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CLERODANE AND LABDANE DITERPENOIDS FROM *BACCHARIS* SPECIES

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Key Word Index—*Baccharis* spp.; Compositae; diterpenes; clerodanes; labdanes; nor-diterpene.

Abstract—The investigation of eight *Baccharis* species afforded, in addition to known compounds, five new clerodanes, three labdane derivatives and a nor-diterpene as well as one hydroperoxide derived from 4α-hydroxygermacra-1(10), 5-diene. The structures were elucidated by spectroscopic methods. The structures of esters isolated previously from *B. cassinaefolia* have to be revised. Chemotaxonomic aspects are discussed briefly.

INTRODUCTION

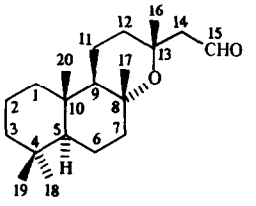
From the large genus *Baccharis* (Compositae, tribe Astereae) already more than 50 species have been investigated chemically. In most cases clerodane derivatives were isolated [1–9]. However, other compounds are also widespread in this genus [9]. There are some indications of possible grouping but still not enough material is available. We have now investigated eight further species, most of them from Peru. The results are presented in this paper.

RESULTS AND DISCUSSION

The aerial parts of *Baccharis scoparia* (L.) Sw., a species widespread in the Caribbean islands, afforded germacrene D, oleanolic acid, baccharis oxide, epi-friedelinol, dihydroeuparin and its 12-hydroxy derivative [10], 8α,15-dihydroxylabdane [11] as well as a new labdane aldehyde (**1**), two clerodanes (**14** and **15**) and the nor-diterpene **9**.

The structure and stereochemistry of **1** could be deduced from careful ^{1}H NMR investigations (Table 1). In deuteriobenzene nearly all signals could be assigned by spin decoupling. The triplet at δ9.96 was obviously due to an aldehyde proton which was coupled with a pair of double-doublets at δ2.30 and 2.13. As the remaining signals were close to those of manoyl oxide, the presence of 15-oxo-14,15-dihydromanoyl oxide was very likely. The stereochemistry was elucidated by spin decoupling and NOE difference spectroscopy. W-Coupling between H-17 and H-7β, between H-20 and H-1β and H-19, between H-18 and H-19, and between H-16 and H-14′ already indicated that all the methyl groups were axial. For assignment of the methyl signals, the NOEs of H-19 with H-18 and H-20 and of H-20 with H-17 were important and these results supported the proposed stereochemistry. Further NOEs were obtained between H-1α and H-9, between H-20 and H-2β, between H-5 and H-9, and between H-18 and H-6α. In the mass spectrum the base peak was at *m/z* 291 ($[M-Me]^+$) while *m/z* 263 obviously was formed by loss of CH_2CHO. Splitting of the 8-*O*- and 9–11 bond followed by loss of a hydrogen led to the strong ion at *m/z* 191 ($C_{14}H_{23}$). As the optical rotation of these labdanes are not very conclusive, the absolute configuration of **1** could not be determined.

The molecular formula of **9** ($C_{19}H_{22}O_5$) indicated that a nor-diterpene was present. The ^{1}H NMR spectrum (Table 2) was in part similar to that of hardwickiic acid-19-lactone [12]. However, the methyl doublet was missing and two pairs of low-field signals between δ2.25 and 3.00 indicated the presence of a keto group which could be placed only at C-7. Furthermore, a broadened double-doublet at δ4.83 was due to H-12. Accordingly, a hydroxyl group was at C-12 and irradiation at δ4.83 collapsed



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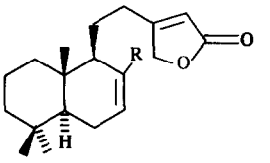
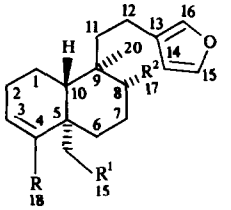
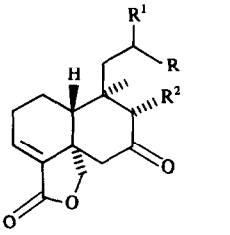


2 R = CH_2OH
3 R = CH_2OAc
4 R = CHO



	5	**6**	**7**
R	Me	Me	CO_2H
R^1	H	H	OH
R^2	Me	CHO	Me



8

9

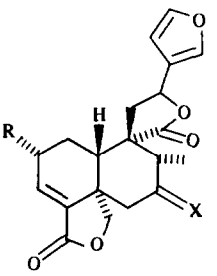
	8	**9**
R^1	H	OH
R^2	Me	H

Table 1. ^{1}H NMR spectral data of 1–4 (400 MHz, $CDCl_3$, TMS as internal standard)

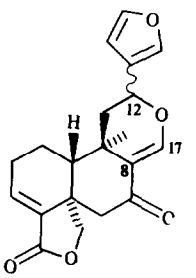
	1 (C_6D_6)	2	3*	4
H-1α	0.66 *ddd*	1.14 *ddd*	1.15 *ddd*	1.18 *ddd*
H-1β	1.37 *m*	1.84 *br d*	1.82 *br d*	1.88 *br d*
H-2α	1.58 *m*	1.53 *m*	1.53 *m*	1.54 *m*
H-2β	1.33 *m*	1.48 *m*	1.48 *m*	1.50 *m*
H-5	0.80 *dd*	1.23 *dd*	1.23 *dd*	1.23 *dd*
H-6α	1.53 *dddd*	2.08 *br d*	2.11 *br d*	2.40 *br d*
H-6β	1.10 *m*	1.94 *m*	1.95 *m*	2.24 *br dd*
H-7α	1.37 *m*	5.80 *br d*	5.88 *br ddd*	6.87 *br ddd*
H-7β	1.79 *ddd*			
H-9	0.98 *dd*	1.89 *m*	1.88 *m*	1.97 *m*
H-11	1.33 *m*	1.74 *dddd*	1.74 *dddd*	1.77 *dddd*
H-11′	1.24 *dddd*	1.57 *m*	1.58 *m*	1.58 *m*
H-12	1.45 *m*	2.80 *br ddd*	2.53 *br ddd*	2.98 *br ddd*
H-12′	1.37 *m*	2.46 *br ddd*	2.37 *br ddd*	2.40 *br ddd*
H-14	2.30 *dd*	5.87 *tt*	5.85 *tt*	5.82 *tt*
H-14′	2.13 *dd*			
H-15	9.96 *t*	—	—	—
H-16	1.10 *s*	4.77 *dd* 4.73 *dd*	4.76 *dd* 4.71 *dd*	4.79 *d*
H-17	1.16 *d*	3.97 *br d* 3.12 *br d*	4.53 *br d* 4.47 *br d*	9.37 *s*
H-18	0.86 *s*	0.88 *s*	0.88 *s*	0.92 *s*
H-19	0.80 *s*	0.86 *s*	0.84 *s*	0.89 *s*
H-20	0.65 *s*	0.75 *s*	0.76 *s*	0.79 *s*

*H-3α 0.95 *ddd*; OAc 2.05 *s*.

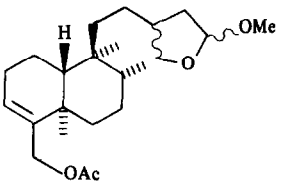
J (Hz): compound **1**: 1α, 1β = 12; 1α, 2α = 3.5; 1α, 2β = 11; 5, 6α = 2.5; 5, 6β = 12; 6α, 6β = 13; 6α, 7β = 6α, 7α ~ 3; 7α, 7β = 12.5; 9, 11 = 2.5; 9, 11′ = 12; 11, 11′ = 13; 11′, 12 ~ 10; 11′, 12′ = 4; 14, 14′ = 14; 14, 15 = 2.5; 14′, 15 = 3.5; (W-coupling: 7α, 17; 1α, 20; 9, 20; 18, 19; 14′, 16 ~ 0.5); compounds **2**–**4**: 1α, 1β = 13; 1α, 2α = 4.5; 1α, 2β = 12; 5, 6α = 5; 5, 6β = 12; 6α, 7 ~ 4; 6β, 7 ~ 2; 7, 9 ~ 2; 9, 12 = 10; 11, 11′ = 13, 11, 12 ~ 10, 11, 12′ ~ 5; 11′, 12 ~ 5; 11′, 12′ ~ 10; 12, 12′ = 14; 12, 14 = 14, 16 ~ 1.5, 16, 16′ = 17.



10 R = H, X = H_2
11 R = H, X = O
12 R = OAng, X = H_2



13 12α H
14 12β H
15 8β, 17 (no Δ), 12β H



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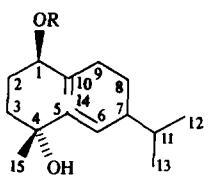

17 R = OH
18 R = H

the double-doublets at δ1.90 and 1.84 to doublets and sharpened the broadened singlet at δ7.39. As the optical rotation had the same sign as hardwickiic acid-19-lactone, the absolute configuration most likely was the same in both compounds. We have named compound **9** bacchascoparone.

The ^{1}H NMR spectral data of **14** (Table 2) were very similar to those of conycephaloide (**13**) from *Conyza* species [13]. However, the chemical shifts of H-20 and H-12 and the couplings of the latter differed considerably. Inspection of a model indicated that **14** was most likely the epimer of **13** with an α-orientated furan ring which shielded the C-9 methyl group. The optical rotations supported again the same absolute configuration as that of **9**.

The third clerodane derivative, **15**, differed from **14** by two additional hydrogens ($C_{20}H_{22}O_5$). The ^{1}H NMR spectrum (Table 2) was very similar to that of **14**; however, the low-field singlet at δ7.51 in the spectrum of **14** was replaced by a pair of double-doublets, which were coupled with a new double-doublet at δ2.66. The chemical shifts of these signals indicated that we were dealing with those of H-8 and H-17. Accordingly, the 8(17)-double bond was hydrogenated in compound **15**. The couplings of H-8 further showed that this proton was β-orientated. The ketone **14** most likely was the precursor of the nor-diterpene **9** since hydrolysis of **14** leads to a formyl ketone which could easily lose C-17.

The aerial parts of *B. eggersii* Hieron gave caryophyllene and its 1,10-epoxide, germacrene D, bicyclogermacrene, umbelliferone, its geranyl ether (auraptene), 3,5-bis-[3′,3′-dimethylallyl]-*p*-coumaric acid, baccharis oxide and the two new labdanes **2** and **4**. The structures of **2**, which also was transformed to the acetate **3**, and **4** followed from the ^{1}H NMR spectra (Table 1) which were in part close to those of similar labdanes from an *Acritopappus* species, where the oxygen function at C-17 was missing or an additional one was present at C-12 [14]. As an oxygen function was at C-17, a pair of doublets at δ4.53 and 4.47 was visible in the spectrum of **3** and in that of **2** at δ3.97 and 3.12. The spectrum of **4** showed a singlet at δ9.37. Furthermore, the H-7 signal was shifted downfield (6.87 *ddd*). All signals in the spectra of **2**–**4** could be assigned by spin decoupling though some were overlapped multiplets.

The aerial parts of *B. hutchisonii* Cuatr. gave germacrene D, δ-cadinene, baccharis oxide, epi-friedelinol and the two clerodanes **5** [15] and **6**. The structure of the latter was easily deduced from the ^{1}H NMR spectrum (Table 2), which was of course similar to that of **5**. The H-17 methyl doublet was replaced by a low-field doublet at δ9.78 and the H-20 signal was slightly shifted downfield (δ1.07 *s*). This effect and the coupling $J_{8,17}$ indicated an 8α-aldehyde group.

The aerial parts of *B. chilco* HBK. afforded oleanolic acid and the corresponding acetate, **7** [12] and **10** [1] while the aerial parts of *B. microcephala* (Less.) DC. gave germacrene D, spathulenol, luteolin and its 7-methyl ether as well as the clerodane **8** [16].

Table 2. ^{1}H NMR spectral data of **6**, **9**, **12**, **14** and **15** (400 MHz, $CDCl_3$, TMS as internal standard)

	6*	9	12†	14	15
H-1α		1.22 *m*	1.24 *dddd*	1.27 *dddd*	1.24 *dddd*
H-1β		1.81 *m*	2.20 *br dd*	1.90 *br d*	1.89 *br d*
H-2α	2.30 *m*	2.46 *dddd*	5.44 *br dd*	2.28 *br dd*	2.37 *br dd*
H-2β	2.05 *m*	2.17 *br dd*		2.52 *br dd*	2.56 *br d*
H-3	5.21 *br s*	6.87 *dd*	6.52 *br s*	6.86 *dd*	6.90 *dd*
H-6α		2.25 *d*	2.10 *ddd*	2.85 *d*	2.69 *d*
H-6β		2.72 *br d*	1.30 *br dd*	2.25 *dd*	2.41 *dd*
H-7α		—	1.85 *m*	—	—
H-7β		—	1.69 *br ddd*	—	—
H-8	2.30 *m*	2.99 *d* 2.38 *dd*	1.78 *ddq*	—	2.66 *dd*
H-10		2.28 *dd*	1.93 *m*	2.07 *dd*	2.95 *br d*
H-11		1.90 *dd*	2.59 *dd*	2.35 *dd*	2.21 *dd*
H-11′		1.84 *dd*	2.52 *dd*	1.97 *dd*	2.48 *dd*
H-12	2.51 *br ddd*	4.83 *br dd*	5.47 *br t*	5.59 *br t*	4.52 *br d*
H-12′	2.38 *m*				
H-14	6.27 *br s*	6.42 *br s*	6.32 *br s*	6.28 *br s*	6.39 *br s*
H-15	7.34 *dd*	7.41 *dd*	7.42 *dd*	7.42 *dd*	7.43 *dd*
H-16	7.21 *br s*	7.39 *br s*	7.45 *br s*	7.31 *br s*	7.41 *br s*
H-17	9.78 *d*	—	1.13 *d*	7.51 *s*	4.05 *dd* 3.97 *dd*
H-19	1.07 *s*	4.15 *dd*	4.68 *d*	4.09 *dd*	4.00 *dd*
H-19′		4.09 *dd*	4.07 *dd*	4.05 *d*	4.10 *d*
H-20	1.00 *s*	0.94 *s*	—	0.69 *s*	0.87 *s*

*H-18, 1.60 *t*, remaining signals not assigned multiplets.

†OAng: 6.12 *qq*, 1.95 *dq*, 1.87 *dq* (J = 7 and 1.5 Hz).

J (Hz): compound **6**: 11, 12 = 13; 11′, 12 = 4; 8, 17 = 3.5; 12, 12′ = 13; 14, 15 = 15, 16 = 1.5; compound **9**: 1α, 10 = 12; 1β, 10 = 2; 1α, 2α ~ 3; 1α, 2β ~ 5; 1β, 2α ~ 4; 1β, 2β ~ 3; 2α, 2β = 19; 2α, 3 ~ 3; 2β, 3 ~ 2; 6α, 6β = 15; 6β, 8β = 1; 8α, 8β = 15; 11, 11′ = 15; 11, 12 = 8; 11′, 12 = 4; 14, 15 = 15, 16 = 1.5; 19, 19′ = 9; compound **12**: 1α, 1β = 13; 1α, 2β = 11; 1α, 10 = 11; 1β, 2β = 3; 2β, 3 ~ 1; 6α, 6β = 13; 6α, 7α = 6α, 7β = 3; 6β, 7α = 12; 6β, 7β ~ 3; 7α, 7β = 14; 7α, 8β ~ 10; 7β, 8β = 3; 8β, 17 = 6.5; 11, 11′ = 14; 11, 12 = 9; 11′, 12 = 7; 14, 15 = 15, 16 = 1.5; 19, 19′ = 10; compound **14**: 1α, 1β = 13; 1α, 2α = 4; 1α, 2β = 12; 1α, 10 = 13; 1β, 10 = 2; 2α, 2β = 18; 2α, 3 = 8; 2β, 3 = 2; 6α, 6β = 17; 6β, 19 = 2.5; 11, 11′ = 14; 11, 12 = 1; 11′, 12 = 7.5; 14, 15 = 15, 16 = 1.5; 19, 19′ = 9; compound **15**: 1α, 1β = 13; 1α, 2α = 4; 1α, 2β = 13; 1α, 10 = 13; 2α, 2β = 18; 2α, 3 = 7.5; 2β, 3 = 2; 6α, 6β = 14; 6β, 19 = 2.5; 8, 17 = 12; 8, 17′ = 6; 11, 11′ = 15; 11, 12 = 12; 11′, 12 = 1.5; 14, 15 = 15, 16 ~ 1.5; 17, 17′ = 13.5; 19, 19′ = 8.

The aerial parts of *B. nitida* (R. et P.) Pers. gave germacrene D, oleanolic acid and the angelate **12** which showed ^{1}H NMR signals (Table 2) which were in part the same as those of an inseparable mixture of esters which were previously isolated from *B. cassinaefolia* [16]. The presence of an angelate followed from the ^{1}H NMR spectrum (Table 2), which was close to that of bacchotricuneatin B (**10**) [1]. However, the presence of an oxygen function at C-2 clearly followed from the broadened double-doublet at δ5.44. Irradiation of this signal sharpened the broadened singlet at δ6.52 and collapsed the signals at δ2.20 and 1.24 to a broad doublet and a double-doublet, respectively (H-1α and H-1β). The couplings required an α-angeloyloxy residue. The ^{13}C NMR spectrum also agreed well with the structure (see Experimental). Accordingly, the structures proposed for the diacyloxyclerodanes from *B. cassinaefolia* [6] have to be revised to the same as **12**, being the corresponding senecioate and 2-methylbutyrate, respectively.

The aerial parts of *B. grandicapitulata* Hieron. gave germacrene D, caryophyllene, α-humulene, spathulenol, γ-cadinene, baccharis oxide, acacetin, kaempferide, epifriedelinol and the corresponding ketone, oplodiol-1-*O*-angelate [17] and the clerodane **16**, which so far has not been isolated but has been prepared from a naturally occurring clerodane [9].

The aerial parts of *B. pylicoides* HBK. also gave germacrene D, α-humulene, spathulenol, oleanolic acid and oblodiol-1-*O*-angelate as well as *ent*-kaurenic acid, sakuranetin and its 7-methyl ether as well as the hydroperoxide **17**, which after addition of triphenylphosphine afforded the diol **18**. The structures followed from the ^{1}H NMR spectral data (Table 3) which were close to similar germacrane derivatives [18].

The investigation of eight further *Baccharis* species again showed that clerodane derivatives and baccharis

Table 3. ^{1}H NMR spectral data of **17** and **18** (400 MHz, TMS as internal standard)

	17* ($CDCl_3$)	17 (C_6D_6)	18
H-1	4.16 *ddd*	4.15 *dd*	3.94 *dd*
H-5	5.30 *m*	5.02 *d*	5.21 *d*
H-6		5.28 *dd*	5.30 *dd*
H-12	0.82 *d*	0.88 *d*	0.82 *d*
H-13	0.87 *d*	0.91 *d*	0.89 *d*
H-14	5.22 *br s*	5.18 *br s*	5.12 *br s*
H-14′	5.09 *br s*	4.95 *br s*	4.89 *br s*
H-15	1.27 *s*	1.09 *s*	1.18 *s*

*OOH 7.60 *s*.

J (Hz): 1, 2 = 8; 1, 2′ = 3; (compound **18**: 1, 2 = 9.5; 1, 2′ = 3.5); 5, 6 = 15.5; 6, 7 = 10; 11, 12 = 11, 13 = 7.

oxide are most widespread. However, as before, some diversity was visible which may be an indication that this large genus is not very homogeneous.

EXPERIMENTAL

The air-dried plant material was worked-up in the usual way [19] and the extracts (with MeOH–Et_2O–petrol, 1:1:1) were separated as usual [19]. Known compounds were identified by comparison of the 400 MHz ^{1}H NMR spectra with those of authentic material and by co-TLC. Sesquiterpene hydrocarbons were identified by GC/MS and ^{1}H NMR spectroscopy. In all cases, also the authentic material was available for direct comparison. The purity of all compounds was determined by their 400 MHz ^{1}H NMR spectra and by TLC or HPLC in different solvent mixtures.

Baccharis scoparia (*L.*) *Sw.* Voucher Jam 18; deposited at the U.S. National Herbarium, Washington, collected in January 1984 near Newcastle, Jamaica. The extract of 400 g aerial parts gave four CC (SiO_2) fractions. Fraction 1 (petrol and Et_2O–petrol, 1:10) afforded, on TLC (SiO_2 PF 254), 12 mg germacrene D and 12 mg baccharis oxide Fraction 2 (Et_2O–petrol, 1:1) gave, on TLC (Et_2O–petrol, 1:4), 8 mg epi-friedelinol and 6 mg **1** (R_f 0.42). Fraction 3 (Et_2O) afforded by TLC (Et_2O–petrol, 2:1) 2 mg dihydroeupatin, 2 mg of its 12-hydroxy derivative, oleanolic acid and a mixture of **14** and **15** which was separated by HPLC (always RP 8, *ca* 100 bar, flow rate 3 ml/min, MeOH–H_2O, 3:2) affording 5 mg **15** (R_t 4.5 min) and 4 mg **14** (R_t 4.0 min). Fraction 4 (Et_2O–MeOH, 10:1 and MeOH) gave, on TLC (Et_2O–petrol, 9:1) and HPLC (MeOH–H_2O, 3:2), 3 mg **9** (R_t 5.0 min) and 7 mg 8α,15-dihydroxylabdane.

Baccharis eggersii. Voucher RMK 9096; collected in Peru. The extract of 100 g aerial parts gave, on TLC (Et_2O–petrol, 2:1), three bands. The first (30 mg) gave by GC/MS caryophyllene, germacrene D, bicyclogermacrene and caryophyllene-1,10-epoxide (*ca* 15:2:1:1). The second band gave, on repeated TLC (Et_2O–petrol, 4:1), 8 mg 3,5-bis-[3′,3′-dimethylallyl]-*p*-coumaric acid, 9 mg auraptene, 12 mg umbelliferone and crude **4**, which was purified by repeated TLC (Et_2O–petrol, 4:1) and HPLC (MeOH–H_2O, 7:3) affording 3 mg **4** (R_t 5.0 min) The most polar band gave, on TLC (Et_2O–petrol, 9:1), 7 mg **2** (R_f 0.4).

Baccharis hutchisonii. Voucher RMK 9129; collected in Peru. The extract of 370 g aerial parts gave three CC fractions. TLC of fraction 1 (petrol) gave 80 mg germacrene D and 30 mg δ-cadinene TLC of fraction 2 (Et_2O–petrol, 1:4) gave 15 mg baccharis oxide, 50 mg epi-friedelinol, 2 mg **5** and 3 mg **6** (R_f 0.5)

Baccharis chilco. Voucher RMK 9030; collected in Peru. The extract of 530 g aerial parts gave a polar CC fraction (Et_2O and Et_2O–MeOH, 9:1) which on TLC (Et_2O) gave 12 mg oleanolic acid acetate, 90 mg oleanolic acid, 1 mg **7** and 5 mg **10**.

Baccharis microcephala. Voucher 3/83; collected in Caaguazu, Paraguay. The extract of 200 g aerial parts gave three CC fractions. Fraction 1 (petrol) gave, on TLC (petrol), 2 mg germacrene D; fraction 2 (Et_2O–petrol, 1:1) gave by TLC (Et_2O–petrol, 1:3) 20 mg spathulenol and fraction 3 (Et_2O and Et_2O–MeOH, 9:1) affording by TLC (Et_2O) 200 mg **8**, 30 mg luteolin, 200 mg **8** and 30 mg of its 7-methyl ether.

Baccharis nitida. Voucher RMK 9191; collected in Peru. The extract of 200 g aerial parts gave a polar CC fraction (Et_2O and Et_2O–MeOH, 9:1) affording by TLC (Et_2O) 30 mg luteolin, 200 mg **8** and 30 mg of its 7-methyl ether.
(MeOH–H_2O, 7:3) 10 mg **12** (R_t 5.5 min).

Baccharis grandicapitulata Voucher RMK 9127; collected in Peru. The extract of 400 g aerial parts gave three CC fractions. TLC (petrol) of fraction 1 (petrol and Et_2O–petrol, 1:10) gave 65 mg germacrene D, 13 mg caryophyllene, 12 mg α-humulene and 6 mg γ-cadinene. TLC (Et_2O–petrol, 1:1) of fraction 2 (Et_2O–petrol, 1:3 and 1:1) gave 15 mg oblodiol-1-*O*-angelate, 5 mg spathulenol, 3 mg epi-friedelinone, crude **16**, which was purified by TLC (Et_2O–petrol, 1:9) affording 8 mg **16** (R_f 0.35) [MS *m/z* (rel. int.): 318.256 $[M-HOAc]^+$ (3) (calc for $C_{21}H_{34}O_2$: 318.256), 286 $[318-MeOH]^+$ (34), 271 $[286-Me]^+$ (9), 189 $[C_{14}H_{21}]^+$ (100); ^{1}H NMR identical with authentic material], and 5 mg spathulenol. Fraction 3 (Et_2O and Et_2O–MeOH, 10:1) gave 130 mg of a crystalline mixture of acacetin and kaempferide, which were separated as their acetates (Ac_2O, 1 hr, 140°).

Baccharis pylicoides. Voucher RMK 9192; collected in Peru. The extract of 240 g aerial parts gave three CC fractions. Fraction 1 (petrol) gave, on TLC, 260 mg germacrene D and 20 mg α-humulene. Fraction 2 (Et_2O–petrol, 1:3 and 1:1) gave on TLC (Et_2O–petrol, 1:4) 40 mg oblodiol-1-*O*-angelate, 32 mg *ent*-kaurenic acid, 45 mg oleanolic acid, 20 mg spathulenol and after repeated TLC (Et_2O–petrol, 1:9) 3 mg **17** (R_f 0.33). Fraction 3 (Et_2O and Et_2O–MeOH, 10.1) gave, on TLC (Et_2O), 25 mg sakuranetin and 25 mg of its 7-methyl ether.

15-*Oxo*-14,15-*dihydromanoyl oxide* (**1**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2730, 1720 (CHO); MS *m/z* (rel. int.): 306.256 $[M]^+$ (10) (calc. for $C_{20}H_{34}O_2$: 306.256), 291 $[M-Me]^+$ (100), 273 $[291-H_2O]^+$ (18), 263 $[M-CH_2CHO]^+$ (20), 245 $[263-H_2O]^+$ (68), 191 $[C_{14}H_{23}]^+$ (76);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-15 \quad -16 \quad -19 \quad -33} \quad (CHCl_3;\ c\ 0.74).$$

17-*Hydroxy-labda*-7,13-*dien*-15-*acid*-16-*lactone* (**2**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 318 $[M]^+$ (0.5), 195 $[M-C_9H_{15}]^+$ (96), 124 $[C_9H_{16}, RDA]^+$ (48), 109 $[124-Me]^+$ (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+12 \quad +12 \quad +14 \quad +23} \quad (CHCl_3;\ c\ 0.18).$$

Acetylation of **2** gave **3** (Ac_2O, 1 hr, Ac_2O); colourless oil; MS *m/z* (rel. int.): 360.230 $[M]^+$ (2.5) (calc. for $C_{22}H_{32}O_4$: 360.230), 300 $[M-HOAc]^+$ (12), 285 $[300-Me]^+$ (9), 237 $[M-C_9H_{15}]^+$ (86), 177 $[237-HOAc]^+$ (35), 124 $[C_9H_{16}, RDA]^+$ (47), 109 $[124-Me]^+$ (100).

17-*Oxolabda*-7,13-*dien*-15-*acid*-16-*lactone* (**4**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1720 (CHO); MS *m/z* (rel. int.). 316.204 $[M]^+$ (6) (calc. for $C_{20}H_{28}O_3$: 316.204), 301 $[M-Me]^+$ (2), 193 $[M-C_9H_{15}]^+$ (100), 124 $[C_9H_{16}, RDA]^+$ (52), 109 $[124-Me]^+$ (98).

17-*Oxocleroda*-3,13(16),14-*trien*-15,16-*oxide* (**6**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2740, 1720 (CHO); MS *m/z* (rel. int.): 300.209 $[M]^+$ (17) (calc. for $C_{20}H_{28}O_2$: 300.209), 285 $[M-Me]^+$ (5), 205 $[M-C_6H_7O]^+$ (8), 149 $[205-CH_2{=}CHCHO]^+$ (100), 95 $[C_6H_7O]^+$ (96), 81 $[C_5H_5O]^+$ (97).

Bacchascoparone (**9**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone), 1720 (C=O); MS *m/z* (rel. int.): 330.147 $[M]^+$ (6) (calc. for $C_{19}H_{22}O_5$: 330.147), 312 $[M-H_2O]^+$ (8), 234 $[M-C_6H_8O]^+$ (40), 219 $[234-Me]^+$ (44), 112 $[C_6H_8O_2]^+$ (85), 94 $[C_6H_6O]^+$ (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-50 \quad -53 \quad -62 \quad -121} (CHCl_3;\ c\ 0.3).$$

2α-*Angeloyloxybacchotricuneatin B* (**12**). Colourless crystals, mp 145°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770 (γ-lactone), 1715 (C=O); MS *m/z* (rel. int.): 440.184 $[M]^+$ (6) (calc. for $C_{25}H_{28}O_7$: 440.184), 422 $[M-H_2O]^+$ (1), 358 $[M-O{=}C{=}C(Me)CH{=}CH_2]^+$ (2), 357 $[M-RCO]^+$ (5), 340 $[M-RCO_2H]^+$ (8), 310 $[340-CH_2O]^+$ (9), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (88);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-34 \quad -36 \quad -42 \quad -74} (CHCl_3;\ c\ 0.23).$$

^{13}C NMR ($CDCl_3$, C-1–C-20): 41.6 *t*, 71.0 *d**, 144.3 *d*, 140.2 *s*, 45.7 *s*, 27.8 *t*, 33.2 *t*, 43.1 *d*, 50.3 *s*, 45.2 *d*, 27.5 *t*, 71.8 *d**, 125.1 *s*, 108.0 *d*, 134.5 *d*, 139.5 *d*, 176.6 *s*, 168.2 *s*, 72.7 *t*, 17.2 *q* (C-1′–C-5′: 167.0 *s*, 127.1 *s*, 139.5 *d*, 20.4 *q*, 15.8 *q*). (Signals labelled with an asterisk may be interchanged.)

12-*epi*-*Conycephaloide* (**14**) Colourless oil; IR $\nu_{mah}^{CHCl_3}$ cm^{-1}: 1775 (γ-lactone), 1700 (C=O); MS *m/z* (rel. int.): 340.131 $[M]^+$ (6) (calc. for $C_{20}H_{20}O_5$: 340.131), 325 $[M-Me]^+$ (1), 311 $[M-CHO]^+$ (2), 246 $[M-C_6H_6O]^+$ (2), 94 $[C_6H_6O]^+$ (100);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-86 \quad -87 \quad -103 \quad -211} (CHCl_3;\ c\ 0.14)$$

12-*epi*-8β,17-*Dihydroconycephaloide* (**15**). Colourless crystals, mp 182°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}. 1780 (γ-lactone), 1715 (C=O), 880 (furane); MS *m/z* (rel. int.): 342.147 $[M]^+$ (40) (calc. for $C_{20}H_{22}O_5$: 342.147), 233 $[M-C_6H_5O_2]^+$ (20), 232 $[M-C_6H_6O_2]^+$ (100), 205 $[233-CO]^+$ (41), 110 $[C_6H_6O_2]^+$ (44), 95 $[C_6H_7O]^+$ (54), 94 $[C_6H_6O]^+$ (52);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-158 \quad -164 \quad -192 \quad -395} (CHCl_3;\ c\ 0.3).$$

4α-*Hydroxygermacra*-5E,10(14)-*dien*-1β-*hydroperoxide* (**17**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 236.178 $[M-H_2O]^+$ (1) (calc. for $C_{15}H_{24}O_2$: 236.178), 220 $[M-H_2O_2]^+$ (4), 162 $[C_{12}H_{18}]^+$ (100). To 3 mg **17** in 0.5 ml $CDCl_3$, 10 mg triphenylphosphine was added. After 10 min, the ^{1}H NMR spectrum of **18** was obtained (see Table 3).

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