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ENT-LABDANE DERIVATIVES FROM *GUTIERREZIA GRANDIS*

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Key Word Index—*Gutierrezia grandis*; Compositae, Astereae, *ent*-labdane derivatives; 3α-angeloyloxy-18-hydroxy-13-furyl-*ent*-labda-8(17)-ene; 3α-hydroxy-18-angeloyloxy-13-furyl-*ent*-labda-8(17)-ene; 3α,18-dihydroxy-13-furyl-*ent*-labda-8(17)-ene

Abstract—Two new diterpenes, 3α-angeloyloxy-18-hydroxy-13-furyl-*ent*-labda-8(17)-ene and 3α-hydroxy-18-angeloyloxy-13-furyl-*ent*-labda-8(17)-ene and an only recently reported third diterpene, 3α,18-dihydroxy-13-furyl-*ent*-labda-8(17)-ene, were isolated from the leaves of *Gutierrezia grandis*. Their structures were determined by mass spectral, IR, ^{1}H NMR and ^{13}C NMR data was well as chemical evidence.

INTRODUCTION

In the course of a chemical investigation of the genus *Gutierrezia* (Compositae: Astereae), we studied the terpenoid constituents of *G. grandis* S. F. Blake, a somewhat rare perennial herb found in the mountains of north central Mexico between Saltillo and Monterrey. Here we report the structures of three *ent*-labdane-type diterpenes.

RESULTS AND DISCUSSION

Compound **1** represents *ca* 0.1% of the leaves of *G. grandis*; compound **2**, 0.001%; and compound **3** *ca* 8%. The evidence established that **1** is the 3-angelic ester of **3**, and that **2** has the angelate moiety at the C-18 position rather than C-3.

The electron impact mass spectrum of **1** showed a molecular ion at *m/z* 400 for $C_{25}H_{36}O_4$. All relevant spectroscopic data indicated that the compound contains an exocyclic methylene group: ^{1}H NMR signals at δ4.89 (*br s*) and 4.59 (*br s*); ^{13}C NMR signals at δ148.0 (*s*) and 106.8 (*t*); and IR ν_{max} bands at 3090, 1620 and 895 cm^{-1}. A furano group was also clearly indicated by: ^{1}H NMR proton signals at δ6.25 (*br s*), 7.35 (*dd*) and 7.19 (*br s*) [1]; ^{13}C NMR signals at δ125.6 (*s*), 111.0 (*d*), 142.8 (*d*), 138.8 (*d*); and IR ν_{max} bands at 1500 and 875 cm^{-1}. The IR absorptions at 3540 and 1060 cm^{-1} supported the presence of a hydroxyl group, the latter signal also suggesting a primary alcohol. The ^{13}C NMR [δ64.4 (*t*)] and ^{1}H NMR [δ3.55 (*d*) and 3.92 (*d*) each for one proton] signals confirmed the primary alcohol group. The angelic ester side chain was characteristically represented in the proton spectrum by signals at δ1.88 (*q*, 3H), 1.99 (*dq*, 3H) and 6.11 (*qq*, 1H). The intense mass spectral fragment at *m/z* 300 [M − MeCH=CMeCO$_2$H]$^+$ strongly supported the angelate moiety. Hydrolysis of **1** in ethanolic potassium hydroxide yielded angelic acid and the diol, **3**, which was also isolated from this extract as a natural product. Comparison of the ^{1}H NMR data of the acetate of **3** with that of **9** [2] and those reported by Bohlmann *et al.* [1, 3] suggested the *ent*-labdane skeleton as most likely. Furthermore, the chemical shifts at δ4.79 (1H, *dd*, *J* = 4.3, 11.5 Hz), and 3.74 and 3.79 (1H, *d*, *J* = 11.5 Hz) suggested that **1** and **3** have the same substitution pattern as that of **9** at the C-3 and C-18 positions. In order to confirm this as well as the angelate side chain attachment, compound **1** was oxidized with Jones reagent. The oxidized product, **4**, was obtained in high yield; it exhibited a ^{1}H NMR signal for an aldehydic proton at δ9.29. Fetizon *et al.* [4] have noted that all equatorial aldehydes at this centre come at an abnormally high field (higher than δ9.3), whereas axial substitutions appeared in the usual proton range (lower than δ9.7). Therefore, the primary hydroxyl in both **1** and **3** should be attached equatorially at the C-18 position. This is in agreement with the recent report by Bohlmann *et al.* [3]. Instead of giving an aldehyde, the oxidation of **3** by the same method gave the acetonide, **8**, as the main product along with compound **7**. The formation of **8** indicated that the two hydroxyl groups in **3** must be in spatial proximity. All the observed NMR coupling data for H-3β (*dd*, *J* = 4.3, 11.5 Hz) in **1**, **4**–**6** and **8** were in accord with these assignments. The mass spectra of compounds **4**–**8**, which were derivatives of **1** and **3**, all exhibited the expected molecular ions and fragmentations (see Experimental). The ^{13}C NMR data (Table 1) also supported the assignment of **1** as 3α-angeloyloxy-18-hydroxy-13-furyl-*ent*-labda-8(17)-ene and **3** as 3α,18-dihydroxy-13-furyl-*ent*-labda-8(17)-ene [2, 5]. Since the completion of this work compound **3** has been reported by Bohlman *et al.* [6].

Compound **2**, like **1**, exhibited a molecular ion at *m/z* 400 for $C_{25}H_{36}O_4$ and gave a characteristic angelate fragment at *m/z* 300 [M − 100]$^+$. While the IR spectra of compounds **1** and **2** were similar, the ^{1}H NMR spectra were significantly different. The AB quartet observed for **1** shifted from δ2.92 and 3.35 to 3.77 and 4.34 for **2**, with the same coupling constants of 11.5 Hz. Moreover, the 3β-proton signal shifted upfield from δ4.99 (1H, *dd*, *J* = 4.5, 11.6 Hz) in **1** to 3.44 (1H, *m*) in **2**. This evidence suggested that the angeloyl ester side chain in **2** is attached at position C-18 instead of C-3 as in **1**. The ^{13}C NMR data of

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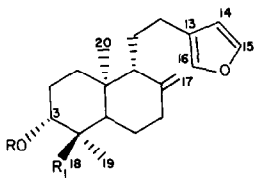
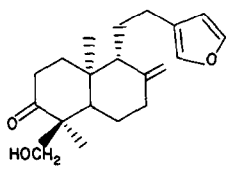


	R_1	R
1	CH_2OH	Ang
2	CH_2OAng	H
3	CH_2OH	H
4	CHO	Ang
5	CH_2OAc	Ang
6	CH_2OAc	Ac



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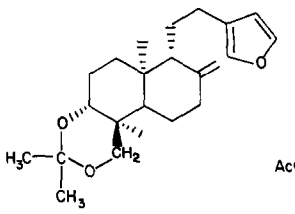

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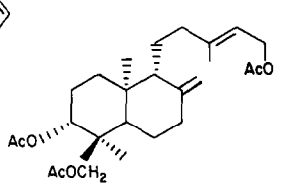

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1 and 2 showed differences primarily for C-3, C-18, C-2 and C-19 (see Table 1).

Alkaline hydrolysis of 2 yielded a single product 3. Thus, compound 2 is 3α-hydroxy-18-angeloyloxy-13-furyl-*ent*-labda-8(17)-ene.

Table 1. ^{13}C NMR chemical shifts* of 3α-angeloyloxy-18-hydroxy-13-furyl-*ent*-labda-8(17)-ene (1), 3α,18-dihydroxy-13-furyl-*ent*-labda-8(17)-ene (3) and 3α-hydroxy-18-angeloyl-oxy-13-furyl-*ent*-labda-8(17)-ene (2) (δ-values in $CDCl_3$ with TMS as int. standard)

C No.	1	2	3
C-1	37.8 *t*	38.0 *t*	37.9 *t*
C-2	24.6 *t*	26.7 *t*	27.2 *t*
C-3	74.4 *d*	72.3 *d*	75.7 *d*
C-4	42.9 *s*	42.7 *s*	42.3 *s*
C-5	46.3 *d*	47.7 *d*	48.6 *d*
C-6	24.5 *t*†	24.4 *t*†	24.3 *t*†
C-7	36.9 *t*	37.0 *t*	36.8 *t*
C-8	148.0 *s*	147.5 *s*	147.6 *s*
C-9	55.9 *d*	56.3 *d*	55.9 *d*
C-10	39.1 *s*	39.2 *s*	39.2 *s*
C-11	23.7 *t*†	23.8 *t*†	24.0 *t*†
C-12	23.5 *t*	23.6 *t*	23.5 *t*
C-13	125.6 *s*	125.5 *s*	125.4 *s*
C-14	111.0 *d*	111.0 *d*	111.0 *d*
C-15	142.8 *d*	142.8 *d*	142.7 *d*
C-16	138.8 *d*	138.8 *d*	138.8 *d*
C-17	106.8 *t*	107.1 *t*	106.9 *t*
C-18	64.6 *t*	66.3 *t*	70.4 *t*
C-19	13.0 *q*	12.0 *q*	11.6 *q*
C-20	15.2 *q*	15.1 *q*	15.0 *q*
OAng C-1′	168.8 *s*	168.4 *s*	—
C-2′	128.2 *s*	127.8 *s*	—
C-3′	138.3 *d*	138.8 *d*	—
C-4′	15.7 *q*	15.9 *q*	—
C-5′	20.6 *q*	20.7 *q*	—

*Assignments were based on compound 9 [2], manool and marrubiin [5].

†These signals may be interchanged within each column

EXPERIMENTAL

Gutierrezia grandis. S. F. Blake was collected in 1984 in the mountains of north central Mexico on the road between Monterrey and Saltillo and was identified by Meredith Lane of the University of Colorado at Boulder. A voucher specimen (Leidig 113) is deposited in the herbarium of the University of Texas at Austin.

Leaves of *G. grandis* (1.66 kg) were extracted with CH_2Cl_2 (2 × 11 l.) for 30 min. The extracts were combined and evaporated under red. pres The residue was then dissolved in Me_2CO and kept in a refrigerator. After filtering to remove the ppt, the resulting soln was then evaporated to yield a dark brown syrup (215 g). Part of the syrup (89 g, equivalent to 0.69 kg plant material) was charged onto a silica gel column, which was eluted with a hexane–EtOAc gradient solvent system. The eluate was monitored by TLC and fractions containing the same compounds were combined. CC over Sephadex LH-20 of the 90% EtOAc eluate yielded 3 in pure form. Further purifications of other fractions from the Sephadex LH-20 column were made on prep. TLC, developed with hexane–EtOAc (2:1), yielding 2 (from the 20% EtOAc eluate) and 1 (from the 15% EtOAc eluate).

3α-Angeloyloxy-18-hydroxy-13-furyl-ent-labda-8(17)-ene (1). Gum (680 mg). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3540, 1060 (OH), 1700, 1240, 1165 (α,β-unsd COOR), 3090, 1640 (C=C), 895 (C=CH_2), 1500, 875 (furan), 850 (C=CH, angelate), 1390 (Me) EIMS (probe) 70 eV, *m/z* (rel. int.): 400 $[M]^+$ ($C_{25}H_{36}O_4$) (51), 385 $[M-Me]^+$ (5), 382 $[M-H_2O]^+$ (5), 300 $[M-MeCH{=}C(Me)CO_2H]^+$ (54), 285 $[M-100-Me]^+$ (21), 282 $[M-100-H_2O]^+$ (22), 270 $[M-100-CH_2O]^+$ (100), 83 $[C_5H_7O]^+$ (81), 82 $[C_5H_6O]^+$ (70), 81 $[C_5H_5O]^+$ (88) ^1H NMR (200 MHz, $CDCl_3$): δ0.69 (3H, *s*, H-20), 0.76 (3H, *s*, H-19), 2.92 (1H, *d*, *J* = 11.5 Hz, H-18a), 3.35 (1H, *d*, *J* = 11.5 Hz, H-18b), 4.59 (1H, *br s*, H-17a), 4.89 (1H, *br s*, H-17b), 4.99 (1H, *dd*, *J* = 4.5, 11.6 Hz, H-3β), 6.25 (1H, *br s*, H-14), 7.19 (1H, *br s*, H-16), 7.35 (1H, *dd*, *J* = 1.6, 1.6 Hz, H-15), 1.88 (3H, *q*, *J* = 1.5 Hz, H-5′), 1.99 (3H, *dq*, *J* = 1.5, 7.3 Hz, H-4′), 6.11 (1H, *qq*, *J* = 1.5, 7.3 Hz, H-3′). ^{13}C NMR: see Table 1.

Acetylation of 1. Compound 1 (52 mg) was dissolved in 1 ml Ac_2O and 0.5 ml C_5H_5N and, after 2.5 hr, the soln was worked-up in the usual manner to yield 55 mg 5. IR ν_{max}^{KBr} cm^{-1}: 3140, 3080, 1650 (C=C), 895, 780 (C=CH_2), 1500, 875 (furan), 850 (C=CH, angelate), 1745 (MeCOOR), 1715 (angelate), 1385 (Me), 1240, 1160. EIMS (probe) 70 eV, *m/z* (rel. int.): 442 $[M]^+$ ($C_{27}H_{38}O_5$) (34), 427 $[M-Me]^+$ (2), 342 $[M-MeCH{=}C(Me)CO_2H]^+$ (21), 83 $[C_5H_7O]^+$ (100), 81 $[C_5H_5O]^+$ (93). ^1H NMR (200 MHz, $CDCl_3$): δ0.76 (3H, *s*, H-20), 0.86 (3H, *s*, H-19), 3.77 (1H, *d*, *J* = 11.5 Hz, H-18a), 3.83 (1H, *d*, *J* = 11.5 Hz, H-18b), 4.61 (1H, *br s*, H-17a), 4.89 (1H, *dd*, *J* = 4.6, 11.6 Hz, H-3β), 4.90 (1H, *br s*, H-17b), 6.27 (1H, *br s*, H-14), 7.20 (1H, *br s*, H-16), 7.36 (1H, *dd*, *J* = 1.6, 1.6 Hz, H-15), 2.08 (3H, *s*, OAc), 1.87 (3H, *q*, *J* = 1.5 Hz, H-5′), 1.97 (3H, *dq*, *J* = 1.5, 7.3 Hz, H-4′), 6.03 (1H, *qq*, *J* = 1.7, 7.3 Hz, H-3′).

Alkaline hydrolysis of 1. Compound 1 (330 mg) was dissolved in 3 ml EtOH, then 2 ml 12.5% KOH–EtOH was added after which the flask was flushed with N_2 and sealed. Work-up after the reaction was complete afforded compound 3 (213 mg)

IR ν_{max}^{KBr} cm^{-1}: 3420, 1160, 1020 (OH), 3080, 1640 (C=C), 890, 780 (C=CH_2), 1500, 870 (furan), 1380 (Me). EIMS (probe) 70 eV, *m/z* (rel. int.): 318 $[M]^+$ ($C_{20}H_{30}O_3$) (42), 303 $[M-Me]^+$ (10), 300 $[M-H_2O]^+$ (11), 285 $[M-18-Me]^+$ (8), 81 $[C_5H_5O]^+$ (100). The ^{1}H NMR spectrum was identical to the one recorded for **3** isolated from the extract. The saponifiable fraction afforded angelic acid. EIMS (probe) 70 eV, *m/z* (rel. int.): 100 $[M]^+$ ($C_5H_8O_2$) (100), 85 $[M-Me]^+$ (39), 55 $[M-COOH]^+$ (85), 45 $[M-(Me)C{=}CHMe]^+$ (47). ^{1}H NMR (90 MHz, $CDCl_3$): δ1.94 (3H, *br s*, H-5'), 2.05 (3H, *br d*, *J* = 7 Hz, H-4'), 6.23 (1H, *br q*, *J* = 7 Hz, H-3').

Oxidation of **1**. Compound **1** (196 mg) was dissolved in 8 ml Me_2CO and Jones reagent was added drop by drop under stirring at 5–10°, monitoring by TLC. The reaction was stopped by adding *iso*-PrOH as soon as there was only a small amount of starting material left. After work-up and purification on prep. TLC, 105 mg pure **4** was obtained. IR ν_{max}^{KBr} cm^{-1}: 3140, 3080, 1640 (C=C), 890, 780 (C=CH_2), 840 (C=CH), 1500, 870 (furan), 2700 (CHO), 1710 (C=O, Vs), 1380 (Me), 1230, 1150. EIMS (probe) 70 eV, *m/z* (rel. int.): 398 $[M]^+$ ($C_{25}H_{34}O_4$) (14), 299 $[M-MeCH{=}C(Me)COO]^+$ (13), 270 $[M-99-CHO]^+$ (100), 255 $[M-128-Me]^+$ (43), 83 $[C_5H_7O]^+$ (86), 81 $[C_5H_5O]^+$ (95). ^{1}H NMR (200 MHz, $CDCl_3$): δ0.78 (3H, *s*, H-20), 1.10 (3H, *s*, H-19), 4.64 (1H, *br s*, H-17a), 4.32 (1H, *br s*, H-17b), 5.04 (1H, *dd*, *J* = 4.3, 11.5 Hz, H-3β), 6.26 (1H, *br s*, H-14), 7.21 (1H, *br s*, H-16), 7.37 (1H, *dd*, *J* = 1.6, 1.6 Hz, H-15), 9.29 (1H, *s*, CHO), 1.82 (3H, *q*, *J* = 1.6 Hz, H-5'), 1.94 (3H, *dq*, *J* = 1.5, 7.3 Hz, H-4'), 6.04 (1H, *qq*, *J* = 1.5, 7.3 Hz, H-3').

3α,18-*Dihydroxy*-13-*furyl*-*ent*-*labda*-8(17)-*ene* (**3**). Gum (3.4 g). IR ν_{max}^{KBr} cm^{-1}: 3400, 1170, 1020 (OH), 3080, 1640 (C=C), 890, 780 (C=CH_2), 1500, 870 (furan), 1380 (Me). EIMS (probe) 70 eV, *m/z* (rel. int.): 318 $[M]^+$ ($C_{20}H_{30}O_3$) (73), 303 $[M-Me]^+$ (5), 300 $[M-H_2O]^+$ (10), 285 $[M-18-Me]^+$ (4), 81 $[C_5H_5O]^+$ (100). ^{1}H NMR (200 MHz, $CDCl_3$): δ0.73 (3H, *s*, H-20), 0.85 (3H, *s*, H-19), 3.40 (1H, *d*, *J* = 10.4 Hz, H-18a), 3.65 (1H, H-3, overlapped by H-18b), 3.67 (1H, *d*, *J* = 10.2 Hz, H-18b), 4.58 (1H, *br s*, H-17a), 4.88 (1H, *br s*, H-17b), 6.25 (1H, *br s*, H-14), 7.19 (1H, *br s*, H-16), 7.35 (1H, *dd*, *J* = 1.6, 1.6 Hz, H-15). ^{13}C NMR: see Table 1

Acetylation of **3**. Compound **3** (105 mg) was acetylated with Ac_2O and C_5H_5N in the usual way. After work-up, 128 mg diacetate (**6**) was obtained. IR ν_{max}^{KBr} cm^{-1}: 3140, 3080, 1640 (C=C), 890, 780 (C=CH_2), 1500, 870 (furan), 1730, 1240 (MeCOOR), 1370 (Me). EIMS (probe) 70 eV, *m/z* (rel. int.): 402 $[M]^+$ ($C_{24}H_{34}O_5$) (26), 387 $[M-Me]^+$ (2), 342 $[M-MeCOOH]^+$ (11), 81 $[C_5H_5O]^+$ (100). ^{1}H NMR (200 MHz, $CDCl_3$): δ0.75 (3H, *s*, H-20), 0.82 (3H, *s*, H-19), 3.74 (1H, *d*, *J* = 11.5 Hz, H-18a), 3.79 (1H, *d*, *J* = 11.5 Hz, H-18b), 4.60 (1H, *br s*, H-17a), 4.90 (1H, *br s*, H-17b), 4.79 (1H, *dd*, *J* = 4.3, 11.5 Hz, H-3β), 6.26 (1H, *br s*, H-14), 7.20 (1H, *br s*, H-16), 7.36 (1H, *dd*, *J* = 1.6, 1.6 Hz, H-15), 2.02 (3H, *s*, OAc), 2.07 (3H, *s*, OAc).

Oxidation of **3** Compound **3** (309 mg) was dissolved in 13 ml Me_2CO and oxidized with Jones reagent in the manner described above. Work-up and separation by prep. TLC, yielded **8** and **7** Compound **8**, 105 mg, gum. IR ν_{max}^{KBr} cm^{-1}: 3140, 3080, 1640 (C=C), 890 (C=CH_2), 1500, 875 (furan), 1380, 1370 [Me(Me)C]. EIMS (probe) 70 eV, *m/z* (rel. int.): 358 $[M]^+$ ($C_{23}H_{34}O_3$) (17), 343 $[M-Me]^+$ (34), 300 $[M-C_3H_6O]^+$ (30), 81 $[C_5H_5O]^+$ (100). ^{1}H NMR (200 MHz, $CDCl_3$): δ0.74 (3H, *s*, H-20), 1.03 (3H, *s*, H-19), 3.44 (1H, *d*, *J* = 10.9 Hz, H-18a), 3.52 (1H, *d*, *J* = 10.3 Hz, H-18b), 3.52 (1H, *dd*, *J* = 4.1, 11.4 Hz, H-3β), 4.59 (1H, *br s*, H-17a), 4.88 (1H, *br s*, H-17b), 6.25 (1H, *br s*, H-14), 7.20 (1H, *br s*, H-16), 7.36 (1H, *dd*, *J* = 1.6, 1.6 Hz, H-15), 1.41, 1.44 (each 3H, *s*, acetonide-Me). Compound **7**, 56 mg, gum. IR ν_{max}^{KBr} cm^{-1}: 3450, 1060 (OH), 3140, 3080, 1640 (C=C), 890 (C=CH_2), 1500, 875 (furan), 1695 (C=O), 1380 (Me). EIMS (probe) 70 eV, *m/z* (rel. int.): 316 $[M]^+$ ($C_{20}H_{28}O_3$) (37), 298 $[M-H_2O]^+$ (4), 286 $[M-CH_2O]^+$, (53), 81 $[C_5H_5O]^+$ (100). ^{1}H NMR (200 MHz, $CDCl_3$): δ0.95 (3H, *s*, H-20), 0.98 (3H, *s*, H-19), 3.37 (1H, *d*, *J* = 11.4 Hz, H-18a), 3.68 (1H, *d*, *J* = 11.5 Hz, H-18b), 4.67 (1H, *br s*, H-17a), 4.96 (1H, *br s*, H-17b), 6.27 (1H, *br s*, H-14), 7.19 (1H, *br s*, H-16), 7.36 (1H, *dd*, *J* = 1.8, 1.8 Hz, H-15).

3α-*Hydroxy*-18-*angeloyloxy*-13-*furyl*-*ent*-*labda*-8(17)-*ene* (**2**). Colourless solid (68 mg). IR ν_{max}^{KBr} cm^{-1}: 3300 (OH), 1710, 1230, 1160 (α,β-unsatd COOR), 3090, 1645 (C=C), 900, 780 (C=CH_2), 1500, 870 (furan), 850 (C=CH, angelate), 1385 (Me). EIMS (probe) 70 eV, *m/z* (rel. int.): 400 $[M]^+$ ($C_{25}H_{36}O_4$) (12), 382 $[M-H_2O]^+$ (3), 300 $[M-MeCH{=}C(Me)CO_2H]^+$ (13), 282 $[M-100-H_2O]^+$ (13), 83 $[C_5H_7O]^+$ (96), 81 $[C_5H_5O]^+$ (100). ^{1}H NMR 200 MHz, $CDCl_3$): δ0.73 (3H, *s*, H-20), 0.78 (3H, *s*, H-19), 3.44 (1H, *m*, H-3), 3.77 (1H, *d*, *J* = 11.6 Hz, H-18a), 4.34 (1H, *d*, *J* = 11.6 Hz, H-18b), 4.60 (1H, *br s*, H-17a), 4.89 (1H, *br s*, H-17b), 6.24 (1H, *br s*, H-14), 7.19 (1H, *br s*, H-16), 7.34 (1H, *dd*, *J* = 1.6, 1.6 Hz, H-15), 1.92 (3H, *q*, *J* = 1.5 Hz, H-5'), 2.01 (3H, *dq*, *J* = 1.5, 7.3 Hz, H-4'), 6.13 (1H, *qq*, *J* = 1.5, 7.3 Hz, H-3'). ^{13}C NMR: see Table 1. Compound **2** (62 mg) was hydrolysed in ethanolic KOH as described above and the work-up yielded 44 mg pure diol (**3**). IR ν_{max}^{KBr} cm^{-1}: 3400, 3080, 1640, 1500, 1380, 1170, 1020, 890, 870, 780. EIMS (probe) 70 eV, *m/z* (rel. int.): 318 $[M]^+$ ($C_{20}H_{30}O_3$) (68), 303 $[M-Me]^+$ (7), 300 $[M-H_2O]^+$ (21), 285 $[M-18-Me]^+$ (10), 81 $[C_5H_5O]^+$ (100). ^{1}H NMR (200 MHz, $CDCl_3$): δ0.73 (3H, *s*, H-20), 0.85 (3H, *s*, H-19), 3.40 (1H, *d*, *J* = 10.4 Hz, H-18a), 3.65 (1H, H-3, overlapped by H-18b), 3.67 (1H, *d*, *J* = 10.3 Hz, H-18b), 4.58 (1H, *br s*, H-17a), 4.88 (1H, *br s*, H-17b), 6.25 (1H, *br s*, H-14), 7.19 (1H, *br s*, H-16), 7.35 (1H, *dd*, *J* = 1.5, 1.5 Hz, H-15). The basic hydrolysis product (30 mg) was subjected to acetylation in the usual way and 34 mg pure diacetate was obtained. IR ν_{max}^{KBr} cm^{-1}: 3140, 3080, 1730, 1640, 1500, 1370, 1240, 1030, 890, 870, 780. EIMS (probe) 70 eV, *m/z* (rel. int.): 402 $[M]^+$ ($C_{24}H_{34}O_5$) (60), 387 $[M-Me]^+$ (4), 342 $[M-MeCOOH]^+$ (22), 81 $[C_5H_5O]^+$ (100). ^{1}H NMR (200 MHz, $CDCl_3$): δ0.75 (3H, *s*, H-20), 0.82 (3H, *s*, H-19), 3.74 (1H, *d*, *J* = 11.5 Hz, H-18a), 3.79 (1H, *d*, *J* = 11.5 Hz, H-18b), 4.60 (1H, *br s*, H-17a), 4.90 (1H, *br s*, H-17b), 4.79 (1H, *dd*, *J* = 4.3, 11.5 Hz, H-3β), 6.26 (1H, *br s*, H-14), 7.20 (1H, *br s*, H-16), 7.36 (1H, *dd*, *J* = 1.6, 1.6 Hz, H-15), 2.02 (3H, *s*, OAc), 2.07 (3H, *s*, OAc).

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