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MACROLIDE DITERPENES AND OTHER *ENT*-LABDANES FROM *CORYMBIUM VILLOSUM*

C. ZDERO and F. BOHLMANN

Institute of Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, F.R.G.

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Key Word Index—*Corymbium villosum*; Compositae; diterpenes, *ent*-labdane derivatives; macrolide diterpenes.

Abstract—The roots of *Corymbium villosum* afforded nine new simple *ent*-labdane derivatives two in which two diterpene units are combined via malonic acid and two in which the hydroxy groups are connected via malonic acid forming macrolide systems. The structures were elucidated by high field NMR spectroscopy and a few chemical transformations. The chemotaxonomic relevance of the results is discussed briefly.

INTRODUCTION

Traditionally *Corymbium* is placed in the tribe Vernonieae, however, recent investigation of the pollen morphology indicated that this genus should be excluded from the tribe (H. Robinson, private communication). Very little is known about the chemistry of this genus. Flavone glycosides have been isolated from *C. glabrum* L. [1] and we have isolated the two polyacetylenes tridecapentaynene and entetraynene from the roots of *C. villosum* Less. [2]. We have now re-examined the root extract of *C. villosum* in more detail.

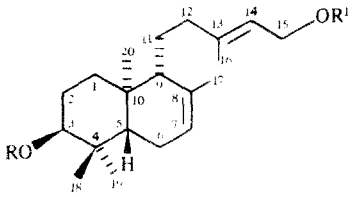
RESULTS AND DISCUSSION

In addition to the polyacetylenes a complex mixture of diterpenes was isolated. The latter yielded the new ent-labdane derivatives **1**–**13**, the acids **7**–**9** only being separated as their methyl esters (**7a**–**9a**). As the signals in the ^{1}H NMR spectra of the main constituents (**1** and **6**) were in part not well resolved we transformed **1** to the diacetate **2**Ac and **6** to the methyl ester **6a**. In the spectrum of **2**Ac (Table 1) nearly all of the signals could be assigned by spin decoupling. However, the relative position of the secondary oxygen function and some stereochemical details required NOE difference spectroscopy. Two methyl singlets gave clear effects with the equatorial proton under the acetoxy group (5%). Accordingly, the singlets were due to H-18 and H-19 while the acetoxy group was at C-3. As saturation at δ0.79 caused a clear effect at δ0.96 (8%) the latter singlet was due to H-19. Furthermore, a small *W*-coupling was observed between H-20 (*s* 0.79) and H-1β (*dt* 1.34). Additional NOEs were observed between H-18, H-5 (8%) and H-6 (4%) as well as between H-15 and H-16 (8%). These effects established the *trans*-annellation of the cyclohexane rings and the presence of a 13*E*-double bond. To determine the absolute configuration, **1** was partial acetylated to **2**, which was identical with the naturally occurring monoacetate. Oxidation of **2** with pyridine dichromate afforded the ketone **2**-one which showed a negative Cotton effect. As 3-ketosteroids as well as dammadienone show positive Cotton effects the diterpenes most likely all belong to the *ent*-labdane series. Thus **1** is 3β, 15-dihydroxy-*ent*-labda-7, 13*E*-diene.

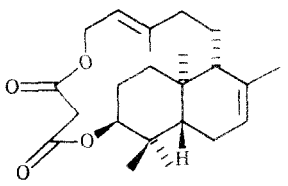
Inspection of the ^{1}H NMR spectra of **2**, **4** and **5** (Table 1) showed that these diterpenes differed from each other only in the nature of the groups at C-15, the identities of which followed from the typical ^{1}H NMR signals. The spectrum of **3** (Table 1) indicated that an isomer of **2** was present as the H-3 signal was shifted down field while that of H-15 was shifted up field. In the case of **4** and **5** the H-15 signal was split into pairs of double doublets. The ^{1}H NMR spectrum of the methyl ester **6a** was in part very close to that of **3** (Table 2). However, the acetoxy singlet was replaced by singlets at δ3.74 (3H) and 3.39 (2H) which led to the proposal that a malonate residue may be present. This was supported by the ^{13}C NMR spectrum of **6a**, especially when it is compared with that of **2**Ac (Table 3). While most carbons showed nearly the same shift that of C-3 was altered and four additional signals (167.2 *s*, 165.8 *s*, 41.8 *t*, 53.7 *q*) confirmed the presence of a methyl malonate residue. As expected, in the mass spectrum of **6** and also in that of **6a** no molecular ion could be detected as elimination of dimethyl allyl alcohol from the side chain followed by loss of methyl malonate is highly favoured.

The ^{1}H NMR spectra of **7a**–**9a** (Table 2) showed that again the corresponding 15-O-acetate, -isovalerate and -3-methyl valerate were present.

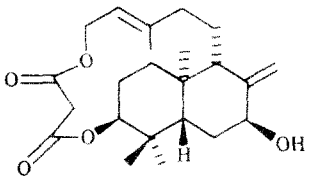
The ^{1}H NMR spectrum of **10** (Table 4) differed markedly from those of the discussed compounds with most of the signals favouring the presence of a similar diterpene. The low field signals between δ5.5 and 4.4 indicated that in addition to two olefinic protons three protons under an ester function should be proposed. However, except for a pair of doublets at δ3.41 and 3.21 no further signals, which could be due to an ester group, were visible. The ^{13}C NMR spectrum (Table 3) indicated 23 carbons and the molecular formula was $C_{23}H_{34}O_4$. A fragment at *m/z* 306 corresponded to $C_{20}H_{34}O_2$ obviously formed by loss of O=C=C=C=O. When the ^{1}H NMR signals were compared with those of **2**Ac it was clear that the side chain at C-9 was part of a ring system as the signals of H-14 and H-15 no longer showed the typical splitting of an open chain compound. Accordingly, a 15-membered lactone ring with a malonate bridge between C-3 and C-15 had to be present. Spin decoupling allowed the assignment of most signals and the oserved NOEs established the proposed



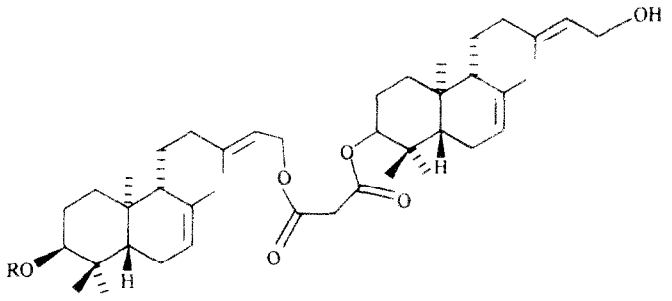
	1	2*	3	4	5	6*	7*	8*	9*
R	H	H	Ac	H	H	$COCH_2CO_2H$	$COCH_2CO_2H$	$COCH_2CO_2H$	$COCH_2CO_2H$
R^1	H	Ac	H	iVal		H	Ac	iVal	



10



11



12 R = H
13 R = Ac

* **6a** – **9a** are the corresponding methylesters, **2**Ac is the diacetate and **2**-one the 3-ketoderivative.

stereochemistry. Thus clear effects were observed between H-14, H-12′ (6%) and H-9 (6%), between H-16 and H-15 (8%), between H-9 and H-12 (4%), between H-19, H-3 (8%), H-6 (7%), H-2α (6%) and H-20 (10%) as well as between H-18, H-3 (8%) and H-6 (7%). The structure was further supported by alanate reduction which afforded the diol **1**, identical in all respects with the natural diol. It is noteworthy that compound **10** seems to be present in a preferred conformation as followed from the couplings and the NOE of H-9 with H-14.

In the ^{1}H NMR spectrum of **11** (Table 4) the signal of one olefinic methyl group was replaced by a pair of methylene singlets (δ5.05 and 4.82). Furthermore, an additional low field triplet at δ4.42 was visible. These results together with the molecular formula, $C_{23}H_{34}O_5$, establish the structure of **11**. Most likely this derivative is formed by oxidation of **10** at C-7. The configuration was supported by comparison of the ^{1}H NMR signals of H-7 and H-17 with those of similar diterpenes. Compound **10** we have named corymbi-7,13*E*-dienolide.

The ^{1}H NMR spectrum of **12** (Table 4) clearly indicated that two diterpene units must be linked by malonic acid. Accordingly, many of the typical signals of **2** and **6a** respectively were doubled and a two proton singlet at δ3.38 was attributed to the methylene group of a malonate residue. From the chemical shifts of H-3 and H-15 the relative position of the free hydroxy groups could be deduced. Thus compound **12** was derived from the diol **1** where two molecules were linked between C-15 and C-3 by malonic acid.

The ^{1}H NMR data of **13** (Table 4) showed that this compound was the corresponding 3-*O*-acetate.

Table 1. ^{1}H NMR spectral data of compounds **1**–**5**,2Ac and **2**-one (400 MHz, $CDCl_3$, δ-values)

H	1	2	2Ac	2-one	3	4	5†	Multiplicity
1α	1.58	*	1.60	2.11	1.60	*	1.57	*m*
1β	1.47	*	1.34	1.45	1.35	1.47	1.48	*ddd*
2α	1.87 *m*	1.9 *m*	1.86	2.71	1.87	*	1.89 *m*	*dddd*
2β	1.72	*	1.71	2.25	1.70	*	*	*m*
3	3.44	3.44	4.68	—	4.67	3.43	3.44	*t*
5	1.61 *dd*	*	1.62	1.60 *dd*	1.62	*	*	*t*
6	1.89	1.90	1.90	2.05 m 1.39 *m*	1.90	1.90	1.89	*m*
7	5.39	5.40	5.41	5.44	5.41	5.39	5.39	*br s*
9	1.70	*	1.71	*	1.70	*	*	*m*
11	1.54 *m*	*	1.54	1.57	1,54	*	1.55 *m*	*ddd*
11′	1.31*dddd*	1.32*dddd*	1.28	1.38	1.28	1.29	1.29	*m*
12	2.22	2.24	2.27	2.25	2.25	2.24	2.24	*ddd*
12′	1.96	2.00	2.00	1.99	1.98	1.98	1.98	*ddd*
14	5.41	5.33	5.35	5.35	5.43	5.32	5.33	*br t*
15	4.14	4.61 *dd*	4.59	4.58	4.16	4.61 *dd*	4.61 *dd*	*br d*
15′		4.56 *dd*				4.56 *dd*	4.56 *dd*	
16	1.69	1.71	1.72	1.72	1.69	1.71	1.72	*br s*
17	1.70	1.70	1.71	1.72	1.72	1.69	1.69	*br s*
18	0.95	0.95	0.85	1.11	0.86	0.90	0.90	*s*
19	0.91	0.91	0.96	1.06	0.97	0.94	0.94	*s*
20	0.79	0.78	0.79	1.01	0.80	0.78	0.77	*s*
OCOR	—	2.06	2.05		2.05	‡		*s*

* Obscured.

†OCOR: 2.31 *dd*, 2.11 *dd*, 1.89 *m*, 1.34 *ddq*, 1.22 *ddq*, 0.89 *t*, 0.93 *d*.

‡2.19 *d*, 2.05 *tqq*, 0.95 *d*.

J[Hz]: 1α,1β = 1β,2α = 2α,2β = 11,11′ = 11,12 = 11′,12′ = 12,12′ ~ 13; 1α,2α = 1β,2β = 3; 1β,18 ~ 0.5; 2α,3 = 2β,3 = 2; 5,6 = 8; 9,11′ = 4; 11,12′ = 11′,12 = 5; 14,15 = 7; OiVal: 2,3 = 3,4 = 7; OMeval: 2,2′ = 14; 2,3 = 6; 2,3′ = 8; 3,4 = 3,6 = 4,5 = 7.

Table 2. ^{1}H NMR spectral data of compounds **6a**–**9a**, **12** and **13** (400 MHz, $CDCl_3$, δ-values).

H	6a	7a	8a	9a*	12	13	Multiplicity
3	4.72	4.73	4.72	4.72	4.73, 4.68	4.73, 3.44	*t*
6	1.89	1.90	1.88	1.88	1.90	1.90	*m*
7	5.39	5.40	5.39	5.39	5.40	5.40	*br s*
12	2.23	2.26	2.25	2.24	2.24 *m*	2.23 *m*	*dt*
12′	1.97	1.97	1.96	1.95	1.98 *m*	1.98 *m*	*dt*
14	5.42	5.35	5.34	5.34	5.42, 5.34	5.42, 5.33	*br t*
15	4.18	4.59*d*	4.59*d*	4.58*d*	4.65*d* 4.19	4.69, 4.20	*dd*
15′	4.13				4.15	4.62, 4.15	*dd*
16	1.68	1.73	1.71	1.71	1.71, 1.69	1.70, 1.68	*br s*
17	1.70	1.70	1.69	1.69	1.71	1.70	*br s*
18	0.96	0.97	0.96	0.95	0.97	0.87, 0.97	*s*
19	0.86	0.87	0.86	0.85	0.87, 0.86	0.90, 0.96	*s*
20	0.79	0.79	0.77	0.77	0.80, 0.79	0.79, 0.78	*s*
OMe	3.74	3.74	3.74	3.74	—		*s*
OCOR	3.39	3.40	3.40		3.38	3.39	s
		2.06 s	2.17 d		2.05 *s*		
			2.09 *tq*				
			0.94 *d* (6*H*)				

*OCOR: 3.40 *s*, 2.29 *dd*, 2.09 *dd*, 1.88 *m*, 1.35 *ddq*, 1.22 *ddq*, 0.87 *t*, 0.91 *d*; *J*[Hz]: see Table 1.

Accordingly, now both H-3 signals were at lower fields. As expected the chemical shifts differed slightly, the second carbonyl group in the malonate unit causing a small down field shift. Compound **12** we have named corymbivillosol.

The isolation of the *ent*-labdane derivatives **1**–**13** together with tridecapentaynene supports the already proposed exclusion of this genus from Veronieae as diterpenes have never been reported from any member of this

Table 3. ^{13}C NMR spectral data of compounds **2Ac**, **6a** and **10** ($CDCl_3$, δ-values*)

C	2Ac	6a	10	Multiplicity
1	31.9	31.7	30.1	*t*
2	23.2	23.2	21.7	*t*
3	78.2	80.0	81.3	*d*
4	36.4	36.2	36.0	*s*
5	44.7	44.6	44.6	*d*
6	25.5	25.4	23.7	*t*
7	122.2	123.9	121.8	*d*
8	135.3	135.3	135.8	*s*
9	54.2	52.4	51.3	*d*
10	36.4	36.4	34.9	*s*
11	22.7	22.6	21.4	*t*
12	42.0	41.8	43.1	*t*
13	142.7	139.7	143.6	*s*
14	118.3	122.0	121.1	*d*
15	61.4	59.4	62.0	*t*
16	22.1	22.1	21.3	*q*
17	16.6	16.3	16.3	*q*
18	27.5	27.5	27.4	*q*
19	22.1	22.1	21.0	*q*
20	13.5	13.5	14.4	*q*
OR	171.1	167.2	166.4	*s*
	170.7	165.8	165.5	*s*
	21.2*q*	53.7*q*	40.2*t*	
	21.1*q*	41.8*t*		

*Assignment by 2D-correlated spectra.

Table 4. ^1H NMR spectral data of compounds **10** and **11** (400 MHz, $CDCl_3$, δ-values)

H	10	C_6D_6	11
1α	1.20 *dt*	1.10 *dt*	1.30 *m*
1β	1.29 *dt*	1.35 *dt*	
2α	1.75 *ddt*	1.59 *ddt*	1.70 *m*
2β	1.84 *dq*	2.00 *dq*	1.86 *dq*
3	4.49 *dd*	4.64 *dd*	4.54 *dd*
5	1.90 *m*	1.78 *dd*	*
6		1.85 *m*	*
7	5.38 *br s*	5.44 *br s*	4.42 *t*
9	1.74 *br s*	1.95 *br s*	*
11	1.45 *m*	1.30 *m*	*
11'	1.34 *br dd*	1.22 *br dd*	*
12	2.20 *br dd*	1.95 *m*	2.17 *m*
12'	1.90 *m*	1.83 *m*	2.11 *m*
14	5.45 *br dd*	5.32 *br dd*	5.41 *br dd*
15	4.82 *t*	4.76 *t*	4.96 *dd*
15'	4.54 *dd*	4.23 *dd*	4.44 *dd*
16	1.73 *br s*	1.55 *br s*	1.77 *br s*
17	1.70 *br s*	1.71 *br s*	5.05 *br s*
			4.82 *br s*
18	0.92 *s*	0.83 *s*	0.92 *s*
19	0.89 *s*	0.75 *s*	0.87 *s*
20	0.75 *s*		0.66 *s*
OCOR	3.41 *d*	3.16 *d*	3.49 *d*
	3.25 *d*	3.08 *d*	3.27 *d*

*obscured.

J [Hz]: 1α,1β = 1β,2α = 12.12' = 13; 1α,2α = 1α,2β = 2β,3 = 3.5; 2α,2β = 14; 2α,3 = 1; 5,6 = 12; 9,11 = 6; 11',12 = 4; 14,15 = 11; 14,15' = 5; OCOR: 2,2' = 14; compound **11**: 6,7 = 2; 14,15 = 10; 14,15' = 6.

tribe. *ent*-Labdanes were widespread in representatives of Eupatorieae and Astereae, less common in Inuleae and Heliantheae while from all other tribes no diterpenes of this type have been reported. As, however, tridecapentaynene has not been found in Astereae, and Heliantheae are not present in South Africa these tribes can be excluded as possible candidates for the placement of *Corymbium*. Further morphological studies may help to decide where this genus should be placed.

EXPERIMENTAL

The air-dried aerial parts (380 g, collected in September 1986, near Hermanus, Rotary Drive, R.S.A., voucher 86/227, deposited in the Compton Herbarium, Kirstenbosch) were extracted with MeOH–Et_2O–petrol (1:1:1) and separated by CC (silica gel) and TLC (silica gel, PF 254) affording 20 mg **1** and 2 mg **2** (see below). The extract from 380 g roots was separated first by CC into three fractions (1; petrol, 2; Et_2O and 3; Et_2O–MeOH, 9:1). TLC of fraction 1 (petrol) gave 1 mg tridecapentaynene and 1 mg trideca-1, 11*E*-dien-3,5,7,9-tetrayne. Fraction 2 gave by TLC (Et_2O–petrol, 1:1) three bands (2/1–2/3). TLC of 2/1 (Et_2O–petrol, 1:3) gave 20 mg **10** (R_f 0.50). HPLC of 2/2 (always RP8, MeOH–H_2O, 9:1, *ca* 100 bar, flow rate *ca* 3 ml/min.) gave 10 mg **4** (R_t 4.4 min.) and 15 mg **5** (R_t 6.5 min). Fraction 2/3 (free of methoxy signals in the ^1H NMR) was reacted with CH_2N_2 in Et_2O. TLC (Et_2O–petrol, 1:1) afforded three bands (2/3/1–2/3/3). HPLC of 2/3/1 gave 2 mg **10** (R_t 4.2 min), 15 mg **8a** (R_t 6.0 min) and 20 mg **9a** (R_t 7.4 min). HPLC of 2/3/2 gave 3 mg **7a** (R_t 3.3 min). HPLC of 2/3/3 afforded 1.5 mg **11** (R_t 1.4 min), 5 mg **3** (R_t 2.7 min), 5 mg **12** (R_t 8.8 min) and 6 mg **13** (R_t 12.3 min). HPLC of fraction 3 gave by HPLC (MeOH–H_2O, 4:1) 30 mg **6** (R_t 3.0 min.) and 30 mg **1** (R_t 8.9 min).

3β, 15-*Dihydroxy*-ent-*labda*-7,13E-*diene* (**1**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH); MS *m/z* (rel. int.): 306.256 $[M]^+$ (0.2) (calc. for $C_{20}H_{34}O_2$: 306.256), 220 $[M - Me_2C{=}CHCH_2OH]^+$ (100), 202 $[220 - H_2O]^+$ (18), 187 $[202 - Me]^+$ (24), 81 $[C_6H_9]^+$ (88). $[\alpha]_D^{24} = -9$ ($CHCl_3$; *c* 2.81).

10 mg **1** were heated for 3 hr with Ac_2O at 70°. TLC (Et_2O–petrol, 1:1) gave 10 mg **2**Ac (R_f 0.75); colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1245 (OAc). MS *m/z* (rel. int.): 390.277 $[M]^+$ (0.06) (calc. for $C_{24}H_{38}O_4$: 390.277), 330 $[M - HOAc]^+$ (0.3), 262 $[M - Me_2C{=}CHCH_2OAc]^+$ (27), 202 $[262 - HOAc]^+$ (28), 187 $[202 - Me]^+$ (26), 99 $[C_6H_{11}O]^+$ (100); $[\alpha]_D^{24} = -7$ ($CHCl_3$; *c* 0.56). 10 mg **1** were dissolved in 100 mg Ac_2O. After 12 hr standing at room temp., TLC of reaction products afforded 9 mg **2**, identical with the natural hydroxyacetate. 9 mg **2** in 2 ml $CHCl_3$ were stirred for 3 hr with 30 mg PDC and 10 mg $NaHCO_3$. TLC (Et_2O–petrol, 1:3) gave 7 mg 2-one (R_f 0.45); colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1235 (OAc), 1710 (C=O); MS *m/z* (rel. int.): 346.251 $[M]^+$ (0.2) (calc. for $C_{22}H_{34}O_3$: 346.251), 286 $[M - HOAc]^+$ (1.4), 218 $[M - Me_2C{=}CHCH_2OAc]^+$ (100), 203 $[218 - Me]^+$ (32); CD (MeCN): $\Delta\varepsilon_{287} = 0.93$.

3β-*Hydroxy*-15-*acetoxy*-ent-*labda*-7,13E-*diene* (**2**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1735, 1240 (OAc); MS *m/z* (rel. int.): 348.266 $[M]^+$ (0.7) (calc. for $C_{22}H_{36}O_3$: 348.266), 288 $[M - HOAc]^+$ (1), 220 $[M - Me_2C{=}CHCH_2OAc]^+$ (100), 202 $[220 - H_2O]$ (14); $[\alpha]_D^{24} = +4$ ($CHCl_3$; *c* 0.53).

3β-*Acetoxy*-15-*hydroxy*-ent-*labda*-7,13E-*diene* (**3**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1740, 1255 (OAc); MS *m/z* (rel.

int.): 262.123 $[M-Me_2C{=}CHCH_2OH]^+$ (100) (calc. for $C_{17}H_{26}O_2$: 262.123), 202 $[262-HOAc]^+$ (86), 187 $[202-Me]^+$ (84), 81 $[C_6H_9]^+$ (80); $[\alpha]_D^{24°}$ − 10 ($CHCl_3$; *c* 0.52).

3*β-Hydroxy*-15-*isovaleryloxy*-ent-*labda*-7,13E-*diene* (**4**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1730 (CO_2R); MS *m/z* (rel. int.): 288.245 $[M-RCO_2H]^+$ (1) (calc. for $C_{20}H_{32}O$: 288.245), 220 $[M-Me_2C{=}CHCH_2OiVal]^+$ (100), 202 $[220-H_2O]^+$ (17), 187 $[202-Me]^+$ (26), 81 $[C_6H_9]^+$ (58); $[\alpha]_D^{24°}$ − 5 ($CHCl_3$; *c* 0.53).

3*β-Hydroxy*-15-[3-*methylvaleryloxy*]-ent-*labda*-7,13E-*diene* (**5**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1730 (CO_2R); MS *m/z* (rel. int.): 404.329 $[M]^+$ (0.2) (calc. for $C_{26}H_{44}O_3$: 404.329), 288 $[M-RCO_2H]^+$ (1), 220 $[M-Me_2C{=}CHCH_2OCOR]^+$ (100), 202 $[220-H_2O]^+$ (11), 187 $[202-Me]^+$ (12).

3*β-Malonyloxy*-15-*hydroxy*-ent-*labda*-7,13E-*diene* (**6**). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 – 2600, 1720 (CO_2H); MS *m/z* (rel. int.): 374.246 $[M-H_2O]^+$ (0.4) (calc. for $C_{23}H_{34}O_4$: 374.246), 306 $[M-Me_2C{=}CHCH_2OH]^+$ (10), 262 $[306-CO_2]^+$ (83), 202 $[306-RCO_2H]^+$ (82), 187 $[202-Me]^+$ (68), 81 $[C_6H_9]^+$ (100). Addition of CH_2N_2 in Et_2O afforded **6a**; colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1730 (CO_2R); MS *m/z* (rel. int.): 320 $[M-Me_2C{=}CHCH_2OH]^+$ (38), 202 $[320-RCO_2H]^+$ (100), 187 $[202-Me]^+$ (68), 81 $[C_6H_9]^+$ (68); $[\alpha]_D^{24°}$ − 19 ($CHCl_3$; *c* 1.62).

Methylester of 3*β-malonyloxy*-15-*acetoxy*-ent-*labda*-7,13E-*diene* (**7a**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750, 1235 (OAc), 1730 (CO_2R); MS *m/z* (rel. int.): 448.284 $[M]^+$ (0.04) (calc. for $C_{26}H_{40}O_6$: 448.284), 417 $[M-OMe]^+$ (0.2), 388 $[M-HOAc]^+$ (0.3), 320 $[M-Me_2C{=}CHCH_2OAc]^+$ (44), 202 $[320-RCO_2H]^+$ (100), 187 $[202-Me]^+$ (52), 81 $[C_6H_9]^+$ (54).

Methylester of 3*β-malonyloxy*-15-*isovaleryloxy*-ent-*labda*-7,13E-*diene* (**8a**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750, 1730 (CO_2R); MS *m/z* (rel. int.): 490.329 $[M]^+$ (0.2) (calc. for $C_{29}H_{46}O_6$: 490.329), 388 $[M-RCO_2H]^+$ (0.4), 357 $[388-OMe]^+$ (0.3), 320 $[M-Me_2C{=}CHCH_2OCOR]^+$ (28), 202 $[320-RCO_2H]^+$ (81), 187 $[202-Me]^+$ (100), 81 $[C_6H_9]^+$ (26); $[\alpha]_D^{24°}$ − 3 ($CHCl_3$; *c* 1.38).

Methylester of 3*β-malonyloxy*-15-[3-*methylvaleryloxy*]-ent-*labda*-7,13E-*diene* (**9a**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1740 (CO_2R); MS *m/z* (rel. int.): 504.345 $[M]^+$ (0.1) (calc. for $C_{30}H_{48}O_6$: 504.345), 473 $[M-OMe]^+$ (0.15), 388 $[M-RCO_2H]^+$ (0.5), 320 $[M-Me_2C{=}CHCH_2OCOR]^+$ (44), 202 $[320-RCO_2H]^+$ (100), 187 $[202-Me]^+$ (44), 81 $[C_6H_9]^+$ (38); $[\alpha]_D^{24°}$ − 2 ($CHCl_3$; *c* 2.0).

Corymbi-7,13E-*dienolide* (**10**). Colourless crystals, mp. 111°; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735, 1715 (CO_2R); MS *m/z* (rel. int.): 374.225 $[M]^+$ (8) (calc. for $C_{23}H_{34}O_4$: 374.225), 306 $[M-O{=}C{=}C{=}C{=}O]^+$ (4), 203 $[M-Me_2C{=}CHCH_2OCOCH_2CO_2]^+$ (60), 202 $[203-H]^+$ (62), 187 $[202-Me]^+$ (100), 81 $[C_6H_9]^+$ (50); $[\alpha]_D^{24°}$ − 161 ($CHCl_3$; *c* 0.54). To 5 mg **10** in 2 ml Et_2O 20 mg $LiAlH_4$ was added. After 5 min, usual work-up gave 3 mg **1**, identical with the natural diol (^1H NMR, Co-TLC).

7*β-Hydroxy-corymbi*-8(17),13*E-dienolide* (**11**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740, 1720 (CO_2R); MS *m/z* (rel. int.): 390.241 $[M]^+$ (6) (calc. for $C_{23}H_{34}O_5$: 390.241), 372 $[M-H_2O]^+$ (6), 357 $[372-Me]^+$ (3), 81 $[C_6H_9]^+$ (100).

Corymbivillosol (**12**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1750, 1720 (CO_2R); MS *m/z* (rel. int.): 662 $[M-H_2O]^+$ (0.05) ($C_{43}H_{66}O_5$), 320 (1), 306 (1.5), 288 (2.5), 262 (10), 220 (95), 202 (38), 187 (50), 81 (100); $[\alpha]_D^{24°}$ − 17 ($CHCl_3$; *c* 0.18).

Corymbivillosol-3-O-*acetate* (**13**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740, 1250 (OAc), 1725 (CO_2R); MS *m/z* (rel. int.): 704 $[M-H_2O]^+$ (0.05) ($C_{45}H_{68}O_6$), 644 $[704-HOAc]^+$ (0.1), 374 (2), 306 (4), 262 (48), 220 (36), 202 (72), 187 (100), 81 (98); $[\alpha]_D^{24°}$ − 18 ($CHCl_3$; *c* 0.16).

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