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DITERPENOIDS FROM *ACACIA LEUCOPHLOEA*

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Key Word Index—*Acacia leucophloea*; Mimosaceae; new pimar-8(14)-ene diterpenoids; ^{13}C NMR data.

Abstract—From the root bark of *Acacia leucophloea* (Mimosaceae) two new pimar-8(14)-ene diterpenoids have been isolated. Their structures have been established by chemical and spectroscopic means as 1β,15*R*,16-trihydroxypimar-8(14)-ene(leucophleol) and 15*R*,16-epoxy-1β,11α-dihydroxypimar-8(14)-ene(leucophleoxol).

INTRODUCTION

Acacia leucophloea (Roxb.) Willd. is a tree very characteristic of the dry regions of India, and its gum is used in indigenous medicine. In previous work on this plant [1, 2], some known substances were characterized. A study of the root bark has now led to the isolation of two new diterpenoids whose structures were established as 1β,15*R*,16-trihydroxypimar-8(14)-ene (**1**, leucophleol) and 15*R*-16-epoxy-1β,11α-dihydroxypimar-8(14)-ene (**2**, leucophleoxol).

RESULTS AND DISCUSSION

The first of the new diterpenoids, leucophleol (**1**), $C_{20}H_{34}O_3$, had an IR spectrum which showed strong hydroxyl (3290, 3200 cm^{-1}) and olefinic (1655, 840 cm^{-1}) absorptions and no CO bands. The ^{1}H NMR spectrum of leucophleol showed signals for one olefinic proton without vicinal hydrogen atoms (1 H, singlet at δ 5.23, $W_{1/2}$ = 4 Hz), four protons geminal to hydroxyl groups (complex signal between 3.76 and 3.26) and four C−Me singlets (0.98, 0.86, 0.83 and 0.80), whereas its MS showed the base peak at *m/e* 261 (loss of a −CHOH·CH_2OH fragment) and loss of water from the molecular and the *m/e* 261 peaks (*m/e* 304 and 243, respectively).

Acetone–anhydrous $CuSO_4$ treatment of **1** yielded an acetonide derivative (**3**) which on acetylation gave compound **4**. The ^{1}H NMR spectrum of **4** showed a 1H quartet ($J_{aa'}$ = 9, $J_{ae'}$ = 6 Hz) at δ 4.66 assigned to the proton geminal to an equatorial acetoxyl group which must be placed between a tetrasubstituted sp^3 carbon atom and a methylene grouping. The protons involved in the acetonide group (3 H) appeared as an ABC system between 3.98 and 3.54.

All the above data suggested a diterpenic structure based on the pimarene or isopimarene skeleton for leucophleol with a 1,2-dihydroxyethyl side chain, a secondary (and equatorial) hydroxyl group at the C-1, C-3 or C-12 position and a double bond between C-8 and C-14. This last assumption was also supported by the fact that the ^{1}H NMR spectrum of **1** showed a clear signal for the C-7 allylic equatorial proton (δ 2.29, *br ddd*, J_{gem} = 14 Hz, $J_{ea'}$ = 5, $J_{ee'}$ = 2 Hz, $J_{allylic} \simeq$ 1 Hz) identical with that observed in some isopimar-8(14)-ene derivatives [3].

The ^{13}C NMR spectrum of the acetonide derivative (**3**) was in complete agreement with structure **1** for leucophleol (Table 1). The location of the carbocyclic hydroxyl group at the C-1 equatorial position was supported mainly by the strong γ-gauche effect (Δδ = −6.4 ppm) shown by the C-20 carbon atom, and also by the fact that the chemical shifts of the C-1, C-2, C-3, C-4, C-5, C-9, C-10 and C-11 carbon atoms in **3** were identical with the calculated values obtained from pimar-8(14)-enes [4] taking into account the introduction of an equatorial −OH group at the C-1 position [5–7] (Table 1). On the other hand, the reported values of the C-8, C-12, C-13, C-14, C-15, C-16 and C-17 carbon resonances in 15*R*,16,18-trihydroxypimar-8(14)-ene (**5**) [8] are almost identical with the same carbon resonances calculated for leucophleol (**1**, Table 1) from the data of its derivative **3** and the observed effects caused by an acetonide group in several diterpenoids with a 1,2-dihydroxyethyl side chain (Rodríguez, B., unpublished results). In particular, the observed value for the C-8 carbon atom in **3** (138.6 ppm), which is not affected by the acetonide grouping (Rodríguez, B., unpublished results), pointed towards a pimar-8(14)-ene skeleton [4, 8] and not its C-13 epimer [9]. The latter shows a C-8 carbon resonance at 136.5 ppm and a possible deshielding δ-effect on this carbon atom in **3**, caused by the C-1 hydroxyl group, may be discarded [10]. The ^{13}C NMR data also provided proof of the stereochemistry at C-15 in leucophleol; a 15*R* configuration showed the C-15 carbon resonance at 78.2 ppm [8], almost identical with the value calculated for compound **1** (79.1 ppm, see Table 1), but very different from those reported for the 15*S* epimer (75.5 ppm) [8].

The absolute configuration of leucophleol (**1**) was established by the application of Horeau's method [11] to compound **3** (see Experimental). The absolute stereochemistry of the equatorial C-1 alcohol was 1*R* (1β-OH) and hence this new diterpenoid belongs to the *normal* series.

The other new diterpenoid isolated from *Acacia leucophloea*, leucophleoxol (**2**), had the formula

Table 1. ^{13}C NMR chemical shifts in ppm relative to TMS

Carbon No.	3	Calc. for 1*	2
1	79.1 *d*	79.1	76.0 *d*
2	29.9 *t*†	30.9	28.1 *t*
3	39.8 *t*	39.8	39.8 *t*
4	33.2 *s*	33.3	33.1 *s*
5	54.1 *d*	54.3	55.1 *d*†
6	22.4 *t*	22.9	24.3 *t*
7	36.3 *t*	36.0	36.6 *t*
8	138.6 *s*	138.3	139.7 *s*
9	52.0 *d*	51.7	59.2 *d*
10	43.9 *s*	43.7	47.4 *s*
11	21.8 *t*	21.9	69.3 *d*
12	31.8 *t*†	31.8	38.2 *t*
13	36.3 *s*	37.4	36.8 *s*
14	126.7 *d*	127.1	123.6 *d*
15	83.4 *d*	79.1	55.7 *d*†
16	65.6 *t*	63.5	44.8 *t*
17	21.7 *q*‡	21.5	24.9 *q*
18	33.2 *q*	33.9	33.5 *q*
19	22.7 *q*‡	22.5	21.4 *q*
20	8.5 *q*	9.4	12.4 *q*

* Values for C-1 to C-11 and C-18, C-19 and C-20 see refs. [4–7]; values for C-12 to C-17 calculated from **3** and ref. [9].

†, ‡ Values in any vertical column may be interchanged, but those given here are considered to be most likely.

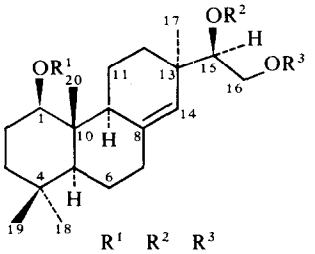
$C_{20}H_{32}O_3$ and its IR spectrum showed absorptions for strong hydrogen-bonded hydroxyl groups (3110 cm^{-1}) and for a trisubstituted olefinic double bond (1670, 865 cm^{-1}). The ^1H NMR spectrum of **2** was very informative and showed signals for one olefinic proton (δ 5.01) without vicinal protons ($W_{1/2}$ = 3 Hz), a pseudo-axial proton geminal to a secondary hydroxyl group (a five-line signal at 3.98) which may be placed in the C-11 position of a pimar-8(14)-ene skeleton with the ring C in a distorted chair conformation ($J_{11\beta,9\alpha} = J_{11\beta,12\beta}$ = 5.5, $J_{11\beta,12\alpha}$ = 11 Hz) [3], and another axial proton also geminal with another secondary hydroxyl group (3.55, $J_{aa'}$ = 8.5, $J_{ae'}$ = 6.5 Hz) which was placed between a tetrasubstituted sp^3 carbon atom and a methylene grouping as in leucophleol (**1**). In addition, the ^1H NMR spectrum of leucophleoxol (**2**) showed signals for a monosubstituted oxirane ring (1H, *q*, J_1 = 4.5, J_2 = 2.5 Hz, at δ 2.79, and a 2H octet at 2.61), for the 7β-allylic proton (equatorial) in pimar-8(14)-enes (2.28, broad eight-line signal, J_{gem} = 13 Hz, $J_{ea'}$ = 5, $J_{ee'}$ = 2, $J_{allylic} \simeq$ 1 Hz), for the H-9 proton (2.03, *br d*, $J_{9\alpha,11\beta}$ = 5.5, $J_{allylic} \simeq$ 1 Hz) (allylic and vicinal to the C-11 hydroxyl group) [3] and finally, for four C—Me singlets at 1.04, 0.98, 0.86 and 0.82. Double resonance experiments confirmed the above assignments because on irradiation at δ 3.98 (H-11) the doublet at 2.03 (H-9) collapsed to a broad singlet, whereas irradiation on H-9 (2.03) caused a narrowing ($W_{1/2}$ = 1.5 Hz) of the olefinic proton signal (5.01) and transformed the quintuplet of the C-11 proton into a quartet ($J_{11\beta,12\beta}$ = 5.5 Hz, $J_{11\beta,12\alpha}$ = 11 Hz). On the other hand, the equatorial H-7 (β) proton was also coupled (allylic coupling) with the olefinic proton (irradiation at δ 5.01 caused a narrowing of the signal at δ 2.28, and vice versa). All these data may be accommodated in structure **2** for leucophleoxol, in which the low IR hydroxyl group absorption and the small $J_{11\beta,9\alpha}$ value (*vide supra*) must be rationalized by a conformational change in ring C caused by 1β-hydroxy and 11α-hydroxy interactions [3].

Moreover, the ^{13}C NMR spectrum of leucophleoxol (Table 1) showed carbon resonances in complete agreement with the proposed structure **2** and the differences with compound **3** must be rationalized by the additional 11α-hydroxy [7, 12, 13] and the 15,16-oxirane [14] functions and also by the conformational change in ring C in the molecule of leucophleoxol (**2**).

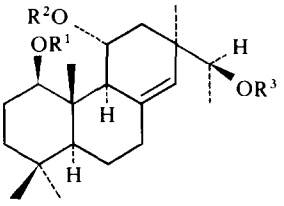
All the above assumptions, the configuration at C-15 of the oxirane ring and the absolute stereochemistry of the molecule of leucophleoxol (**2**) were confirmed as follows.

Acetic anhydride–pyridine treatment of **2** yielded a diacetate (**6**). $LiAlH_4$ reduction of leucophleoxol gave a triol (**7**), the ^1H NMR spectrum of which showed a typical pattern of a —C—CHOH—Me grouping (δ 3.56, 1 H, *q* J = 6.5 Hz, H-15; 1.14, 3 H, *d*, J = 6.5 Hz, 3H-16). Thus the presence of an oxirane ring in **2** was confirmed. Acetone–anhydrous $CuSO_4$ treatment of triol **7** yielded an acetonide derivative (**8**) which was acetylated to give **9**, the ^1H NMR spectrum of which showed the H-15 quartet paramagnetically shifted (δ 4.79, J = 6.5 Hz). Thus the acetonide formation occurred between the C-1 and C-11 hydroxyl groups.

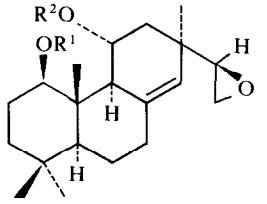
On the other hand, CrO_3–pyridine oxidation of triol **7** gave a mixture of two compounds easily separated on PLC. One of these compounds (less polar component) was the expected triketone **10** (no —OH absorption in its IR spectrum: a 3 H singlet at δ 2.20, 3 H-16; no protons geminal to hydroxyl groups) whereas the other one had structure **11** (hydroxyl group bands at 3590, 3450 cm^{-1}; δ 3.75, 1 H, *q*, $J_{aa'}$ = 9 Hz, $J_{ae'}$ = 6 Hz, H-1) (see also Experimental). Treatment of the triketone (**10**) with oxalic



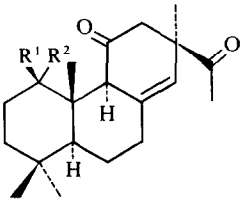
	R^1	R^2	R^3
1	H	H	H
3	H	—CMe_2—	
4	Ac	—CMe_2—	



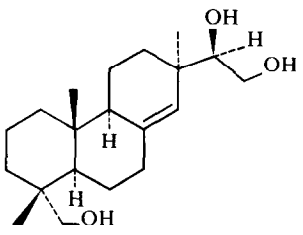
	R^1	R^2	R^3
7	H	H	H
8	—CMe_2—		H
9	—CMe_2—		Ac



2 $R^1 = R^2 = H$
6 $R^1 = R^2 = Ac$



10 $R^1, R^2 = O$
11 $R^1 = OH$; $R^2 = H$



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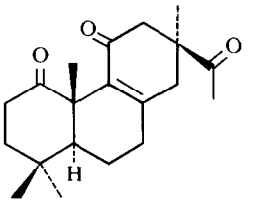

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acid in EtOH solution yielded an isomeric compound which possessed an α,β-unsaturated keto group [IRν_{max} 1663 cm^{-1}, UVλ_{max}^{EtOH} 242 nm (ε 6700)] with a tetrasubstituted olefinic double bond (no ^{1}H NMR signals below δ 3.5). Thus, structure **12** must be assigned to this compound which is in complete agreement with all the above deductions.

Finally, application of the Horeau's method [11] to compound **8** (see Experimental) defined the configuration of this centre as 15*S*, and hence as 15*R* the stereochemistry of the C-15–C-16 epoxide ring in leucophleoxol (**2**). The same procedure [11] applied to the C-1 equatorial alcohol in compound **11** (see Experimental) established the absolute configuration of this function as 1*R* (1βOH), and thus leucophleoxol belongs to the *normal* series as does leucophleol (**1**).

EXPERIMENTAL

Mps were determined in a Kofler apparatus and are uncorr. ^{1}H NMR and ^{13}C NMR spectra were measured at 100 and 25.2 MHz, respectively, in $CDCl_3$ soln with TMS as int. standard. Assignments of ^{13}C chemical shifts were made with the aid of off-resonance and noise-decoupled ^{13}C NMR spectra. Elemental analyses were carried out in Madrid, with the help of an automatic analyser. Plant materials were collected in December 1977 from the out-skirts of Jaipur (India) and voucher specimens were deposited in Rajasthan University Botanical Laboratories (Herbarium Sheet No. 11342).

Isolation of the diterpenoids. Finely ground root bark of *Acacia leucophloea* (5 kg) was extracted with C_6H_6 and the extract concd. The brownish semi-solid obtained (100 g) was chromatographed on a Si gel (Merck, No. 7734) column (150 g). Elution with C_6H_6–EtOAc (4:1) gave leucophleoxol (**2**, 450 mg); further elution with C_6H_6–EtOAc (3:1) yielded leucophleol (**1**, 250 mg).

Leucophleol (**1**). Mp 176–178° (Me_2CO–*n*-hexane); $[\alpha]_D^{19}$ + 6.5° (*c* 0.25, EtOH). IRν_{max}^{KBr} cm^{-1}: 3290, 3200, 1655, 1090, 1015, 840. ^{1}H NMR: see Discussion. MS (70 eV, direct inlet) *m/e* (rel. int.): 322 (M^+, 0.6), 304 (0.8), 289 (1), 273 (2.5), 261 (100), 243 (46), 233 (6), 187 (14), 158 (14), 121 (57), 105 (62), 95 (70), 81 (56). [Found: C, 74.37; H, 10.69. $C_{20}H_{34}O_3$ requires: C, 74.49; H, 10.63%].

Leucophleoxol (**2**). Mp 185–187° (Me_2CO–*n*-hexane); $[\alpha]_D^{20}$ − 131.0° (*c* 0.28, EtOH). IRν_{max}^{KBr} cm^{-1}: 3110, 3070, 3005, 2840, 1670, 1064, 1050, 880, 865, 828. ^{1}H NMR: see Discussion. ^{13}C NMR: see Table 1. MS (75 eV, direct inlet) *m/e* (rel. int.): 320 (M^+, 3), 305 (3), 302 (8), 287 (7), 284 (5), 271 (100), 269 (8), 257 (15), 119 (68), 105 (99), 91 (53), 81 (53), 69 (60), 55 (63), 43 (62). [Found: C, 74.95; H, 10.15. $C_{20}H_{32}O_3$ requires: C, 74.96; H, 10.06%].

Leucophleol acetonide (**3**). Leucophleol (**1**, 260 mg) was dissolved in dry Me_2CO (80 ml) and $CuSO_4$ (500 mg) was added

to the soln. The mixture was heated under reflux for 12 hr. The reaction product **3** was crystallized from *n*-hexane, mp 61–63°; $[\alpha]_D^{20}$ + 1.9° (*c* 0.48, $CHCl_3$). IR ν_{max}^{NaCl} cm^{-1}: 3490, 1660, 1220, 1170, 1070, 870, 830. ^1H NMR: δ 5.30 (1H, *br s*, $W_{1/2}$ = 4 Hz, H-14), 3.96–3.38 (4H, 16 lines, H-1, H-15 and 2H-16), 2.28 (1H, *br ddd*, J_{gem} = 14.5, $J_{ea'}$ = 5, $J_{ee'}$ = 2.5, $J_{allylic} \simeq$ 1 Hz, βH-7), 1.40 and 1.32 (3H each, *s*, acetonide), C—Me singlets at 1.01, 0.86, 0.83 and 0.81. ^{13}C NMR: see Table 1. MS (75 eV, direct inlet) *m/e* (rel. int.): 362 (M^+, 1.5), 347 (3), 329 (1.5), 304 (2), 287 (5), 269 (5), 261 (100), 243 (45), 121 (57), 105 (65), 101 (77), 95 (75), 81 (54). [Found: C, 76.28; H, 10.49. $C_{23}H_{38}O_3$ requires: C, 76.19; H, 10.57%].

Application of Horeau's method [11] *to* **3**. A mixture of (±)-α-phenylbutyric anhydride (0.43 mmol) and **3** (0.055 mmol) in Py soln (2 ml) was kept at room temp. for 16 hr. α_1 = +0.363; α_2 = +0.282; $\alpha_1 - 1.1\alpha_2$ = +0.053. Configuration 1*R*.

Acetyl derivative **4**. The hydroxyacetonide **3** (54 mg) was acetylated in the usual manner yielding **4** (53 mg): mp 127–129° (MeOH); $[\alpha]_D^{21}$ + 30.7° (*c* 0.14, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1730, 1660, 1250, 1165, 1070, 1030, 870, 830. ^1H NMR: δ 5.34 (1H, *br s*, $W_{1/2}$ = 4 Hz, H-14), 4.66 (1H, *q*, $J_{aa'}$ = 9 Hz, $J_{ae'}$ = 6 Hz, H-1), 3.98–3.54 (3H, ABC system, H-15 and 2H-16), 2.03 (3H, *s*, —OAc), 1.41 and 1.33 (3H each, *s*, acetonide), C—Me singlets at 1.02, 0.92, 0.88 and 0.86. MS (70 eV, direct inlet) *m/e* (rel. int.): 404 (M^+, 0.3), 389 (0.7), 346 (0.5), 344 (0.2), 329 (1.3), 303 (18), 302 (14), 269 (7), 261 (3), 243 (100), 227 (4), 121 (23), 101 (97), 81 (28). [Found: C, 74.33; H, 10.03. $C_{25}H_{40}O_4$ requires: C, 74.21; H, 9.97%].

Leucophleoxol diacetate (**6**). Treatment of **2** (10 mg) with Ac_2O–Py in the usual manner gave the diacetate **6**, a syrup, $[\alpha]_D^{19}$ + 17.2 (*c* 0.40, $CHCl_3$). IR ν_{max}^{NaCl} cm^{-1}: 1725, 1250, 850. ^1H NMR: δ 5.13 (2 H, complex signal, H-14 and H-11), 4.56 (1 H, *q*, $J_{aa'}$ = 10, $J_{ae'}$ = 4 Hz, H-1), 2.74–2.43 (3H, *m*, H-15 and 2H-16), 2.00 (6H, *s*, two —OAc), C—Me singlets at 1.09 (6H) and 0.87 (6H).

$LiAlH_4$ *reduction of leucophleoxol to yield triol* **7**. Compound **2** (120 mg) in Et_2O soln (30 ml) was reduced with $LiAlH_4$ (200 mg) at room temp. for 1 hr and gave **7** (118 mg). Mp 196–198° (Me_2CO–*n*-hexane); $[\alpha]_D^{21}$ – 93.9° (*c* 0.37, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3320, 3200, 1095, 1060, 910, 880. ^1H NMR: δ 5.14 (1H, *br s*, $W_{1/2}$ = 5 Hz, H-14), 4.19 (1H, *m*, $W_{1/2}$ = 18 Hz, H-11), 3.56 (1H, *q*, *J* = 6.5 Hz, H-15), 3.59 (1H, *q*, $J_{aa'}$ = 9, $J_{ae'}$ = 6 Hz, H-1), 1.14 (3H, *d*, *J* = 6.5 Hz, 3H-16), C—Me singlets at 0.99, 0.96, 0.86 and 0.82. MS (75 eV, direct inlet) *m/e* (rel. int.): 322 (M^+, 0.4), 304 (0.7), 289 (0.7), 277 (36), 259 (44), 241 (39), 145 (43), 131 (37), 123 (80), 105 (100), 95 (34), 81 (34), 69 (48). [Found: C, 74.68; H, 10.71. $C_{20}H_{34}O_3$ requires: C, 74.49; H, 10.63%].

Acetonide **8**. Triol **7** (90 mg) was treated as previously described for **1**, yielding 90 mg of the hydroxyacetonide **8**. Mp 110–112° (Me_2CO–*n*-hexane); $[\alpha]_D^{20}$ – 32.4° (*c* 0.54, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3300, 1665, 1215, 1170, 1085, 920, 885, 880, 870, 855. ^1H NMR: δ 5.13 (1H, *br s*, $W_{1/2}$ = 5 Hz, H-14), 4.35 (1H, 8 lines, *br ddd*, $J_{11\beta,9\alpha}$ = 12, $J_{11\beta,12\alpha}$ = 6.5, $J_{11\beta,12\beta}$ = 4.5, $J_{allylic} \simeq$ 1 Hz, H-11), 3.57 (2H, complex signal, H-1 and H-15), 2.31 (1H, *br ddd*, $J_{7\beta,7\alpha}$ = 14, $J_{7\beta,6\beta}$ = 5, $J_{7\beta,6\alpha}$ = 2, $J_{allylic} \simeq$ 1 Hz, equatorial H-7), 1.71 (1H, *d*, *J* = 12 Hz, with small allylic coupling, H-9), 1.44 (6H, *s*, acetonide), 1.14 (3H, *d*, *J* = 6.5 Hz, 3H-16), C—Me singlets at 1.02, 0.94, 0.86 and 0.83. MS (75 eV, direct inlet) *m/e* (rel. int.): M^+ absent, 317 (M^+ – $CHOHCH_3$ side chain, 57), 304 (2), 300 (3), 287 (2), 259 (100), 241 (70), 145 (48), 119 (45), 109 (65), 105 (87), 81 (63), 69 (48). [Found: C, 76.24; H, 10.68. $C_{23}H_{38}O_3$ requires: C, 76.19; H, 10.57%].

Application of Horeau's method [11] *to* **8**. A mixture of (±)-α-phenylbutyric anhydride (0.43 mmol) and **8** (0.066 mmol) in Py soln (2 ml) was kept at room temp. for 20 hr. α_1 = –0.600; α_2 = –0.403; $\alpha_1 - 1.1\alpha_2$ = –0.157. Configuration 15*S* (for leucophleoxol **2**, 15*R*).

Acetyl acetonide derivative **9**. Obtained from **8** (20 mg) in the usual manner. **9** (20 mg) had mp 117–119° (MeOH); $[\alpha]_D^{19}$ – 68.2° (*c* 0.43, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3030, 1737, 1240, 1095, 885, 860, 820. ^1H NMR (δ): 5.13 (1H, *br s*, $W_{1/2}$ = 4 Hz, H-14), 4.79 (1H, *q*, *J* = 6.5 Hz, H-15), 4.32 (1H, *ddd*, $J_{11\beta,9\alpha}$ = 12.5 Hz, $J_{11\beta,12\alpha}$ = 7 Hz, $J_{11\beta,12\beta}$ = 5 Hz, H-11), 3.56 (1H, *q*, $J_{1\alpha,2\beta}$ = 10 Hz, $J_{1\alpha,2\alpha}$ = 6.5 Hz, H-1), 2.31 (1H, *br ddd*, $J_{7\beta,7\alpha}$ = 13 Hz, $J_{7\beta,6\beta}$ = 5 Hz, $J_{7\beta,6\alpha}$ = 2 Hz, $J_{7\beta,14} \simeq$ 1 Hz, equatorial H-7), 2.00 (3H, *s*, —OAc), 1.68 (1H, *br d*, *J* = 12.5 Hz, $J_{allylic}$ = 1 Hz, H-9), 1.44 (6H, *s*, acetonide), 1.15 (3H, *d*, *J* = 6.5 Hz, 3H-16), C—Me singlets at 1.00, 0.98, 0.86 and 0.83. MS (75 eV, direct inlet) *m/e* (rel. int.): 404 (M^+, 0.3), 389 (0.4), 344 (0.6), 317 (48), 269 (8), 259 (100), 241 (56), 187 (48), 159 (33), 145 (53), 119 (42), 109 (53), 105 (80), 81 (68), 69 (35). [Found: C, 74.36; H, 10.04. $C_{25}H_{40}O_4$ requires: C, 74.21; H, 9.97%].

Triketone **10** *and hydroxydiketone* **11**. To a suspension of CrO_3 (300 mg) in Py (3 ml) was added triol **7** (45 mg) in Py soln (3 ml). The mixture was left 24 hr at room temp. The soln was diluted with H_2O and extracted with Et_2O. The Et_2O extract was dried and evapd. The residue was a mixture of two compounds which were easily separated by PLC on Si gel plates developed with $CHCl_3$–MeOH (19:1). *Triketone* **10** (16 mg, less polar component): mp 97–100° (MeOH); $[\alpha]_D^{20}$ + 78.7 (*c* 0.16, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1700 (strong), 1100, 955, 875, 840. ^1H NMR: δ 5.79 (1H, *br s*, $W_{1/2}$ = 5 Hz, H-14), 3.40 (1H, *br s*, $W_{1/2}$ = 5 Hz, H-9), 2.20 (3H, *s*, 3H-16), C—Me singlets at 1.24, 1.12, 1.10 and 0.92. MS (75 eV, direct inlet) *m/e* (rel. int.): 316 (M^+, 5), 301 (2), 287 (9), 273 (70), 255 (18), 161 (42), 121 (44), 113 (86), 95 (44), 43 (100). [Found: C, 75.87; H, 9.03. $C_{20}H_{28}O_3$ requires: C, 75.91; H, 8.92%]. *Hydroxydiketone* **11** (12.7 mg, most polar component): mp 147–149° (Me_2CO–*n*-hexane); $[\alpha]_D^{20}$ – 217.2° (*c* 0.21, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3595, 3450, 1715, 1690, 1287, 1140, 1050, 1040, 980, 865. ^1H NMR: δ 5.53 (1H, *br s*, $W_{1/2}$ = 5 Hz, H-14), 3.75 (1H, *q*, $J_{1\alpha,2\beta}$ = 9 Hz, $J_{1\alpha,2\alpha}$ = 6 Hz, H-1), 2.05 (3H, *s*, 3H-16), C—Me singlets at 1.35, 1.03, 0.89 and 0.85. MS (75 eV, direct inlet) *m/e* (rel. int.): 318 (M^+, 0.6), 303 (1), 300 (0.4), 275 (36), 257 (31), 161 (35), 147 (40), 135 (32), 123 (54), 121 (100), 69 (29), 43 (36). [Found: C, 75.61; H, 9.46. $C_{20}H_{30}O_3$ requires: C, 75.43; H, 9.50%].

Application of Horeau's method [11] *to* **11**. A mixture of (±)-α-phenylbutyric anhydride (0.12 mmol) and **11** (0.036 mmol) in Py soln (2 ml) was kept at room temp. for 20 hr. α_1 = –0.404; α_2 = –0.458; $\alpha_1 - 1.1\alpha_2$ = +0.100. Configuration 1*R*.

Double bond isomerization of **10** *to produce* **12**. Compound **10** (9 mg) and oxalic acid (3 mg) in EtOH soln (5 ml) were heated under reflux for 24 hr. The solvent was evapd and the residue was chromatographed on a TLC aluminium sheet of Si gel 60 F_{254} (Merck, Art. 5554) eluted with EtOAc–*n*-hexane (1:1) yielding **12** (6 mg): mp 137–138° (EtOAc–*n*-hexane); $[\alpha]_D^{19}$ + 68.1° (*c* 0.066, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 1703 *br*, 1660, 1630 (double bond), 1300, 1112, 1030, 1006, 965, 890, 735. ^1H NMR: δ 2.26 (3H, *s*, 3H-16), C—Me singlets at 1.58, 1.15, 1.12 and 0.92. UV λ_{max}^{EtOH} nm (ε): 242 (6700). MS (75 eV, direct inlet) *m/e* (rel. int.): 316 (M^+, 40), 301 (6), 273 (89), 260 (41), 255 (26), 242 (16), 232 (7), 217 (58), 199 (45), 175 (74), 161 (64), 147 (40), 113 (77), 43 (100). [Found: C, 76.04; H, 8.91. $C_{20}H_{28}O_3$ requires: C, 75.91; H, 8.92%].

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