int.): 222.198 $[M-H_2O]^+$ (8) (calc. for $C_{15}H_{26}O$: 222.198), 109 (100), 82 (39), 69 (64); ^1H NMR ($CDCl_3$): δ 1.43 (*m*, H-3), 1.33 (*tt*, H-6), 1.49 (*dd*, H-8), 2.05 (*m*, H-9), 5.13 (*br t*, H-10), 1.69 (*br s*, H-12), 1.63 (*br s*, H-13), 1.12 (*s*, H-14), 3.45, (*d*, H-15); (*J* [Hz): 2, 3 = 3, 4 = 3.5; 2′, 3 = 3, 4 = 12; 3, 15 = 8, 9 = 9, 10 = 7; 8, 9′ = 10). Acetylation (Ac_2O, 1 hr, 70°) gave **39Ac**; coloulrss oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1750, 1250 (OAc); MS *m/z* (rel. int.): 264.209 $[M-H_2O]^+$ (6) (calc. for $C_{17}H_{28}O_2$: 264.209), 204 (2), 161 (4), 109 (100), 82 (34), 69 (57); ^1H NMR ($CDCl_3$): δ 1.58 (*m*, H-3), 1.32 (*tt*, H-6), 1.48 (*dd*, H-8), 2.05 (*m*, H-9), 5.13 (*br t*, H-10), 1.67 (*br s*, H-12), 1.62 (*br s*, H-13), 1.11 (*s*, H-14), 3.88 (*d*, H-15), 2.05 (*s*, OAc); (*J* [Hz]: 2, 3 = 3, 4 = 3.5; 2′, 3 = 3, 4′ = 12, 13, 15 = 8, 9 = 9, 10 = 7; 8, 9′ = 10);

^{13}C NMR ($CDCl_3$, C-1–C-15): δ 26.6$^+$, 29.71$^+$, 37.1, 29.66$^+$, 25.9$^+$, 47.1, 74.3, 39.7, 22.1, 124.5, 131.8, 25.7, 17.6, 23.8, 69.5; OAc: 20.9, 171.2 (assigned by ^{1}H/^{13}C correlation); $[\alpha]_D^{24}$ −3 ($CHCl_3$; *c* 1.29).

7, 10, 15-*Trihydroxybisabol*-11-*ene* (**41**). Isolated as its diacetate **41**Ac; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1740, 1240 (OAc); MS *m/z* (rel. int.): 280.204 [M − HOAc]$^+$ (1.8) (calc. for $C_{17}H_{28}O_3$: 280.204), 265 (1.3), 220 (1.5), 125 (100), 109 (57), 82 (94); ^{1}H NMR ($CDCl_3$): δ 1.68 (*m*, H-9), 5.13 (*br t*, H-10), 4.93 (*br s*, H-12), 4.88 (*br s*, H-12′), 1.70 (*br s*, H-13). 1.08 (*s*, H-14), 3.87 (*d*, H-15); (*J* [Hz]: 9, 10 = 3, 15 = 7).

6-*Oxo-germacra*-1(10)E,4(15)-*diene* (**43**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3080, 1640, 910 (C=CH$_2$), 1710 (CO); MS *m/z* (rel. int.): 220.183 [M]$^+$ (38) (calc. for $C_{15}H_{24}O$: 220.183), 205 (30), 177 (69), 159 (78), 97 (82), 81 (100), 69 (86); ^{1}H NMR ($CDCl_3$): δ 5.25 (*br dd*, H-1), 2.07 (*m*, H-2), 2.21 (*m*, H-2′), 3.32 (*d*, H-5), 2.97 (*br d*, H-5′), 2.30 (*br dd*, H-7), 2.12 (*m*, H-8), 1.34 (*m*, , H-8′), 1.71(*dq*, H-11), 0.92 (*d*, H-12), 0.87 (*d*, H-13), 1.40 (*br s*, H-14), 5.02 and 4.88 (*br s*, H-15); $[\alpha]_D^{24}$ +53 ($CHCl_3$; *c* 0.69).

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