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DITERPENES FROM *BACCHARIS* SPECIES*

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Key Word Index—*Baccharis* species; Compositae; diterpenes; *ent*-labdanes; clerodane; *ent*-kauranes; *p*-hydroxyacetophenone derivatives; acetylenes; flavone; 3′-methoxyxanthomicrol.

Abstract—The investigation of ten *Baccharis* species afforded in addition to known compounds eight new diterpenes, four *ent*-labdanes, three kaurenes and a clerodane derivative. Furthermore, two new *p*-hydroxyacetophenones, a flavone, 3′-methoxyxanthomicrol and two matricaria ester derivatives were isolated. The structures were elucidated by spectroscopic methods and a few chemical transformations. The chemotaxonomic situation of the large genus is discussed briefly.

INTRODUCTION

So far, chemical investigations of the large American genus *Baccharis* (Compositae, tribe Astereae) [1] have shown that the chemistry of this genus is not very uniform. The investigation of nine further species and the investigation of *B. ramosissima* roots again showed this diversity.

RESULTS AND DISCUSSION

While the roots of *Baccharis oxydonta* DC. afforded squalene, baccharis oxide (**35**) [2] and small amounts of further triterpenes, probably closely related to euphol, the aerial parts contained germacrene D, β-farnesene, squalene, squalene-2,3-epoxide, α-humulene, bicyclogermacrene, unidentified triterpenes, the flavanones pinocembrin **12** and pinobanksin **13**, *ent*-manool (**1**) [3] and its derivatives **2**, **3**, **6** and **7**. The structures followed from the ^{1}H NMR data and from those of some transformation products, the acetates **4** and **5** and the methyl ester **8** (Table 1). **2** and **3** are obviously epimeric at C-2, as could be deduced from the ^{1}H NMR data of the corresponding acetates **4** and **5** (Table 1). Furthermore, oxidation of **2** and **3** both afforded the ketone **9**; its structure clearly followed from the ^{1}H NMR data too. Obviously the side chain was transformed by allylic rearrangement and subsequent oxidation to the conjugated aldehyde. The signals assigned to H-1 and H-3 required a carbonyl group at C-2. **7** clearly was a succinate. Consequently lithium aluminium hydride reduction afforded **2**. The ^{1}H NMR data of **6** (Table 1) showed that the keto group was at C-2. In the ^{1}H NMR spectra of **5**–**9** the assignment of H-1 and H-3 could not really be established; perhaps assignments may be interchangeable. Although the absolute configuration was not determined, the proposed one is very probable since *ent*-manool (**1**) was isolated too.

The roots of *B. subdentata* DC. afforded baccharis oxide (**35**), matricaria ester (**51**) and the dilactone **10**, already isolated from another *Baccharis* species, its structure being confirmed by X-ray analysis [4]. Furthermore, the corresponding 7β-angeloyloxy derivative **11** was present, its ^{1}H NMR data being very close to those of **10** (Table 1). The couplings of H-7 allowed the assignment of the proposed stereochemistry. The aerial parts gave germacrene D, bicyclogermacrene, *p*-methoxycinnamic acid, oleanolic acid and β-amyrin acetate.

The roots of *B. leptocephala* DC. afforded again **35** and the aerial parts germacrene D, bicyclogermacrene, benzyl benzoate and the flavanones naringenin 7-methyl ether **14** [5] and naringenin 4′-methyl ether **15** [5]. The roots of *B. latifolia* (R. et P.) Pers. also afforded **35** and the thymol derivative **29** as well as the *p*-hydroxyacetophenones **21** [6], **22** [7] and **23** [8].

The roots of *B. concinna* Barroso gave lupeol, lupenone, squalene, **28** [7], **36** [9] and **43** [10], while the aerial parts afforded germacrene D, bicyclogermacrene, α-humulene, lupeol, lupenone, squalene, **12**, **36** and **41** [18]. The aerial parts of *B. helichrysioides* DC. gave the coumarin **30** only, while those of *B. trinervis* (Lam.) Pers. afforded phytene, caryophyllene, germacrene D, bicyclogermacrene, α- and γ-humulene, squalene, lupeol and its Δ12,13-isomer, lupenone, β-amyrin, lupeyl acetate and lachnophyllum ester (**56**). The roots gave lupeyl acetate only. A reinvestigation of the roots of *B. ramoisissima* Gardn. afforded, in addition to euphol-like triterpenes, *ent*-kaurenic acid (**36**), *ent*-kaurenal (**37**), **24** [11], **26** [11] and a further unusual substituted *p*-hydroxyacetophenone derivative, the ester **27**. The structure clearly followed from the ^{1}H NMR data (see Experimental). The roots of *B. truncata* Gardn. afforded germacrene D, bicyclogermacrene, α- and γ-humulene, lupeol, **35**, **36** and **50** [12] as well as **24**, **26** and the corresponding alcohol **25**, its structure following from the ^{1}H NMR data (see Experimental). The aerial parts gave germacrene D, bicyclogermacrene, lupeol, lupenone, **17** [13], **36**, **37** [14], **40** [15] and **42** [10].

*Part 359 in the series "Naturally Occurring Terpene Derivatives". For Part 358 see Bohlmann, F., Kramp, W., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, (in press).

Table 1. ^{1}H NMR spectral data of compounds **2**, **4**–**9** and **11** (400 MHz, TMS as internal standard)

	2 ($CDCl_3$)	**4** ($CDCl_3$)	**4** (C_6D_6)	**5** (C_6D_6)*	**6** (C_6D_6)*	**7** ($CDCl_3$)*	**8** ($CDCl_3$)*	Δ	**9** (C_6D_6)*	**11** (C_6D_6)
H-1α				1.91 *d* (*br*)	2.54 *dd*	1.99 *d* (*br*)	2.00 *d* (*br*)	0.25	2.34 *dd*	
H-1β				1.28 *m*	1.88 *d*	1.44 *m*	1.45 *m*	0.14	1.72 *d*	
H-2	4.15 *dddd*	5.16 *dddd*	5.29 *dddd*	5.31 *dddd*	—	5.19 *dddd*	5.19 *dddd*	0.28		—
H-3α				2.28 *d* (*br*)	2.14 *dd*	1.75 *d* (*br*)	1.75 *d* (*br*)	0.16	2.13 *dd*	6.26 *dd*
H-3β				1.20 *m*	2.01 *d*	1.44 *m*	1.45 *m*	0.07	2.01 *d*	
H-5	1.15 *dd*	1.20 *dd*		1.18 *dd*		1.18 *dd*	1.18 *dd*	0.06		—
H-7α	2.38 *ddd*	2.41 *ddd*	2.42 *ddd*	2.38 *d* (*br*)	2.33 *ddd*	2.39 *ddd*	2.40 *ddd*	0.03	2.25 *ddd*	5.53 *ddd*
H-7β	1.94 *ddd*	2.00 *m*	1.96 *ddd*	1.91 *m*		1.97 *m*	1.97 *m*	0.04	1.80 *ddd*	—
H-14	5.91 *dd*	5.91 *dd*	5.85 *dd*	5.83 *dd*	5.82 *dd*	5.89 *dd*	5.90 *dd*	0.15	5.82 *dq*	5.97 *s* (*br*)
H-15	5.06 *dd*	5.08 *dd*	5.02 *dd*	5.01 *dd*	5.01 *dd*	5.07 *dd*	5.08 *dd*	0.06	9.98 *d*	6.99 *dd*
H-15′	5.21 *dd*	5.22 *dd*	5.26 *dd*	5.25 *dd*	5.22 *dd*	5.21 *dd*	5.21 *dd*	0.13		
H-16	1.27 *s*	1.28 *s*	1.18 *s*	1.16 *s*	1.16 *s*	1.27 *s*	1.27 *s*	0.17	1.60 *d*	7.01 *s* (*br*)
H-17	4.84 *s* (*br*)	4.87 *s* (*br*)	5.03 *s* (*br*)	4.98 *s* (*br*)	4.92 *s* (*br*)	4.86 *s* (*br*)	4.86 *s* (*br*)	0.04	4.85 *s* (*br*)	0.86 *d*
H-17′	4.51 *s* (*br*)	4.53 *s* (*br*)	4.78 *s* (*br*)	4.74 *s* (*br*)	4.69 *s* (*br*)	4.54 *s* (*br*)	4.52 *s* (*br*)	0.09	4.40 *s* (*br*)	
H-18	0.98 *s*	0.98 *s*	0.85 *s*	0.85 *s*	0.78 *s*	0.97 *s*	0.97 *s*	0.09	0.76 *s*	3.92 *dd*
H-19	0.91 *s*	0.93 *s*	1.04 *s*	0.85 *s*	0.75 *s*	0.92 *s*	0.92 *s*	0.07	0.73 *s*	5.00 *d*
H-20		0.88 *s*	1.01 *s*	0.82 *s*	0.72 *s*	0.86 *s*	0.86 *s*	0.12	0.63 *s*	—
OCOR	—	—			—	2.58 *t*	2.61 *m*	0.27	—	5.78 *qq*
						2.67 *t*	3.69 *s*	0.17	—	1.99 *dq*
										1.86 *dq*
OAc		2.02 *s*		1.81 *s*	—	—	—	—	—	—

Compound **11**: H-6α 2.54 *dd*, H-6β 0.92 *dd*, H-10 1.25 *d* (*br*), H-11 1.69 *dd*, H-11′ 1.74 *dd*, H-12 4.77 *dd* (*br*).

J (Hz): Compounds **2**, **4**–**8**: 5β,6α = 12; 5β,6β = 3; 6α,7α = 4; 6α,7β = 12; 6β,7α = 2; 6β,7β = 5; 7α,7β = 12; 14,15 = 10.5; 14,15′ = 17; 15,15′ = 1.5; compounds **2**, **4**–**8**: 1α,2β = 1β,2β = 2β, 3α = 2β,3β = 4; compound **5**: 1α,1β = 1β, 2α = 2α,3β = 12; 1α,2α = 2α,3α = 4; compounds **6** and **9**: 1α,1β = 12.5; 1α,3α = 2; 3α,3β = 13; (**9**: 14,15 = 8; 14,16 = 1.5); compound **11**: 1α,10 = 12; 2,3 = 7; 2′,3 = 2.5; 6α,6β = 12; 6α,7α = 4; 6β,7α = 11; 6β,19 = 2; 7α,8β = 11; 8β,17 = 7; 11,11′ = 14; 11,12 = 9.5; 11′,12 = 7.5; 14,15 = 15,16 = 1.5; 19,19′ = 9.5.

*The assignments of H-1 and H-3 may be interchangeable.

The roots of *B. quitensis* HBK afforded germacrene D, euphol-like triterpenes, **21**, **28**, **51**, **52** and in addition to **53** [16] the isomers **54** and **55**, their structures following from the spectroscopic data (see Experimental). While the chromophoric system could be deduced from the UV spectra, the stereochemistry of the double bonds followed from the ^{1}H NMR data. Furthermore, the *iso*-kaurenic derivative **46** was present. Acetylation gave the diacetate **47**. The ^{1}H NMR data (Table 2) were close to those of similar diterpenes, while the nature of the ester residue clearly followed from the corresponding ^{1}H NMR signals. The aerial parts gave germacrene D, α-humulene, lupeol and its Δ9,11- and Δ12,13-isomers, **31** [17] and **32**, containing **33** and **34**, as could be deduced from the mass spectrum. In addition to the *ent*-kaurane derivatives **36**, **38** [14] and **46**, two further *p*-hydroxyhydrocinnamic esters were present, **44** and **48**. **44** on acetylation afforded acetate **45**, while **48** on lithium aluminium hydride reduction gave **49** and *p*-hydroxyphenylpropanol. Again the structures followed from the ^{1}H NMR data (Table 2), especially if compared with those of similar kaurane derivatives. In addition to xanthomicrol (**19**) [19] the methoxy derivative **20** (6,7,8,3′-tetramethoxy-5,4′-dihydroxyflavone) was isolated in minute amounts too. The ^{1}H NMR data (see Experimental) clearly showed that an additional O-function had to be placed at C-3′. The changes in the UV maxima after addition of sodium acetate showed that a free 4′-hydroxy group was present. As the ^{1}H NMR signal at 12.54 ppm required a free 5-hydroxy group, the additional methoxy group must be at C-3′. The overall picture of the chemistry of *Baccharis* is still not very uniform. One group of species contain the typical triterpene **35**, others kaurene, *ent*-labdane or clerodane derivatives, sometimes together with flavanoids or *p*-hydroxyacetophenone derivatives with an unusually placed acetyl group. The other triterpenes isolated so far are widespread in the family, except those related to euphol; their structures, however, could not be assigned with certainty. New taxonomic investigations are desirable to see whether this large genus should be separated or not.

EXPERIMENTAL

The air-dried plant material was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by column chromatography (Si gel) and further by TLC (Si gel). Known compounds were identified by comparing the IR and ^{1}H NMR (400 MHz) spectra with those of authentic material.

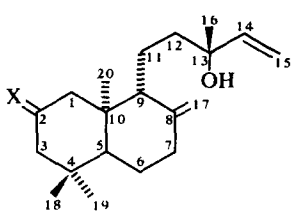
Baccharis oxydonta (*voucher RMK* 8331). The roots (120 g) afforded 3 mg of an unidentified triterpene alcohol, 3 mg of its acetate, 10 mg of its ketone, 4 mg squalene and 7 mg **35**, while the aerial parts (260 g) gave 20 mg germacrene D, 5 mg β-farnesene, 16 mg squalene, 10 mg squalene-2,3-epoxide, 5 mg bicyclogermacrene, 5 mg α-humulene, 8 mg **1**, (laevorotatory) 95 mg **2** (Et_2O–petrol, 1:1), 48 mg **3** (Et_2O–petrol, 1:1), 15 mg **6** (Et_2O–petrol, 1:3), 440 mg **7** (Et_2O), 20 mg **12** and 20 mg **13**.

Baccharis subdentata (*voucher RMK* 8225). The roots (15 g) afforded 4 mg **10**, 2 mg **11** (Et_2O), 9 mg **35** and 1 mg **51**, while the

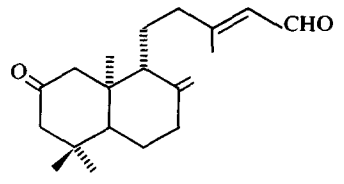
Table 2. ^{1}H NMR spectral data of compounds **44–49** ($CDCl_3$, 270 MHz, TMS as internal standard)

	44	**45**	**46**	**47**	**48**	**49**
H-13	2.64 *s* (*br*)	2.64 *s* (*br*)	2.67 *s* (*br*)	2.54 *d* (*br*)	2.56 *s* (*br*)	2.08 *s*(*br*)
H-15	2.05 *s* (*br*)	2.05 *s* (*br*)	5.34 *s* (*br*)	5.40 *s* (*br*)		
H-17	4.79 *s* (*br*)	4.80 *s* (*br*)	4.19 *s* (*br*)	4.67 *dd*	9.65 *d*	3.42 *m*
H-17′	4.73 *s* (*br*)	4.74 *s* (*br*)		4.68 *dd*		
H-18	1.01 *s*	1.02 *s*	1.02 *s*	1.03 *s*	0.99 *s*	1.01 *s*
H-19	4.22 *d*	4.24 *d*	4.21 *d*	4.22 *d*	4.21 *d*	3.75 *d*
H-19′	3.86 *d* (*br*)	3.87 *d* (*br*)	3.86 *d* (*br*)	3.86 *d* (*br*)	3.86 *d* (*br*)	3.45 *d*
H-20	0.90 *s*	0.90 *s*	0.90 *s*	0.90 *s*	0.90 *s*	0.90 *s*
OCOR	2.60 *t*	2.63 *t*	2.59 *t*	2.63 *t*	2.60 *t*	—
	2.89 *t*	2.95 *t*	2.87 *t*	2.95 *t*	2.87 *t*	—
	7.07 *d*	7.21 *d*	7.04 *d*	7.21 *d*	7.05 *d*	—
	6.75 *d*	7.00 *d*	6.75 *d*	7.00 *d*	6.75 *d*	—
OAc	—	2.29 *s*	—	2.29 *s*	—	—
				2.08 *s*		

J (Hz): 19,19′ = 11; 2′,3′ = 7.5; 5′,6′ = 8.5; compound **47**: 15,17 = 1.3; 15,17′ = 13; compound **48**: 16,17 = 1.5.



1 X = H_2
2 X = αOH, H
3 X = βOH, H
4 X = αOAc, H
5 X = βOAc, H
6 X = O
7 X = $\alpha OCOCH_2CH_2CO_2H$, H
8 X = $\alpha OCOCH_2CH_2CO_2Me$, H



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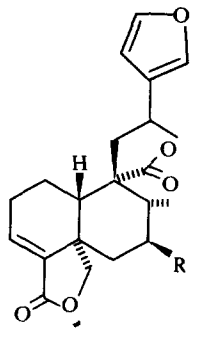
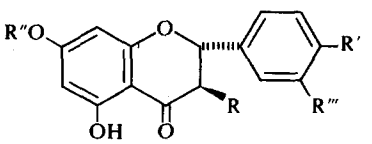
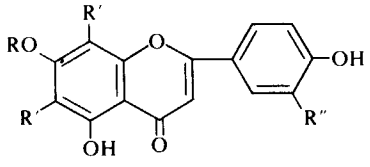


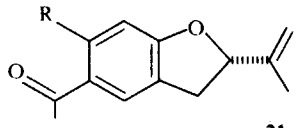
10 R = H
11 R = OAng



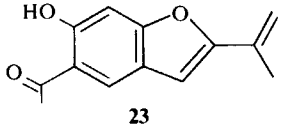
	12	**13**	**14**	**15**	**16**	**17**
R	H	OH	H	H	H	H
R′	H	H	OH	OMe	OH	H
R″	H	H	Me	H	H	H
R‴	H	H	H	H	H	OMe



	18	19	20
R	H	Me	Me
R′	H	OMe	OMe
R″	H	H	OMe



21 R = H
22 R = OH



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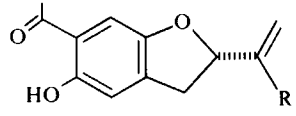
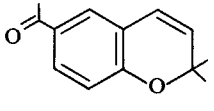


24 R = CH_2OAc
25 R = CH_2OH
26 R = CHO
27 R = CO_2Me



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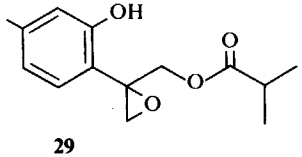

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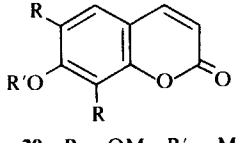
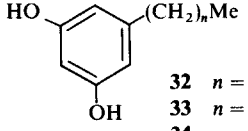
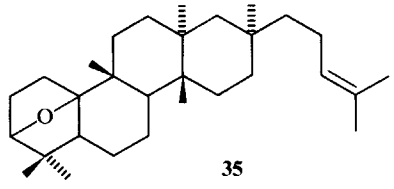


30 R = OMe, R′ = Me
31 R = H, R′ = Geranyl



32 *n* = 14
33 *n* = 13
34 *n* = 12



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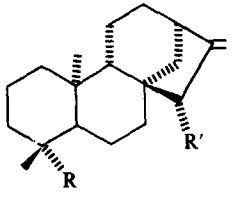
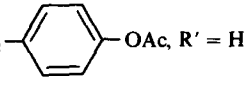
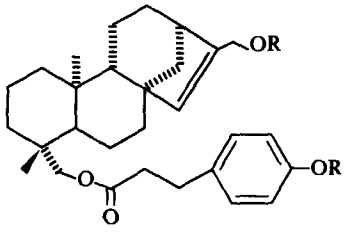
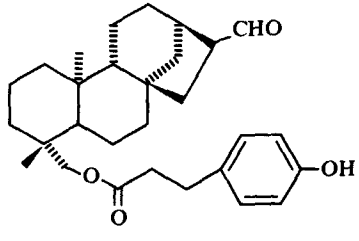


	36	37	38	39	40	41	42	43	44
R	CO_2H	CHO	CH_2OH	CO_2H	CO_2H	CO_2H	CO_2H	CO_2Me	$CH_2OCOCH_2CH_2$
R'	H	H	H	OSen	OTigl	OAng,	OAc	OH	H

45 R = $CH_2OCOCH_2CH_2$  OAc, R' = H



46 R = H
47 R = Ac



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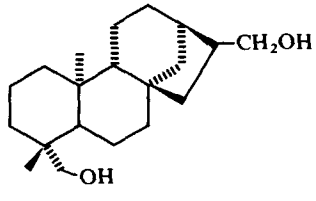

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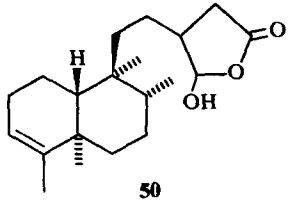

50

MeCH=CH[C≡C]$_2$CH=CHCO$_2$Me
51 *c* *c*
52 *c* *t*
AngOCH$_2$CH=CH[C≡C]$_2$CH=CHCO$_2$Me
53 *t* *t*
54 *t* *c*
55 *c* *t*
EtCH$_2$[C≡C]$_2$CH=CHCO$_2$Me **56**
t

aerial parts (645 g) gave 48 mg germacrene D, 17 mg bicyclogermacrene, 30 mg *p*-methoxycinnamic acid, 15 mg: β-amyrin acetate and 180 mg oleanolic acid.

Baccharis leptocephala (*voucher RMK* 8085). The roots (25 g) afforded 30 mg **35** and the aerial parts (100 g) 75 mg benzylbenzoate, 56 mg germacrene D, 29 mg bicyclogermacrene, 7 mg **14** and 7 mg **15**.

Baccharis latifolia (*voucher RMK* 7851). The roots (200 g) afforded 6 mg **21**, 21 mg **22**, 7 mg **23**, 8 mg **29** and 60 mg **35**.

Baccharis concinna (*voucher RMK* 8365). The roots (50 g) afforded 4 mg lupeol, 5 mg lupenone, 4 mg squalene, 4 mg **28**, 8 mg **36** and 3 mg **43**, while the aerial parts (410 g) gave 86 mg germacrene D, 16 mg bicyclogermacrene, 94 mg α-humulene, 45 mg lupenone, 16 mg squalene, 273 mg lupeol, 13 mg **12**, 42 mg **28**, 8 mg **36** and 3 mg **41**.

Baccharis helichrysoides (*voucher RMK* 8399). The aerial parts (120 g) afforded 1 mg **30**.

Baccharis trinervis (*voucher RMK* 8028). The roots (45 g) gave 4 mg lupeyl acetate and the aerial parts (540 g) 2 mg phytene, 9 mg caryophyllene, 3 mg germacrene D, 5 mg bicyclogermacrene, 5 mg α- and 5 mg γ-humulene, 10 mg squalene, 140 mg lupeyl acetate, 6 mg lupeol and 8 mg of its Δ12,13-isomer, 12 mg β-amyrin and 86 mg **56**.

Baccharis ramosissima (*voucher RMK* 8293). The roots (250 g) afforded 4 mg of an unidentified triterpene alcohol and 5 mg of its acetate, 4 mg of its ketone, 1 mg **24**, 1 mg **26**, 1 mg **27** (Et_2O–petrol, 1:3), 12 mg **35**, 52 mg **36** and 0.5 mg **37**.

Baccharis quitensis (*voucher RMK* 7942). The roots (340 g) afforded 1 mg germacrene D, 10 mg of euphol-like triterpenes, 4 mg **21**, 1 mg **28**, 4 mg **46** (Et_2O–petrol, 3:1), 6 mg **51**, 8 mg **52**, 4 mg **53**, 2 mg **54** and **55**, while the aerial parts (630 g) gave 80 mg germacrene D, 5 mg α-humulene, 15 mg lupeol and its Δ9,11- and Δ12,13-isomer (*ca* 1:1:1), 6 mg **19**, 1 mg **20**, 5 mg **31**, 15 mg **32**–**34** (*ca* 1:1:5) (Et_2O–petrol, 1:1), 8 mg **36**, 5 mg **38**, 15 mg **44** (Et_2O–petrol, 1:1), 45 mg **46** and 19 mg **48** (Et_2O–petrol, 1:1).

Baccharis truncata (*voucher RMK* 8175). The roots (60 g) afforded 12 mg germacrene D, α- and β-humulene and bicyclogermacrene (*ca* 2:1:1:1), 5 mg lupeol, 2 mg **24**, 5 mg **25** (Et_2O–petrol, 1:1), 3 mg **26**, 73 mg **35**, 15 mg **36** and 6 mg **50**, while the aerial parts (145 g) gave 70 mg germacrene D, 10 mg bicyclogermacrene, 83 mg lupeol 80 mg lupenone, 14 mg **17**, 1 mg **36**, 1 mg **37**, 150 mg **40** and 150 mg **42**.

Ent-2β-*hydroxymanool* (**2**). Only isolated as its acetate (Ac_2O, 2 hr, 70°) (**4**), colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1740, 1260 (OAc); MS *m/z* (rel. int.): 330.256 $[M - H_2O]^+$ (2) ($C_{22}H_{34}O_2$), 288 $[M - HOAc]^+$ (2), 270 $[288 - H_2O]^+$ (10), 262 $[330 - H_2C{=}C(Me)CH{=}CH_2]^+$ (15), 255 $[270 - Me]^+$ (14), 202 $[262 - HOAc]^+$ (24), 135 $[C_{10}H_{15}]^+$ (100).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-16 \quad -18 \quad -20 \quad -34} \quad (c = 0.7, CHCl_3).$$

10 mg **2** in 1 ml CH_2Cl_2 was stirred for 6 hr with 20 mg pyridine chlorochromate. TLC (Et_2O–petrol, 1:1) afforded 5 mg **9**, colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1715 (C=O), 2730, 1675, 1640 (C=CCHO); MS *m/z* (rel. int.): 302 $[M]^+$ (4), 287 $[M - Me]^+$ (18), 269 $[287 - H_2O]^+$ (6), 219 $[M - MeC(Me){=}CHO]^+$ (31), 151 $[C_{10}H_{15}O]^+$ (100).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-18 \quad -18 \quad -22 \quad -45} \quad (c = 0.5, CHCl_3).$$

Ent-2-*hydroxymanool* (**3**). Only isolated as its acetate (**5**), colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3590 (OH), 1735, 1250 (OAc), 1640, 930 (CH=CH_2); MS *m/z* (rel. int.): 330 $[M - H_2O]^+$ (1), 288.245 $[M - HOAc]^+$ (2) ($C_{20}H_{32}O$), 270 $[288 - H_2O]^+$ (8), 255 $[270 - Me]^+$ (20), 202 (12), 135 $[C_{10}H_{15}]^+$ (100). $[\alpha]_D$ $-13°$ ($c = 0.58$, $CHCl_3$). 10 mg **3** (containing *ca* 2 mg **2**) were oxidized as above. TLC (Et_2O–petrol, 1:1) afforded 5 mg **9**, identical with the ketone from **2**.

2-*Oxo*-ent-*manool* (**6**). Colourless gum: IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1715 (C=O); MS *m/z* (rel. int.): 303 $[M]^+$ (1), 286. 230 $[M - H_2O]^+$ (10) ($C_{20}H_{30}O$), 271 $[286 - Me]^+$ (19), 258 $[286 - CO]^+$ (6), 151 $[C_{10}H_{15}O]^+$ (51), 57 (100); $[\alpha]_D = -10°$ ($c = 0.3$, $CHCl_3$).

Ent-2β-*Succinyloxymanool* (**7**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3500–2600, 1710 (CO_2H), 1735 (CO_2R), 1635, 925 (CH=CH_2); MS *m/z* (rel. int.): 388 $[M - H_2O]^+$ (4), 360 $[388 - CO]^+$ (1), 270 $[388 - HO_2CCH_2CH_2CO_2H]^+$ (11), 255 $[270 - Me]^+$ (14), 135 $[C_{10}H_{15}]^+$, (100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-25 \quad -26 \quad -30 \quad -50} \quad (c = 2.3, CHCl_3).$$

Addition of CH_2N_2 in Et_2O afforded **8** (TLC: Et_2O–petrol, 1:1), colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1735 (CO_2R), 1640, 940 (CH=CH_2); MS *m/z* (rel. int.): 402.277 $[M - H_2O]^+$ (2), 387 $[402 - Me]^+$ (1), 288 $[M - RCO_2H]^+$ (2), 270 $[288 - H_2O]^+$ (12), 135 $[C_{10}H_{15}]^+$ (100). $LiAlH_4$ reduction of **8** (Et_2O) afforded **2**, colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1640, 925 (CH=CH_2); MS *m/z* (rel. int.): 288.245 $[M - H_2O]^+$ (9) ($C_{20}H_{32}O$), 220 $[288 - \text{isoprene}]^+$ (31), 135 $[C_{10}H_{15}]^+$ (100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-33 \quad -34 \quad -39 \quad -66} \quad (c = 0.8, CHCl_3).$$

7β-*Angeloyloxybacchotricunetin B* (**11**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (γ-lactone), 1725 (C=CCO_2R), 1505, 880 (furane); MS *m/z* (rel. int): 440 $[M]^+$ (1), 410 $[M - CH_2O]^+$ (56), 310 $[410 - AngOH]^+$ (82), 83 $[C_4H_7CO]^+$ (79), 55 $[83 - CO]^+$ (100).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-10 \quad -11 \quad -14 \quad -39} \quad (c = 0.1, CHCl_3).$$

3′-*Methoxyxanthomicrol* (**20**). Inseparable from **19**, UV (MeOH) λ_{max} nm: 332, 282; + NaOAc 415, 330; + $AlCl_3$ (414), 364, 409, 288; MS *m/z* (rel. int.): 374.100 $[M]^+$ (91) ($C_{19}H_{18}O_8$), 359 $[M - Me]^+$ (100); ^1H NMR ($CDCl_3$): H-3 6.61 *s*, H-2′ 7.43 *d*, H-5′ 7.07 *d*, H-6′ 7.56 *dd*, OMe 4.12 *s*, 4.01 *s*, 3.98 *s*, 3.96 *s*, OH 12.54 *s* (*J*(Hz): 2′,6′ = 2; 5′,6′ = 8).

2-[1-*Hydroxymethyl*]-*vinyl*-6-*acetyl*-5-*hydroxycumarane* (**25**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3500–2700, 1650, 1635, 1595 (hydrogen-bonded PhCO); MS *m/z* (rel. int.): 234.089 $[M]^+$ (100) ($C_{13}H_{14}O_4$), 216 $[M - H_2O]^+$ (10), 203 $[M - CH_2OH]^+$ (91); ^1H NMR ($CDCl_3$): H-2 5.22 *dd*, H-3 3.41 *d*, H-3 3.18 *ddd*, H-4 6.83 *t*, H-7 7.08 *s*, H-9 2.58 *s*, H-11 5.17 *s*(*br*), H-12 4.30 *d* and 4.24 *d* (*J*(Hz): 2,3 = 9,2,3′ = 8.5; 3,3′ = 17; 3′,6′ = 1; 12, 12′ = 12.5).

(2-[1-*Methoxycarbonyl*]-*vinyl*-6-*acetyl*-5-*hydroxycumarane*) (**27**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2700, 1660, 1635, 1595 (hydrogen-bonded PhCO), 1725 (C=CCO_2R); MS *m/z* (rel. int.): 262.084 $[M]^+$ (100) ($C_{14}H_{14}O_5$), 230 $[M - MeOH]^+$ (21), 215 $[230 - Me]^+$ (11), 202 $[230 - CO]^+$ (42), 187 $[202 - Me]^+$ (62), 176 $[M - C_4H_6O_2]^+$ (10) (McLafferty), 161 $[176 - Me]^+$ (23).

Tridecyl-, tetradecyl- and pentadecyl-resorcinol (**32**–**34**). Inseparable oily mixture; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1600 (aromate); MS *m/z* (rel. int.): 320.342 $[M]^+$ (2) ($C_{21}H_{36}O_2$), 306.259 $[M]^+$ (2) ($C_{20}H_{34}O_2$), 292.239 $[M]^+$ (12), 124 ($C_7H_8O_2$, 100); ^1H NMR ($CDCl_3$): H-2 6.18 *t*, H-4,5 6.25 *d* (*J* = 2.5 Hz), H-1′ 2.49 *t* (*J* = 8 Hz); CH_2 1.59 *m*, 1.28 *m*, Me 0.89 *t* (*J* = 6 Hz).

19-[p-*Hydroxyhydrocinnamoyloxy*]-ent-*kaurenic acid* (**44**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1735 (CO_2R); acetylation (Ac_2O, 1 hr, 70°) afforded **45**, colourless crystals, mp 93° (Et_2O–petrol); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (OAc), 1740 (CO_2R), 1660, 890 (C=CH_2); MS *m/z* (rel. int): 478.308 $[M]^+$ (38) ($C_{31}H_{42}O_4$), 463 $[M - Me]^+$ (8), 436 $[M - ketene]^+$ (7), 270 $[M - RCO_2H]^+$ (31), 107 ($C_7H_7O^+$, 100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-38 \quad -43 \quad -47 \quad -79} \quad (c = 0.15,\ CHCl_3).$$

17-*Hydroxy*-19-[p-*hydroxyhydrocinnamoyloxy*]-iso-*kaurene* (**46**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH), 1740 (CO_2R); MS *m/z* (rel. int.): 452.293 $[M]^+$ ($C_{29}H_{38}O_4$), 434 $[M - H_2O]^+$ (6), 286 $[M - RCO_2H]^+$ (6), 107 $[C_7H_7O]^+$ (61), 55 $[C_4H_7]^+$ (100). Acetylation (Ac_2O, 1 hr, 70°) afforded **47**, colourless crystals, mp 55° (Et_2O–petrol); MS *m/z* (rel. int.): 536.314 $[M]^+$ (21) ($C_{33}H_{44}O_6$), 476 $[M - HOAc]^+$ (28), 461 $[476 - Me]^+$ (10), 268 $[476 - RCO_2H]^+$ (47), 107 $[C_7H_7O]^+$ (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-13 \quad -14 \quad -15 \quad -18} \quad (c = 0.84,\ CHCl_3).$$

19-[p-*Hydroxyhydrocinnamoyloxy*]-ent-*kauran*-17-*al* (**48**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 2700, 1725 (CHO), 1725 (CO_2R); MS *m/z* (rel. int.): 452.293 $[M]^+$ (19) ($C_{29}H_{40}O_4$), 286 $[M - RCO_2H]^+$ (20), 107 $[C_7H_7O]^+$ (62), 55 $[C_4H_7]^+$ (100). 10 mg **48** in 2 ml Et_2O was reduced with 20 mg $LiAlH_4$. TLC (Et_2O) afforded 5 mg **49**; MS *m/z* (rel. int.): 306 $[M]^+$ (7), 288 $[M - H_2O]^+$ (10), 275 $[M - CH_2OH]^+$ (100), 257 $[275 - H_2O]^+$ (8) and 2 mg 3-[*p*-hydroxylphenyl]-propanol, ^{1}H NMR ($CDCl_3$): H-2,6 7.07 *d*, H-3,5 6.76 *d*, H-1′ 2.65 *t*, H-2′ 1.87 *tt*, H-3′ 3.68 *t* (*J* (Hz): 2,3 = 8; 1′,2′ = 7.5; 2′,3′ = 6.5); MS *m/z* (rel. int.): 152 $[M]^+$ (29), 133 $[M - CHO]^+$ (13), 107 $[C_7H_7O]^+$ (100).

10-*Angeloyloxy*-2c,8t-*matricaria ester* (**54**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2210 (C≡C), 1715 (C=CCO_2R), 1615 (C=C); UV (Et_2O) nm: 330, 308, 290; MS *m/z* (rel. int.): 272.105 $[M]^+$ (17), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (83); ^{1}H NMR ($CDCl_3$): H-2,3 6.23 AB*q*, H-8 5.88 *d*(*br*), H-9 6.41 *dt*, H-10 4.73 *dd*, OAng: 6.12 *qq*, 2.00 *dq*, 1.92 *dq* (*J* (Hz): 8,9 = 15; 8,10 = 1.5; 9,10 = 6; 3′,4′ = 7; 3′,5′ = 4′, 5′ = 1.5).

10-*Angeloyloxy*-2t,8c-*matricaria ester* (**55**). Colourless oil, inseparable from **53**; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2220 (C≡C), 1730 (C=CCO_2R), 1620 (C=C); UV (Et_2O) nm: 330, 308, 290; MS *m/z* (rel. int.): 272.105 $[M]^+$ (28), 257 $[M - Me]^+$ (10), 189 $[M - C_4H_7CO]^+$ (22), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (65); ^{1}H NMR ($CDCl_3$): H-2 6.35 *d*, H-3 6.82 *dd*, H-8 5.78 *d*(*br*), H-9 6.28 *dt*, H-10 4.92 *dd*, OAng 6.13 *qq*, 2.00 *dq*, 1.92 *dq* (*J* (Hz): 2,3 = 15; 3,8 = 1; 8,9 = 10; 8,10 = 1.5; 9,10 = 6.5).

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