Phytochemistry, Vol. 29, No. 8, pp. 2611–2616, 1990.
Printed in Great Britain.

0031–9422/90 $3.00+0.00

ENT-LABDANE GLYCOSIDES FROM *BACCHARIS PINGRAEA*

C. ZDERO, F. BOHLMANN and H. M. NIEMEYER*

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, F.R.G.; *Faculdad de Ciencias, Universidad de Chile, Santiago, Casilla 653, Chile

(*Received* 1 *December* 1989)

Key Word Index—*Baccharis pingraea*; Compositae; diterpenes; *ent*-labdane glycosides.

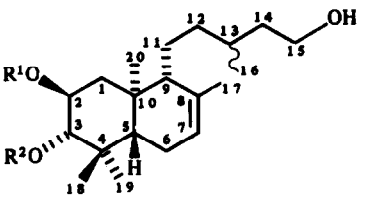
Abstract—The aerial parts of *Baccharis pingraea*, collected in Chile, afforded, in addition to two diterpene glycosides isolated previously, 14 new ones and two of the corresponding desacyl aglycones. The structures were elucidated by high field ^{1}H NMR spectroscopy. The differences between the collections from Argentina and Chile are discussed.

INTRODUCTION

In continuation of our studies on the chemistry of the large genus *Baccharis* (Compositae, tribe Astereae) [1–3] we have investigated again the aerial parts of *B. pingraea* DC., this time collected in northern Chile. The results are compared with those from a collection in Argentina and presented in this paper.

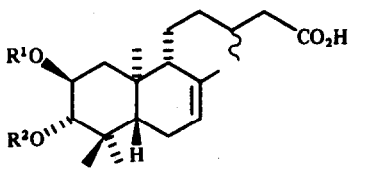
RESULTS AND DISCUSSION

The aerial parts of *Baccharis pingraea*, collected in the Region del Libertador Bernardo O'Higgins in northern Chile, gave a very complex mixture of diterpenes which only could be separated after some chemical transformations. Finally, the glycosides **2**–**10** and **12**–**18** as well as two desacyl aglycones (**1** and **11**) were isolated, **7** only



	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
R^1	H	Rha	Rha	Rha	Fuc	Fuc	Fuc	Xyl	Xyl	Glc
R^2	H	Ang	Meacr	Ang Δ^{13E}	Ang	*i*Bu	Ang Δ^{13E}	Ang	Ang Δ^{13E}	Ang Δ^{13E}

1Ac 2,15-*O*-Ac; **2**Ac –**5**Ac and **7**Ac –**9**Ac are the corresponding tetraacetates, **10**Ac the pentaacetate



	11	**12**	**13**	**14**	**15**	**16**	**17**	**18**
R^1	H	Rha	Fuc	Fuc	Fuc	Fuc	Fuc	Glc
R^2	H	Ang	Ang	Meacr	Tigl	Sen	*i*Bu	Ang

11a–**18a** are the methylesters, **11**Ac –**18**Ac the methylester acetates

as its tetraacetate, **12–17** as their methyl esters **12a–17a** and **18** as its methyl ester tetraacetate **18a**Ac. The glycosides **7** and **9** have been isolated previously from the same species from the collection in Argentina [1].

The main constituent was the β-fucopyranoside **5**. The ^{1}H NMR spectra of **5** and its tetraacetate **5**Ac (Table 1) were in part similar to those of **7** and **7**Ac [1]. However, the absence of the 13,14-double bond was indicated by the *methyl* doublet at δ0.90 and 0.93, respectively. Spin decoupling showed that these signals were due to H-16 as the coupling partner (δ1.52 *m*) was coupled with multiplets which itself were coupled with multiplets which were due to H-15, as followed from the chemical shifts in the spectra of **5** and **5**Ac. In the latter case a downfield shift of 0.44 ppm was observed if compared with the corresponding shift of **5**. Thus the fucopyranoside **5** was the 13,14-dihydro derivative of **7** [1]. The configuration at C-13 could not be determined. The optical rotation of **5** and of all the other labdanes indicated that *ent*-labdanes were present. This was supported previously by the Cotton-effect of a related ketone and by the Horeau-method [1].

The ^{1}H NMR spectrum of **6** (Table 1) differs from that of **5** only by the signals of the ester residue. The angelate signals were replaced by those of an isobutyrate and the H-3 signal was slightly shifted up field. The ^{1}H NMR spectra of **8** and **8**Ac (Table 1) were in part similar to those of **9** and **9**Ac [1]. The presence of the corresponding 13,14-dihydro derivatives followed from the signals of H-16 and H-15 which were more or less identical with those in the spectra of **5** and **5**Ac. Similarly the spectrum of **2**Ac (Table 1) differed from that of **4**Ac only in the signals of the side chain, indicating that again the Δ^{13}-double bond was hydrogenated. The spectrum of **3** (Table 1) showed that this rhamnopyranoside was a 3α-methacryloyloxy derivative. Accordingly, the spectrum was similar to that of **2** except the signals of the ester residue. The 4′-*O*-acetate of the rhamnopyranoside **4** was already isolated from a *Baccharis* species [1]. The ^{1}H NMR spectra of the tetraacetates were identical (Table 1).

The ^{1}H NMR spectrum of **10**Ac (Table 1) showed that again an angelate of a labdane with oxygen functions at C-2, C-3 and C-15 was present. Accordingly, the spectrum was close to those of **4**, **7** and **9**. However, the signals of the sugar part required the presence of a β-glucopyranoside.

The ^{1}H NMR spectra of **1** and the 3,15-*O*-diacetate (Table 1) indicated that compound **1** most likely was the 3-desacyl aglycone of the glycosides **2**, **3**, **5**, **6** and **8**. The 3-*epi* derivative was isolated previously from a *Baccharis* species [1]. The couplings of H-2 and H-3 differ in the expected way.

The ^{1}H NMR spectrum of **11a**Ac (Table 2) showed that a 2β,3α-diacetoxylabdane with an ester group in the side chain must be present. Accordingly, a pair of double doublets at δ2.28 and 2.16 were coupled with a multiplet at δ1.92 which itself was coupled with the methyl doublet at δ0.93 (H-16). Thus compound **11** was an oxidation product of **1**. The configuration at C-13 could not be determined.

The ^{1}H NMR spectra of **12a** and **12a**Ac (Table 1) indicated that again a rhamnopyranoside was present. The chemical shifts of H-2 and H-3, which could be assigned by spin decoupling, required that the sugar moiety was at C-2 and an ester group at C-3. The typical signals showed that the latter was an angelate. Accordingly, the spectra were in part similar to those of **2** and **2**Ac.

The spectra of **13a** and **13a**Ac (Table 2) differed from those of **12a** and **12a**Ac only by the signals of the sugar moiety. The couplings required the presence of a fucopyranoside. In the spectra of **14a** and **14a**Ac the signals of the angelate group were replaced by those of a methacrylate. From the spectra of **15a–17a** (Table 2) the presence of the corresponding tiglate, senecioate and isobutyrate, respectively, was deduced. In addition to the changed signals of the ester group, as in many similar cases, small shift differences of H-3 were visible. The ^{1}H NMR spectrum of the glycoside **18a**Ac (Table 2) showed that a β-glucopyranoside was present as followed from the typical splitting of the signals of the sugar part.

The mass spectra of the glycosides show some characteristic common features. In most cases only the acetylated compounds gave molecular ions. Furthermore, in all cases typical fragments were due to loss of the sugar moiety followed by elimination of the acids. Only the acetates gave clear fragments of the sugar moiety. Base peaks are always the acyl cations.

In both collections from Argentina [1] and Chile, all *ent*-labdanes are of the same type with oxygen functions at C-2, C-3 and C-15. Also the position and the nature of the sugars are nearly identical, with the exception that the Chilean material also gave small amounts of glucopyranosides. However, in the collection from Argentina the side chain was always unsaturated and never had a carboxyl group. Thus the chemistry of the two collections is very similar but differs in some aspects characteristically. Surely the accumulation of *ent*-labdane glycosides is the important chemotaxonomic feature.

EXPERIMENTAL

The air-dried aerial part (595 g), collected in February 1989 in Termas del Flaco, Region del Libertador Bernardo O'Higgins, voucher Niemeyer 8914, deposited in the Herbarium of the University of Chile, Santiago, was extracted with MeOH–Et_2O–petrol (1:1:1). After treatment with MeOH to remove long chain saturated compounds separation by CC (silica gel) afforded, in addition to fatty acids and triglycerides, a polar fraction (15 g). A small amount was separated by HPLC (MeOH–H_2O, 17:3, always RP 8, flow rate 3 ml min^{-1}, *ca* 100 bar). The ^{1}H NMR spectra of the complex mixtures showed no acetate Me or Me ester singlets, but indicated the presence of different glycosides. Therefore the whole fraction was acetylated (Ac_2O, $CHCl_3$, DMAP, 2 hr, 70°). From the obtained mixture the acidic part was separated by shaking with $NaHCO_3$ soln. Medium pressure chromatography (silica gel Φ 60 μ) of the neutral part gave 90 fractions (20 ml each), which were combined, after monitoring by TLC, into 6 fractions. The first one contains 100 mg **2**Ac, the next one was separated by HPLC (MeOH–H_2O, 9:1) affording 10 mg **1**Ac (R_t 3.5 min), two mixtures (2/1 and 2/2) and 10 mg **2**Ac (R_t 8.1 min). TLC of 2/1 ($CHCl_3$–C_6H_6–Et_2O, 2:3:1) gave 10 mg **7**Ac (R_f 0.59) and 20 mg **9**Ac (R_f 0.68). TLC of 10% of 2/2 (Et_2O–petrol, 3:2) gave 10 mg **5**Ac (R_f 0.55) and 50 mg **8**Ac (R_f 0.65). Saponification of **1**Ac (MeOH–H_2O, 10% KOH, 3 min, 70°) gave, after HPLC (MeOH–H_2O, 17:3), the triol **1** (R_t 4.4 min) and saponification (see above) of **5**Ac after HPLC (MeOH–H_2O, 17:3) the rhamnoside **5** (R_t 9.7 min). The remaining fraction 2/2 gave after saponification (see above) by HPLC (MeOH–H_2O, 17:3) 30 mg **4** (R_t 7.2 min), 5 mg **3** (R_t 8.0 min), 400 mg **8** (R_t 9.2 min), 4 mg **6** (R_t 10.5 min) and 100 mg **5** (R_t 12.7 min). Fraction 3 contained

Table 1. ^{1}HNMR spectral data of **1–6**, **8**, **10**, **1Ac**, **2Ac**, **5Ac**, **8Ac** and **10Ac** (400 MHz, $CDCl_3$ δ-values)

H	1	1Ac	2	2Ac	3	4*	5	5Ac	6	8	8Ac	10†	10Ac	Multiplicity
1α	2.19	2.14	2.27	2.22	2.27	2.24	2.32	2.14	2.29	2.31	2.15	2.23	2.16	*dd*
1β	1.11	1.13	1.16	1.20	1.16	1.12	1.26 *m*	1.19	1.25 *m*	1.22 *m*	1.17	1.24	1.18	*t*
2	3.71	4.93	3.88	3.88	3.90	3.88	3.86	3.82	3.84	3.88	3.82	3.83	3.83	*ddd*
3	3.04	3.19	4.78	4.90	4.75	4.77	4.72	4.77	4.61	4.72	4.78	4.72	4.76	*d*
6	1.97	1.97	1.96	1.95	1.97	1.96	1.96	1.95	1.96	1.95	1.95	1.96	1.95	*m*
7	5.39	5.38	5.38	5.39	5.38	5.39	5.36	5.39	5.38	5.37	5.39	5.41	5.41	*br s*
13	1.55	1.50	1.53	1.53	1.53	—	1.52	1.52	1.50	1.53	1.53	—	—	*m*
15	3.68	4.07	3.66	4.10	3.68	4.17 *br d*	3.64	4.08	3.67	3.64	4.09	4.16 *br d*	4.59 *br d*	*m*
16	0.92	0.90	0.91	0.91	0.91	1.70 *br s*	0.90	0.93	0.91	0.90	0.93	1.71 *br s*	1.72 *br s*	*d*
17	1.67	1.65	1.67	1.68	1.68	1.67	1.67	1.68	1.67	1.67	1.68	1.65	1.67	*br s*
18[a]	0.88	0.91	0.87	0.89	0.87	0.87	0.87	0.86	0.84	0.87	0.86	0.89	0.87	*s*
19[a]	1.01	1.01	0.97	0.96	0.97	0.97	0.95	0.94	0.95	0.96	0.95	0.97	0.95	*s*
20[a]	0.83	0.84	0.82	0.81	0.83	0.81	0.81	0.83	0.81	0.81	0.82	0.83	0.84	*s*
OCOR			6.14 *qq*	6.12 *qq*	6.14 *br s*	6.14 *qq*	6.02 *qq*	6.01 *qq*	2.61 *qq*	6.03 *qq*	6.07 *qq*	6.07 *qq*	6.04 *qq*	
			2.03 *dq*	2.04 *dq*	5.60 *br s*	2.03 *dq*	1.98 *dq*	2.03 *dq*	1.20 *d*	1.97 *dq*	2.02 *dq*	1.99 *dq*	2.02 *dq*	
			1.92 *dq*	1.93 *dq*	1.97 *br s*	1.91 *dq*	1.91 *dq*	1.93 *dq*	1.19 *d*	1.90 *dq*	1.91 *dq*	1.92 *dq*	1.90 *dq*	
OAc	—	2.10	—	2.13	—	—	—	2.14	—	—	2.05	—	2.07	*s*
		2.04	—	2.03	—	—	—	2.04	—	—	2.05	—	2.05	*s*
				2.01	—	—	—	2.02	—	—	2.04	—	2.02	*s*
				1.94	—	—	—	1.96	—	—	2.03	—	2.00, 1.98	*s*
1′	—	—	4.88 *br s*	4.87	4.92 *br s*	4.89 *br s*	4.19	4.49	4.20	4.34	4.60	4.31	4.59	*d*
2′	—	—	3.83 *br s*	5.15	3.85 *br s*	3.83 *br s*	3.41	5.03	3.43	3.48	4.74	‡	4.82	*dd*
3′	—	—	3.57	5.09	3.56 *m*	3.57	3.53 *m*	4.98	3.58 *m*	3.64 *m*	5.08	‡	5.18	*dd*
4′	—	—	3.39	4.99	3.38	3.39	3.53 *m*	5.16	3.58 *m*	3.54 *m*	4.83 *ddd*	‡	5.04	*dd*
5′	—	—	3.54	3.84	3.56 *m*	3.55	3.53 *m*	3.72	3.58 *m*	3.85 *dd* 3.21 *dd*	4.01 *dd* 3.31 *dd*	3.33 *m*	3.65 *ddd*	*dq*
6′	—	—	1.22	1.14	1.23	1.23	1.22	1.12	1.29	—	—	‡	4.19 *dd* 4.03 *dd*	*d*

[a]May be interchangeable.

*H-14 5.39 *br t*.

†H-14 5.44 *br t*.

‡Overlapped multiplets.

J [Hz]: 1α,1β = 1β,2 = 12; 1α,4 = 4; 2,3 = 10; 13,16 = 6.5; compounds **2–4**, **2Ac** and **3Ac**: 1′,2′ = 1.5; 2′,3′ = 3.5; 3′,4′ = 4′,5′ = 10; 5′,6′ = 6; compound **4**: 14,15 = 6; compounds **5–7** and **5Ac**: 1′,2′ = 7; 2′,3′ = 10; 3′,4′ = 3.5; 4′,5′ = 1; 5′,6′ = 6.5; compounds **8** and **8Ac**: 1′,2′ = 6; 2′,3′ = 3′,4′ = 8; 4′,5′$_1$ = 4.5; 4′, 5′$_2$ = 7; 5′$_1$,5′$_2$ = 12; compound **10Ac**: 1′,2′ = 7.5; 2′,3′ = 3′,4′ = 4′,5′ = 9.5; 5′,6′$_1$ = 4.5; 5′,6′$_2$ = 2.5; 6′$_1$,6′$_2$ = 12; OAng: 3,4 = 7; 3,5 = 4,5 = 1.5; *O*iBu: 2,3 = 2,4 = 7.

Table 2. ^{1}H NMR spectral data of **11a**Ac–**14a**Ac, **12a**–**17a** and **18a**Ac (400 MHz, $CDCl_3$, δ-values)

H	**11a**Ac	**12a**	**12a**Ac	**13a**	**13a**Ac	**14a**	**14a**Ac	**15a**	**16a**	**17a**	**18a**Ac	Multiplicity
1α	2.15	2.27	2.23	2.25	2.14	2.20 *m*	2.14 *m*	2.20 *m*	2.20 *m*	2.20 *m*	2.15 *m*	*dd*
1β	1.23	1.12	1.18	1.23	1.18	1.25 *m*	1.21 *m*	1.25 *m*	1.25 *m*	1.25 *m*	1.20 *m*	*t*
2	5.10	3.92	3.88	3.92	3.84	3.94	3.85	3.95	3.92	3.92	3.86	*ddd*
3	4.74	4.80	4.90	4.73	4.77	4.71	4.74	4.71	4.69	4.63	4.75	*d*
6	1.95	1.95	1.95	1.95	1.95	1.95	1.95	1.96	1.96	1.96	1.95	*m*
7	5.38	5.39	5.38	5.38	5.39	5.39	5.39	5.39	5.39	5.39	5.39	*br s*
13	1.92	1.95	1.95	1.95	1.95	1.95	1.95	1.96	1.96	1.96	1.95	*m*
14	2.28	2.29	2.34	2.27	2.28	2.28	2.28	2.29	2.28	2.28	2.28	*dd*
14′	2.16	2.19	2.15	2.16	2.14	2.20	2.14	2.19	2.19	2.19	2.14 *m*	*dd*
16	0.93	0.97	0.95	0.95	0.95	0.96	0.96	0.96	0.96	0.96	0.97	*d*
17	1.66	1.68	1.67	1.66	1.67	1.67	1.67	1.67	1.67	1.67	1.67	*br s*
18[a]	0.86	0.83	0.81	0.82	0.83	0.83	0.83	0.84	0.83	0.83	0.84	*s*
19[a]	0.96	0.98	0.96	0.96	0.94	0.96	0.95	0.98	0.95	0.95	0.95	*s*
20[a]	0.87	0.88	0.89	0.88	0.87	0.88	0.85	0.87	0.86	0.87	0.88	*s*
OCOR	—	6.14	6.13	6.03	6.01	6.14 *br s*	6.13 *br s*	6.89	5.69	2.63 *qq*	6.03	*qq*
		2.05	2.06	1.99	2.02	5.54 *br s*	5.57 *br s*	1.80	2.17 *d*	1.20 *d*	2.01	*dq*
		1.92	1.94	1.91	1.93	1.97 *br s*	1.98 *br s*	1.80	1.90 *d*	1.21 *d*	1.90	*dq*
QAc	2.05	—	2.12	—	2.14	—	2.13	—	—	—	2.06	*s*
	2.01	—	2.01	—	2.03	—	2.04	—	—	—	2.03	*s*
					1.95	—	1.96	—	—	—	2.01	*s*
											1.98	*s*
1′	—	4.94	4.87	4.25	4.50	4.26	4.50	4.27	4.27	4.30	4.62	*d*
2′	—	3.88	5.17	3.58 *m*	5.04	3.60 *m*	5.05	3.59 *m*	3.60 *m*	3.60 *m*	4.83	*dd*
3′	—	3.57 *m*	5.09		4.99		4.99				5.20	*dd*
4′	—	3.39	5.01	3.40	5.17	3.40	5.16	3.39	3.41	3.42	5.04	*dd*
5′	—	3.57 *m*	3.85	3.58 *m*	3.75	3.60 *m*	3.73	3.59 *m*	3.60 *m*	3.60 *m*	3.70 *ddd*	*dq*
6′	—	1.25	1.14	1.26 *d*	1.13	1.27	1.13	1.27	1.29	1.32	4.19 *dd*	*d*
											4.04 *dd*	
OMe	3.65	3.66	3.66	3.65	3.66	3.66	3.66	3.66	3.66	3.66	3.67	*s*

[a]Signals may be interchangeable.

J[Hz]: 13,14 = 6; 13,14′ = 8; 14,14′ = 14; OTigl: 3,4 = 7; 3,5 = 4,5 = 1; OSen: 2,4 = 2,5 = 1; O*i*Bu: 2,3 = 2,4 = 7; others as the corresponding ones in Table 1.

1.5 g **5**Ac and fraction 4 gave after saponification (see above) and HPLC (MeOH–H_2O, 17:3) 5 mg **1** (R_t 4.5 min), 2 mg **10** (R_t 4.9 min), 10 mg **4** (R_t 7.6 min) and 50 mg **2** (R_t 9.9 min). Fraction 5 gave after saponification (see above) and HPLC (MeOH–H_2O, 17:3) 100 mg **2** and 400 mg **8**.

The acid fraction was acetylated and esterified with CH_2N_2. Separation by HPLC (MeOH–H_2O, 17:3) gave 20 mg **11a**Ac (R_t 10.1 min), 10 mg **14a**Ac (R_t 15.5 min), 6 mg **18a**Ac (R_t 16.5 min), 100 mg **13a**Ac (R_t 19.3 min), 40 mg **12a**Ac (R_t 23.5 min) and a mixture (R_t 17.8 min) which gave after saponification (see above) and esterification with CH_2N_2 by HPLC (MeOH–H_2O, 17:3) 1 mg **16a**, not free from **17a** (R_t 16.3 min), 1 mg **17a**, not free from **16a** (R_t 16.5 min) and 2 mg **15a** (R_t 17.7 min). Similar saponification and esterification (see above) of **12a**Ac–**14a**Ac gave after HPLC (MeOH–H_2O, 9:1) the glycosides **12a**–**14a**. The 400 MHz ^1H NMR spectra of **4**Ac, **7**Ac and **9**Ac were identical with those isolated previously [1].

2β,3α,15-*Trihydroxy*-ent-*labd*-7-*ene* (**1**). Gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH). MS *m/z* (rel. int.): 324.266 $[M]^+$ (10) (calc. for $C_{20}H_{36}O_3$: 324.266), 306 $[M-H_2O]^+$ (12), 291 $[306-Me]^+$ (24), 288 $[306-H_2O]^+$ (10), 273 $[288-Me]^+$ (9), 223 $[M-CH_2CH_2CH(Me)CH_2CH_2OH]^+$ (38), 205 $[C_{14}H_{21}O]^+$ (74), 187 $[205-H_2O]^+$ (34), 135 (70), 121 (93), 95 (84), 81 (100), 69 (84). 2,15-*O-Diacetate* (1Ac). Gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1755 (OAc). MS *m/z* (rel. int.): 408.288 $[M]^+$ (1.7) (calc. for $C_{24}H_{40}O_5$: 408.288), 390 $[M-H_2O]^+$ (0.2), 348 $[M-HOAc]^+$ (32), 333 $[348-Me]^+$ (34), 205 $[348-CH_2CH_2CH(Me)CH_2CH_2OAc]^+$ (90), 187 $[205-H_2O]^+$ (46), 121 (100). $[\alpha]_D^{24°}$ −31 ($CHCl_3$; *c* 1.81).

3α-*Angeloyloxy*-2β,15-*dihydroxy*-ent-*labd*-7-*ene*-2-O-α-*rhamnopyranoside* (**2**). Crystals, mp 93°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420 (OH), 1710, 1640 (C=CCO_2R). MS *m/z* (rel. int.): 552.366 $[M]^+$ (0.4) (calc. for $C_{31}H_{52}O_8$: 552.366), 406 $[M-C_6H_{10}O_4]^+$ (10), 389 $[M-$sugar moiety$]^+$ (14), 289 $[389-AngOH]^+$ (60), 187 (11), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (92); $[\alpha]_D^{24°}$ −29 ($CHCl_3$; *c* 0.68). *Tetraacetate* (**2**Ac). Gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (OAc). MS *m/z* (rel. int.): 720.408 $[M]^+$ (0.1) (calc. for $C_{39}H_{60}O_{12}$: 720.408), 431 $[M-$sugar moiety$]^+$ (2), 331 $[431-AngOH]^+$ (6), 273 $[M-$sugar moiety$]^+$ (44), 213 $[273-HOAc]^+$ (6), 153 $[213-HOAc]^+$ (30), 111 $[153-$ketene$]^+$ (26), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (42); $[\alpha]_D^{24°}$ −29 ($CHCl_3$; *c* 7.71).

3α-*Methacryloyloxy*-2β,15-*dihydroxy*-ent-*labd*-7-*ene*-2-O-α-*rhamnopyranoside* (**3**). Gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3440 (OH), 1720, 1640 (C=CCO_2R). MS *m/z* (rel. int.): 538.350 $[M]^+$ (0.1) (calc. for $C_{30}H_{50}O_8$: 538.350), 392 $[M-C_6H_{10}O_4]^+$ (20), 375 $[M-$sugar moiety$]^+$ (36), 289 $[375-RCO_2H]^+$ (81), 205 $[C_{14}H_{21}O]^+$ (32), 187 (43), 121 (67), 69 $[C_3H_5CO]^+$ (100).

3α-*Angeloyloxy*-2β,15-*dihydroxy*-ent-*labda*-7,13E-*diene*-2-O-α-*rhamnopyranoside* (**4**). Gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580, 3420 (OH), 1715, 1640 (C=CCO_2R); MS *m/z* (rel. int.): 387.290 $[M-$sugar moiety$]^+$ (5) (calc. for $C_{25}H_{39}O_3$: 387.290), 287 $[387-AngOH]^+$ (8), 269 $[287-H_2O]^+$ (18), 201 (48), 187 (23), 121 (41), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (82).

3α-*Angeloyloxy*-2β,15-*dihydroxy*-ent-*labd*-7-*ene*-2-O-β-*fucopyranoside* (**5**). Crystals, mp 119°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3460 (OH), 1710, 1650 (C=CCO_2R). MS *m/z* (rel. int.): 406 $[M-C_6H_{10}O_4]^+$ (5), 389.305 $[M-$sugar moiety$]^+$ (7) (calc. for $C_{25}H_{41}O_3$: 389.305), 371 $[389-H_2O^+$ (2), 289 $[389-AngOH]^+$ (26), 201 (6), 187 (7), 121 (11), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (48); $[\alpha]_D^{24°}$ −17 ($CHCl_3$; *c* 0.58). *Tetraacetate* (**5**Ac). Gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (OAc). MS *m/z* (rel. int.): 720.408 $[M]^+$ (0.2) (calc. for $C_{39}H_{60}O_{12}$: 720.408), 431 $[M-$sugar moiety$]^+$ (5), 331 $[431-AngOH]^+$ (12), 273 [sugar part]$^+$ (28), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (27). $[\alpha]_D^{24°}$ −6 ($CHCl_3$; *c* 1.85).

3α-*Isobutyryloxy*-2β,15-*dihydroxy*-ent-*labd*-7-*ene*-2-O-β-*fucopyranoside* (**6**). Crystals, mp 110°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420 (OH), 1720 (CO_2R). MS *m/z* (rel. int.): 394 $[M-C_6H_{10}O_4]^+$ (20), 377.305 $[M-$sugar moiety$]^+$ (34) (calc. for $C_{24}H_{41}O_3$: 377.305), 289 $[377-RCO_2H]^+$ (86), 205 $[C_{14}H_{21}O]^+$ (46), 187 (56), 12 (80), 71 $[C_3H_7CO]^+$ (100).

3α-*Angeloyloxy*-2β,15*dihydroxy*-ent-*labd*-7-*ene*-2-O-β- *xylopyranoside* (**8**). Crystals, mp 213°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3420 (OH), 1710, 1645 (C=CCO_2R). MS *m/z* (rel. int.): 406 $[M-C_6H_{10}O_4]^+$ (8), 389.306 $[M-$sugar moiety$]^+$ (6) (calc. for $C_{25}H_{41}O_3$: 389.306), 289 $[389-AngOH]^+$ (28), 205 $[C_{14}H_{21}O]^+$ (10), 187 (12), 121 (20), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (81). $[\alpha]_D^{24°}$ −24 ($CHCl_3$; *c* 0.24). *Tetraacetate* (**8**Ac). Gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1765, 1750 (OAc), 1720, 1650 (C=CCO_2R). MS *m/z* (rel. int.): 706.390 $[M]^+$ (0.4) (calc. for $C_{38}H_{58}O_{12}$: 706.390), 431 $[M-$sugar moiety$]^+$ (8), 331 $[431-AngOH]^+$ (24), 302 $[431-CH_2CH_2(Me)CH_2CH_2OAc]^+$ (24), 259 [sugar part]$^+$ (72), 199 $[259-HOAc]^+$ (68), 139 $[199-HOAc]^+$ (67), 97 $[139-$ketene$]^+$ (62), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (66); $[\alpha]_D^{24°}$ −27 ($CHCl_3$; *c* 1.29).

3α-*Angeloyloxy*-2β, 15-*dihydroxy*-ent-*labda*-7, 13E-*diene*-2-O-β-*glucopyranoside* (**10**). Crystals, mp 161°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3420 (OH), 1710, 1640 (C=CCO_2R). *Pentaacetate* (**10**Ac). Gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (OAc), 1710 (C=CCO_2R). MS *m/z* (rel. int.): 716 $[M-HOAc]^+$ (0.1), 429.300 $[M-$sugar moiety$]^+$ (2.5) (calc. for $C_{27}H_{41}O_4$: 429.300), 369 $[429-HOAc]^+$ (1), 331 [sugar part]$^+$ (12), 302 $[429-CH_2CH_2C(Me)=CHCH_2OAc]^+$ (13), 202 $[302-AngOH]^+$ (8), 211 $[331-2\times HOAc]^+$ (1), 187 (5), 169 $[211-$ketene$]^+$ (23), 109 $[169-HOAc]^+$ (14), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (51).

2β,3α-*Dihydroxy*-ent-*labd*-7-*en*-15-*oic acid* (**11**). Isolated as its Me ester diacetate **11a**Ac. Gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1755 (OAc, CO_2R). MS *m/z* (rel. int.): 436.282 $[M]^+$ (2.5) (calc. for $C_{25}H_{40}O_6$: 436.282), 421 $[M-Me]^+$ (1), 405 $[M-OMe]^+$ (4), 376 $[M-HOAc]^+$ (15), 316 $[376-HOAc]^+$ (96), 301 $[316-Me]^+$ (66), 247 $[376-CH_2CH_2CH(Me)CH_2CO_2Me]^+$ (62), 187 $[247-HOAc]^+$ (100), 159 (73), 122 (94), 95 (90), 82 (99), 81 (90), 69 (90); $[\alpha]_D^{24°}$ −4 ($CHCl_3$; *c* 1.97).

3α-*Angeloyloxy*-2β-*hydroxy*-ent-*labd*-7-*en*-15-*oic acid*-2-O-α-*rhamnopyranoside* (**12**). Isolated as its Me ester **12a**. Gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1745 (CO_2R), 1720 (C=CCO_2R). MS *m/z* (rel. int.): 580.361 $[M]^+$ (0.02) (calc. for $C_{32}H_{52}O_9$: 580.361), 548 $[M-MeOH]^+$ (0.2), 434 $[M-C_6H_{10}O_4]^+$ (8), 417 $[M-$sugar moiety$]^+$ (6), 317 $[417-RCO_2H]^+$ (14), 205 $[C_{14}H_{21}O]^+$ (7), 187 $[205-H_2O]^+$ (6), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (42); $[\alpha]_D^{24°}$ −28 ($CHCl_3$; *c* 0.94). *Triacetate* (**12a**Ac). Gum, MS *m/z* (rel. int.): 706.388 $[M]^+$ (1.5) (calc. for $C_{38}H_{58}O_{12}$: 706.388), 675 $[M-OMe]^+$ (2), 575 $[675-AngOH]^+$ (1.5), 417 $[M-$sugar moiety$]^+$ (10), 317 $[417-AngOH]^+$ (37), 273 [sugar part]$^+$ (95), 213 $[273-HOAc]^+$ (47), 153 $[213-HOAc]^+$ (76), 111 $[153-$ketene$]^+$ (67), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (65).

3α-*Angeloyloxy*-2β-*hydroxy*-ent-*labd*-7-*en*-15-*oic acid*-2-O-β-*fucopyranoside* (**13**). Isolated as its Me ester **13a**. Crystals, mp 85°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CO_2R), 1720 (C=CCO_2R). MS *m/z* (rel. int.): 434.303 $[M-C_6H_{10}O_4]^+$ (20) (calc. for $C_{26}H_{42}O_5$: 434.303), 417 $[M-$sugar moiety$]^+$ (12), 317 $[417-RCO_2H]^+$ (42), 205 $[C_{14}H_{21}O]^+$ (28), 187 $[205-H_2O]^+$ (16), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (82); $[\alpha]_D^{24°}$ −18 ($CHCl_3$; *c* 0.17). *Triacetate* (**13a**Ac). Gum, MS *m/z* (rel. int.): 674.366 $[M-MeOH]^+$ (1) (calc. for $C_{37}H_{54}O_{11}$: 674.366), 574 $[674-HOAng]^+$ (1), 434 $[M-C_6H_{10}O_4]^+$ (20), 417 $[M-$sugar moiety$]^+$ (7), 317 $[417-HOAng]^+$ (24), 273 [sugar part]$^+$(76), 213 $[273-HOAc]^+$ (33), 187 (18), 153 $[213-HOAc]^+$ (70), 111 $[153-$ketene$]^+$(70), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (68).

3α-*Methacryloyloxy*-2β-*hydroxy*-ent-*labd*-7-*en*-15-*oic acid*-2-O-β-*fucopyranoside* (**14**). Isolated as its Me ester **14a**. Crystals, mp 173°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1745 (CO_2R), 1730

(C=CO_2R). MS *m/z* (rel. int.): 420.288 [M−$C_6H_{10}O_4$]$^+$ (12) (calc. for $C_{25}H_{40}O_5$: 420.288), 403 [M−sugar moiety]$^+$ (10), 317 [403−RCO_2H]$^+$ (52), 205 [$C_{14}H_{21}O$]$^+$ (26), 187 [205−H_2O]$^+$ (18), 69 [C_3H_5CO]$^+$ (100). *Triacetate* (**14a**Ac). MS *m/z* (rel. int.): 660.351 [M−MeOH]$^+$ (1) (calc. for $C_{36}H_{52}O_{11}$: 660.351), 574 [660−$C_3H_5CO_2H$]$^+$ (1.5), 403 [M−sugar moiety]$^+$ (8), 317 [403−RCO_2H]$^+$ (52), 273 [sugar part]$^+$ (98), 213 [273−HOAc]$^+$ (64), 187 (37), 153 [213−HOAc]$^+$ (92), 111 [153−ketene]$^+$ (81), 69 [C_3H_5CO]$^+$ (100).

3α-*Tigloyloxy-2β-hydroxy*-ent-*labd-7-en-15-oic acid*-2-O-*β-fucopyranoside* (**15**). Isolated as its Me ester **15a**. Gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CO_2R), 1720 (C=CCO_2R). MS *m/z* (rel. int.): 434.303 [M−$C_6H_{10}O_4$]$^+$ (21) (calc. for $C_{26}H_{42}O_5$: 434.303), 417 [M−sugar moiety]$^+$ (16), 317 [417−RCO_2H]$^+$ (62), 205 [$C_{14}H_{21}O$]$^+$ (33), 187 [205−H_2O]$^+$ (27), 83 [C_4H_7CO]$^+$ (100), 55 [83−CO]$^+$ (52).

3α-*Senecioyloxy-2β-hydroxy*-ent-*labd-7-en-15-oic acid*-2-O-*β-fucopyranoside* (**16**). Isolated as its Me ester **16a**, not free from **17a**. Gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CO_2R), 1725 (C=CCO_2R). MS *m/z* (rel. int.): 434.303 [M−$C_6H_{10}O_4$]$^+$ (1) (calc. for $C_{26}H_{42}O_5$: 434.303), 417 [M−sugar moiety]$^+$ (8), 205 [$C_{14}H_{21}O$]$^+$ (8), 187 [205−H_2O]$^+$ (8), 83 [C_4H_7CO]$^+$ (100), 55 [83−CO]$^+$ (40).

3α-*Isobutyryloxy-2β-hydroxy*-ent-*labd-7-en-15-oic acid*-2-O-*β-fucopyranoside* (**17**). Isolated as its Me ester **17a**, not free from **16a**. Gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R). MS *m/z* (rel. int.): 422.303 [M−$C_6H_{10}O_4$]$^+$ (1) (calc. for $C_{25}H_{42}O_5$: 422.303), 405 [M−sugar moiety]$^+$ (1), 317 [405−RCO_2H]$^+$ (7), 205 [$C_{14}H_{21}O$]$^+$ (10), 187 [205−H_2O]$^+$ (9), 71 [C_3H_7CO]$^+$ (100).

3α-*Angeloyloxy-2β-hydroxy*-ent-*labd-7-en-15-oic acid*-2-O-*β-glucopyranoside* (**18**). Isolated as its Me ester tetraacetate **18a**Ac. Gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1755 (OAc, CO_2R). MS *m/z* (rel. int.): 732.372 [M−MeOH]$^+$ (0.5) (calc. for $C_{39}H_{56}O_{13}$: 732.372), 633 [732−OAng]$^+$ (0.5), 417 [M−sugar moiety]$^+$ (3), 331 [sugar part]$^+$ (63), 317 [417−AngOH]$^+$ (17), 271 [331−HOAc]; (17), 211 [271−HOAc]$^+$ (12), 169 [211−ketene]$^+$ (81), 83 [C_4H_7CO]$^+$ (100), 55 [83−CO]$^+$ (69); $[\alpha]_D^{24°}$ −13 ($CHCl_3$; *c* 0.55).

Acknowledgements—We thank the VW-foundation for financial support and Mrs C. Fernandez, Mrs A. Hoffmann and Mr M. Quezada for help in collection and identification of plant material.

REFERENCES

1. Zdero, C., Bohlmann, F., King, R. M. and Robinson, H. (1986) *Phytochemistry* **25**, 2841.
2. Zdero, C., Bohlmann, F., Solomon, J. C., King, R. M. and Robinson, H. (1989) *Phytochemistry* **28**, 531.
3. Jakupovic, J., Schuster, A., Ganzer, U., Bohlmann, F. and Boldt, P. E. (1990) *Phytochemistry* **29**, 2217.