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EUDESMANOLIDES FROM *CHAMAEMELUM FUSCATUM*

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Key Word Index—*Chamaemelum fuscatum*; Compositae; sesquiterpene lactones; eudesmanolides.

Abstract—The aerial parts of *Chamaemelum fuscatum* afforded, in addition to the known sesquiterpene lactones santamarine and armexifolin, six new related eudesmanolides, 8α-methacryloyloxybalchanin, 8α-isobutyryloxybalchanin, 8α-methacryloyloxyarmexifolin, 8α-isobutyryloxyarmexifolin, 8α-methacryloyloxyarmefolin and 8α-isobutyryloxyarmefolin. The structures were elucidated by spectroscopic methods and chemical transformations.

INTRODUCTION

In a previous paper on the essential oil of *Chamaemelum fuscatum* (Brot.) Vasc.* [1], we described the isolation, identification and synthesis of some new natural esters, whose structures were very close to those described in other species of the genus *Anthemis* [2, 3].

Following on from there studies we have analysed the chloroform extract of the aerial parts of *C. fuscatum* which afforded, besides the previously known santamarine (**1**) [4] and armexifolin (**2**) [5], six new related eudesmanolides **3a**, **4a**, **5a**, **6a**, **7a** and **8a**.

RESULTS AND DISCUSSION

Compounds **3a** and **4a** were obtained as a crystalline dextrorotatory mixture. They could not be separated from each other. The IR spectrum of the mixture showed absorption bands of α,β-unsaturated-γ-lactone (1765 cm^{-1}), ester (1725 cm^{-1}) and hydroxyl (3510 cm^{-1}) groups. The ^1H NMR spectrum (Table 1) showed signals corresponding to H-5 (*d*), H-6 (*dd*), H-7 (*dddd*) and H-8 (*ddd*), besides those of an olefinic hydrogen. These signals denoted the presence of a C-6-*trans* fused lactone ring, a C-8 α-equatorial ester and Δ^3 unsaturation. A signal at δ3.62 (*dd*) was assigned to a hydrogen geminal to a β-equatorial hydroxyl group at C-1. In the acetylated mixture (**3b** and **4b**) this signal was deshielded at δ4.87 (*dd*). This spectrum was very similar to that of 8α-hydroxybalchanin (**6**) except for the H-8 signal which appeared at δ5.25. The remaining signals correspond to those of methacrylate (δ6.07, 5.57 and 1.90) and isobutyrate (δ2.50, 1.14 and 1.12) esters. The ^{13}C NMR spectrum (Table 2) was also very close to that of 8α-hydroxybalchanin with the C-8 signal at δ69.6, methacrylate signals at δ166.4, 136.3 126.3 and 18.2 and isobutyrate signals at δ176.4, 34.5, 19.2 and 19.2. This was in agreement with the mass spectrum which in addition to the base peak at *m/z* 228 ($[M - H_2 - MacOH]^+$ for **3a**, and $[M - H_2O - BuOH]^+$ for **4a**) displayed two peaks at *m/z* 314 ($[M - H_2O]^+$ for **3a** and *m/z* 316 $[M - H_2O]^+$ for **4a**). With these data we assigned the structure of 8α-methacryloyloxybalchanin (**3a**) and 8α-isobutyryloxybalchanin (**4a**) to these new natural products. On saponification of the mixture in the usual way (KOH–MeOH), **3c** was produced by saponification of the ester group at C-8 in **3a** or **4a** and addition of methanol to the α-methylene-γ-lactone group. Treatment with aqueous KOH afforded a small amount of saponification product identical to the known 8α-hyroxybalchanin. These facts confirmed the proposed structures for **3a** and **4a**.

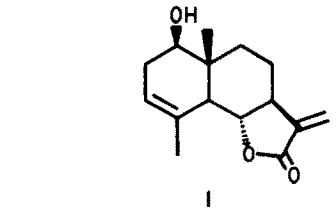
Compound **5a**, mp 206°, also gave rise to IR absorption bands of α,β-unsaturated-γ-lactone, ester and hydroxyl groups, and another band at 1680 cm^{-1} corresponding to an α,β-unsaturated ketone, that absorbs at 240 nm in the UV. On acetylation no hydroxyl band was observed in the IR spectrum. In the ^1H NMR spectrum (Table 1) of **5a** the signals corresponding to H-6 (*dq*) coupled with Me-15 (δ2.07 *d*, $J = 1.7$ Hz), H-7 (*dddd*) and H-8 (*ddd*) suggested a eudesmanolide structure with Δ^4 unsaturation, *trans*-fusion of the lactone ring system and an equatorial ester group at C-8. The signal at δ3.93 (*dd*), which on acetylation was deshielded (δ5.12, *dd*), was assigned to a hydrogen geminal to an equatorial hydroxyl at C-1. In the ^{13}C NMR spectrum (Table 2) the signal of the α,β-unsaturated-γ-lactone, α,β-unsaturated ketone, two oxygenated methynes, a quaternary carbon, two methylene and two methyl groups were observed. These spectra were almost superimposable upon those of 8α-acetoxyarmexifolin (**7**) except for the signals of the ester at C-8, which in **5a** corresponded to methacrylate. Consequently **5a** must be 8α-methacryloyloxyarmexifolin. No molecular ion was observed in the mass spectrum but the fragments at *m/z* 260 $[M - C_4H_6O_2]^+$ and 242 $[M - H_2O - C_4H_6O_2]^+$ were in agreement with the formula $C_{19}H_{22}O_6$. The absolute configuration of compound **5a** was determined on the basis of the observed maxima in the CD spectrum: 325 ($\Delta\varepsilon$ −1.68), 382 ($\Delta\varepsilon$ +0.90) and 216 ($\Delta\varepsilon$ +2.12) for the enone corresponding with the double bond in the first quadrant, the positive dihedral angle and the *P* absolute configuration [8] of the bicyclic system respectively, and 267 ($\Delta\varepsilon$ −0.63) for the *trans*-fused α-methylene-γ-lactone corresponding with an *R* configuration at C-7.

*The material was identified by Prof. B. Casaseca Mena, from the Botany Department of Salamanca University, where a specimen is held (Herbarium no. 6679).

Table 1. ^{1}H NMR spectral data of compounds 3–9 (200 MHz, $CDCl_3$, TMS as internal standard)

H	3a + 4a	3c	5a	6a	5b	6b	7a	8a	7b	8b	9
1	3.62 *dd* (9.7, 6.5)	3.69 *dd* (9.8, 6.8)	3.93 *dd* (12.3, 5.4)	3.92 *dd* (12.2, 5.4)	5.12 *dd* (12.7, 5.2)	5.10 *dd* (12.7, 5.1)	3.83 *t* (8)	3.80 *t* (8)	5.02 *m*		5.02 *dd* (9.7, 6.7)
2	2.5–2.2 *m*	2.5–2.2 *m*	2.72 *dd* (16.6, 5.4)		2.78 *dd* (16.5, 5.1)		1.90–1.75 *m*		2.0–1.8 *m*		2.0–1.8 *m*
2′	2.0–1.8 *m*	2.0–1.8 *m*	2.60 *dd* (16.6, 12.3)		2.58 *dd* (16.5, 13.0)		1.90–1.75 *m*		2.0–1.8 *m*		2.0–1.8 *m*
3	5.31 *m*	5.37 *m*					3.99 *br s*	3.98 *br s*	5.21 *br s*	5.20 *br s*	5.20 *br s*
5	2.34 *d* (11.6)	2.5–2.2 *m*									
6	4.01 *dd* (11.6, 10.8)	4.06 *dd* (10.7, 10.6)	4.87 *dq* (12.5, 1.7)	4.89 *dq* (2.5, 1.7)	4.87 *dq* (12.2, 1.7)	4.89 *dq* (12.3, 1.7)	4.68 *dq* (11.7, 1.7)	4.69 *dq* (11.7, 1.7)	4.73 *dq* (11.9, 1.9)	4.72 *dq* (11.9, 1.9)	4.73 *dq* (11.6, 1.4)
7	2.82 *dddd* (10.8, 10.8 3.2, 3.0)	2.5–2.2 *m*	3.17 *dddd* (12.5, 10.7, 3.1, 2.9)		3.18 *dddd* (12.2, 10.6, 3.1, 2.9)		3.02 *dddd* (11.7, 10.9, 3.0, 2.9)	3.01 *dddd* (11.7, 10.9, 3.0, 2.9)	3.11 *dddd* (11.9, 10.7, 3.3, 3.0)		2.58 *ddd* (10.7, 10.7, 10.6)
8	5.25 *ddd* (10.8, 10.8, 4.5)	3.91 *dt* (10.4, 10.4, 4.6)	5.34 *ddd* (10.7, 10.7, 4.7)	5.27 *ddd* (10.7, 10.7, 4.7)	5.31 *ddd* (10.6, 10.6, 4.6)	5.25 *ddd* (10.6, 10.6, 4.6)	5.22 *ddd* (10.9, 10.9, 4.5)	5.16 *ddd* (10.9, 10.9, 4.5)	5.27 *ddd* (10.7, 10.7, 4.4)	5.22 *ddd* (10.7, 10.7, 4.4)	5.13 *ddd* (10.7, 10.7, 4.6)
9	2.47 *dd* (12.7, 4.5)	2.37 *dd* (13.0, 4.5)	2.71 *dd* (12.8, 4.7)		2.42 *dd* (12.7, 4.6)		2.57 *dd* (13.7, 4.5)		2.28 *dd* (13.5, 4.4)		2.2–1.9 *m*
9′	1.25 *dd* (12.7, 10.8)	1.3–1.1 *m*	1.50 *dd* (12.8, 10.7)		1.51 *dd* (12.7, 10.6)		1.36 *dd* (13.7, 10.9)		1.46 *dd* (13.5, 10.7)		1.46 *dd* (13.5, 10.7)
11		2.82 *ddd* (12.3, 10.3, 3.7)									2.70 *ddd* (10.7, 2.9, 2.9)
13	6.06 *d* (3.2)		6.30 *d* (3.1)		6.30 *d* (3.1)		6.20 *d* (3.0)		6.22 *d* (3.3)		3.78 *dd* (9.8, 2.9)
13′	5.47 *d* (3.0)	4.00 *m*	5.74 *d* (2.9)		5.73 *d* (2.9)		5.65 *d* (2.9)		5.67 *d* (3.0)		3.52 *dd* (9.8, 2.9)
14	0.90 *s*	0.92 *s*	1.39 *s*		1.45 *s*		1.13 *s*		1.28 *s*		1.24 *s*
15	1.79 *s*	1.83 *s*	2.07 *d* (1.7)		2.05 *s* (1.7)		2.01 *d* (1.7)		1.97 *d* (1.9)		1.89 *d* (1.4)
Mac	6.07 *br s* 5.57 *t* (1.5) 1.90 *br s*		6.17 *br s* 5.70 *t* (1.6) 1.99 *br s*		6.17 *br s* 5.71 *t* (1.6) 1.98 *br s*		6.13 *br s* 5.65 *t* (1.5) 1.95 *br s*		6.15 *br s* 5.66 *t* (1.5) 1.94 *br s*		
iso-Bu	2.50 *m* 1.14 *d* (7.1) 1.12 *d* (6.9)			2.60 *m* 1.15 *d* (6) 1.11*d* (6)		2.60 *m* 1.28 *d* (7.1) 1.21 *d* (6.9)		2.57 *m* 1.20 *d* (7.0) 1.18 *d* (6.9)		2.60 *m* 1.22 *d* (6.9) 1.20 *d* (7.0)	
OAc					2.10 *s*				2.07 *s* 2.10 *s*		2.07 *s* 2.07 *s* 2.11 *s*
OMe		3.48 *s*									3.36 *s*

*J in Hz.



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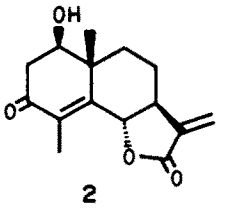

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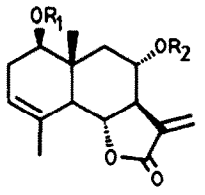
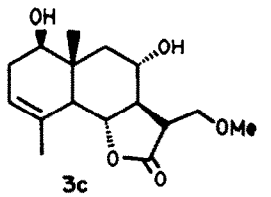
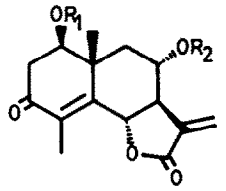


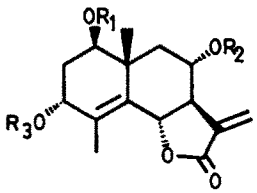
3a R_1 =H ; R_2 =Mac
3b R_1 =Ac ; R_2 =Mac
4a R_1 =H ; R_2 = i Bu
4b R_1 =Ac ; R_2 = i Bu



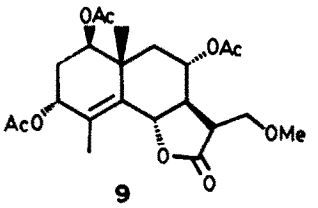
3c



5a R_1 =H ; R_2 =Mac
5b R_1 =Ac ; R_2 =Mac
6a R_1 =H ; R_2 = i Bu
6b R_1 =Ac ; R_2 = i Bu



7a R_1 = R_3 =H ; R_2 =Mac
7b R_1 = R_3 =Ac ; R_2 =Mac
8a R_1 = R_3 =H ; R_2 = iBu
8b R_1 = R_3 =Ac ; R_2 = iBu



9

Compound **6a**, mp 225° was very similar to **5a** (Tables 1 and 2), except that the methylacrylate group at C-8 had been replaced by isobutyrate (^{1}H NMR: δ2.61 (1H), 1.15 (3H) and 1.11 (3H); ^{13}C NMR: δ176.1, 34.2, 19.0 and 18.3).

Compound **7a** showed in the MS an ion at m/z 330 $[M - H_2O]^+$ in agreement with the formula $C_{19}H_{24}O_6$. In its IR spectrum bands of α,β-unsaturated-γ-lactone and ester groups were observed, besides a strong hydroxyl absorption which was absent from the acetylated product. The ^{1}H NMR spectrum (Table 1) corresponded with a eudesmanolide related to the other isolated compounds of the extract, having a *trans*-fused lactone ring ($J_{6,7}$ = 11.2 Hz), Δ^4-unsaturation, an α-equatorial ester at C-8 and a β-equatorial hydroxyl at C-1; in addition, a broad singlet at δ3.99 was assigned to an allylic proton geminal with a hydroxyl. The acetylated product **7b** showed two acetate methyls (δ2.07 and 2.10) and the deshielding to δ5.02 (*dd*) and 5.21 (*br s*) of the hydrogens geminal with oxygenated functions. The ^{13}C NMR spectrum (Table 2) showed, besides other signals, those of an α,β-unsaturated-γ-lactone, a tetrasubstituted double bond and three oxygenated methynes. These data and the H/H (COSY) two-dimensional correlations led us to assign the depicted structure for **7a**. The presence of a C-1 β-equatorial and a C-3 α-quasiaxial hydroxyl group have been observed in the related eudesmanolide armefolin, but this substance has no oxygenated function at C-8.

Compound **8a** showed in the MS an ion at m/z 332 $[M - H_2O]^+$ in agreement with the formula $C_{19}H_{26}O_6$. From a comparison of its spectroscopic properties and those of its diacetate **8b** with those of **7a** and **7b** it was deduced that **8a** was the corresponding C-8 isobutyrate ester. Chromic acid oxidation of **7a** and **8a** afforded the above described ketones **5a** and **6a**. This fact confirmed the proposed structures for **7a** and **8a**, that have not been previously described in the literature, as the mono esterified derivatives of the same triol.

Saponification of **7a** and **8a** followed by addition of 4-phenylphenacyl bromide and acetylation gives the product **9**, and the phenacylic esters of methacrylic and isobutyric acids. Compound **9** was a methoxy triacetate produced by saponification of the ester group at C-8 and acetylation of the C-1, C-3 and C-8 hydroxyls accompanied by the usual conjugated addition of a methoxy group to the α,β-unsaturated-γ-lactone. The structure of **9** was determinated by means of its spectroscopic properties and H/H (COSY) two dimensional correlations.

The coexistence of these structurally related com-

Table 2. ^{13}C NMR spectral data of compounds 3–9 (50.3 MHz, $CDCl_3$, chem. shifts are in δ-values from TMS)

C No	3a + 4a		3c	5a	6a	7a	8a	9
1	74.9		75.2	74.1	74.4	70.7	70.1	70.1
2	32.6		32.4	42.3	42.3	35.7	35.8	29.5
3	121.8		121.9	196.5	196.5	72.5	72.5	72.5
4	132.5		132.6	130.4	130.4	131.7	131.7	133.4
5	50.4		49.8	150.1	150.2	128.4	128.4	125.1
6	78.9		79.5	78.5	78.4	79.1	79.1	78.1
7	53.7		60.2	51.0	51.0	51.8	51.8	49.5
8	69.6		66.7	70.0	70.2	71.4	71.3	74.4
9	41.0		43.1	44.1	44.1	44.2	44.3	43.3
10	40.5		40.3	43.3	43.5	41.8	41.9	40.2
11	135.9		46.6	135.4	135.4	136.1	136.3	45.9
12	169.7		174.7	168.2	168.2	169.5	169.5	169.9
13	119.3		71.5	122.5	122.5	121.6	121.6	68.7
14	12.1		12.3	18.7	18.7	18.2	18.9	19.4
15	23.1		23.1	11.1	11.1	17.6	17.6	17.1
1′	166.4	176.4	—	166.2	176.1	169.2	176.3	—
2′	136.3	34.5	—	135.3	34.2	136.0	34.2	—
3′	126.3	19.2	—	126.7	18.3	126.5	18.4	—
4′	18.2	19.2	—	18.1	19.0	18.4	18.4	—
OCOMe	—	—	—	—	—	—	—	170.4
OCOMe	—	—	—	—	—	—	—	20.9
OCOMe	—	—	—	—	—	—	—	170.4
OCOMe	—	—	—	—	—	—	—	20.9
OCOMe	—	—	—	—	—	—	—	170.1
OCOMe	—	—	—	—	—	—	—	20.9
OMe	—	—	59.3	—	—	—	—	59.1

pounds is usually found in the sesquiterpene lactone field and indicates a common biosynthetic pathway.

EXPERIMENTAL

Mps: uncorr; optical rotations: $CHCl_3$; UV: EtOH; IR: KBr or film; ^1H NMR: 200 MHz, $CDCl_3$, TMS as int. standard; ^{13}C NMR: 50.3 MHz; MS: 70 eV; CD: EtOH.

Extraction and separation of compounds. Air-dried plant material (14 kg) (collected in Zarza de Granadilla, Cáceres, SW Spain, in April 1983) was extracted with $CHCl_3$ and the neutral fraction of the EtOH–H_2O (2:3) soluble extract chromatographed over silica gel developed with C_6H_6, C_6H_6–Et_2O and C_6H_6–EtOAc mixtures of increasing polarity to give 3 + 4 (600 mg; C_6H_6–Et_2O, 7:3), 5 + 6 (500 mg; C_6H_6–Et_2O, 1:1) and 7 + 8 (800 mg; C_6H_6–EtOAc, 2:3). The different components were purified by repeated prep. CC or TLC or crystallization.

8α-Methacryloyloxybalchanin (**3a**) *and 8α-isobutyryloxybalchanin* (**4a**). The mixture of **3a** and **4a** was chromatographed and crystallized (CH_2Cl_2–hexane) several times, but no separation of **3a** from **4a** was obtained. IR ν_{max}^{KBr} cm^{-1}: 3510, 3040, 1765, 1725, 1680, 1640; MS *m/z* (rel. int.): 316 (4), 314 (5), 246 (16), 228 (100), 213 (25), 150 (31), 122 (68), 71 (32), 69 (100).

Acetylation of **3a** *and* **4a**. Treatment of a crystalline mixture of **3a** and **4a** with Ac_2O–C_5H_5N in the usual way afforded a mixture of the acetates **3b** and **4b**. IR ν_{max} cm^{-1}: 3040, 1780, 1750, 1735, 1230, 890.

Saponification of **3a** *and* **4a**. (a) A mixture (90 mg) of **3a** and **4a** was treated with 2 ml 2M KOH (MeOH) and the mixture kept at room temp. for 12 hr. After acidification, EtOAc extraction and CC, 43 mg **3c** were obtained. IR ν_{max} cm^{-1}: 3425, 3030, 1770, 1670, 1270, 1050;

$$[\alpha]^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436}{+83.8 \quad +87.3 \quad +99.8 \quad +171.7} \ (c\ 0.7).$$

(b) A mixture (90 mg) of **3a** and **4a** was treated with 8 ml 0.2 M KOH in H_2O and the mixture was stirred at room temp. for 38 hr. After acidification, EtOAc extraction and CC, 12 mg 8α-hydroxybalchanin (**6**) were obtained.

8α-Methacryloyloxyarmexifolin (**5a**). Colourless crystals, mp 206° (CH_2Cl_2–hexane). IR ν_{max} cm^{-1}: 3480, 1770, 1730, 1680, 1640, 880; UV λ_{max} nm: 247 (ε 3680); MS *m/z* (rel. int.): 260 (33), 242 (23), 216 (50), 188 (28), 145 (17), 85 (46), 69 (100);

$$[\alpha]^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436}{+161.2 \quad +187.6 \quad +213.4 \quad +351.1} \ (c\ 1.9).$$

Acetylation of **5a** afforded the monoacetate **5b**. Colourless crystals mp 152° (Et_2O–hexane). IR ν_{max} cm^{-1}: 1775, 1745, 1720, 1675, 1630, 1230.

8α-Isobutyryloxyarmexifolin (**6a**). Colourless crystals, mp 225° (CH_2Cl_2–hexane). IR ν_{max} cm^{-1}: 3525, 1780, 1740, 1680, 1640; UV λ_{max} nm: 242 (ε 2246);

$$[\alpha]^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436}{+113.4 \quad +119.5 \quad +135.1 \quad +220.8} \ (c\ 1).$$

Acetylation of **6a** gave the monoacetate **6b**. Colourless crystals, mp 158 (Et_2O–hexane). IR ν_{max} cm^{-1}: 1780, 1745, 1680, 1630, 1230.

8α-Methacryloyloxyarmexifolin (**7a**). Obtained as a colourless

gum. IR ν_{max} cm^{-1}: 3400, 1785, 1730, 1650; MS *m/z* (rel. int.): 330 (3), 262 (1), 244 (9), 226 (22), 211 (22), 124 (15), 85 (27), 69 (61), 41 (100);

$$[\alpha]^{\lambda} = \frac{589 \quad 568 \quad 546 \quad 436}{+171.6 \quad +179.2 \quad +205.1 \quad +356.3} (c\ 1.1)$$

Acetylation of **7a** afforded the diacetate **7b**. Colourless gum. IR ν_{max} cm^{-1}: 1785, 1750, 1730, 1645, 1240;

$$[\alpha]^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436}{+124.4 \quad +132.8 \quad +150.2 \quad +273.2} (c\ 0.6)$$

8α-Isobutyryloxyarmefolin (**8a**). Obtained as a colourless gum. IR ν_{max} cm^{-1}: 3400, 1780, 1730, 1640. MS *m/z* (rel. int.): 332 (5), 262 (2), 244 (24), 226 (33), 211 (56), 161 (22), 87 (50), 71 (45);

$$[\alpha]^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436}{+179.2 \quad +204.0 \quad +354.2 \quad +401.8} (c\ 1).$$

Acetylation of **8a** afforded the diacetate **8b**. Colourless gum. IR ν_{max} cm^{-1}: 1780, 1740, 1725, 1645, 1240;

$$[\alpha]^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436}{+167.6 \quad +174.1 \quad +200.7 \quad +360.0} (c\ 1.2).$$

Saponification of **7a** *and* **8a**. A mixture (360 mg) of **7a** and **8a** in 2 ml of methanolic KOH (2M) was kept at room temp. for 12 hr. It was then acidified (phenolphtalein) with 2 M HCl, and after the addition of 290 mg 4-phenyl phenacylbromide in EtOH (15 ml) was refluxed for 30 min, evaporated to dryness, dissolved in H_2O and extracted with Et_2O. The organic layer (350 mg) was chromatographed (silica gel) to afford **10** (90 mg) and **11** (60 mg).

4-Phenylphenacylisobutyrate (**10**). White crystals, mp 83°. IR ν_{max} cm^{-1}: 3040, 1760, 1710, 1625, 1510, 1230, 1175, 990, 710, 680; ^{1}H NMR (60 MHz): δ1.28 (6H, *d*, *J* = 7 Hz), 2.75 (1H, *m*), 5.35 (2H, *s*), 7.40–8.00 (9H).

4-Phenylphenacyl-3-methoxy-2-methylpropionate (**11**). White crystals mp 125° IR ν_{max} cm^{-1}: 3050, 1750, 1705, 1620, 1500, 1230, 1130, 990, 710, 680; ^{1}H NMR (60 MHz): δ1.26 (3H, *d*, *J* = 6.5 Hz), 2.90 (1H, *c*, *J* = 6.5 Hz), 3.30 (3H, *s*), 5.32 (2H, *s*), 7.30–8.00 (9H).

The water-soluble fraction was acidified with 2 M HCl, heated for 5 min at 90°, neutralized, evaporated to dryness and acetylated. The reaction product (350 mg) was chromatographed (silica gel) to afford 253 mg **9**. Colourless gum. IR ν_{max} cm^{-1}: 1775, 1745, 1730, 1240, 1170, 1120, 1030, 970;

$$[\alpha]^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436}{-175.4 \quad -184.5 \quad -218.3 \quad -515.2} (c\ 1).$$

Oxidation of **7a** *and* **8a**. A mixture 200 mg of **7a** and **8a** was disolved in C_5H_5N (0.5 ml) and added to a soln of CrO_3 (200 mg) in C_5H_5N (2 ml) and CH_2Cl_2 (8 ml). The mixture was stirred for 3.5 hr in an ice water bath under N_2. The oxidation product was chromatographed over silica gel. Elution with C_6H_6–MeOH (99:1) afforded 64 mg of a crystalline product, mp 206° and 12 mg of another crystalline product, mp 225°. The identity of the compounds with **5a** and **6a** was established by direct comparison.

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