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DITERPENE GLYCOSIDES AND OTHER CONSTITUENTS FROM ARGENTINIAN *BACCHARIS* SPECIES

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Key Word Index—*Baccharis* ssp.; Compositae; diterpenes; clerodane derivatives; labdane derivatives; friedolabdanes; diterpene glycosides; fucopyranosides; xylopyranosides; rhamnopyranoside; nor-labdane derivative; umbelliferone derivatives; coumaric acid derivatives; furocadinenes; nor-sesquiterpene.

Abstract—The investigation of the aerial parts of nine *Baccharis* species from Argentina gave 37 new compounds, seven *ent*-clerodanes, 13 *ent*-labdanes, two friedolabdanes, a nor-labdane ketone, seven coumaric acid derivatives, two umbelliferone derivatives, a flavanone, three sesquiterpenes including a nor-furanocadinene and a propiophenone derivative. Ten of the diterpenes were glycosides. The structures and the configurations were determined by highfield NMR spectroscopy and some chemical transformations. The absolute configurations of the diterpenes were proposed following observed Cotton-effects and in one case by using the Horeau-method together with ^{1}H NMR determination of the configuration of the main phenylbutyrate obtained. The chemotaxonomy is discussed.

INTRODUCTION

From the large genus *Baccharis* (Compositae, tribe Astereae) already more than 50 species have been investigated chemically. The most widespread compounds are clerodane derivatives but also labdane and kaurane derivatives are isolated. Furthermore typical acetylenic compounds, baccharis oxide, an unique triterpene, and derivatives of *m*-hydroxyacetophenone are present. In continuation of our investigations of South American representatives [1] we have studied nine species from Argentina, one of them from three different locations. The results are discussed in this paper.

RESULTS AND DISCUSSION

From *Baccharis salicifolia* Pers. baccharis oxide [2] and some flavanones [3] have been reported. We now have studied three samples from different locations in Argentina. The aerial parts of a collection near Rio Colorado gave baccharis oxide, germacrone [4], the flavanones eriodictyol [5], 4′-methoxypinostrobin [6], sakuranetin [7], isosakuranetin [8] and **43**, the cadinene derivatives **27** [9] and **28**, *cis*-α-copaen-8-ol [10], the elemene **31** and two clerodane derivatives, the acids **12** and **13**. The structure of the flavanone **43** followed from the ^{1}H NMR spectrum and from that of the corresponding tetraacetate (Experimental). The ^{1}H NMR signals for H-6 and H-8 in the spectrum of **43** differed from those of the corresponding isomer with a 7-methoxy group [11] but agreed with those of 5,7-dihydroxy flavanones. The structure of the epoxide **28** was deduced from the ^{1}H NMR data (Experimental) which were in part close to those of **27** [9]. The presence of an epoxide followed from the absence of an olefinic signal. Spin decoupling allowed the assignment of all signals. Inspection of a model showed that the small coupling $J_{5,6}$ required an α-epoxide. The presence of *cis*-α-copaen-8-ol was established by ^{1}H NMR spectroscopy. As no sample for comparison was available the stereochemistry was determined by NOE difference spectroscopy. The ^{1}H NMR data agreed with those in the literature [10].

The structure of **31** was deduced from the ^{1}H NMR spectrum (Experimental). The presence of an elemene derivative followed from the typical lowfield signals. Spin decoupling allowed the assignment of all signals. The large coupling $J_{5,6}$ further indicated the stereochemistry at C-5.

The structures of **12** and **13** which have been transformed to their methyl esters **12a** and **13a** followed from the molecular formulae and the ^{1}H NMR spectra (Table 1) which were in part close to those of similar clerodanes. All signals could be assigned by spin decoupling and the stereochemistry was established by NOE difference spectroscopy. In the case of the acetate **12aAc**, which was prepared by acetylation of **12a**, clear effects were observed between H-20, H-19 and H-11′, between H-6β and H-8, between H-10 and H-8, between H-16 and H-15 as well as between H-8 and H-12. The structure of **12aAc** was further supported by the ^{13}C NMR spectrum (Experimental). The ^{1}H NMR spectrum of **13a** was close to that of **12a**. Clear differences of the signals of the side chain indicated that in **13a** a 15-*O*-acetate of a 16-hydroxy derivative of **12a** was present (H-15, δ4.65 and 4.60 *dd*; H-16, 4.23 and 4.18 *dd*). The acid **12** has been named bacchasalicyclic acid. A clerodane with a carboxyl group at C-8 with the same stereochemistry was isolated from *B. hutchisonii* [1].

The aerial parts collected near San Raphael gave 5-hydroxy-7,3′,4′-trimethoxyflavone [12], corymbosin [13] and 5-hydroxy-6,7,3′,4′,5′-penta-methoxyflavone [14]. The structures followed from the ^{1}H NMR signals and those of the corresponding acetates. The shift differences of the methoxy signals and of H-8 only agreed with the

Table 1. ^{1}H NMR spectral data of compounds **12a**, **12aAc** and **13a** (400 MHz, $CDCl_3$)

H	12a	12aAc	13a
1α	1.43 *dddd*	1.43 *dddd*	1.43 *dddd*
1β	1.59 *m*	1.58 *m*	1.59 *m*
2	2.03 *m*	2.05 *m*	2.05 *m*
3	5.19 *br s*	5.19 *br s*	5.18 *br s*
6α	1.77 *ddd*	1.78 *ddd*	1.77 *ddd*
6β	1.14 *ddd*	1.14 *ddd*	1.13 *ddd*
7α	1.98 *dddd*	1.98 *dddd*	1.98 *ddd*
7β	1.62 *m*	1.62 *dddd*	1.63 *m*
8	2.48 *m*	2.48 *dd*	2.52 *dd*
10	1.36 *d*	1.37 *d*	1.37 *d*
11	1.55 *ddd*	1.56 *ddd*	1.63 *ddd*
11′	1.24 *ddd*	1.24 *ddd*	1.30 *m*
12	2.09 *br ddd*	2.10 *br ddd*	2.33 *ddd*
12′	1.83 *ddd*	1.85 *ddd*	1.90 *ddd*
14	5.41 *br t*	5.33 *br t*	5.40 *br t*
15	4.18 *br d*	4.57 *br d*	4.65 *dd* 4.60 *dd*
16	1.68 *br s*	1.70 *br s*	4.23 *dd* 4.18 *dd*
18	1.58 *br s*	1.58 *br s*	1.57 *br s*
19	1.04 *s*	1.04 *s*	1.04 *s*
20	0.88 *s*	0.88 *s*	0.86 *s*
OMe	3.64 *s*	3.65 *s*	3.66 *s*
OAc	—	2.05 *s*	2.04 *s*

J (Hz): 1α,1β = 1α,2β = 1α,10 = 6α,6β = 6β,7α = 7α,7β = 7α,8β = 11,11′ = 11,12′ = 11′,12 = 12, 12′ ~ 13; 2,3 = 2.5 and 4.5; 3,18 ~ 1.5; 6α,7α = 6α,7β = 6β,7β = 7β,8β = 3; 11,12 = 11′,12′ = 4.5; 14,15 = 7.

proposed position of the methoxy groups. Furthermore, the labdane derivatives **7** and **8** as well as a complex mixture of glycosides were isolated. Finally the fucopyranosides **1**, **1a**, **1b** and the rhamnoside **5** were obtained.

The structure of **8** was deduced from its ^{1}H NMR spectrum (Experimental). The presence of a furolabdane followed from the typical lowfield signals of a β-substituted furane and from the four methyl signals, one being olefinic as followed from the chemical shift. The position of two hydroxy groups could be determined by spin decoupling and by comparison of the ^{1}H NMR data with those of similar labdanes. The ^{1}H NMR spectrum of **7** (Experimental) was in part similar to that of **8**. However, the presence of an angelate caused a downfield shift of the H-3 signal. Furthermore, the furan moiety was replaced by an open chain group with a 15-hydroxy group as clearly followed from the typical ^{1}H NMR signals. To establish the configuration of the Δ^{13}-double bond and the absolute configuration we have transformed **7** to the keto aldehyde **7a**. The chemical shift of H-16 (δ2.18) indicated an *E*-configuration of the double bond. The negative Cotton-effect of the ketone indicated the presence of an *ent*-labdane.

The ^{1}H NMR spectrum of **1** (Table 2) was in part close to that of compound **7**. Additional overlapped lowfield signals indicated the presence of a glycoside. Acetylation afforded the tetraacetate **1Ac** with the molecular formula $C_{39}H_{58}O_{12}$. All ^{1}H NMR signals of the latter could be assigned by spin decoupling. The sequences which were obtained in this way clearly showed that a fucopyranoside of **7** was present. In the spectrum of **1Ac** only the H-1′ signal was not shifted downfield showing that the sugar was connected at C-1 with the 2-hydroxy group of the diterpene. Starting with the H-1′ signal, the remaining signals of the sugar moiety could be assigned. The observed couplings nicely agreed with those of 1-*O*-alkylfucopyranoside triacetates [15].

The ^{1}H NMR spectrum of the main constituent **1a** differed from that of **1** mainly by the presence of an acetate methyl singlet and the downfield shift of one of the sugar protons (δ5.09 *br d*). This signal obviously corresponded to the double doublet at 3.66 in the spectrum of **1**. Spin decoupling showed that these signals were due to H-4′. Thus **1a** is the 4′-*O*-acetate of **1** which was established by acetylation which afforded **1Ac**. The ^{13}C NMR spectrum of **1a** (Experimental) could be assigned by 2D-correlation (^{1}H–^{13}C NMR) and the stereochemistry of the sugar was established by NOE difference spectroscopy. Clear NOEs were observed between H-1′, H-3′, H-5′ and H-2. Acid catalysed methanolysis of **1a** followed by acetylation gave the epimeric 1-*O*-methyl fucopyranoside triacetates. The optical rotation indicated that we were dealing with L-fucopyranosides if compared with the rotation of triacetyl-β-methyl-D-fucoside [16]. The ^{1}H NMR spectrum of **1b** (Table 2) differed from that of **1a** by the chemical shift of two of the protons of the sugar moiety. The lowfield double doublet at δ4.80 showed the same splitting as the H-3′ signal in the spectrum of **1a**. Spin decoupling indicated that this signal really was that of H-3′. Accordingly, the acetate **1b** was the corresponding 3′-*O*-acetate of **1**.

The last glycoside **5** also was an acetate. However, the ^{1}H NMR signals of the sugar moiety differed more remarkably from those of **1a** and **1b** (Table 2). As the signals were in part overlapped we have prepared the tetraacetate (**5Ac**). The ^{1}H NMR signals of the latter (Table 2) could be completely assigned by spin decoupling. The couplings of the protons of the sugar moiety showed that an α-rhamnopyranoside was present. Accordingly, the H-1′ signal now showed a very small coupling. As $J_{2',3'}$ also was small the acetoxy group of C-2′ was axial. The other couplings all were around 10 Hz indicating equatorial orientations of the substituents at C-3′–C-5′. The ^{1}H NMR data nicely agreed with those of other rhamnopyranosides [17]. Inspection of the ^{1}H NMR spectrum of the natural compound itself indicated that a 4-*O*-acetyl rhamnoside was present. Accordingly, the lowfield triplet at δ4.75 was decoupled by irradiation of the easily detectable H-5 signal. Though the absolute configuration of the sugar was not determined it is very likely that an L-rhamnoside was present since L-rhamnosides as well as L-fucosides are more common in plant sources [18].

The fragmentation pattern in the mass spectra of **1**, **1a**, **1b** and **5** is very similar. The base peak is always at *m/z* 83 (acyl cation). Furthermore, loss of the sugar moiety, which itself is represented by its onium ion, is typical. Also a McLafferty fragmentation of the side chain can be observed. Loss of angelic acid is not very pronounced.

The aerial parts of a collection near Catamarca afforded several known compounds (Experimental) including in high concentration the acid **9** which seemed to be identical with a reported labdane derivative, 2α,3-dihydroxycativic acid [19]. As all the other diterpenes were derivatives of the *ent*-series we have investigated the absolute configur-

Table 2. ^{1}H NMR spectral data of compound **1**, **1a**, **1b**, **1Ac**, **4**, **5** and **5Ac** (400 MHz, $CDCl_3$)

H	1*	1a	1b	1Ac	4	5	5Ac
2	3.87 *ddd*	3.85 *ddd*	3.89 *ddd*	3.78 *ddd*	3.91 *ddd*	3.88 *ddd*	3.87 *ddd*
3	4.72 *d*	4.68 *d*	4.73 *d*	4.75 *d*	4.71 *d*	4.80 *d*	4.88 *d*
5	1.40 *dd*	1.37 *dd*	1.40 *dd*	1.37 *dd*	1.37 *dd*	1.37 *dd*	1.42 *dd*
6	1.97 *m*	1.96 *m*	1.98 *m*	1.98 *m*	1.98 *m*	1.95 *m*	1.95 *m*
7	5.40 *br s*	5.37 *br s*	5.41 *br s*	5.38 *br s*	5.41 *br s*	5.39 *br s*	5.39 *br s*
11	1.53 *m*	1.50 *m*	1.53 *m*	1.48 *m*	1.53 *m*	1.49 *m*	1.53 *m*
11′	1.40 *m*	1.37 *m*	1.40 *m*	1.36 *m*	1.37 *m*	1.40 *m*	1.33 *m*
12 12′	2.23 *m*	2.18 *m*	2.25 *m*	2.25 *br ddd* 2.02 *ddd*	2.3 *m*	2.25 *m*	2.25 *m*
14	5.43 *br t*	5.40 *br t*	5.43 *br t*	5.31 *br t*	5.33 *br t*	5.42 *br t*	5.36 *br t*
15	4.13 *dd* 4.18 *dd*	4.12 *m*	4.16 *d*		4.48 *br dd* 4.71 *br dd*	4.18 *dd* 4.14 *dd*	4.59 *d*
16	1.70 *br s*	1.65 *br s*	1.71 *br s*	1.68 *br s*	1.73 *br s*	1.70 *br s*	1.72 *br s*
17	1.71 *br s*	1.68 *br s*	1.69 *br s*	1.67 *br s*	1.69 *br s*	1.67 *br s*	1.69 *br s*
18	0.88 *s*	0.85 *s*	0.88 *s*	0.84 *s*	0.87 *s*	0.87 *s*	0.87 *s*
19	0.96 *s*	0.93 *s*	0.96 *s*	0.92 *s*	0.94 *s*	0.96 *s*	0.95 *s*
20	0.82 *s*	0.78 *s*	0.82 *s*	0.81 *s*	0.80 *s*	0.81 *s*	0.80 *s*
1′	4.19 *d*	4.19 *d*	4.29 *d*	4.45 *d*	4.24 *d*	4.93 *br s*	4.85 *d*
2′	3.39 *dd*	3.36 *dd*	3.56 *dd*	5.01 *dd*	3.44 *dd*	3.85 *br s*	5.13 *dd*
3′	3.55 *dd*	3.70 *dd*	4.80 *dd*	4.96 *dd*	3.74 *dd*	3.68 *dd*	5.09 *dd*
4′	3.66	5.09 *br d*	3.77 *d*	5.13 *br d*	5.14 *br d*	4.75 *t*	4.98 *t*
5′	3.57 *br q*	3.63 *br q*	3.64 *br q*	3.68 *br q*	3.67 *br q*	3.71 *dp*	3.83 *dq*
6′	1.25 *d*	1.06 *d*	1.24 *d*	1.09 *d*	1.11 *d*	1.12 *d*	1.13 *d*
OAc	—	2.08 *s*	2.15 *s*	2.09, 2.02, 1.98, 1.92 *s*	2.10 *s*	2.07 *s*	2.13, 2.06, 2.00, 1.94 *s*
OAng	6.04 *qq*	5.95 *qq*	6.05 *qq*	5.98 *qq*	5.98 *qq*	6.13 *qq*	6.11 *qq*
	1.99 *dq*	1.96 *dq*	2.01 *dq*	1.98 *dq*	1.98 *dq*	2.05 *dq*	2.05 *dq*
	1.92 *dq*	1.90 *dq*	1.92 *dq*	1.90 *dq*	1.93 *dq*	1.92 *dq*	1.93 *dq*

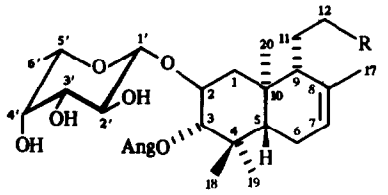
*2′-OH 3.78 *br s*, 3′-OH 3.05 *d*, 4′-OH 2.28.

J (Hz): 1α,1β = 13; 1α,2 = 4; 1β,2 = 11; 2,3 = 10; 5,6 = 6; 5,6′ = 10; 14,15 = 7; compounds **1**, **1a** and **1b**: 1′,2′ = 7.5; 2′,3′ = 10; 3′,4′ = 3; 4′,5′ ~ 0.5; 5′,6′ = 6.5; (compound **1**: 2′, OH ~ 1.5; 3′, OH = 5; 4′, OH = 6); compound **5Ac**: 1′,2′ = 1.5; 2′,3′ = 3.5; 3′,4′ = 10; 5′,6′ = 6; OAng: 3′,4′ = 7; 3′,5′ = 4′,5′ = 1.5.

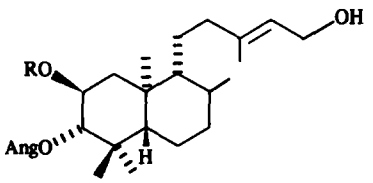
ation of **9**. Partial chromic acid oxidation of the methyl ester of **9** afforded **9b** only, the axial hydroxy group being oxidized. A positive Cotton-effect indicated by application of the octant rule the presence of an *ent*-labdane. By using the Horeau method, reaction of the methyl ester of **9** gave excess of (−)-α-phenyl butyric acid and the derivative **9a** as the main reaction product. This also supported the presence of an *ent*-labdane. As followed from the ^{1}H NMR spectrum only the 2-hydroxy group was esterified. NOE difference spectroscopy with the main α-phenyl butyrate **9a** gave effects between H-1β and the aromatic protons indicating that the preferred conformation was **9c**. Furthermore the observed NOEs allowed the assignment of the methyl signals. A *W*-coupling between H-20 and H-1β established the *trans*-fusion of the six membered rings. Also the highfield shift of H-1α and H-1β supported the stereochemistry of the main product. The upfield shift of H-3 in the minor ester agreed with the preferred conformations in such cases [20, 21]. All results therefore showed that **9** was an *ent*-labdane (Experimental).

Furthermore, the *ent*-labdanes **10** and **10a** and the xylopyranosides **11** and **14**, which were isolated as their acetates **10Ac**, **10aAc**, **11a**, **11b**, **11c** and **14a**, were present. The structure of **10Ac** followed from the ^{1}H NMR data, which were close to those of a labdane triol obtained by alanate reduction [22]. However, the Δ^{13}-double bond had the *E*-configuration as could be shown by a NOE between H-15 and H-16. The molecular formula of **10Ac** indicated, together with the ^{1}H NMR spectrum, that a 13,14-dihydro derivative of **10Ac** was present. Accordingly, the signal of the olefinic methyl (H-16) was replaced by a doublet at δ0.91. The configurations at C-2 and C-3 followed from the observed couplings which clearly indicated the presence of an equatorial hydroxy group at C-2 and an axial one at C-3.

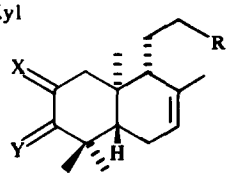
The acetates **11a**–**11c**, which were obtained by acetylation of the crude glycoside **11**, could be separated by HPLC. The ^{1}H NMR spectra (Table 3) showed that we were dealing with derivatives of 8,15-dihydroxylabd-13-ene where the 8-hydroxy group was connected with a sugar moiety. Spin decoupling allowed the assignment of nearly all signals. The sequences obtained in this way supported the presence of 8,15-dihydroxylabdane-8-*O*-glycosides. The couplings of the sugar moiety clearly showed that β-xylopyranosides were present. The values observed nicely agreed with those of other xylopyranosides [23]. The stereochemistry at C-8 was established by NOE difference spectroscopy. Clear effects were obtained between H-17, H-20, H-9 and H-1′, between H-18 and H-3α as well as between H-16 and H-15. This also established



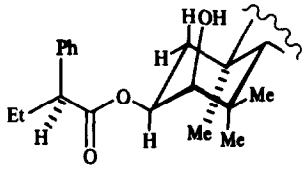
1*§ R = A
1a R = A, 4′ - OAc
1b R = A, 3′ - OAc
2 R = B, 4′ - OAc
3 R = A, 16 - OH, 4′ - OAc
4 R = C, 4′ - OAc



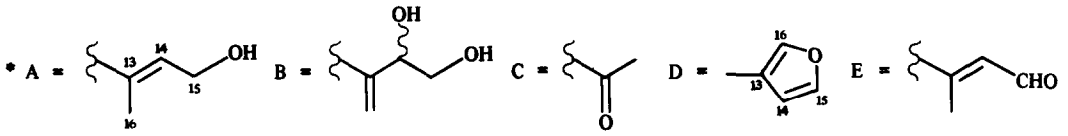
5 R = Rham - 4 - OAc †
6 R = Xyl

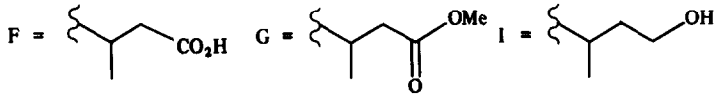


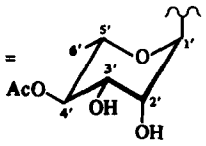
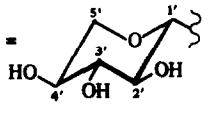
	7	7a	8	9	9a	9b	10	10a
X	βOH,H	O	βOH,H	βOH,H	βOPhbu,H†	βOH,H	βOH,H	βOH,H
Y	αOAng,H	αOAng,H	αOH,H	βOH,H	βOH,H	O	βOH,H	βOH,H
R	A	E	D	F	G	G	A	I



9c



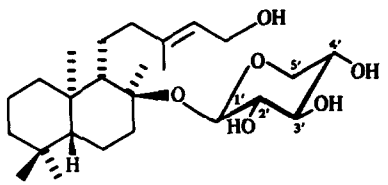


† Rham - 4 - OAc =  † Xyl = 

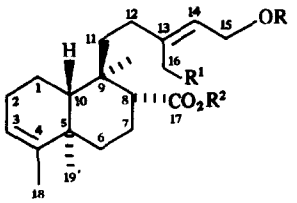
† Phbu = $C_6H_5CH(C_2H_5)CO$

the position of the sugar moiety, the configuration of the Δ^{13}-bond and allowed the assignment of the methyl singlets at C-4 and C-10. Acetylation by more drastic conditions transformed **11a–11c** into the tetraacetate **11Ac**.

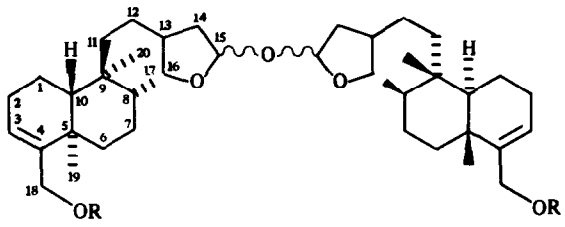
The structure of the minor glycoside **14**, which was transformed to the triacetate **14a**, also followed from the ^{1}H NMR spectrum (Experimental) which was in part very close to that of **12a**. However, in addition to the signals of the clerodane moiety those of a xylopyranoside also were present. All signals again could be assigned by spin decoupling. This gave clear sequences which only agreed with the proposed structure. The downfield shift of the H-1′ signal required an acyloxy group at C-1′. The observed shifts and couplings agreed with those of similar β-xylopyranosides [23]. As the couplings of the diterpene moiety were the same as in **12a**, identical stereochemistry was assumed.



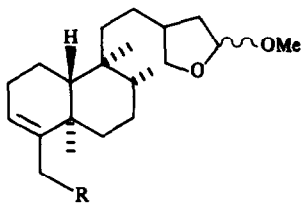
11
11a 15,4'-OAc
11b 15,3'-OAc
11c 15,3',4'-OAc



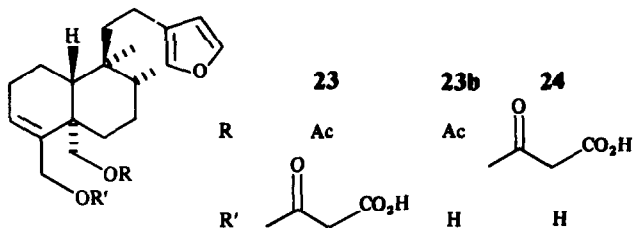
	12	12a	13	13a	14	14a
R	H	H	Ac	Ac	H	Ac
R^1	H	H	OH	OH	H	H
R^2	H	Me	H	Me	Xyl†	Xyl-3',4'-OAc



15 ‖ R = $COCH_2CO_2H$ (Mal)
16 R = $COCH_2CH_2CO_2H$ (Suc)
17 R = H
18 R = Ac

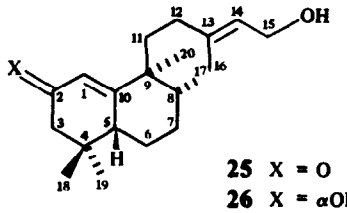


19 R = OMal
20 R = OSuc
21 R = OMe
22 R = H (Δ^1)



23 **23b** **24**

	23	23b	24
R	Ac	Ac	
R'		H	H



25 X = O
26 X = αOH,H

§ **1Ac – 6Ac, 11Ac, 12aAc** and **24aAc** are the peracetylated derivatives, **10Ac** and **10aAc** are 2,15-*O*-diacetates.

‖ **15a, 16a, 19a, 20a, 23a, 24a** and **36a – 40a** are the corresponding methyl esters

The chemistry of the three different collections showed some similarities but the differences are remarkable. Further investigations are necessary to see whether these are chemotypes or varieties.

The aerial parts of *B. darwinii* Hook. et Arn. afforded β-farnesene and large amounts of umbelliferone geranyl ether (auraptene) [24]. Furthermore, several derivatives of the latter were present, the 6',7'-epoxide [25], the corresponding diol [26], 5'-oxo-auraptene (**32**) [27] as well as two new compounds, the 5'-hydroxy derivative **33** and the ketone **34**. The structure of **33** was deduced from the ^{1}H NMR spectrum (Experimental) and established by manganese dioxide oxidation to **32**. The ^{1}H NMR spectrum of **34** (Experimental) showed the presence of an isopropyl group. The chemical shift of the methine proton indicated a neighbouring keto group. This assumption was supported by spin decoupling and also by the fragmentation pattern. In the mass spectrum the butyryl

cation (m/z 71) was visible and loss of C_4H_6O was indicated by the ion at m/z 244. Most likely **34** is formed biogenetically by epoxide isomerization. From this species no diterpenes were obtained.

From the aerial parts of *B. gilliesii* A. Gray so far only some flavones were obtained [28]. A reinvestigation gave in high concentration the clerodane derivative bacchotricuneatin B [29] but no other diterpenes.

The aerial parts of *B. magellanica* (Lam.) Pers. gave several known compounds (Experimental) and the diacetate of dehydrodiconiferyl alcohol previously only isolated from a *Lasiolaena* species [30]. The configuration at C-7′ and C-8′ was supported by NOE difference spectroscopy, as a clear effect between H-7′ and H-8′ and not between H-7′ and H-9′ was observed. The polar fractions contained a mixture of acids (**15** and **16**) which were transformed to the corresponding methyl esters (**15a** and **16a**). These compounds could not be acetylated or oxidized and they gave no molecular ions in the mass spectrometer. Saponification gave **17** which was transformed by acetylation to **18**. Also these derivatives gave no molecular ions. However, heating of **18** in methanol with *p*-toluene sulphonic acid afforded the dimethyl ether **21** and the elimination product **22**. The structures of these compounds could be elucidated by their ^{1}H NMR spectra (Table 4). The spectrum of **21** was very close to that of the corresponding 18-hydroxy derivative [31] which also was present as a mixture of epimeric acetals. Mild treatment of **15** and **16** with *p*-toluene sulphonic acid in methanol afforded after esterification the methyl esters **19a** and **20a** which could be separated by HPLC. The ^{1}H NMR spectral data (Table 4) indicated that the oxygen functions at C-18 were methyl malonate and methyl succinate, respectively. NOE difference spectroscopy confirmed the proposed stereochemistry. Thus clear effects were observed between H-20, H-19, H-17, H-1α and H-7α, between H-19, H-18, H-20 and H-1α, between OMe and H-15, between OMe and H-15′, between H-16β and H-13, between H-15 and H-14 as well as between H-15′ and H-14′. The last NOEs agreed with the proposal that in the main epimer H-13 and H-15 are *trans*- and in the minor epimer *cis*-orientated. This is supported by the observed chemical shifts and the couplings of H-15. As the natural compounds **15** and **16**, which we have named bacchomagellin A and B, are also epimeric at C-15, a mixture of

Table 3. ^{1}H NMR spectral data of compounds **11a–11c*** and **11Ac** (400 MHz, $CDCl_3$, TMS as internal standard)

H	11a	11b	11c	11Ac
1′	4.65 *d*	4.49 *d*	4.51 *d*	4.64 *d*
2′	3.39 *ddd*	3.40 *ddd*	3.42 *ddd*	4.84 *dd*
3′	3.73 *ddd*	4.82 *dd*	5.11 *dd*	5.15 *dd*
5′	4.81 *ddd*	3.76 *dddd*	4.91 *ddd*	4.94 *ddd*
$5'_1$	4.10 *dd*	3.97 *dd*	4.01 *dd*	4.05 *dd*
$5'_2$	3.32 *dd*	3.26 *dd*	3.25 *dd*	3.26 *dd*
OH	3.04 *d*	2.62 *d* (4′)	2.13 *d*	—
	2.44 *d*	2.15 *d* (2′)		
OAc	2.10 *s*	2.18 *s*	2.09 *s*	2.03 *s*
			2.02 *s*	2.01 *s*
				1.99 *s*

*H-14 5.31 *br t* (J = 7 Hz), H-15 4.56 *br d*, H-16 1.69 *br s*, H-17 1.19 *s* (**11Ac**: 1.14 *s*), H-18 0.84 *s*, H-19 0.76 *s*, H-20 0.81 *s*; OAc 2.05 *s*; J (Hz): 1′,2′ = 7.5; 2′,3′ = 3′,4′ = 9; 4′,$5'_1$ = 5; 4′,$5'_2$ = 10; $5'_1$,$5'_2$ = 12; (compound **11a**: 2′,OH = 5; 3′,OH = 4.5; compound **11b**: 2′,OH = 1.5; 4′,OH = 4.5; compound **11c**: 2′,OH = 2.5).

Table 4. ^{1}H NMR spectral data of compounds **15a**, **16a**, **17***, **18**, **19a**, **20a**, **21** and **22** (400 MHz, $CDCl_3$, TMS as internal standard)

H	15a/16a	19a†	20a	21	22‡
2	2.15 *br d* 2.05 *m*	2.16 *br ddd* 2.03 *m*	2.14 *br ddd* 2.03 *m*	2.15 *br ddd* 2.05 *m*	5.90 *br dd*
3	5.58 *br s* 5.55 *br s*	5.59 *br t*	5.55 *br t*	5.53 *br t*	5.58 *br d*
13	2.25 *m*	2.28 *m* 2.03 *m*	2.27 *m* 2.03 *m*	2.27 *m* 2.05 *m*	2.28 *m*
15	5.06 *m*	4.99 *dd* 4.97 *br d*	4.98 *dd* 4.96 *br d*	4.99 *dd* 4.97 *br d*	5.00 *dd* 4.97 *br d*
16	4.10 *t* 4.02 *t*	4.04 *t* 3.41 *t*	4.03 *t* 3.95 *t*	4.04 *t* 3.95 *t*	4.02 *t* 3.93 *t*
16′	3.47 *t* 3.42 *t*	3.43 *t* 3.96 *t*	3.41 *dd* 3.43 *t*	3.43 *t* 3.41 *t*	3.42 *t* 3.37 *t*
17	0.78 *d*	0.77 *d*	0.76 *d*	0.77 *d*	0.77 *d*
18	4.53 *br s* 4.57 *br s*	4.57 *br s*	4.54 *br d*	3.85 *br d*	1.66 *br s*
18			4.49 *br d*	3.77 *br d*	
19	1.05 *s*	1.03 *s*	1.02 *s*	1.04 *s*	0.81 *s*
20	0.71 *s* 0.70 *s*	0.68 *s*	0.68 *s* 0.67 *s*	0.69 *s* 0.68 *s*	0.77 *s*
OCOR	3.36 *s* 3.62 *s*	3.39 *s*	2.63 *br s*	—	—
OMe	3.73 *s* 3.67 *s*	3.74 *s*	3.68 *s*	3.39 *s*	3.32 *s* 3.30 *s*
		3.31 *s* 3.33 *s*	3.32 *s* 3.30 *s*	3.34 *s* 3.31 *s*	—

*Compound **17**: H-3 5.49 *br s*, H-15 5.02 *m*, H-17 0.73 *d*, H-18 4.01 *br s*, H-19 1.00 *s*, H-20 0.64 *s*; compound **18**: OAc 2.06 *s*, H-15 5.07 *dd*, 5.02 *d*, H-18 4.53 and 4.47 *br d*.

†H-14 2.03, 1.42 *m*, H-14′ 1.52, 2.28 *m*.

‡H-1 5.67 *br d*, H-10 2.13 *br s*.

J (Hz): 1,2 = 5; 2,2′ = 18; 2,3 = 2′,3 = 3.5; 8,17 = 7; 13,16 = 16,16′ = 7.5; 14,15 = 5.5; 14′,15 = 2.5; (14,15-epi = 5; 14′,15-epi ~ 0.5); 18,18′ = 12; ^{13}C (**15a/16a**): CO_2R 172.8 *s* (172.3 *s*), 166.8 *s* (166.3 *s*); OMe 52.5 *q* (52.0 *q*); CH_2O 72.8 *t* (72.2 *t*), 66.0 *t* (65.2 *t*); acetal-H 104.5 *d* (104.0 *d*).

eight compounds was present. Compounds **17–21** are also pairs of epimers at C-15. Dimeric diterpenes are rare. So far only a few examples have been reported [32, 33]. However, in no case have dimeric acetals been isolated.

The roots gave in addition to the diconiferylalcohol derivative the propiophenone **35**; its structure followed from the spectral data. The aerial parts of *B. patagonica* H. et A. gave several known compounds (Experimental) and again **15** containing *ca* 15% of **16**.

The aerial parts of *B. pingraea* DC afforded as the main constituent the fucopyranoside **1a**. Furthermore, the glycosides **1**, **1b**, **2–4** and **6** were present. The structure of **3**, which was transformed to the pentaacetate **3Ac**, was deduced from the ^{1}H NMR spectrum (Table 5). All signals except those of H-14–H-16 were nearly identical with those of the acetate of **1a**. The presence of an additional 16-acetoxy group followed from the corresponding ^{1}H NMR signal and the stereochemistry of the double bond was deduced by the NOE between H-15 and H-16.

The ^{1}H NMR spectrum of the pentaacetate of **2** (Table 5) also was similar to that of the acetate of **1a**. Again only the signals of the side chain were altered. Spin decoupling showed that most signals were doubled indicating the presence of epimers. In agreement with the mass spectrum, all ^{1}H NMR data agreed with the presence of **2** epimeric at C-14. A diterpene with the same side chain has been isolated from a *Juniperus* species [34]. The published ^{1}H NMR data of H-14–H-16 nicely agreed with those of **2**.

The molecular formula of triacetate of **4** was $C_{35}H_{52}O_{11}$ indicating the presence of a nor-diterpene. The ^{1}H NMR data (Table 5) were in part very close to those of the acetate of **1a**. However, the signals of the side chain were completely different. In addition to a methyl singlet at δ2.13 a pair of doublet triplets at 2.69 and 2.40 indicated the presence of $-CH_2CH_2Ac$ as side chain. This was supported by the mass spectrum which showed elimination of acetone by a McLafferty fragmentation. Thus **4** probably was formed by oxidative degradation of **1a**.

The ^{1}H NMR spectrum of the tetraacetate of **6** (Table 5) showed that the sugar moiety was changed while the remaining signals indicated that again a derivative of **1a** was present. As already followed from the mass spectrum **6** was a pentose derivative. The ^{1}H NMR signals of the sugar moiety were nearly identical with those of **11Ac**. Accordingly, a 2-*O*-β-xylopyranoside was present. Surprisingly, the couplings of **6Ac** all were somewhat smaller than those of **11Ac**.

The aerial parts of *B. polifera* Griseb. gave in addition to widespread compounds (Experimental) several derivatives of coumaric acid. In addition to large amounts of 3-[dimethylallyl] and 3,5-bis-[dimethylallyl]-coumaric acid [35] also the corresponding acetates **36** and **40** were present. The structures were deduced from the spectroscopic data and the compounds also were prepared by acetylation of the phenols. Furthermore, the corresponding isobutyrate **37**, the β-phenylpropionate **38**, and the β-[*p*-hydroxyphenyl]-propionate **39**, were isolated as their methyl esters. The structures followed from the mass spectra and the ^{1}H NMR spectral data (Experimental). The polar fraction further gave the ferulyl derivatives **41** and **42**. These compounds gave identical mass spectra and differed in the ^{1}H NMR spectra only in a few signals (Experimental). The main fragments in the mass spectra

Table 5. ^{1}H NMR spectral data of compounds **2Ac**, **3Ac**, **4Ac** and **6Ac** (400 MHz, $CDCl_3$)

H	2Ac*	3Ac	4Ac†	6Ac
2	3.85 *ddd*	3.78 *ddd*	3.83 *ddd*	3.80 *ddd*
3	4.77 (4.78) *d*	4.72 *d*	4.77 *d*	4.78 *d*
7	5.41 *br s*	5.35 *br s*	5.42 *br s*	5.39 *br s*
14	5.38 (5.37) *t*	5.50 *br t*	—	5.34 *br t*
15	4.26 *dd* 4.08 (4.06) *dd*	4.61 *br d*	—	4.57 *br d*
16	5.11 *br s* 5.09 *br s*	4.61 *d* 4.56 *d*	2.13 *s*	1.70 *br s*
17	1.70 (1.69) *br s*	1.64 *br s*	1.66 *br s*	1.69 *br s*
18	0.86 *s*	0.80 *s*	0.85 *s*	0.85 *s*
19	0.94 *s*	0.88 *s*	0.94 *s*	0.93 *s*
20	0.84 *s*	0.77 *s*	0.84 *s*	0.80 *s*
1′	4.53 (4.51) *d*	4.45 *d*	4.48 *d*	4.58 *d*
2′	6.02 *dd*	4.98 *dd*	5.04 *dd*	4.73 *dd*
3′	4.98 *dd*	4.93 *dd*	4.98 *dd*	5.06 *dd*
4′	5.16 *br d*	5.10 *br d*	5.17 *br d*	4.81 *ddd*
5′	3.75 *br q*	3.69 *br q*	3.74 *br q*	4.00 *dd* 3.30 *dd*
6′	1.11 *d*	1.06 *d*	1.12 *d*	—
OAc	2.12, 2.09, (2.08), 2.05, 1.88 (1.98) 1.94 *s*	2.07, 2.00, 1.95, 1.89 *s*	2.13 *s* 2.02 *s* 1.95 *s*	2.04, 2.03, 2.01 (2×) *s*
OAng	6.00 *qq*	5.96 *qq*	6.01 *qq*	6.06 *qq*
	2.01 *dq*	2.00 *dq*	2.02 *dq*	2.00 *dq*
	1.92 *dq*	1.88 *dq*	1.93 *dq*	1.90 *dq*

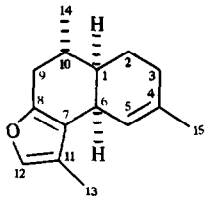
*Values of the epimer in parentheses.

†H-12. 2.69 and 2.40 *dt*.

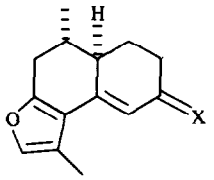
J (Hz): see compound **1** except for **2Ac**: 14,15 = 14,15′ = 3; 15,15′ = 12; compound **4Ac**: 11,12 = 12,12′ = 13; 11′,12 = 11,12′ = 5; compound **6**: 1′,2′ = 6; 2′,3′ = 3′,4′ = 8; 4′,5′$_1$ = 4.5; 4′,5′$_2$ = 7; 5′$_1$,5′$_2$ = 12.

(*m/z* 194 and 177) represented the ions of ferulic acid and the corresponding acyl-cation. The ^{1}H NMR data showed that the ester parts were isomeric 3-oxo-hexanols. A clear NOE between the methoxy group and H-2 established the position of the former group. Thus **41** and **42** were unusual esters of ferulic acid.

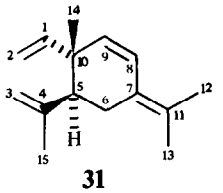
From the polar fractions two diterpenes were isolated. The major compound was the ketone **25** as followed from the molecular formula, the ^{1}H NMR spectrum (Experimental), spin decoupling and 2D-correlations. Furthermore, the data were close to those of related rearranged labdanes [36–38]. The second diterpene was the corresponding diol **26**. The structure also followed from the spectral data. The stereochemistry was determined by NOE difference spectroscopy. Clear effects were obtained between H-19, H-2, H-18, H-12 and H-5, between H-20, H-1, H-12, H-11 and H-17, between H-15 and H-16 as well as between H-18, H-19, H-3α, H-3β and H-6β. These data led to a conformation with H-2β and H-3α axial as well as C-17 and C-19 axial and C-20 equatorially orientated. This explained the pronounced shift differences of H-11, H-12 and H-17–H-20 in the spectra of **25** and **26**. A *W*-coupling between H-11 and H-20 and the large shift differences of H-11, as well as a clear NOE between H-11 and H-5, indicated a fixed conforma-



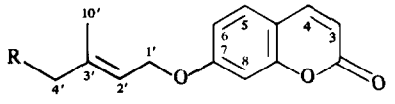
27 **28** 4α,5α - epoxide



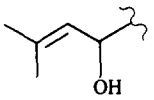
29 X = CH_2
30 X = O



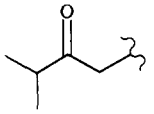
31



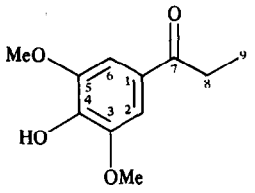
32 R =



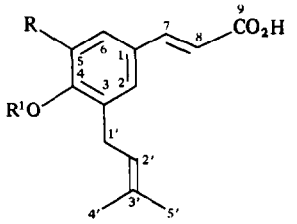
33 R =



34 R =

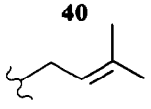


35



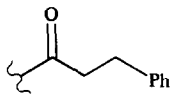
36 **37** **38** **39** **40**

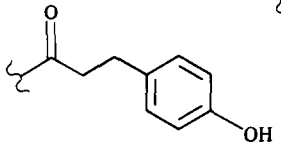
R H H H H

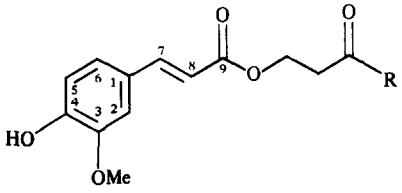


Ac

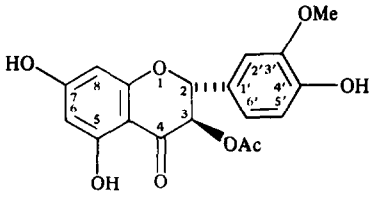
R^1 Ac iBu







41 R = iC_3H_7
42 R = nC_3H_7



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tion of the C-9 side chain. Alanate reduction of **25** only gave **26**. Accordingly, **26** was the 2α-hydroxy derivative. As followed from inspection of a model, the β-attack of hydride was favoured.

The aerial parts of *B. rhetinodes* Meyen et Walp. gave baccharis oxide and as the main constituent the clerodane derivative **23**. The ^{1}H NMR spectrum (Experimental) was similar to that of kingidiol [39]. However, the signals of H-18 and H-19 were shifted downfield indicating that the hydroxy groups were esterified. Only one acetate singlet (δ 1.99) was visible. Addition of diazomethane gave a methylester and a two proton singlet at δ 3.35 could be due to a malonate residue. This was established by the mass spectrum. After loss of CH_2OAc elimination of malonate led to the base peak (*m/z* 269). This fragmentation pattern also showed that a 19-acetoxy-18-malonyloxy derivative was present. This was further supported by partial saponification which gave the 18-hydroxy derivative **23b**, as followed from the changes in the ^{1}H NMR spectrum. Complete saponification gave kingidiol [39]. Furthermore, bacchotricuneatin A [29] and the malonate **24** were isolated. The latter was transformed to the methyl ester

Table 6. Sections in genus *Baccharis* and typical constituents

	Main constituents
Alatae	furoclerodanes (flavanoids)
Cuneifoliae	furoclerodanes*
Cylindricae	furoclerodanes (flavanoids, *p*-coumaric acid derivatives)
Nitidae	furoclerodanes
Pseudobaccharis	furoclerodanes (flavanoids)
Tarchonanthoides	furoclerodanes
Involucratae	clerodanes* (flavanoids)
Glomeruliflorae	clerodanes
Angustifoliae	furoclerodanes (furocadinenes)
Discolores	furoclerodanes (flavanoids, β-coumaric acid derivatives, friedolabdanes)
Sergilae	clerodanes* (flavones, labdanes)
Baccharis	clerodanes, labdanes, kauranes (flavones)
Trinervatae	labdanes, kauranes, flavanoids, umbelliferone der.
Paniculatae	clerodanes, labdanes (flavanoids)
Axillaris	*ent*-kauranes (*p*-coumaric acid der., flavanoids, clerodanes)
Racemosae	*ent*-kauranes (*p*-coumaric acid der.)
Molinae	*ent*-labdanes (flavanoids, furocadinenes)
Illinitae	flavanoids
Myricifolia	*m*-hydroxyacetophenones
Leucopappa	umbelliferone derivatives
Stephananthus	toxol derivatives (*p*-coumaric acid der.)

*Including tetrahydrofurane acetals.

24a. The ^{1}H NMR spectrum (Experimental) differed characteristically from that of **23a** and in the mass spectrum now after loss of water elimination of $CH_2OCOCH_2CO_2Me$ was observed. Accordingly, the malonate residue now was at C-19. Acetylation of **24a** gave a compound which was an isomer of **23a**. The ^{1}H NMR spectra were slightly different and the fragmentation in the mass spectra differed typically.

The aerial parts of *B. ulicina* H. et A. gave chromolaenin [40], the isomeric dihydro derivatives [41] and a norsesquiterpene, the furanoketone **30**. The structure followed from the molecular formula ($C_{14}H_{16}O_2$) and the characteristic ^{1}H NMR spectrum (Experimental). All signals could be assigned by spin decoupling. Together with the IR and UV spectra the only possible structure was **30**. As $J_{1\alpha,2\beta}$ and $J_{1\alpha,10}$ were large the conformation was clear. A negative Cotton-effect therefore supported the proposed absolute configuration of the chromolaenin derivatives. The ketone **30** is a further example of a norcadinene derivative which have only been isolated from Astereae [41–44].

CONCLUSIONS

One of the main problems in the tribe Astereae is still the delimition of the subtribes. Bentham says "the Astereae are not divisible into distinct subtribes". But he nevertheless divided the tribe into six subtribes. The subtribe Baccharinae is one of the most derived ones and is said to be a natural grouping by the presence of dioecious heads [45]. Only three genera are placed in this group, the small genera *Heterothalamus* (8 sp. now often treated as part of *Baccharis*) and *Parastrephia* (5 sp. recently reinterpreted to include most of *Lepidophyllum* not necessarily close to *Baccharis*) and the large genus *Baccharis* (400 sp.). The overall picture of the chemistry of the latter genus shows a tendency of accumulation of baccharis oxide, *ent*-clerodanes and, less common, *ent*-labdanes or *ent*-kauranes. As shown in this paper probably diterpene glycosides may be characteristic. Widespread are also *m*-hydroxyacetophenones which in part replace the common *p*-hydroxy derivatives. A relationship to *Heterothalamus* and *Parastrephia* is indicated by the presence of umbelliferone geranyl ether derivatives in these genera [46, 47] and some *Baccharis* species [1, 48] though these compounds also have been reported from a few other species placed in *Solidago*, *Haplopappus*, *Nidorella*, *Conyza* and *Aster*. Similarly cadinenes have been isolated from some *Baccharis* species and from *Heterotheca* [43] species which are placed in the Solidaginae. As *ent*-clerodanes and *ent*-labdanes are present in other genera of the tribe Astereae, especially in those placed in the subtribe Solidaginae and Conyzinae, the chemistry does not indicate clear limits of the proposed subtribes. The same seems to be true for proposed sections in the totally American genus *Baccharis*. Attempts of understand relationships within this genus, all having separate male and female plants, have resulted in various sectional classifications during the last 150 years. The sections that have been proposed in most recent treatments tend to divide the genus into many small groups, which are probably usually phyletic, but overall groupings are not as certain. If a system is used which is derived primarily from two regional treatments of the genus, the Colombian and the Argentina species 21 sections or groups can be erected [49–52]. The species investigated now are placed in four different sections. Representatives of the section Cuneifolia DC are *B. magellanica*, *B. patagonica* and *B. rhetinodes*, which all contain furanoclerodanes. This is true also for *B. tricuneata* which was investigated previously [29]. The chemistry of those species which are placed in the section Molinae Pers. differs clearly. Both species, *B. pingraea* and *B. salicifolia*, gave *ent*-labdane glycosides. The two

species, *B. gilliesii* and *B. ulicina* belonging to the section Angustifoliae Baker, differ in the chemistry, one affording furanoclerodanes and one furanocadinenes. The chemistry of *B. polifolia* (section Discolores DC) again is different from that of the other sections. The unusually high concentration of prenyl-*p*-coumaric acid derivatives is remarkable. Furthermore, the usual diterpenes are replaced by minute amounts of partially rearranged *ent*-labdanes. The overall picture of the chemotaxonomy of *Baccharis* is still somewhat diverse. In several cases the chemistry agrees with the proposed sections (Table 6). Thus in 11 sections *ent*-furanoclerodanes, in one section *ent*-labdanes and in two sections *ent*-kauranes predominate. In three sections different types of diterpenes are present and in four sections no diterpenes so far could be detected. Flavanoids, baccharis oxide and *m*-hydroxyacetophenones as well as acetylenic compounds are distributed over all sections.

EXPERIMENTAL

The air dried plant material was collected in February 1985 in Argentina and extracted with MeOH–Et_2O–petrol (1:1:1). The extracts obtained were defatted with MeOH and separated as reported previously [53]. For CC silica gel, for preparative TLC silica gel, PF 254 and for HPLC RP 8 columns, flow rate 3 ml/min, *ca* 100 bar, were used.

The extract of the aerial parts of *B. salicifolia* (650 g, collected 70 km W of Rio Colorado, 250 ft, voucher RMK 9344, all deposited in the US National Herbarium, Washington) gave by CC four fractions (1: petrol, 2: Et_2O–petrol, 1:3, 3: Et_2O and 4: Et_2O–MeOH, 9:1). Preparative TLC (silica gel, $AgNO_3$ coated, Et_2O–petrol, 1:20) of fraction 1 gave 10 mg **27** (R_f 0.75) and 30 mg **31** (R_f 0.32). Preparative TLC of fraction 2 (Et_2O–petrol, 1:9) gave 10 mg **28** (R_f 0.55), 5 mg baccharis oxide and 400 mg germacrone. Preparative TLC of fraction 3 (Et_2O–petrol, 1:1) gave 600 mg 4'-methoxypinostrobin, 100 mg sakuranetin and 200 mg isosakuranetin. Flash chromatography of fraction 4 (silica gel, ϕ 30–60 μ, Et_2O–petrol 1:1, Et_2O and Et_2O–MeOH, 9:1) gave 250 mg crude **12**, 30 mg **13**, 30 mg eriodictyol and 350 mg **43**. Compound **12** was transformed by addition of CH_2N_2 to the methyl ester **12a** which was purified by preparative TLC (Et_2O–petrol, 1:1, R_f 0.75).

The extract of aerial parts of *B. salicifolia* (500 g, collected 11 km NW of San Rafael, 2200 ft, voucher RMK 9429) was extracted as above and separated first by CC (silica gel) affording three polar fractions (1: Et_2O, 2: Et_2O–MeOH, 100:1 and 3: Et_2O–MeOH, 10:1). Preparative TLC of fraction 1 (Et_2O) gave 50 mg corymbosin, mp 188° (lit. [12] 188°). Preparative TLC of fraction 2 (Et_2O–petrol, 3:1) gave a mixture which by HPLC (MeOH–H_2O, 4:1) gave 7 mg **8** (R_t 5.4 min) and 200 mg **7** (R_t 8.0 min). Fraction 3 gave on standing in Et_2O crystals which by preparative TLC (Et_2O–petrol, 3:1) afforded 20 mg 5-hydroxy-7,3',4'-trimethoxyflavone and 150 mg 5-hydroxy-6,7,3',4',5'-pentamethoxyflavone. HPLC of the mother liquor of fraction 3 (MeOH–H_2O, 17:3) gave a mixture (R_t 3.6 min) and 2 g **1a** (R_t 4.2 min). Preparative TLC of the mixture (Et_2O–MeOH, 30:1) gave 60 mg **1b** (R_f 0.62), a mixture of **1b** and **5**, 40 mg **5** (R_f 0.45) and 10 mg **1** (R_f 0.20).

The extract of the aerial parts of *B. salicifolia* (250 g, collected in the city limits of Catamarca, 1600 ft, voucher RMK 9448) was separated by CC into three fractions (1: Et_2O–petrol, 1:3, 2: Et_2O and 3: Et_2O–MeOH, 10:1). Preparative TLC (Et_2O–petrol, 1:1) of fraction 1 gave 300 mg 4β-hydroxygermacra-5*E*,1(10)*E*-diene and 1.2 g 6α-hydroxygermacra-4*E*,1(10)*E*-diene. Preparative TLC of fraction 2 (Et_2O) gave 50 mg 5,4'-dihydroxy-7,3'-dimethoxyflavanone. The ^{1}H NMR spectrum of fraction 3 indicated the presence of acids which were separated by extraction with diluted K_2CO_3 soln affording 2 g **9**. The neutral parts showed no acetoxy signals in the ^{1}H NMR. Acetylation (Ac_2O, $CHCl_3$, *p*-dimethylaminopyridine, 2 hr, 65°) gave a mixture which was separated by HPLC (MeOH–H_2O, 17:3) affording 40 mg **10Ac** (R_t 3.3 min), 30 mg **10aAc** (R_t 3.9 min), 5 mg **14a** (R_t 4.4 min), 10 mg **11b** (R_t 4.7 min), 15 mg **11a** (R_t 5.6 min) and 5 mg **11c** (R_t 6.3 min).

The extract of the aerial parts of *B. darwinii* (850 g, collected near Neuquen, 1800 ft, voucher RMK 9376) afforded by CC and preparative TLC 3 mg β-farnesene, 1.5 g auraptene (Et_2O–petrol, 1:3), 300 mg 6',7'-epoxyauraptene, 20 mg 5'-oxo-auraptene (both Et_2O–petrol, 1:1), 500 mg 6',7'-dihydroxy-auraptene (Et_2O–MeOH, 9:1), 1 g **33** (Et_2O) (preparative TLC, Et_2O–petrol, 3:1, R_f 0.3) and 30 mg **34** (preparative TLC, Et_2O–petrol, 3:1, R_f 0.45).

The extract of the aerial parts of *B. gilliesii* (800 g, collected Rio Negro, 7 km E of Choele Choel, 375 ft, voucher RMK 9348) gave by CC 4 g bacchotricuneatin B, identical with authentic material (mp, ^{1}H NMR).

The extract of aerial parts of *B. magellanica* (200 g, collected in the Banos de Copahue, 4600 ft, voucher RMK 9398) gave by CC 20 mg baccharisoxide, 20 mg *p*-hydroxyacetophenone, 4 mg 4-[1-methoxyethyl]-phenol and 10 mg dehydrodiconiferyl alcohol diacetate and a polar fraction which gave by TLC (Et_2O–MeOH, 50:1) a mixture of 1.5 g **15** and **16** (*ca* 3:2) and 40 mg bacchotricuneatin B. The roots (150 g) gave by CC and TLC 150 mg baccharisoxide and a polar fraction which gave by TLC (Et_2O–petrol, 3:1, two developments) 10 mg dehydrodiconiferyl alcohol diacetate and 2 mg **35** (R_f 0.50).

The aerial parts of *B. patagonica* (300 g, collected 20 km S of Confluencia, 2000 ft, voucher RMK 9374) gave 5 mg germacrene D, 5 mg β-farnesene, 100 mg *p*-hydroxyacetophenone, 50 mg acacetin, 50 mg genkwanin and 600 mg **15** containing *ca* 15% **16**.

The aerial parts of *B. pingraea* (250 g, collected 36 km W of Rio Colorado, 200 ft, voucher RMK 9339) afforded a polar CC fraction (Et_2O and Et_2O–MeOH, 9:1) which was separated again by flash chromatography (silica gel, ϕ 30–60 μ, Et_2O and Et_2O–MeOH, 9:1). The fractions were combined into four groups (F1–F4). HPLC of F1 (MeOH–H_2O, 17:3) gave 40 mg **1b** (R_t 5.1 min). The fraction F2 contained 2 g **1a**. HPLC of F3 (MeOH–H_2O, 17:3) gave 100 mg **1** (R_t 5.2 min) and a mixture (R_t 4.2 min) (F3/2). TLC of 10% of F3/2 (Et_2O–petrol, 3:1, two developments) gave 3 mg **6** (R_f 0.45) and a mixture. The whole fraction F3/2 therefore was acetylated. TLC (Et_2O–petrol, 3:1, two developments) gave after HPLC (MeOH–H_2O, 9:1) 27 mg **6** acetate (R_t 2.5 min), 15 mg **2Ac** (R_f 0.58) and 10 mg **4Ac** (R_f 0.38). Fraction F4 contained crude **3** which gave by acetylation and TLC (Et_2O–petrol, 3:1) 200 mg of the pentaacetate **3Ac** (R_f 0.68).

The extract of the aerial parts of *B. polifolia* (400 g, collected in the province Rio Negro, voucher RMK SIV) gave by CC three crude fractions (F1: Et_2O–petrol, 3:1, F2: Et_2O and F3: Et_2O–MeOH, 20:1). Flash chromatography and PTLC of F1 gave 5 mg spathulenol, 2.8 g 3,5-bis-[3',3'-dimethylallyl]-coumaric acid, 2.3 g of the corresponding acetate **40**, 30 mg of the acetate **36** and 100 mg of the isobutyrate **37** (isolated as its methyl ester, TLC: Et_2O–petrol, 1:3, R_f 0.4), 100 mg **38** (isolated as its methyl ester; TLC: Et_2O–petrol, 1:1, R_f 0.62) and a crude fraction which was combined with F2 and separated with $NaHCO_3$ in an acid part which gave 14 g crystalline 3-[3',3'-dimethylallyl]-coumaric acid and a neutral part which was separated by flash chromatography affording 150 mg isosakuranetin, 700 mg nevadensin, 20 mg of the 7-*O*-methyl ether and

two crude fractions (F2/1 and F2/2). HPLC of F2/1 (MeOH–H_2O, 3:1) gave 6 mg **41** and **42** (*ca* 1:1) which could be separated by TLC (Et_2O–petrol, 1:1, eight developments). HPLC of one tenth of F2/2 (MeOH–H_2O, 3:1) gave 60 mg **25** (R_t 4.8 min), a mixture of **25** and **26** and 30 mg **26** (R_t 6.0 min).

The extract of the aerial parts of *B. rhetinodes* (300 g, collected 4 km E of Junin de los Andes, 2300 ft, voucher RMK 9380) gave by CC 150 mg baccharis oxide and two polar fractions (1: Et_2O and 2: Et_2O–MeOH, 9:1). Fraction 1 gave 10 g **23**. Fraction 2 was separated again by flash chromatography (Et_2O–petrol, 3:1–Et_2O–MeOH, 100:1, 20 ml fractions). Fractions 17–19 gave 100 mg **24**, which was purified as its methyl ester, and fractions 32–35 afforded 20 mg bacchotricuneatin A.

The aerial parts of *B. ulicina* (300 g, collected 70 km W of Rio Colorado, 250 ft, voucher RMK 9342) gave a CC fraction with Et_2O–petrol, 1:20, which afforded by preparative TLC ($AgNO_3$–silica gel) 2 mg chromolaenin, 4 mg of the 1,2-dihydro derivative and 6 mg 1,2-dihydroisochromolaenin (45). The CC fraction with Et_2O–petrol (1:1) gave by preparative TLC ($CHCl_3$–C_6H_6–Et_2O, 1:1:1) 5 mg **28** (R_f 0.35). The roots (50 g) afforded 5 mg baccharisoxide.

3α-*Angeloyloxy*-2β-,15-*dihydroxy*-ent-*labd*-7,13E-*dien*-2-O-β-*fucopyranoside* (**1**). Colourless crystals, mp 145°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1715 (C=CCO_2R); MS *m/z* (rel. int.): 532.340 [M $-H_2O]^+$ (0.1) (calc. for $C_{31}H_{48}O_7$: 532.340), 464 [532 – isoprene]$^+$ (0.5), 387 (2), 319 (6), 318 (4), 302 (8), 219 (7), 201 (12), 189 (7), 83 $[C_4H_7CO]^+$ (100), 55 [83 – CO]$^+$ (26); $[\alpha]_D^{24°}$ = −18.5 ($CHCl_3$; *c* 1.25). Acetylation (Ac_2O, *p*-dimethyl aminopyridine, 1 hr, 100°) gave the tetraacetate **1Ac**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750, 1235 (OAc); MS *m/z* (rel. int.): 718.393 [M]$^+$ (0.5) (calc. for $C_{39}H_{58}O_{12}$: 718.393), 658 [M – HOAc]$^+$ (0.5), 590 [M – Me_2C=$CHCH_2OAc]^+$ (2), 429 [M – sugar]$^+$ (1.5), 369 [429 – HOAc]$^+$ (1.5), 302 [429 – CH_2C(Me)=$CHCH_2Ac]^+$ (22), 273 [sugar onium cation]$^+$ (28), 213 [273 – HOAc]$^+$ (5), 202 [302 – AngOH]$^+$ (12), 153 [213 – HOAc]$^+$ (28), 111 [153 – ketene]$^+$ (37), 83 $[C_4H_7CO]^+$ (100); $[\alpha]_D^{24°}$ = +5.1 ($CHCl_3$; *c* 5.84). ^{13}C NMR (100.61 MHz, $CDCl_3$, C-1–C-20): 42.8 *t*, 73.2 *d*, 81.0 *d*, 37.3 *s*, 53.4 *d*, 23.4 *t*, 121.7 *d*, 138.8 *s*, 49.2 *d*, 38.9 *s*, 25.1 *t*, 40.7 *t*, 135.0 *s*, 124.7 *d*, 59.1 *t*, 16.7 *q*, 21.9 *q*, 28.2 *q*, 17.5 *q*, 14.5 *q*; (C-1′–C-6′): 100.3 *d*, 71.4 *d*, 72.0 *d*, 72.5 *d*, 69.1 *d*, 16.3 *q*; OAc: 171.1 *s*, 20.7 *q*; OAng: 168.6 *s*, 129.0 *s*, 136.0 *d*, 15.7 *q*, 20.7 *q* (assigned by ^1H–^{13}C shift correlation).

3α-*Angeloyloxy*-2β,15-*dihydroxy*-ent-*labd*-7,13E-*dien*-2-O-β-[*fucopyranoside*-4′-O-*acetate*] (**1a**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3420 (OH), 1740, 1240 (OAc), 1710, 1640 (C=CCO_2R); MS *m/z* (rel. int.): 592.361 [M]$^+$ (0.1) (calc. for $C_{33}H_{52}O_9$: 592.361), 574 [M – $H_2O]^+$ (0.5), 536 [574 – $H_2O]^+$ (0.1), 506 [574 – isoprene]$^+$ (2), 488 [506 – $H_2O]^+$ (3), 387 (6), 319 (9), 318 (8), 302 (18), 219 $[C_{15}H_{23}O]^+$ (6), 201 (8), 189 $[C_8H_{13}O_3]^+$ (8), 129 [189 – AcOH]$^+$ (6), 83 $[C_4H_7CO]^+$ (100), 55 [83 – CO]$^+$ (26); $[\alpha]_D^{24°}$ = −14° ($CDCl_3$; *c* 3.05). Acetylation afforded **1Ac**; 50 mg **1a** in 2 ml MeOH were boiled for 2 hr with 20 mg *p*-Ts. After addition of $NaHCO_3$ the solvent was removed and the residue was extracted with $CHCl_3$. The extract was acetylated affording a mixture of triacetyl-α- and β-methyl-fucopyranoside which was separated by preparative TLC ($CHCl_3$–Et_2O, 4:1). α-Methyl derivative: $[\alpha]_D^{24°}$ = +109 ($CHCl_3$; *c* 0.6); MS *m/z* (rel. int.): 273.097 (6) [M – OMe]$^+$ (calc. for $C_{12}H_{17}O_7$: 273.097), 244 [M – HOAc]$^+$ (2), 184 [244 – HOAc]$^+$ (26), 157 [AcCHCH=CHOAc]$^+$ (100). ^1H NMR ($CDCl_3$): δ4.94 (*d*, H-1), 5.15 (*dd*, H-2), 5.35 (*dd*, H-3), 5.29 (*br d*, H-4), 4.12 (*br q*, H-5), 1.16 (*d*, H-6), OAc: 2.17, 2.08, 1.98 (*s*); OMe: 3.39 (*s*); [*J* (Hz): 1,2 = 4; 2,3 = 11; 3,4 = 3.5; 5,6 = 6.5). β-Methyl derivative: $[\alpha]_D^{24°}$ = +7° ($CHCl_3$; *c* 0.4) (lit. [16] for triacetyl-β-methyl-D-fucopyranoside, −6°); ^1H NMR ($CDCl_3$): δ4.36 (*d*, H-1), 5.18 (*dd*, H-2), 5.01 (*dd*, H-3), 5.23 (*br d*, H-4), 3.80 (*br q*, H-5), 1.23 (*d*, H-6), OAc: 2.17, 2.05, 1.98 (*s*); OMe: 3.51 (*s*); [*J* (Hz): 1,2 = 7.5; 2,3 = 10; 3,4 = 3.5; 4,5 = 0.5; 5,6 = 6.5]; MS *m/z* (rel. int.): 273.097 [M – OMe]$^+$ (3) (calc. for $C_{12}H_{17}O_7$: 273.097), 244 [M – HOAc]$^+$ (3), 184 [244 – HOAc]$^+$ (26), 157 (100).

3α-*Angeloyloxy*-2β,15-*dihydroxy*-ent-*labd*-7,13E-*dien*-2-O-β-[*fucopyranoside*-3′-O-*acetate*] (**1b**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3420 (OH), 1740 (OAc), 1710, 1640 (C=CCO_2R); MS *m/z* (rel. int.): 574.351 [M – $H_2O]^+$ (0.1) (calc. for $C_{33}H_{50}O_8$: 574.351), 506 (0.3), 488 (1), 387 (2.5), 319 (4), 318 (4.5), 302 (8), 287 (4), 269 (3), 219 (5), 83 (100); $[\alpha]_D^{24°}$ = +9° ($CHCl_3$; *c* 0.18).

3α-*Angeloyloxy*-2β,14,15-*trihydroxy*-ent-*labd*-7,13(16)-*dien*-2-O-[*fucopyranoside*-4′-O-*acetate*] (**2**). Crude compound showed ^1H NMR signals indicating the presence of 4′-*O*-acetate (5.09 *br d*, 2.09 *s*). Acetylation afforded the pentaacetate **2Ac**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750, 1240 (OAc); MS *m/z* (rel. int.): 776.398 [M]$^+$ (0.1) (calc. for $C_{41}H_{60}O_{14}$: 776.398), 656 (0.2), 487 (1), 387 (0.6), 302 (1), 273 (22), 213 (5), 153 (27), 111 (22), 83 (100).

3α-*Angeloyloxy*-2β,15,16-*trihydroxy*-ent-*labd*-7,13E-*dien*-2-O-β-[*fucopyranoside*-4′-O-*acetate*] (**3**). Colourless oil; MS *m/z* (rel. int.): 590 [M – $H_2O]^+$ (0.2), 419 [M – sugar moiety]$^+$ (1.5), 319 [419 – AngOH]$^+$ (25), 189 [sugar]$^+$ (62), 171 [189 – $H_2O]^+$ (58), 111 [171 – AcOH]$^+$ (38), 83 $[C_4H_7CO]^+$ (100). Acetylation afforded the pentaacetate (**3Ac**); colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750, 1235 (OAc); MS *m/z* (rel. int.): 776.398 [M]$^+$ (0.1) (calc. for $C_{41}H_{60}O_{14}$: 776.398), 716 (0.4), 656 (1), 590 [M – $AcOCH_2C$(Me)=$CHCH_2OAc]^+$ (1), 487 [M – sugar moiety]$^+$ (1.5), 345 (1.5), 302 [487 – CH_2C(Me)=$CHCH_2OAc]^+$ (11), 273 [sugar]$^+$ (48), 213 (7), 153 (22), 111 (24), 83 (100); $[\alpha]_D^{24°}$ = −2.1° ($CHCl_3$; *c* 6.2).

3α-*Angeloyloxy*-2-*hydroxy*-13-*oxo*-14,15-*nor*-ent-*labd*-7-*en*-2-O-[*fucopyranoside*-4′-O-*acetate*] (**4**). Crude compound showed ^1H NMR signals of a 4′-*O*-acetate (5.07 *br d*, 2.08 *s*). Acetylation gave the triacetate (**4Ac**); MS *m/z* (rel. int.): 648.341 [M]$^+$ (0.1) (calc. for $C_{35}H_{52}O_{11}$: 648.341), 590 [M – $Me_2CO]^+$ (0.1), 359 [M – sugar moiety]$^+$ (2), 302 (1.2), 273 (45), 213 (8), 153 (32), 111 (26), 83 (100); $[\alpha]_D^{24°}$ = −2.3° ($CHCl_3$; *c* 0.69).

3α-*Angeloyloxy*-2β,15-*dihydroxy*-ent-*labd*-7,13E-*dien*-2-O-*rhamnopyranoside*-4′-O-*acetate* (**5**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3420 (OH), 1745 (OAc), 1710 (C=CCO_2R); MS *m/z* (rel. int.): 592.361 [M]$^+$ (0.1) (calc. for $C_{33}H_{52}O_9$: 592.361), 574 (0.3), 506 (2), 488 (1), 387 (4), 369 (2.5), 319 (10), 318 (7), 302 (26), 287 (12), 269 (12), 201 (33), 83 (100); $[\alpha]_D^{24°}$ = −16° ($CHCl_3$; *c* 1.48). Acetylation afforded the tetraacetate **5Ac**; colourless oil; MS *m/z* (rel. int.): 718.393 [M]$^+$ (0.2) (calc. for $C_{39}H_{58}O_{12}$: 718.393), 658 (1.5), 590 (5), 371 (2), 302 (22), 273 (44), 83 (100).

3α-*Angeloyloxy*-2β,15-*dihydroxy*-ent-*labd*-7,13E-*dien*-2-O-β-*xylopyranoside* (**6**). Colourless oil; MS *m/z* (rel. int.): 518 [M – $H_2O]^+$ (0.2), 420 (6), 387 (11), 302 (61), 202 (58), 133 (40), 83 (100). Acetylation afforded the tetraacetate (**6Ac**); colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750, 1240 (OAc); MS *m/z* (rel. int.): 704.346 [M]$^+$ (0.1) (calc. for $C_{38}H_{56}O_{12}$: 704.346), 644 (0.2), 357 (1), 302 (12), 259 (10), 83 (100); $[\alpha]_D^{24°}$ = −26° ($CHCl_3$; *c* 1.75).

3α-*Angeloyloxy*-ent-*labda*-7,13-*dien*-2β,15-*diol* (**7**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1720, 1650 (C=CCO_2R); MS *m/z* (rel. int.): 404.293 [M]$^+$ (0.4) (calc. for $C_{25}H_{40}O_4$: 404.293), 386 [M – $H_2O]^+$ (0.4), 318 [386 – isoprene]$^+$ (94), 218 [318 – $RCO_2H]^+$ (20), 203 [218 – Me]$^+$ (41), 83 $[C_4H_7CO]^+$ (100), 55 [83 – CO]$^+$ (64); $[\alpha]_D^{24°}$ = +32° ($CHCl_3$; *c* 3.44). ^1H NMR ($CDCl_3$): δ2.24 (*dd*, H-1α), 1.17 (*t*, H-1β) 3.82 (*ddd*, H-2), 4.59 (*d*, H-3), 1.36 (*dd*, H-5), 1.95 (*m*, H-6), 5.38 (*br s*, H-7), 2.20 (*m*, H-12), 5.40 (*br s*, H-14), 4.14 (*br d*, H-15), 1.67 (*br s*, H-16), 1.69 (*br s*, H-17), 0.87 (*s*, H-18), 0.95 (*s*, H-19), 0.81 (*s*, H-20), OAng: 6.09 (*qq*), 2.00 (*dq*), 1.92 (*dq*); [*J* (Hz): 1α,1β = 1β,2 = 13; 1α,2 = 4; 2,3

= 10; 5,6 = 6; 5,6′ = 10; 14,15 = 7; OAng: 3,4 = 7; 3,5 = 4,5 = 1.5]. Compound **7** (10 mg) in 2 ml CH_2Cl_2 were stirred 2 hr with 20 mg pyridine chlorochromate and 10 mg $NaHCO_3$. Preparative TLC of the reaction product gave 2 mg **7a**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2730, 1680 (C=O), 1720 (C=CCO_2R); MS *m/z* (rel. int.): 400 $[M]^+$ (0.3), 316.204 $[M - Me_2C{=}CHCHO]^+$ (21) (calc. for $C_{20}H_{28}O_3$: 316.204), 83 $[C_4H_7CO]^+$ (100), 55 [83 $-CO]^+$ (38); ^1H NMR ($CDCl_3$): δ2.34 (*br d*, H-1α), 2.59 (*d*, H-1β), 5.04 (*s*, H-3), 1.41 (*dd*, H-5), 2.00 (*m*, H-6), 5.48 (*br s*, H-7), 2.70 and 2.45 (*m*, H-12), 5.87 (*br d*, H-14), 9.99 (*d*, H-15), 2.18 (*br s*, H-16), 1.74 (*br s*, H-17), 0.91 (*s*, H-18), 1.16 (*s*, H-19), 0.81 (*s*, H-20), OAng: 6.14 (*qq*), 2.01 (*br d*), 1.96 (*br s*); [*J* (Hz) as **7** except 1α,1β = 13]; CD (MeCN): $\Delta\varepsilon_{277} = -0.45$.

15,16-*Epoxy*-ent-*labda*-7,13(16),14-*trien*-2β,3α-*diol* (**8**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 880 (furane); MS *m/z* (rel. int.): 318.219 $[M]^+$ (3) (calc. for $C_{20}H_{30}O_3$: 318.219), 300 $[M - H_2O]^+$ (1), 236 $[M - C_5H_6O]^+$ (8), 218 $[236 - H_2O]^+$ (2), 82 $[C_5H_6O]^+$ (100); ^1H NMR ($CDCl_3$): δ3.69 (*ddd*, H-2), 3.02 (*d*, H-3), 1.29 (*dd*, H-5), 1.98 (*m*, H-6), 5.42 (*br s*, H-7), 2.62 and 2.37 (*ddd*, H-12), 6.28 (*br s*, H-14), 7.35 (*t*, H-15), 7.21 (*br s*, H-16), 1.74 (*br s*, H-17), 0.88 (*s*, H-18), 1.00 (*s*, H-19), 0.82 (*s*, H-20); [*J* (Hz) as **7** except 14,15 = 15,16 = 1.5]; $[\alpha]_D^{24°} = -11°$ ($CHCl_3$; *c* 0.74).

2β,3β-*Dihydroxy*-ent-*cativic acid* (**9**). Colourless oil which was transformed to the methyl ester; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CO_2R); ^1H NMR ($CDCl_3$): δ3.98 (*ddd*, H-2), 3.42 (*d*, H-3), 5.36 (*br s*, H-7), 1.92 (*m*, H-13), 2.23 (*dd*) and 2.12 (*dd*, H-14), 0.91 (*d*, H-16), 1.63 (*br s*, H-17), 0.96 (*s*, H-18), 0.88 (*s*, H-19), 0.76 (*s*, H-20), OMe: 3.64 (*s*); [*J* (Hz): 1,2 = 4; 1′,2 = 11; 2,3 = 2; 13,14 = 6; 13,14′ = 8; 14,14′ = 15); MS *m/z* (rel. int.): 498.335 $[M]^+$ (4) (calc. for $C_{31}H_{46}O_5$: 498.335), 480 $[M - H_2O]^+$ (1.5), 334 $[M - RCO_2H]^+$ (32), 119 $[C_9H_{11}]^+$ (96), 91 $[C_7H_7]^+$ (100). To 50 mg of the methyl ester of **9** in 2 ml AcOH 25 mg CrO_3 in 0.5 ml H_2O were added. After 12 hr usual work-up gave by TLC (Et_2O–petrol, 3:1) 20 mg **9b**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3480 (OH), 1740 (CO_2R), 1710 (C=O); MS *m/z* (rel. int.): 350.246 $[M]^+$ (17) (calc. for $C_{21}H_{34}O_4$: 350.246), 332 $[M - H_2O]^+$ (8), 317 $[332 - Me]^+$ (10), 203 [332 $- CH_2CH_2CH(Me)CH_2CO_2Me]^+$ (23), 121 (62), 83 (100); CD (MeCN): $\Delta\varepsilon$ 307 = +0.38, $\Delta\varepsilon$ 267 = −0.32; ^1H NMR ($CDCl_3$): δ2.51 (*dd*, H-1), 1.27 (*m*, H-1′), 4.57 (*ddd*, H-2), 1.58 (*dd*, H-5), 2.30 and 2.10 (*m*, H-6) 5.41 (*br s*, H-7), 1.92 (*m*, H-13), 2.29 and 2.14 (*dd*, H-14), 0.94 (*d*, H-16), 1.67 (*br s*, H-17), 1.07, 1.11, 1.14 (*s*, H-18, H-19, H-20), OMe: 3.66 (*s*). To 44.1 mg of the methyl ester of **9** in 2 ml pyridine 114.2 mg α-phenyl butyric acid anhydride was added. After 12 hr H_2O was added, the neutral and acid parts separated. The acid showed a negative rotation (optical yield 10%). The esters obtained were separated by TLC (Et_2O–petrol, 3:1) affording as the less polar band the minor compound (**13b/1**) and 30 mg **9a**; colourless oil; $[\alpha]_D^{24°} = -8.0°$ ($CHCl_3$; *c* 2.4); ^1H NMR ($CDCl_3$, in parentheses **9a/1**): δ1.60 (*dd*, H-1α) (1.73), 1.50 (*t*, H-1β) (1.60), 5.20 (*ddd*, H-2) (5.20), 3.50 (*d*, H-3) (3.32), 5.37 (*br s*, H-7) (5.37), 2.27 and 2.14 (*dd*, H-14) (2.30, 2.10), 0.93 (*d*, H-16) (0.91), 1.64 (*br s*, H-17) (1.63), 0.96 (*s*, H-18) (0.97), 0.95 (*s*, H-19) (0.95), 0.80 (*s*, H-20) (0.78); $OCOCH(Et)C_6H_5$: 3.48 (*t*), 2.14 (*dq*), 0.91 (*t*), 7.26 (*m*), 7.32 (*m*); OMe: 3.64 (*s*) (3.67) (couplings as in the methyl ester of **9**).

2β,15-*Diacetoxy*-3β-*hydroxy*-ent-*labd*-7,13E-*diene* (**10Ac**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1745 (OAc); MS *m/z* (rel. int.): 406.272 $[M]^+$ (1) (calc. for $C_{24}H_{38}O_5$: 406.272), 346 (0.5), 278 [346 − isoprene]$^+$ (100), 218 $[278 - HOAc]^+$ (63), 203 (48), 149 (78), 81 (98); ^1H NMR ($CDCl_3$): see **10a**Ac except 2.24 (*br ddd*, H-12) and 2.00 (*m*, H-12), 5.34 (*br t*, H-14), 4.58 (*br d*, H-15), 1.70 (*br s*, H-16), OAc: 2.10 and 2.06 (*s*); [*J* (Hz): 1α,2β = 12; 1β,2β = 4; 2β,3β = 2; 14,15 = 7].

2β,15-*Diacetoxy*-3β-*hydroxy*-ent-*labd*-7-*ene* (**10aAc**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1745, 1245 (OAc); MS *m/z* (rel. int.): 408.286 $[M]^+$ (2) (calc. for $C_{24}H_{40}O_5$: 408.286), 390 $[M - H_2O]^+$ (1), 348 $[M - HOAc]^+$ (14), 333 (18), 330 (12), 205 [348 $- CH_2CH_2C(Me){=}CHCH_2OAc$) (100), 187 (41), 121 (84), 95 (94), 81 (76); $[\alpha]_D^{24°} = -15°$ ($CHCl_3$; *c* 0.63); ^1H NMR ($CDCl_3$): δ5.22 (*ddd*, H-2), 3.51 (*br s*, H-3), 5.39 (*br s*, H-7), 4.11 and 4.08 (*dt*, H-15), 0.91 (*d*, H-16), 1.66 (*br s*, H-17), 0.99 (*s*, H-18), 0.97 (*s*, H-19), 0.85 (*s*, H-20), OAc: 2.10, 2.05 (*s*); [*J* (Hz): 1α,2α = 4; 1β,2α = 12; 2α,3α = 2; 14,16 = 7; 14,15 = 14,15′ = 7; 15,15′ = 10].

8β,15-*Dihydroxy*-ent-*labd*-13E-*ene*-8-O-β-*xylopyranoside* (**11**). The crude glycoside was acetylated affording **11a–11c** (^1H NMR, Table 3). Compound **11c**: colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1745, 1245 (OAc); MS *m/z* (rel. int.): 506.324 $[M - HOAc]^+$ (0.1) (calc. for $C_{29}H_{46}O_7$: 506.324), 333 (3), 273 (23), 217 $[C_9H_{13}O_6]^+$ (21), 192 (81), 177 (57), 157 [217 $- HOAc]^+$ (58), 97 $[157 - HOAc]^+$ (100), 81 (73). Acetylation of **11a–11c** (Ac_2O, *p*-dimethylaminopyridine, 2 hr, 100°) gave **11Ac**; colourless crystals, mp. 125°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1250 (OAc); MS *m/z* (rel. int.): 548.335 $[M - HOAc]^+$ (0.1) (calc. for $C_{31}H_{48}O_8$: 548.335), 333 (3), 273 (20), 259 (24), 192 (100), 177 (44); $[\alpha]_D^{24°} = -35°$ ($CHCl_3$; *c* 0.35).

Bacchasalicyclic acid (**12**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3605 (OH), 3500–2600, 1700 (CO_2H); MS *m/z* (rel. int.): 320.235 $[M]^+$ (6) (calc. for $C_{20}H_{32}O_3$: 320.235), 302 $[M - H_2O]^+$ (6.5), 287 $[302 - Me]^+$ (6.5), 95 (100) which was purified as its methyl ester **12a**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1730 (CO_2R), 1660 (C=C); MS *m/z* (rel. int.): 334.251 $[M]^+$ (5) (calc. for $C_{21}H_{34}O_3$: 334.251), 316 $[M - H_2O]^+$ (7), 285 $[316 - OMe]^+$ (2.5), 95 (100). Acetylation (Ac_2O, 1 hr, 70°) gave **12aAc**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735, 1235 (OAc), 1660 (C=C); MS *m/z* (rel. int.): 376 $[M]^+$ (0.5), 316.240 $[M - HOAc]^+$ (6) (calc. for $C_{21}H_{32}O_2$: 316.240), 285 $[316 - OMe]^+$ (3), 95 (100); ^{13}C NMR ($CDCl_3$, C-1–C-20): 21.8 *t*, 35.8 *t*, 118.3 *d*, 143.8 *s*, 37.8 *s*, 33.0 *t*, 17.9 *t*, 49.1 *d*, 38.6 *s*, 46.3 *d*, 38.7 *t*, 26.6 *t*, 142.9 *s*, 120.6 *d*, 61.4 *t*, 16.4 *q*, 175.1 *s*, 17.9 *q*, 20.0 *q*, 20.1 *q*; OAc: 171.1 *s*, 21.1 *q*; OMe: 50.9 *q*; $[\alpha]_D^{24°} = -50°$ ($CHCl_3$; *c* 0.80).

16-*Hydroxybacchasalicylic acid*-15-O-*acetate* (**13**). Colourless oil; ^1H NMR ($CDCl_3$): δ5.18 (*br s*, H-3), 2.51 (*dd*, H-8), 5.41 (*br t*, H-14), 4.56 and 4.59 (*dd*, H-15), 4.25 and 4.20 (*d*, H-16), 1.57 (*br s*, H-18), 1.03 (*s*, H-19), 0.91 (*s*, H-20); [*J* (Hz): see **13a**, Table 1]. Addition of CH_2N_2 gave **13a**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1740 (CO_2R, OAc), 1645 (C=C); MS *m/z* (rel. int.): 332.235 $[M - HOAc]^+$ (12) (calc. for $C_{21}H_{32}O_3$: 332.235), 301 [332 $- OMe]^+$ (11), 95 (100); $[\alpha]_D^{24°} = -45°$ ($CHCl_3$; *c* 2.0).

Bacchasalicylic acid-15-O-[1′-β-*xylopyranoside*] (**14**). Acetylation gave **14a**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1745 (OAc); MS *m/z* (rel. int.): 518.288 $[M - HOAc]^+$ (0.5) (calc. for $C_{29}H_{42}O_8$: 518.288), 500 $[M - H_2O]^+$ (0.2), 345 $[M - sugar]^+$ (1.5), 333 (2.5), 302 (10), 285 (12), 278 (10), 217 $[C_9H_{13}O_6]^+$ (41), 157 (11), 97 (44), 55 (100); ^1H NMR ($CDCl_3$): δ5.19 (*br s*, H-3), 2.55 (*dd*, H-8), 5.37 (*br t*, H-14), 4.57 and 4.52 (*dd*, H-15), 1.71 (*br s*, H-16), 1.58 (*br s*, H-18), 1.04 (*s*, H-19), 0.91 (*s*, H-20), 5.59 (*d*, H-1′), 3.62 (*ddd*, H-2′), 5.11 (*t*, H-3′), 4.95 (*ddd*, H-4′), 4.09 (*dd*, H-5′$_1$), 3.46 (*dd*, H-5′$_2$), OAc: 2.09, 2.04 (6H, *s*); 2′-OH: 2.95 (*d*); [*J* (Hz): 7α,8 = 13; 7β,8 = 3.5; 14,15 = 7; 15,15′ = 12; 1′,2′ = 7.5; 2′,3′ = 3′,4′ = 9; 4′,5′$_1$ = 5; 4′,5′$_2$ = 9; 5′$_1$,5′$_2$ = 11.5; 2′,OH = 4′,OH = 5]; $[\alpha]_D^{24°} = -25°$ ($CHCl_3$; *c* 0.37).

Bacchomagellins A and B (**15** *and* **16**). Colourless oil which was transformed by addition of CH_2N_2 to the methyl esters **15a** and **16a** which could not be separated by TLC or HPLC. Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R); MS *m/z* (rel. int.): 404 (8) [M $- C_{25}H_{39}O_6 - Me]^+$, 389 $[404 - Me]^+$ (10), 255 [389 $- HO_2CCH_2CH_2CO_2Me]^+$ (21), 189 $[C_{14}H_{21}]^+$ (100).

Compounds **15/16** (100 mg) in 2 ml MeOH were heated for 30 min with 100 mg KOH in 0.5 ml H_2O. The neutral fraction

(**17**) was colourless oil; MS *m/z* (rel. int.): 626 $[M]^+$ (0.2) ($C_{40}H_{66}O_5$), 608 $[M-H_2O]^+$ (0.3), 593 $[608-Me]^+$ (0.6), 577 $[608-CH_2OH]^+$ (2.5), 304 $[C_{20}H_{22}O_2]^+$ (5), 189 $[C_{14}H_{21}]^+$ (66), 69 (100). Acetylation (Ac_2O, DMAP, $CHCl_3$) gave the acetate **18**; colourless oil; MS *m/z* (rel. int.): 348 $[C_{22}H_{36}O_3]^+$ (2), 346 $[C_{22}H_{34}O_3]^+$ (2), 189 $[C_{14}H_{21}]^+$ (66), 69 (100).

Compound **18** (50 mg) was heated for 30 min in 2 ml MeOH with 50 mg *p*-Ts. TLC (Et_2O–petrol, 1:1) gave **21** (R_f 0.60); colourless oil; MS *m/z* (rel. int.): 350.282 $[M]^+$ (2) (calc. for $C_{22}H_{38}O_3$: 350.282), 318 $[M-MeOH]^+$ (12), 286 $[318-MeOH]^+$ (37), 189 $[C_{14}H_{21}]^+$ (100) and small amounts of the 1,3-diene **22** formed by elimination of MeOH; colourless oil; MS *m/z* (rel. int.): 318.256 $[M]^+$ (8) (calc. for $C_{21}H_{34}O_2$: 318.256), 286 $[M-MeOH]^+$ (42), 271 $[286-Me]^+$ (37), 189 $[C_{14}H_{21}]^+$ (64), 119 (100).

Compounds **15/16** (100 mg) in 3 ml MeOH were heated for 5 min with 10 mg *p*-Ts. The crude product gave after addition of CH_2N_2 by TLC (Et_2O–petrol, 1:1) 50 mg **19a** and **20a** which were separated by HPLC (MeOH–H_2O, 9:1) affording 15 mg **19a** (R_t 2.7 min) and 10 mg **20a** (R_t 3.9 min).

19a: Colourless oil; MS *m/z* (rel. int.): 404.256 $[M-MeOH]^+$ (2) (calc. for $C_{24}H_{36}O_5$: 404.256), 286 $[404-RCO_2H]^+$ (66), 271 $[286-Me]^+$ (17), 189 $[C_{14}H_{21}]^+$ (75), 69 $[RCO-MeOH]^+$ (100).

20a: Colourless oil; MS *m/z* (rel. int.): 418.272 $[M-MeOH]^+$ (1.7) (calc. for $C_{25}H_{38}O_5$: 418.272), 286 $[M-RCO_2H]^+$ (44), 189 (72), 115 $[RCO]^+$ (100).

18-O-*Malonyl-kingidiol*-19-O-*acetate* (**23**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2500, 1715 (CO_2H), 1740 (CO_2R); MS *m/z* (rel. int.): 373.194 $[M-CH_2OAc]^+$ (0.7) (calc. for $C_{22}H_{29}O_5$: 373.194), 342 $[M-HOOCCH_2CO_2H]^+$ (3), 269 $[373-HO_2CCH_2CO_2H]^+$ (68), 187 $[269-C_5H_6O]^+$ (43), 175 $[269-C_6H_8O]^+$ (42), 105 (58), 81 $[C_5H_5O]^+$ (100). Addition of CH_2N_2 gave the methyl ester **23a**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R, OAc), 880 (β-furan); MS *m/z* (rel. int.): 387.217 $[M-CH_2OAc]^+$ (5) (calc. for $C_{23}H_{31}O_5$: 387.217), 365 $[M-CH_2CH_2C_4H_3O]^+$ (3), 342 $[M-RCO_2H]^+$ (5.5), 283 $[342-OAc]^+$ (7), 282 $[342-HOAc]^+$ (7), 269 $[387-RCO_2H]^+$ (100), 187 (48), 175 (28), 105 (31), 81 (44); ^1H NMR ($CDCl_3$): δ2.22 (*br d*) and 2.13 (*m*, H-2), 5.73 (*br t*, H-3), 1.92 (*ddd*, H-6α), 1.26 (*ddd*, H-6β), 1.38 (*m*, H-7), 1.56 (*m*, H-8), 1.63 and 1.49 (*m*, H-11), 2.28 (*ddd*) and 2.13 (*ddd*, H-12), 6.20 (*br s*, H-14), 7.29 (*dd*, H-15), 7.14 (*br s*, H-16), 0.80 (*d*, H-17), 4.70 and 4.61 (*br d*, H-18), 4.43 and 4.04 (*d*, H-19), 0.73 (*s*, H-20), OAc: 1.99 (*s*), OCOR: 3.35 (*s*, 2H), 3.70 (*s*, 3H); [*J* (Hz): 2, 2′ = 17; 2, 3 = 2′, 3 = 3; 6α, 6β = 6β, 7α = 12.5; 6α, 7 = 3; 6β, 7β = 5; 8, 17 = 7; 11, 12′ = 11′, 12 = 12, 12′ = 13; 11, 12 = 11′, 12′ = 5; 14, 15 = 15, 16 = 1.5; 18, 18′ = 13; 19, 19′ = 11). $[\alpha]_D^{24°} = -53°$ ($CHCl_3$; *c* 8.73). To 30 mg **23** in 2 ml MeOH was added 50 mg K_2CO_3 in 1 ml H_2O. After 2 hr standing at 22° the neutral part was extracted with Et_2O affording by preparative TLC (Et_2O–petrol, 1:1), 6 mg kingidiol and 12 mg **23b**; colourless oil; MS *m/z* (rel. int.): 360.230 $[M]^+$ (4.5) (calc. for $C_{22}H_{32}O_4$: 360.230), 342 $[M-H_2O]^+$ (8), 269 $[342-CH_2OAc]^+$ (65), 81 $[C_5H_5O]^+$ (100); ^1H NMR ($CDCl_3$) as **23a** except 0.85 (*d*, H-17), 4.19 and 4.04 (*br d*, H-18), 4.64 and 4.10 (*d*, H-19), 0.82 (*s*, H-20), OAc: 2.04 (*s*); [*J* (Hz) as **23a**].

19-O-*Malonyl-kingidiol* (**24**). Colourless oil, which was purified as its methyl ester **24a**; colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1725 (CO_2R), 880 (furan); MS *m/z* (rel. int.): 418.236 $[M]^+$ (1.2) (calc. for $C_{24}H_{34}O_6$: 418.236), 400 $[M-H_2O]^+$ (4.5), 269 $[400-CH_2OCOCH_2CO_2Me]^+$ (66), 187 $[269-MeC_4H_3O]^+$ (43), 81 $[C_5H_5O]^+$ (100); ^1H NMR ($CDCl_3$) as **23a** except 5.78 (*br t*, H-3), 0.84 (*d*, H-17), 4.16 and 4.02 (*br d*, H-18), 4.64 and 4.25 (*d*, H-19), 0.80 (*s*, H-20), OCOR: 3.37 (*s*, 2H), 3.73 (*s*, 3H); [*J* (Hz) as **23a**]; $[\alpha]_D^{24°} = -71°$ ($CHCl_3$; *c* 0.72). Acetylation (Ac_2O, $CHCl_3$, *p*-dimethylaminopyridine) gave **24aAc**; MS *m/z* (rel. int.): 400.125 $[M-AcOH]^+$ (4) (calc. for $C_{24}H_{32}O_5$: 400.125), 269 $[400-CH_2OCOCH_2CO_2Me]^+$ (72), 187 (78), 81 (100); ^1H NMR ($CDCl_3$) as **23a** except 0.80 (*d*, H-17), 4.59 and 4.51 (*br d*, H-18), 4.54 and 4.16 (*d*, H-19), 0.73 (*s*, H-20), OAc: 2.03 (*s*); OCOR: 3.35 (*s*), 3.73 (*s*); [*J* (Hz) as **23a**].

2-*Oxo-friedolabd*-1(10),13E-*dien*-15-*ol* (**25**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH), 1675 (C=CC=O); MS *m/z* (rel. int.): 304.240 $[M]^+$ (31) (calc. for $C_{20}H_{32}O_2$: 304.240), 286 $[M-H_2O]^+$ (20), 271 $[286-Me]^+$ (6), 206 $[M-C_6H_{10}O]^+$ (81), 205 $[M-C_6H_{11}O]^+$ (100), 191 $[206-Me]^+$ (40); ^1H NMR ($CDCl_3$): δ5.83 (*br s*, H-1), 2.28 and 2.05 (*d*, H-3), 2.45 (*br dd*, H-5), 1.75 (*m*) and 1.49 (*ddd*, H-6), 2.04 and 1.40 (*m*, H-7), 1.75 (*ddq*, H-8) (determined by 2 DJ resolved spectrum), 1.60 and 1.39 (*m*, H-11), 2.02 (*br dd*) and 1.90 (*ddd*, H-12), 5.34 (*br t*, H-14), 4.12 (*br d*, H-15), 1.62 (*br s*, H-16), 0.77 (*d*, H-17), 0.98, 0.97, 0.93 (*s*, H-18, H-19, H-20); [*J* (Hz): 3, 3′ = 16; 5, 6α = 13; 5, 6β = 4; 6α, 6β = 6α, 7β = 13; 6β, 7β = 4; 7, 8 = 3; 7′, 8 = 4; 8, 17 = 7; 11, 12 = 12, 12′ = 13; 11′, 12 = 11, 12′ = 4; 14, 15 = 7].

2α,15-*Dihydroxy-friedolabd*-1(10),13E-*diene* (**26**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH); MS *m/z* (rel. int.): 306.256 $[M]^+$ (12) (calc. for $C_{20}H_{34}O_2$: 306.256), 288 $[M-H_2O]^+$ (13), 273 $[288-Me]^+$ (7), 206 (70), 205 (100), 189 (63), 81 $[C_6H_9]^+$ (66); ^1H NMR ($CDCl_3$): δ5.33 (*br s*, H-1), 4.22 (*dddd*, H-2), 1.56 (*dd*) and 1.27 (*m*, H-3), 1.64 (*m*, H-5), (+C_6D_6 1.52, *dd*), 1.58 and 1.21 (*m*, H-6), 1.98 (*dddd*) and 1.34 (*br d*, H-7), 1.58 (*m*, H-8), 1.64 and 1.27 (*m*, H-11), 2.06 and 1.87 (*ddd*, H-12), 5.36 (*br t*, H-14), 4.12 (*br d*, H-15), 1.64 (*br s*, H-16), 0.81 (*d*, H-17), 0.93 (*s*, 3H) and 0.87 (*s*, 6H, H-18, H-19, H-20); [*J* (Hz) as **25**, except 1, 2 = 1, 5 = 1.5; 2, 3 = 6; 2, 3′ = 8; 3, 3′ = 12].

Verboccidentafurane-4α,5α-*epoxide* (**28**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1550 (furane); MS *m/z* (rel. int.): 232.146 $[M]^+$ (74) (calc. for $C_{15}H_{20}O_2$: 232.146), 203 $[M-CHO]^+$ (28), 161 $[203-C_3H_6]^+$ (100), 119 (78); $[\alpha]_D^{24°} = +24°$ ($CHCl_3$; *c* 0.25); ^1H NMR ($CDCl_3$): δ1.58 (*m*, H-1α), 1.67 (*m*, H-1β), 1.85 (*dddd*, H-2α), 1.70 (*m*, H-2β), 2.83 (*br s*, H-4), 2.93 (*dd*, H-5), 2.17 (*br dd*, H-8α), 2.66 (*dd*, H-8β), 1.78 (*m*, H-9), 1.43 (*dddd*, H-10), 7.07 (*br s*, H-12), 2.04 (*d*, H-13), 1.03 (*d*, H-14), 1.29 (*s*, H-15); [*J* (Hz): 1α, 1β = 1β, 2α = 2α, 10 ~ 2; 2α, 2β = 14; 5, 8α = 1; 5, 10 = 5; 8α, 8β = 16; 8α, 9 = 11; 8β, 9 = 5; 9, 14 = 7).

4-*Oxo*-1,2,3,4-*tetrahydro-nor*-15-*chromolaenin* (**30**). Colourless crystals, mp 125°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1670, 1620 (C=CC=O), 870 (furan); UV $\lambda_{max}^{Et_2O}$: 296 nm; MS *m/z* (rel. int.): 216.115 $[M]^+$ (100) (calc. for $C_{14}H_{16}O_2$: 216.115), 188 $[M-CO]^+$ (37), 173 $[188-Me]^+$ (85), 145 $[173-CO]^+$ (25); ^1H NMR ($CDCl_3$): δ2.21 (*dddd*, H-1), 2.36 (*dddd*, H-2α), 1.61 (*dddd*, H-2β), 2.36 (*ddd*, H-3α), 2.56 (*ddd*, H-3β), 6.28 (*br d*, H-5), 2.46 (*dd*, H-9α), 2.83 (*dd*, H-9β), 1.83 (*dddq*, H-10), 7.08 (*br s*, H-12), 2.14 (*d*, H-13), 1.14 (*d*, H-14); [*J* (Hz): 1, 2α = 4; 1, 2β = 2α, 2β = 12; 1, 5 = 2; 2α, 3α = 2; 2α, 3β = 4; 2β, 3α = 12; 3α, 3β = 17.5; 9α, 9β = 17; 9α, 10 = 12; 9β, 10 = 5; 10, 14 = 7; 12, 13 = 1.3]; CD (MeCN) $\Delta\varepsilon_{341} = -4.06$.

Elema-1,3,7(11),8-*tetraene* (**31**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3080, 920 (CH=CH_2), 1645 (C=C), 895 (C=CH_2); MS *m/z* (rel. int.): 202.172 $[M]^+$ (39) (calc. for $C_{15}H_{22}$: 202.172), 187 $[M-Me]^+$ (37), 159 (50), 145 (57), 121 (82), 119 (100), 105 (82), 91 (96); $[\alpha]_D^{24°} = +8°$ ($CHCl_3$; *c* 2.9); ^1H NMR ($CDCl_3$): δ5.72 (*dd*, H-1), 4.97 (*d*, H-2*c*), 4.96 (*d*, H-2*t*), 4.85 (*dq*, H-3), 4.69 (*br s*, H-3′), 2.22 (*dd*, H-5), 2.45 (*br dd*, H-6α), 2.29 (*br dd*, H-6β), 6.32 (*d*, H-8), 5.24 (*d*, H-9), 1.78 (*br s*, H-12), 1.74 (*br s*, H-13), 1.02 (*s*, H-14), 1.73 (*br s*, H-15); [*J* (Hz): 1, 2*c* = 11; 1, 2*t* = 17; 3, 5 = 3, 15 = 1; 5, 6α = 3; 5, 6β = 11; 6α, 6β = 14; 8, 9 = 10].

5′-*Hydroxyauraptene* (**33**). Colourless crystals, mp 86°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1745, 1615 (coumarin); MS *m/z* (rel. int.): 314.152 $[M]^+$ (0.4) (calc. for $C_{19}H_{22}O_4$: 314.152), 296 [M

$-H_2O]^+$ (5), 246 $[M-C_4H_6O]^+$ (3), 162 [umbelliferone]$^+$ (100), 134 $[C_{10}H_{14}]^+$ (62), 119 $[134-Me]^+$ (38); ^{1}H NMR ($CDCl_3$): δ6.24 (*d*, H-3), 7.62 (*d*, H-4), 7.36 (*d*, H-5), 6.83 (*dd*, H-6), 6.79 (*d*, H-8), 4.60 (*d*, H-1'), 5.56 (*br t*, H-2'), 2.30 and 2.22 (*dd*, H-4'), 4.51 (*dddd*, H-5'), 5.17 (*br d*, H-6'), 1.70 (*br s*, H-8'), 1.69 (*br s*, H-9'), 1.80 (*br s*, H-10'), OH: 1.50 (*d*); [*J* (Hz): 3, 4 = 9.5; 5, 6 = 8; 6, 8 = 1.5; 1', 2' = 6.5; $4'_1, 4'_2$ = 14; $4'_1, 5'$ = 8; $4'_2, 5'$ = 5; 5', 6' = 8; 5', OH = 2.5].

Compound **33** (20 mg) in 2 ml Et_2O was stirred for 2 hr with 200 mg MnO_2. Usual work-up gave 12 mg **32**, identical with the natural product (^{1}H NMR, mp).

5-Oxo-6',7'-dihydroauraptene (**34**). Colourless crystals, mp 78°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1620 (coumarin), 1715 (C=O); MS *m/z* (rel. int.): 314.152 $[M]^+$ (0.7) (calc. for $C_{19}H_{22}O_4$: 314.152), 244 $[M-C_4H_6O]^+$ (1), 162 [umbelliferone]$^+$ (18), 153 $[M-$umbelliferyl$]^+$ (100), 71 $[C_3H_7CO]^+$ (90); ^{1}H NMR ($CDCl_3$): δ6.25 (*d*, H-3), 7.63 (*d*, H-4), 7.35 (*d*, H-5), 6.82 (*dd*, H-6), 6.79 (*d*, H-8), 4.58 (*d*, H-1'), 5.46 (*br t*, H-2'), 2.35 (*br t*, H-4'), 2.62 (*t*, H-5'), 2.61 (*qq*, H-7'), 1.08 (*d*, H-8', H-9'), 1.76 (*br s*, H-10'); [*J* (Hz): 3, 4 = 9.5; 5, 6 = 8; 6, 8 = 1.5; 1', 2' = 4', 5' = 7', 8' = 7', 9' = 7].

3,5-Dimethoxy-4-hydroxypropiophenone (**35**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OH), 3500–2700, 1680 (HOC_6H_4COR); MS *m/z* (rel. int.): 210.089 $[M]^+$ (33) (calc. for $C_{11}H_{14}O_4$: 210.089), 181 $[M-Et]^+$ (100), 153 $[181-CO]^+$ (7), 138 $[153-Me]^+$ (10), 123 $[138-Me]^+$ (17); ^{1}H NMR ($CDCl_3$): δ7.26 (*s*, H-2, H-6), 2.96 (*q*, H-8), 1.23 (*t*, H-9, *J* = 7 Hz), OMe: 3.95 (*s*, 6H).

3-[3',3'-Dimethylallyl]-coumaric acid acetate (**36**). Colourless crystals, mp 142°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (AcOPh), 3400–2500, 1690, 1630 ($C=CCO_2H$); MS *m/z* (rel. int.): 274.121 $[M]^+$ (26) (calc. for $C_{16}H_{18}O_4$: 274.121), 232 $[M-$ketene$]^+$ (100), 177 $[232-C_4H_7]^+$ (92); ^{1}H NMR ($CDCl_3$): δ7.40 (*br s*, H-2), 7.05 (*d*, H-5), 7.41 (*dd*, H-6), 7.75 (*d*, H-7), 6.39 (*d*, H-8), 3.25 (*br d*, H-1'), 5.22 (*tqq*, H-2'), 1.74 (*br s*, H-4'), 1.68 (*br s*, H-5'), OAc: 2.31 (*s*); [*J* (Hz): 2, 6 = 2; 5, 6 = 8.5; 7, 8 = 16; 1', 2' = 7; 2', 4' = 2', 5' = 1]. Compound **36** was identical with the acetylation product of the corresponding phenol. Addition of CH_2N_2 to **36** gave the methyl ester; colourless crystals, mp 48°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (PhOAc), 1720, 1640 ($C=CCO_2R$); MS *m/z* (rel. int.): 288.136 $[M]^+$ (22) (calc. for $C_{17}H_{20}O_4$: 288.136), 246 $[M-$ketene$]^+$ (100), 191 $[246-C_4H_7]^+$ (65); ^{1}H NMR ($CDCl_3$) as **36**, except 7.63 (*d*, H-7), 6.37 (*d*, H-8), OMe: 3.80 (*s*).

Methyl-3-[3'-3'-dimethylallyl]-4-isobutyryloxy-cinnamate (**37a**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1765 (PhOCOR), 1720, 1645 ($C=CCO_2R$); MS *m/z* (rel. int.): 316.167 $[M]^+$ (12) (calc. for $C_{19}H_{24}O_4$: 316.167), 246 $[M-O=C=CMe_2]^+$ (100), 191 $[246-C_4H_7]^+$ (32), 71 $[C_3H_7CO]^+$ (34).

Methyl-3-[3',3'-dimethylallyl]-4-[dihydrocinnamoyloxy]-cinnamate (**38a**). Colourless crystals, mp 56°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (PhOCOR), 1720, 1645 ($C=CCO_2R$); MS *m/z* (rel. int.): 378.183 $[M]^+$ (6) (calc. for $C_{24}H_{26}O_4$: 378.183), 347 $[M-OMe]^+$ (1.3), 246 $[M-O=C=CHCH_2Ph]^+$ (100), 191 (43), 91 $[C_7H_7]^+$ (22); ^{1}H NMR ($CDCl_3$): δ7.34 (*br s*, H-1), 6.93 (*d*, H-5), 7.35 (*dd*, H-6), 7.63 (*d*, H-7), 6.33 (*d*, H-8), 3.13 (*br d*, H-1'), 5.17 (*tqq*, H-2'), 1.74 (*br s*, H-4'), 1.66 (*br s*, H-5'), 7.15–7.3 (*m*, H-2''–H-6''), 3.08 (*br t*, H-7''), 2.91 (*t*, H-8''), OMe: 3.79 (*s*); [*J* (Hz) see data for **36**].

Methyl-3-[3',3'-dimethylallyl]-4-[4'-hydroxydihydrocinnamoyloxy]-cinnamate (**39a**). Colourless crystals, mp 115°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (PhOCOR), 1715, 1645 ($C=CCO_2R$); MS *m/z* (rel. int.): 394.178 $[M]^+$ (6) (calc. for $C_{24}H_{26}O_5$: 394.178), 363 $[M-OMe]^+$ (2), 246 $[M-O=C=CHCH_2C_6H_4OH]^+$ (100), 191 (26), 107 [hydroxytropylium]$^+$ (66); ^{1}H NMR ($CDCl_3$): δ7.33 (*br s*, H-2), 6.93 (*d*, H-5), 7.34 (*br d*, H-6), 7.63 (*d*, H-7), 6.33 (*d*, H-8), 3.13 (*br d*, H-1'), 5.16 (*tqq*, H-2'), 1.74 (*br s*, H-4'), 1.65 (*br s*, H-5'), 7.10 (*d*, H-2'', H-6''), 6.75 (*d*, H-3'', H-5''), 3.00 (*br t*, H-7''), 2.85 (*t*, H-8''), OMe: 3.79 (*s*).

3,5-Bis-[3',3'-dimethylallyl]-coumaric acid acetate (**40**). Colourless crystals, mp 171°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3300–2500, 1690, 1630 ($C=CCO_2H$), 1765 (PhOAc); MS *m/z* (rel. int.): 342.183 $[M]^+$ (21) (calc. for $C_{21}H_{26}O_4$: 342.183), 300 $[M-$ketene$]^+$ (74), 245 $[300-C_4H_7]^+$ (100), 69 $[C_5H_9]^+$ (44). Addition of CH_2N_2 gave the methyl ester **40a**; colourless oil; MS *m/z* (rel. int.): 356.199 $[M]^+$ (1.3) (calc. for $C_{22}H_{28}O_4$: 356.199), 314 $[M-$ketene$]^+$ (20), 259 $[314-C_4H_7]^+$ (100); ^{1}H NMR ($CDCl_3$): δ7.21 (*br s*, H-2, H-6), 7.62 (*d*, H-7), 6.35 (*d*, H-8), 3.19 (*br d*, 4H, H-1'), 5.21 (*tqq*, 2H, H-2'), 1.73 (*br s*, 6H, H-4'), 1.66 (*br s*, 6H, H-5'); [*J* (Hz) see data for **36**]. Compound **40** also was prepared from the corresponding phenol by acetylation (Ac_2O, 1 hr, 70°).

[4-Methyl-3-oxo-pentyl]-ferulate (**41**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OH), 1720, 1635 ($C=CCO_2R$), 1720 (C=O); MS *m/z* (rel. int.): 292.131 $[M]^+$ (84) (calc. for $C_{16}H_{20}O_5$: 292.131), 194 $[M-H_2C=CHCOC_3H_7]^+$ (84), 177 $[RCO]^+$ (100); 55 $[H_2C=CHCO]^+$ (90); CIMS *m/z* (rel. int.): 293 $[M+1]^+$ (100), 177 $[RCO]^+$ (86), 99 $[CH_2=CHCOC_3H_7+1]^+$ (41); ^{1}H NMR ($CDCl_3$): δ7.00 (*d*, H-1), 6.89 (*d*, H-5), 7.04 (*dd*, H-6), 7.59 (*d*, H-7), 6.22 (*d*, H-8), 4.47 (*t*, H-1'), 2.85 (*t*, H-2'), 2.63 (*qq*, H-4'), 1.10 (*d*, H-5', H-6'), OMe: 3.91 (*s*), OH: 5.87 (*s*); [*J* (Hz): 1, 6 = 1.5; 5, 6 = 8; 7, 8 = 16; 1', 2' = 6.5; 4', 5' = 7].

3-Oxohexyl ferulate (**42**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540 (OH), 1720, 1635 ($C=CCO_2R$), 1720 (C=O); MS *m/z* (rel. int.): 292.131 $[M]^+$ (88), 194 (88), 177 (100), 55 (95); ^{1}H NMR ($CDCl_3$) as **41**, except 4.46 (*t*, H-1'), 2.80 (*t*, H-2'), 2.43 (*t*, H-4'), 1.63 (*q*, H-5'), 0.90 (*t*, H-6'); [*J* (Hz): 4', 5' = 5', 6' = 7]; ^{13}C NMR ($CDCl_3$): 219.1 *s*, 167.1 *s*, 148.0 *s*, 146.8 *s*, 145.1 *d*, 126.9 *s*, 123.1 *d*, 115.1 *d*, 114.7 *d*, 109.4 *d*, 59.3 *t*, 56.0 *q*, 45.1 *t*, 44.6 *t*, 17.1 *t*, 13.7 *q*.

3,5,7,4'-Tetrahydroxy-3'-methoxyflavanone-3-O-acetate (**43**). Colourless crystals, mp 218°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540 (OH), 1640 (PhCO); ^{1}H NMR ($CDCl_3$): δ5.23 (*d*, H-2), 5.82 (*d*, H-3), 5.98 (*d*, H-6), 6.03 (*d*, H-8), 6.99 (*br s*, H-2'), 6.91 (*br s*, 2H, H-5', H-6'); OMe: 3.89 (*s*); OAc: 2.02 (*s*); [*J* (Hz): 2, 3 = 12; 6, 8 = 1.5]; $[\alpha]_D^{24°}$ = +26° ($CHCl_3$; *c* 0.54); MS *m/z* (rel. int.): 360.085 $[M]^+$ (10) (calc. for $C_{18}H_{16}O_8$: 360.085), 300 $[M-HOAc]^+$ (76), 166 (92), 153 (100). Acetylation (Ac_2O, 1 hr, 100°) gave the tetraacetate; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (PhOAc), 1660 (PhCO); ^{1}H NMR ($CDCl_3$): δ5.42 (*d*, H-2), 5.73 (*d*, H-3), 6.60 (*d*, H-6), 6.79 (*d*, H-8), 7.09 (*br s*, H-2'), 7.00 (*dd*, H-5'), 7.08 (*d*, H-6'); OMe: 3.86 (*s*); OAc: 2.37, 2.32, 2.30, 2.02 (*s*); [*J* (Hz): 2, 3 = 12; 6, 8 = 2; 2', 6' = 1.5; 5', 6' = 8]; MS *m/z* (rel. int.): 444.106 $[M]^+$ (3) (calc. for $C_{22}H_{20}O_{10}$: 444.106), 384 $[M-HOAc]^+$ (3), 342 $[384-$ketene$]^+$ (59), 300 $[342-$ketene$]^+$ (32), 166 (100).

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