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18-MALONYLOXY-9-*EPI-ENT*-ISOPIMAROL, A DITERPENE FROM *CALCEOLARIA GLANDULOSA**

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Key Word Index—*Calceolaria glandulosa*, Scrophulariaceae, diterpenes, 9-epimeric pimarane diterpenes

Abstract—A new pimarane diterpene, 18-malonyloxy-9-*epi-ent*-isopimarol, was isolated from the aerial parts of *Calceolaria glandulosa* The structure of the new compound was established by spectroscopic evidence, chemical transformations and X-ray analysis

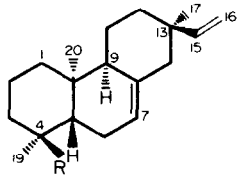
INTRODUCTION

Calceolaria is a genus mostly of medium size herbs widespread in South America, 10% of which are endemic to Chile [2] In continuation of our investigation of the genus *Calceolaria* [1, 3, 4] we have now examined *C. glandulosa*, an uncommon taxon distributed in the coastal hills of central Chile This paper deals with the structural determination of the major compound, a new pimarane diterpene named 18-malonyloxy-9-*epi-ent*-isopimarol (**1**), isolated from the aerial parts of the plant

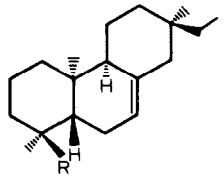
RESULTS AND DISCUSSION

The chloroform extract of the fresh aerial parts of *C. glandulosa* was subjected to CC on silica gel using increasing proportions of ethyl acetate in petrol Compound **1**, obtained from the intermediate fractions as a colourless oil, showed a molecular formula $C_{23}H_{34}O_4$ by mass spectrometry ($[M]^+$ at *m/z* 374) and ^{13}C NMR, and its IR spectrum exhibited carboxyl, ester and olefinic group absorptions The acidic nature of this substance was evident from its characteristic chromatographic behaviour and because, by reaction with ethereal diazomethane, the methyl ester **1a** was easily obtained (see Experimental and Table 1)

The ^1H NMR spectrum of **1** showed the presence of a vinyl group (δ5 84, *dd*, H-15, 4 96, *dd*, H-16*c*; 4 94, *dd*, H-16*t*), a primary ester group (δ3 95, *d*, H-18, 3 78, *d*, H-18′) and three tertiary methyl groups In addition, a methine signal (δ5.25, *t*, H-7) indicated a trisubstituted double bond The foregoing evidence suggested that **1** possessed a pimaradiene-type structure and the other carbon atoms (C_3) in the molecule must be part of the acyl moiety That the ester side chain of **1** is a malonate residue was deduced by a singlet at δ3 43 accounting for two hydrogen atoms in its ^1H NMR spectrum [1, 5] The ^{13}C NMR spectrum of **1** (Table 1) confirmed the presence of this residue by signals at δ166.8 (*s*, C-1′), 40.7 (*t*, C-2′) and 171.4 (*s*, C-3′) [1, 6]. The remaining ^{13}C NMR absorptions were consistent with the structural features of an 7,15-pimaradiene-type skeleton with the primary ester group equatorially orientated (δ74.7, *t*, C-18) at C-4 [7] However, since a methine carbon (APT) occurs at an unusually upfield position (δ38 1 *d*), a normal isopimaradiene structure for **1** was tentatively discarded [7]. Lithium aluminium hydride reduction or alkaline hydrolysis of **1** yielded the same diterpenic alcohol **2**. As expected, the ^1H NMR spectrum of **2** lacked resonances



	R
1	CH_2OCOCH_2COOH
1a	CH_2OCOCH_2COOMe
2	CH_2OH
4	CHO
5	Me
7	COOH



	R
3	CH_2OH
6	Me

* Part 2 in the series 'Diterpenoids from *Calceolaria* species' For part 1 see ref [1]

Table 1 ^{13}C NMR spectral data of compounds **1**, **1a**, **2**, **3**, **5**–**7** ($CDCl_3$, TMS)

Carbon	1*	1a†	2	3	5	6	7
1	36 4	36 5	36 5	36 5	36 9	36 9	35 8
2	18 0	18 3	18 2	18 2	18 9	18 9	18 0
3	37 0	37 1	36 6	36 6	43 1	43 1	37 9
4	36 5	36 5	37 5	37 5	33 1	32 9	46 2
5	38 1	38 2	37 3	37 3	43 6	43 7	38 7
6	23 8	24 0	23 7	23 7	23 8	23 8	25 2
7	118 9	119 1	119 2	118 5	119 6	119 0	118 8
8	137 0	137 0	137 1	137 7	136 9	137 4	137 0
9	53 2	53 2	53 3	53 5	53 3	53 5	53 5
10	35 0	35 1	35 0	34 9	35 2	35 3	34 7
11	25 4	25 5	25 5	25 2	25 4	25 1	25 3
12	39 4	39 5	39 6	38 2	39 7	38 2	39 6
13	39 0	39 1	39 0	35 4	38 9	35 4	38 8
14	49 6	49 7	49 7	48 8	49 7	48 8	49 7
15	146 0	145 7	145 9	28 0	145 9	28 0	145 6
16	111 4	111 4	111 3	7 8	111 1	7 7	111 3
17	30 0	30 0	29 8	28 1	29 7	27 9	29 6
18	74 7	74 5	72 6	72 5	33 5	33 5	185 4
19	18 2	18 2	18 4	18 5	22 2	22 2	17 5
20	22 6	22 7	22 8	22 8	22 7	22 7	22 5

* Malonate carbons at 166 8 (s), C-1′, 40 7 (*t*), C-2′, 171 4 ppm (s), C-3′

† Malonate carbons at 166 4 (s), C-1′, 41 4 (*t*), C-2′, 166 7 ppm (s), C-3′ Methyl ester carbon at 52 4 ppm (*q*)

for the malonate protons and the H-18 and H-18′ signals shifted upfield from δ3 95 and 3 78 to 3.34 and 3 13, respectively

The ^{13}C NMR data of **2** (Table 1) were very similar to the skeletal carbon absorptions of **1** with the exception of the signals near C-18 The spectrum showed, apart from other signals, a doublet (SFORD and APT) at δ37 3 ppm which was displaced, on going from **1** to **2**, upfield by 0 8 ppm, whilst the other doublet (δ53.3 ppm) in the spectrum appeared to be unaffected ($\Delta\delta$ = 0 1 ppm) These differences could be rationalized by considering the neighbourhood effects of the acyl group on the carbon absorption at δ38 1, which was, therefore, tentatively assigned to C-5 However, apart from the known endocyclic homoallylic effect of the Δ^7 bond [8] and the γ-gauche effect due to the C-18 oxy-methylene group, another interaction must operate in order to justify this unusually upfield absorption of C-5

Comparison of the carbon signals tentatively assigned to C-1, C-20 and C-11 of **2** with those of isopimarol [7], shows C-1 to be shielded ($\Delta\delta$ = − 3 1 ppm), C-20 to be deshielded ($\Delta\delta$ = 6 9 ppm) and C-11 to be deshielded ($\Delta\delta$ = 5 0 ppm) These effects, which are also observed in dihydromomilactone A and other related compounds [9], can be explained by the interaction imposed by an uncommon orientation of C-11, which also produces an additional γ-effect on C-5, thus indicating the increased shielding of this carbon atom (compared with Dreiding molecular models) The assignments of the remaining signals in the ^{13}C NMR spectrum of **2** (Table 1), especially those of the A and C rings, were made on the basis of the observed multiplicities, empirical shift rules (α, β and γ effects) [10] and comparison with the corresponding carbon atoms of some derivatives (see Table 1) In fact, by catalytic reduction of 9-*epi*-*ent*-isopimarol (**2**), the vinyl group at C-13 was selectively reduced to give 15,16-dihydrò-9-*epi*-*ent*-isopimarol (**3**) As anticipated from a Dreiding model, the remaining double bond (Δ^7) in ring B was sterically hindered, resisting catalytic reduction under the usual conditions Also as expected, the ^{1}H NMR spectrum of **3** lacked resonances for vinyl protons and its ^{13}C NMR spectrum clearly exhibited the characteristics of an ethyl group (28 0, *t*, C-15, 7 8, *q*, C-16) instead of a vinyl group Treatment of 9-*epi*-*ent*-isopimarol (**2**) with Jones reagent [11] gave the aldehyde **4**, $C_{20}H_{34}O$ ([M]$^+$ at *m/z* 286) the spectra of which (see Experimental) are in full accordance with the assigned structure

Huang–Minlon reduction [12] of **4** gave a mixture of two products, **5** and **6**, which were purified by chromatography on silica gel impregnated with silver nitrate The ^{1}H NMR spectrum of **5** showed four methyl-group protons (C-13, C-18, C-19 and C-20), and an olefinic proton appearing at δ5 33 was assigned to H-7 and an ABC system (δ5 95, H-15, 4 98, H-16*c*, and 4 97, H-16*t*) was attributed to the vinylic protons

Obviously, the replacement of the OH group at C-18 of **2** by one hydrogen atom caused the loss of a γ-gauche interaction producing, as appeared in the ^{13}C NMR spectrum of **5** (Table 1), an upfield shift of 6 3, 6 5 and 3 8 ppm on the C-5, C-3 and C-19 carbon atoms, respectively Also, a shielding effect of 4.4 ppm on C-4 was observed Therefore, compound **5** is shown to be 9α-H-*ent*-7,15-isopimaradiene

That **6** is the 15,16-dihydro derivative of **5** was evident from the ^{1}H and ^{13}C NMR data of this product In fact, the ^{1}H NMR spectrum of **6** exhibited four tertiary methyl groups, a methine proton, and the signals due to the vinyl group were missing In addition, all the ^{13}C NMR signals of **6** (Table 1) were in good agreement with the proposed structure The formation of compound **6** on treatment of aldehyde **4** with hydrazine must be due, in part, to the

generation of a diimide under the reaction conditions The diimide reduction of olefins is a well-known reaction [13] Finally, treatment of aldehyde **4** with excess of Jones reagent gave acid **7**, the spectra of which are in full accordance with the assigned structure.

In order to remove any ambiguity concerning the structure and stereochemistry of 9α-H-ent-isopimarol, the compound was subjected to X-ray analysis which confirmed the structure shown in **2** (Fig 1). Details of the X-ray analysis are given in the Experimental

9-Epimeric diterpenoids constitute a relatively rare group of secondary metabolites with twelve examples known prior to the present work. These are annonalide [14], momilactones A, B, C, [8, 15], icacinol [16], icacinone [17], humirianthenolides A, B, C, D, E and F [18]. From a biogenetic point of view, the formation of these compounds might involve a chair–boat rather than a chair–chair cyclization of geranylgeranyl pyrophosphate to form a bicyclic intermediate possessing a 10α-methyl group and a 9α-hydrogen atom or its enantiomer, i e with H-9 and C-20 in a *cis* relationship In particular, subsequent formation of ring C, elimination of a 7-hydrogen and oxidation of C-18 could afford the alcohol **2** [19] On the other hand, the acumulation of malonyl-esters in members of the *Calceolaria* genus may be of chemotaxonomic interest

EXPERIMENTAL

Mps uncorr, ^{1}H NMR 60, 100 and 400 MHz in $CDCl_3$ with TMS as int standard, ^{13}C NMR 100 MHz, $CDCl_3$ with TMS as int std Assignments of ^{13}C NMR chemical shifts were made with the aid of APT and SFORD IR film on NaCl or KBr pellets, MS direct inlet 70 eV

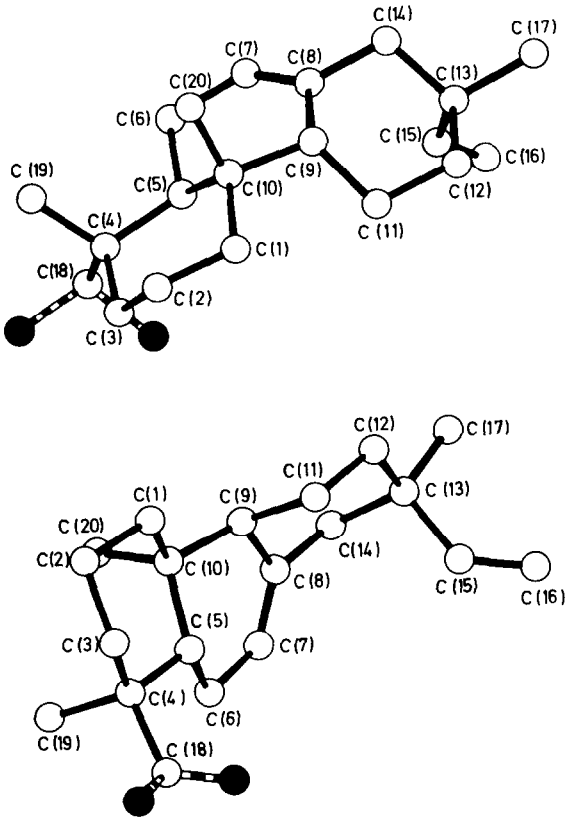


Fig 1 X-Ray crystal structure of 9-*epi-ent*-isopimarol (**2**)

Calceolaria glandulosa Poepp ex Benth, collected in Cuesta Zapata, V-Región, Chile, in November 1985, was identified at the Universidad Federico Santa Maria, where a voucher specimen is deposited

The aerial parts of *C glandulosa* (500 g) were extracted at room temp with $CHCl_3$ for 12 hr, affording 12 3 g of a syrup This crude material was chromatographed on a silica gel column (400 g) and eluted with mixts of petrol and EtOAc of increasing polarity Fractions of 100 ml were taken and combined based upon TLC monitoring Fractions 5–9 gave a mixture of two unknown substances Fractions 12–14 provided a mixt which contained a third unknown compound **1** Fractions 16–28, contained a single substance (gummy, 6 8 g) **1**

18-*Malonyloxy*-9-epi-ent-*isopimarol* (**1**) Viscous colourless oil, $[\alpha]_D^{25}$ −105 1 ($CHCl_3$, *c* 1 0) IR ν_{max}^{film} cm^{-1} 3400–3200, 3060, 2960–2840, 1740, 1715, 1450, 1375, 1310, 1150, 1000, 910, 845, 820 ^{1}H NMR (400 MHz) δ5 84 (1H, *dd*, *J* = 11 2, 17 6 Hz, H-15), 5 25 (1H, *t*, *J* = 4 0 Hz, H-7), 4 96 (1H, *dd*, *J* = 11 2, 1 5 Hz, H-16*c*), 4 94 (1H, *dd*, *J* = 17 6, 1 5 Hz, H-16*t*), 3 95 (1H, *d*, *J* = 10 8 Hz, H-18), 3 78 (1H, *d*, *J* = 10 8 Hz, H-18′), 3 43 (2H, *s*, H_2-malonyl), 1 00 (3H, *s*, Me-17), 0 97 (3H, *s*, Me-20), 0 94 (3H, *s*, Me-19) ^{13}C NMR see Table 1, MS *m/z* (rel int) 374 $[C_{23}H_{34}O_4, M]^+$ (2), 359 $[M-Me]^+$ (3), 330 $[M-CO_2]^+$ (1), 288 $[M-C_3H_2O_3]^+$ (7), 270 $[M-HOOCCH_2COOH]^+$ (45), 255 $[270-Me]^+$ (76), 187 (32), 148 (50), 133 (49), 119 (70), 109 (100), 105 (73), 81 (74), 54 (77)

Methyl 18-*malonyloxy*-9-epi-ent-*isopimarol* (**1a**) After addition of $CH_2N_2Et_2O$, **1** (300 mg) was transformed to **1a** Gummy, $[\alpha]_D^{25}$ −115 3° ($CHCl_3$, *c* 1 1) IR ν_{max}^{film} cm^{-1}, 3080, 2960–2840, 1740, 1720, 1460, 1430, 1375, 1280, 1150, 1020, 910, ^{1}H NMR (100 MHz) δ5 86 (1H, *dd*, *J* = 11 0, 17 0 Hz, H-15), 5 26 (1H, *t*, *J* = 4 0 Hz, H-7), 4 95 (1H, *dd*, *J* = 11 0, 1 5 Hz, H-16c), 5 93 (1H, *dd*, *J* = 17 0, 1 5 Hz, H-16 *t*), 3 93 (1H, *d*, *J* = 11 0 Hz, H-18), 3 74 (1H, *d*, *J* = 11 0 Hz, H-18′), 3 72 (3H, *s*, COOMe), 3 38 (2H, *s*, H_2-malonyl), 1 02 (3H, *s*, Me-17), 0 98 (3H, *s*, Me-20), 0 96 (3H, *s*, Me-19) ^{13}C NMR see Table 1, MS *m/z* (rel int) 388 $[C_{24}H_{36}O_4, M]^+$ (4), 370 (5), 270 $[M-HO_2CCH_2CO_2Me]^+$ (57), 255 $[270-Me]^+$ (100), 251 (25), 187 (38), 148 (39), 133 (49), 119 (74), 109 (88), 105 (70), 81 (67), 55 (70)

9-epi-ent-*Isopimarol* (**2**) **1** (1 g) was treated with $LiAlH_4$ in dry Et_2O After usual work-up and crystallization from MeOH H_2O, **2** was obtained as white crystals (700 mg) On the other hand, **1** (1 g) was also treated with K_2CO_3 in MeOH at room temp under N_2 After 4 hr the mixt was filtered, concd and crystallized from MeOH–H_2O to yield the same compound **2** (530 mg) Mp 113–114° $[\alpha]_D^{25}$ −168.0° ($CHCl_3$, *c* 1 0) IR ν_{max}^{KBr} cm^{-1} 3350, 3080, 2960–2840, 1630, 1460, 1445, 1380, 1150, 1040, 1010, 920, 845, 820 ^{1}H NMR (400 MHz) δ5 89 (1H, *dd*, *J* = 10 6, 18 0 Hz, H-15), 5 26 (1H, *t*, *J* = 3 0 Hz, H-7), 4 95 (1H, *dd*, *J* = 10 6, 1.5 Hz, H-16c), 4 93 (1H, *dd*, *J* = 18 0, 1 5 Hz, H-16 *t*), 3 34 (1H, *d*, *J* = 10 9 Hz, H-18), 3 13 (1H, *d*, *J* = 10 9 Hz, H-18′), 1.00 (3H, *s*, Me-17), 0 97 (3H, *s*, Me-20), 0 87 (3H, *s*, Me-19) ^{13}C NMR see Table 1, MS *m/z* (rel int) 288 $[C_{20}H_{32}O, M]^+$ (64), 273 $[M-Me]^+$ (58), 270 $[M-H_2O]^+$ (67), 257 (92), 255 (67), 241 (59), 147 (77), 134 (60) 121 (75), 109 (100), 91 (78), 55 (83), 41 (78)

15,16-*Dihydro*-9-epi-ent-*isopimarol* (**3**) **1** (200 mg) was dissolved in 100 ml of MeOH PtO_2 (50 mg) was added and the mixt hydrogenated in a Parr apparatus at an initial press of 50 psi After 4 hr, the mixt was filtered, concd and chromatographed on a silica gel column (10 g) and eluted with petrol–EtOAc (9 1) yielding pure **3** (160 mg) Mp 115–116° (MeOH–H_2O) $[\alpha]_D^{25}$ −154 8° ($CHCl_3$, *c* 1.00) IR ν_{max}^{KBr} cm^{-1} 3320, 2960–2840,

1450, 1380, 1060, 1030, 1000, 845, 820 ^{1}H NMR (400 MHz) δ5.25 (1H, *t*, J = 4.0 Hz, H-7), 3.36 (1H, *d*, J = 11.0 Hz, H-18), 3.18 (1H, *d*, J = 11.0 Hz, H-18'), 1.00 (3H, *s*, Me-17), 0.93 (3H, *s*, Me-20), 0.87 (3H, *s*, Me-19), 0.77 (3H, *t*, J = 7.0 Hz, Me-16) ^{13}C NMR see Table 1, MS *m/z* (rel int) 290 $[C_{20}H_{34}O, M]^+$ (100), 275 $[M-Me]^+$ (86) 272 $[M-H_2O]^+$ (58), 260 (92), 259 (78), 257 (75), 243 (57), 190 (71), 187 (83), 151 (73), 147 (74), 135 (76), 133 (79), 95 (89), 93 (78), 81 (86), 55 (82), 41 (84)

9-epi-ent-*Isopimaral* (**4**) **1** (300 mg) was dissolved in 100 ml of Me_2CO and treated with Jones reagent for 20 min at 0°. Excess oxidant was reduced with MeOH and the products isolated with $CHCl_3$. This crude material was evapd and chromatographed on a silica gel column (20 g) and eluted with petrol–EtOAc (19:1) yielding pure **4** (210 mg) Mp 79–80° (MeOH–H_2O) $[\alpha]_D^{25}$ −112.8° ($CHCl_3$, *c* 1.00) IR ν_{max}^{KBr} cm^{-1} 3080, 2960, 2840, 2680, 1720, 1630, 1450, 1380, 980, 930, 850, 820 ^{1}H NMR (60 MHz) δ9.27 (1H, *s*, H-18), 5.95 (1H, *dd*, J = 10.0, 18.0 Hz, H-15), 5.25 (1H, *t*, J = 4.0 Hz, H-7), 4.96 (1H, *dd*, J = 10.0, 1.5 Hz, H-16*c*), 4.93 (1H, *dd*, J = 18.0, 1.5 Hz, H-16*t*), 1.10 (3H, *s*, Me-19), 0.97 (6H, *s*, Me-17, Me-20) MS *m/z* (rel int) 286 $[C_{20}H_{30}O, M]^+$ (100), 271 $[M-Me]^+$ (22), 257 $[M-CHO]^+$ (35), 243 (30), 187 (33), 145 (22), 133 (20), 131 (33), 119 (30), 105 (39), 91 (30), 81 (34), 55 (25), 43 (18), 41 (26)

9-epi-ent-7,15-*Isopimaradiene* (**5**) *and* 9-epi-ent-7-*isopimaraene* (**6**) **4** (1.3 g) was treated with 2.5 g of KOH, 5 ml of 95% hydrazine hydrate and 25 ml of diethylene glycol. The mixt was refluxed for 4 hr and the condenser changed to a dist column while slow boiling was continued to removed H_2O. A white solid deposited in the column. When the pot temp had reached 240°, 2 ml of hydrazine was added and refluxing was continued for an additional 2 hr. The mixt was then cooled, acidified with concd HCl and extracted with Et_2O. The Et_2O soln and the white solid were mixed and subjected to silica gel CC (80 g, HF_{254} for TLC) impregnated with $AgNO_3$ (10%), using *n*-pentane (1 l) and *n*-pentane–EtOAc (49:1), (2 l). Fractions of 50 ml were collected and combined based upon TLC monitoring. Fractions 12–14, containing a single compound, were mixed and afforded **6** (83 mg). Fractions 20–29, containing another pure compound, were mixed affording **5** (350 mg). **5**, white crystals, mp 73–74° $[\alpha]_D^{25}$ −170.2° ($CHCl_3$, *c* 1.00) IR ν_{max}^{KBr} cm^{-1} 2960–2840, 1630, 1450, 1390, 1370, 1000, 920, 850, 820 ^{1}H NMR (400 MHz) δ5.95 (1H, *dd*, J = 18.0, 10.5 Hz, H-15), 5.33 (1H, *br d*, J = 5, 5 Hz, H-7), 4.98 (1H, *dd*, J = 10, 5, 1, 5 Hz, H-16*c*), 4.97 (1H, *dd* J = 18.0, 1.5 Hz, H-16*t*), 1.00 (3H, *s*, Me-17), 0.95 (3H, *s*, Me-18), 0.92 (3H, *s*, Me-19), 0.90 (3H, *s*, Me-20) ^{13}C NMR see Table 1, MS *m/z* (rel int) 272 $[C_{20}H_{32}, M]^+$ (85), 257 $[M-Me]^+$ (85), 229 (34), 148 (80), 133 (77), 119 (78), 105 (100), 93 (99), 81 (91), 79 (86), 55 (92), 41 (58) Compound **6**, amorphous powder IR ν_{max}^{KBr} cm^{-1} 2960–2840, 1450, 1390, 1380, 1000, 845, 820 ^{1}H NMR (60 MHz) δ5.30 (1H, *t*, J = 4.0 Hz, H-7), 0.95 (3H, *s*, Me-18), 0.90 (9H, *br s*, Me-17, Me-19, Me-20), 0.82 (3H, *t*, J = 7.0 Hz, Me-16) ^{13}C NMR see Table 1, MS *m/z* (rel int) 274 $[C_{20}H_{34}, M]^+$ (96) 259 $[M-Me]^+$ (99), 245 (84), 189 (85), 177 (64), 163 (94), 135 (94), 121 (93), 105 (100) 95 (91), 93 (94), 83 (86), 81 (92), 69 (95), 67 (90), 43 (87), 41 (86)

9-epi-ent-7,15-*Isopimaradiene*-18-*oic acid* (**7**) **4** (200 mg) was dissolved in 50 ml of Me_2CO and treated with Jones reagent for 1 hr at room temp. The mixt was dissolved in $CHCl_3$, evapd and chromatographed by silica gel CC (20 g) and eluted with petrol–EtOAc (9:1) yielding pure **7** (110 mg) Mp 170–173° (petrol–EtOAc) $[\alpha]_D^{25}$ −124.5° ($CHCl_3$, *c* 0.50) IR ν_{max}^{KBr} cm^{-1} 3200, 3080, 2960, 2840, 1700, 1630, 1450, 1380, 1280, 1010, 915, 850, 825 ^{1}H NMR (400 MHz) δ5.92 (1H, *dd*, J = 11.0, 18.0 Hz, H-15), 5.25 (1H, *br d*, J = 5.5 Hz, H-7), 4.97 (1H, *dd*, J = 11.0, 1.5 Hz, H-16*c*), 4.94 (1H, *dd*, J = 11.0, 1.5 Hz, H-16*c*), 4.94 (1H, *dd*, J = 18.0, 1.5 Hz, H-16*t*), 1.26 (3H, *s* Me-19), 1.01 (3H, *s*, Me-17), 0.98 (3H, *s*, Me-20) ^{13}C NMR see Table 1 MS *m/z* (rel int) 302 $[C_{20}H_{30}O_2, M]^+$ (66), 287 $[M-Me]^+$ (78), 260 (74), 259 (74), 257 (60), 241 (63), 221 (81), 187 (71), 175 (64) 133 (86), 121 (82), 119 (100), 107 (79), 105 (71), 95 (78) 81 (84) 67 (87) 55 (74), 43 (73), 41 (77)

Crystallographic data for 9-epi-ent-*isopimarol* (**2**) A prismatic crystal (0.6 × 0.4 × 0.2 mm) was mounted on an automatic four-circle diffractometer (Philips PW 1100), using CuK_α radiation. The system was monoclinic, and the data collected assuming a C2 space group a = 28.812 (12) b = 7.351 (4), c = 17.882 (8) Å and β = 112.08 (8)°. The unit cell contains eight molecules. Out of 3420 measured reflections, only 2831 were considered as observed [$I > 3\sigma(I)$]. The structure was solved by direct methods [20] and the parameters refined to an R value of 5.8% [21]. The two independent molecules of the asymmetric unit appear on Fig. 1. In both, the hydroxy group takes two positions, occupied equally, corresponding to two hydrogen bonding schemes. The relative configuration is obviously the same and is represented by the formula **2**.

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