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TRIACYL GLUCOPYRANOSES FROM *BAHIA SCHAFFNERI*

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Key Word Index—*Bahia schaffneri*; Bahiinae; Heliantheae; Compositae; triterpene, flavonoids, germacranolides; triacyl glucopyranoses

Abstract—The aerial parts of *Bahia schaffneri* afforded some known compounds and three new triacyl glucopyranoses, 2-*O*-acetyl-1-*O*-isobutyryl-6-*O*-tiglyl-β-D-glucopyranose, 2-*O*-acetyl-1-*O*-isovaleryl-6-*O*-tiglyl-β-D-glucopyranose and 2-*O*-acetyl-1-*O*-isobutyryl-6-*O*-(2-methylbutyryl)-β-D-glucopyranose. Their structures were deduced by spectroscopic methods and chemical transformations.

INTRODUCTION

Previous chemical investigations have shown that the genus *Bahia* elaborates flavonoids [1, 2], diterpenes [2], guaianolides [3, 4] and heliangolides [1, 2]. The presence of an eudesmanolide glucoside has also been reported [2]. In continuation of our studies of this genus, we examined chemically *B. schaffneri* S. Wats. var. *schaffneri*, collected in the arid lands of northern Mexico. This plant afforded three triacyl glucopyranoses, **3a–c** and the known compounds eupatolide (**1a**) [5], eupatoriopicrin (**1b**) [5], bonanzin (**2a**) [6] and centaureidin (**2b**) [7]. The acylated glucopyranoses are probably involved in the protection of *B. schaffneri* against desiccation in the dry conditions of its habitat [8].

RESULTS AND DISCUSSION

The hexane extract of *B. schaffneri* var. *schaffneri* afforded Ψ-taraxasterol and a mixture of **3a–c**. These glucolipids were also obtained from the chloroform–dichloromethane–ethyl acetate extract along with the known compounds eupatolide (**1a**) [5], eupatoriopicrin (**1b**) [5] and centaureidin (**2b**) [7], which were characterized spectroscopically and compared with authentic samples. We also obtained the flavone **2a** whose mp and spectroscopic data are similar to those reported for bonanzin [6]. Its UV spectra (in MeOH, MeOH + $AlCl_3$ and MeOH + $AlCl_3$ + HCl) are in complete agreement with the published data [9].

The major component of the mixture **3a**, $C_{17}H_{26}O_9$, was separated by HPLC and column chromatography (see Experimental). It showed in the IR, bands at 3500, 1760, 1730 and 1710 cm^{-1} which indicated the presence of alcohol groups and three ester groups. The ^1H and ^{13}C NMR spectra (Tables 1 and 2) showed the signals of acetyl, isobutyryl and tiglyl groups attached to a glucopyranose. That the monosaccharide is a β-D-glucopyranose with an acyl group bonded to C-1 was indicated by the typical chemical shifts of acylated glucopyranoses [10, 11]. The other two acyl groups had to be attached to C-2 and C-6 as indicated by the chemical shift of H-2, H-6a and H-6b (δ4.92, 4.65 and 4.25). Therefore the glucolipid possesses the structure **3a** although at this stage of the characterization the positions of the different ester groups remained to be established.

Compound **3b**, $C_{18}H_{28}O_9$, has a structure similar to that of **3a**, the only difference being the presence of an isovalerate ester instead of an isobutyrate. The presence of the isovalerate ester was established by ^1H NMR and MS spectra.

Compound **3c**, $C_{17}H_{28}O_9$, differs from **3a** in having two more hydrogen atoms. It contains a 2-methylbutyryl group instead of a tiglyl group. The relationship between both compounds was confirmed when **3c** was obtained by hydrogenation of **3a**. This reaction also proves that the tiglate in **3a** and the 2-methylbutyrate of **3c** occupy the same position.

Due to the small amount of pure glucolipids available, we decided to acetylate the mixture and work with the acetates. The IR spectrum of the acetylated mixture did not exhibit OH-bands and the ^1H NMR showed the expected downfield shift of the signals corresponding to H-3 and H-4 thus indicating that the new mixture is constituted by the peracetylated compounds **4a–c**.

The acetylated mixture was hydrogenated and the resulting mixture (**4c** and **4d**) was subsequently treated with phenol and tin tetrachloride in order to substitute the acyl group attached to C-1 with a phenyl group [12]. Two compounds were isolated from the reaction mixture (**5a** and **6a**) neither of which contain isobutyroxy or isovaleroxy groups, thus indicating the position C-1 for these groups in the original compounds **3a–c**.

The less polar compound **5a**, showed in the ^1H NMR spectrum a very low-field signal for H-1, which in conjunction with the CIMS peaks at *m/z* 409, 411 and 373 indicated the presence of a chlorine atom. The above data and the rest of the ^1H NMR spectrum (Table 1) are in agreement with the structure of an α-D-glucopyranose with a chlorine atom at C-1 as depicted in **5a** The position for the 2-methylbutyryl group, however, still remained to be established.

The more polar compound (**6a**) showed in its ^1H NMR spectrum the presence of the same acyl groups as in **5a**.

Table 1 ^{1}H NMR spectral

	H	3a	3b	3c	4a–c	4c–d	5a
Glc	1	5 62 *d* (8)	5 65 *d* (8)	5 6 *d* (8)	5 7 *d* (7)	5 67 *d* (8)	6 26 *d* (4)
	2	4.92 *dd* (8, 8 5)	4 9 *dd* (8, 8.5)	4.87 *dd* (8, 8 5)	4 95–5 4	4 9–5 35	4 97 *dd* (4, 12)
	3	3 71 *t* (8 5)	3 7 *t* (8 5)	3.67 *t* (8 5)	4 95–5 4	4 9–5 35	5 55 *t* (12)
	4	3 37 *t* (8 5)	3 35 *t* (8 5)	3.35 *t* (8 5)	4 95–5 4	4 9–5 35	5 1 *t* (12)
	5	3.55 *m*	3 55 *m*	3 55 *m*	3.85 *m*	3 83 *m*	4 2 *m*
	6a	4 65 *dd* (3, 13)	4 65 *dd* (3, 13)	4 55 *dd* (4, 12)	4 25	4 2	4 22
	6b	4 25 *dd* (2, 13)	4 23 *dd* (2, 13)	4 18 *dd* (2, 12)	4 2	4 15	
i-Bu	2	2 57 *hep* (7)		2 5 *hep* (7)	2 5 *m*	2 45 *m*	
	3	1 16 *d* (7)		1 15 *d* (7)	1 17 *d* (7)	1 12 *d* (7)	
Tigl	3	6 92 *bq* (7)	6.9 *bq* (7)		6 86 *bq* (7)		
	4	1 83 *bd* (7)	1 8 *bd* (7)		1 8 *bd* (7)		
	5	1 85 *b*	1 82 *b*		1 85 *b*		
i-Val	2				2 5 *m*	1 5 *m*	
	3		1.5 *m*		1 5 *m*	2 45 *m*	
	4		0 92 *d* (7)		0 95 *d* (7)	0 92 *d* (7)	
2-MeBu	2			2 45 *hex* (7)	2 5 *m*	2 45 *m*	2 43 *hex* (7)
	3			1 55 *pent* (7)	1 5 *m*	1 5 *m*	1 54 *pent* (7)
	4			0.9 *t* (7)	0 9 *t* (7)	0 87 *t* (7)	0 9 *t* (7)
	5			1 15 *d* (7)	1 17 *d* (7)	1 12 *d* (7)	1 15 *d* (7)
Ac		2 1	2 05	2 07	2 03	2 0	2 03 2 05 2 1

Run at 80 MHz, $CDCl_3$, TMS as int standard Values are in ppm Unmarked signals are singlets Values in
*Phenolic hydrogens as complex multiplet at δ6 9–7 4

The difference in chemical shift for H-1 (δ5.14, *d*, J = 9.5 Hz) and the signals for five aromatic hydrogens are indicative of the existence of a C-1 phenoxy group in **6a**.

With the establishment of the identity of the ester group attached to C-1 in the parent compounds, we went on to determine which ester groups were attached to C-2 and C-6

The acetylated mixture of the glucolipids was hydrogenated using a lower proportion of catalyst. The ^{1}H NMR spectrum of the reaction mixture showed the presence of a small amount of tiglyl derivatives.

Treatment [12] of the hydrogenated mixture of acetates with phenol and tin tetrachloride afforded six products, among them substances **5a** and **6a**. Two more compounds, **5b** and **6b**, were similar to **5a** and **6a** respectively, the only difference being the presence of a tiglyl instead of 2-methylbutyryl group Finally two additional compounds **5c** and **5d** corresponded to α-D-glucopyranosides with a 2-methylbutyryl and a tiglyl group, respectively

Saponification (K_2CO_3–MeOH) of the major product **6b** afforded substance **7** whose ^{1}H NMR spectrum exhibited a complex signal between δ3 3 and 3 9 (H-2, H-3, H-4 and H-5), a broad doublet at δ4 85 (J = 9 Hz) which was assigned to the anomeric hydrogen and a broad triplet at δ4 4 (J = 13 Hz) which was attributed to H-6 The signals of the tiglyl group were also observed These signals are in agreement with structure **7**, therefore the original compounds **3a** and **3b** contain a tigloxy group at C-6, and acetoxy at C-2 and a third different ester at C-1 (iso-

data of compounds **3–7**

	H	5b	5c*	5d*	6a*	6b*	7*
Glc	1	6.27 *d* (4)	5.72 *d* (3.5)	5 7 *d* (4)	5 14 *d* (9.5)	5.15 *d* (10 5)	4.85 *br d* (9)
	2	5 0 *dd* (4, 12)	5.98 *dd* (3.5, 12)	4.98 *dd* (4, 12)	4.95–5 35	4 95–5 35	3.3–3.9
	3	5 57 *t* (12)	5 7 *t* (12)	5 67 *t* (13)	4.95–5.35	4.95–5.35	3.3–3.9
	4	5.15 *t* (12)	5.15 *t* (12)	5.12 *t* (13)	4.95–5 35	4.95–5.35	3.3–3.9
	5	4.15 *m*	4.15 *m*	4.15 *m*	3.86 *m*	3 9 *m*	3 3–3 9
	6a				4 2	4 35 *dd* (3.5, 12.5)	
			4.26	4.15 *m*	4.15 *m*		4.4 *br t* (13)
	6b				4.15 *d* (1.5)	4.1 *d* (12.5)	
i-Bu	2						
	3						
	4						
Tigl	3	6.9 *m*		6.75 *br q* (8)		6 86 *m*	6.87 *m*
	4	1.82 *br d* (7)		1 75 *br d* (8)		1.8 *br d* (8)	1 77 *br d* (7)
	5	1.85 *br*		1.77 *br*		1.82 *br*	1.8 *br*
i-Val	2						
	3						
	4						
	5						
2-MeBu	2		2.3 *m*		2.35 *hex* (7)		
	3		1 5 *m*		1.52 *pent* (7)		
	4		0.87 *t* (7)		0 82 *t* (7)		
	5		1.07 *d* (7)		1 12 *d* (7)		
Ac		2.04	2.04	2.02	1.99	2 01	
		2.1	2.1	2 04	2.01	2.02	
				2.05	2.03	2.04	

parentheses are coupling constants in Hz

butyroxy in **3a** and isovaleroxy in **3b**). The less polar compound **3c** differs from **3a** in having a 2-methylbutyroxy group at C-6.

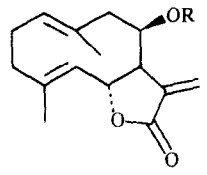
EXPERIMENTAL

Mps: uncorr Chromatography was carried out over Kieselgel G. Known compounds were identified by direct comparison with authentic samples and spectroscopic data.

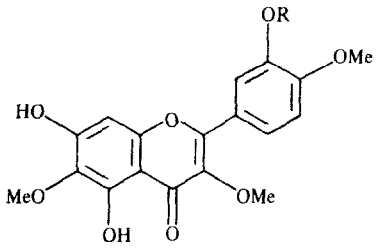
Plant material. Bahia schaffneri S. Wats var. *schaffneri* was collected in the State of San Luis Potosí (Voucher MEXU 432414, deposited in the Herbarium of the Instituto de Biología, UNAM).

Extraction and separation. Air-dried parts (1.33 kg) were extracted with hexane and CH_2Cl_2–$CHCl_3$–EtOAc (5:4:1). The hexane extract (35 g) was chromatographed and eluted with hexane followed by a hexane–EtOAc gradient. The hexane–EtOAc (9.1) fractions yielded 752 mg Ψ-taraxasterol. The hexane–EtOAc (7.3) fractions afforded 447.3 mg of a mixture of **3a–c** The CH_2Cl_2–$CHCl_3$–EtOAc extract (30 g) was chromatographed and the fractions were collected as follows: 1–33 (hexane–EtOAc, 4:1), 34–67 (hexane–EtOAc, 3:2), 68–99 (hexane–EtOAc, 2·3), 100–114 (hexane–EtOAc, 1 4), 115–122 (EtOAc) Fractions 12–14 yielded 55.9 mg eupatolide (**1a**). Fractions 15–25 afforded 38.2 mg bonanzin (**2a**). Fractions 37–42 contained a mixture (2.618 g) of **3a–c**. Fractions 43–58 afforded 455.6 mg eupatoriopicrin (**1b**). Chromatography of 1.6 g of the mixture of **3a–c** eluting with hexane–Me_2CO (4.1) afforded 525 mg **3a**. 13 mg **3a**, 10.1 mg **3b** and 3 mg **3c** were obtained by HPLC on a Si 10 column (50 × 8 cm) eluted with hexane–EtOAc (3.2) at a flow-rate of 200 ml/hr.

Compound **3a**. White crystals from hexane–EtOAc, mp 147–148°. $[\alpha]_D = -60\,16°$ ($CHCl_3$; *c* 0.241). UV λ_{max}^{MeOH} nm· 216 ε = 11 012, IR $\nu_{max}^{CHCl_3}$ cm^{-1}· 3500, 1760, 1730, 1710, 1650; EIMS 70 eV, *m/z* (rel. int): 287 $[M-i\text{-BuO}]^+$ (1.5), 226 $[M-i\text{-BuOH}-HOAc]^+$ (2 1), 126 $[226-TiglOH]^+$ (2 8), 83 $[C_5H_7O]^+$

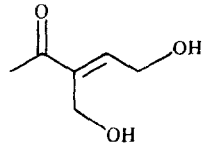


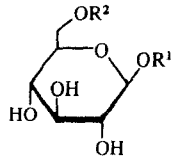
1a R = H



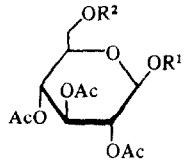
2a R = Me
2b R = H

1b R =

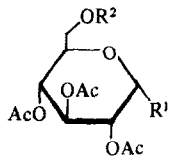


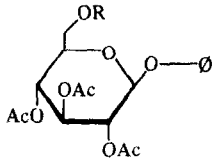


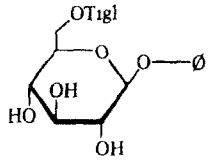
3a R^1 = *t*-Bu R^2 = Tigl
3b R^1 = *t*-Val R^2 = Tigl
3c R^1 = *t*-Bu R^2 = 2-MeBu



4a R^1 = *t*-Bu R^2 = Tigl
4b R^1 = *t*-Val R^2 = Tigl
4c R^1 = *t*-Bu R^2 = 2-MeBu
4d R^1 = *t*-Val R^2 = 2-MeBu







5a R^1 = Cl R^2 = 2-MeBu
5b R^1 = Cl R^2 = Tigl
5c R^1 = O—Ø R^2 = 2-MeBu
5d R^1 = O—Ø R^2 = Tigl

6a R = 2-MeBu
6b R = Tigl

7

(100), 71 $[C_4H_7O]^+$ (50.5), 55 $[C_4H_7]^+$ (19 9), 43 $[C_2H_3O]^+$ (59.5)

Compound **3b**. White crystals from hexane–EtOAc, mp 93–98° $[\alpha]_D = -42\,2°$ ($CHCl_3$, *c* 0.225). UV λ_{max}^{MeOH} nm 212 $\varepsilon = 90\,53$, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3460, 1751, 1711, EIMS 70 eV, *m/z* (rel int) 287 $[M-i\text{-ValO}]^+$ (2 7), 269 $[287-H_2O]^+$ (2.8), 226 $[M-i\text{-ValOH}-HOAc]^+$ (4.2), 126 $[226-TiglOH]^+$ (4 0), 85 $[C_5H_9O]^+$ (61.4), 83 $[C_5H_7O]^+$ (100), 57 $[C_4H_9]^+$ (55 7), 55 $[C_4H_7]^+$ (25), 43 $[C_2H_3O]^+$ (33 1).

Compound **3c** White crystals from hexane–EtOAc, mp 93–95° $[\alpha]_D = -35\,39°$ ($CHCl_3$; *c* 0.238). UV λ_{max}^{MeOH} nm 208 $\varepsilon = 370$; IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3599, 3490, 1752, EIMS 70 eV, *m/z* (rel int). 289 $[M-i\text{-BuO}]^+$ (1 1), 271 $[289-H_2O]^+$ (1 3), 229 $[289-HOAc]^+$ (1 0), 186 $[M-i\text{-BuOH}-TiglOH]^+$ (3.8), 126 $[186-HOAc]^+$ (4 1), 85 $[C_5H_9O]^+$ (58 8), 71 $[C_4H_7O]^+$ (59 5), 57 $[C_4H_9]^+$ (54.5), 43 $[C_2H_3O]^+$ (100)

Hydrogenation of **3a** 97 5 mg of **3a** in EtOAc (10 ml) was hydrogenated for 4 hr over 20 mg of 5% Pd-C at room temp and pres After the usual work-up, 96 3 mg of **3c** were obtained

Acetylation of the mixture of **3a–c** The mixture (171 8 mg) was acetylated with 1 7 ml of Ac_2O and 1 7 ml of pyridine for 4 hr at room temp and worked-up in the usual manner Chromatography of the residue afforded, after elution with $CHCl_3$–Me_2CO (93 3), 190 mg of a mixture of **4a–c** White crystals from hexane–EtOAc, mp 90–93° IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1759, 1715, 1651, EIMS 70 eV, *m/z* (rel int.) 373 $[M-i\text{-BuO}]^+$ (0 5), 371 $[M-i\text{-BuO}]^+$ and $[M-i\text{-ValO}]^+$ (2.7), 85 $[C_5H_9O]^+$ (8 2), 83 $[C_5H_7O]^+$ (56 3), 71 $[C_4H_7O]^+$ (35 7), 57 $[C_4H_9]^+$ (8 1), 55 $[C_4H_7]^+$ (16 7), 43 $[C_2H_3O]^+$ (100)

Hydrogenation of the mixture of **4a–c** 180 mg of the above mixture in 10 ml EtOAc, were hydrogenated over 40 mg of 5% Pd-C for 3 hr at room temp and pres The usual work-up yielded 176 mg of a mixture of **4c** and **4d** White crystals, mp 49–53° IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1760, EIMS 70 eV *m/z* (rel int) 373 $[M-i\text{-BuO}]^+$ and $[M-i\text{-ValO}]^+$ (1.6), 85 $[C_5H_9O]^+$ (76 3), 71 $[C_4H_7O]^+$ (86 9), 57 $[C_4H_9]^+$ (44 9) 43 $[C_3H_7]^+$ and $[C_2H_3O]^+$ (100)

*Phenyl tetra-acyl-*D*-glucopyranoside* A soln of **4c** and **4d** (170 mg) and phenol (98 mg) in dry CH_2Cl_2 (100 ml) was treated with $SnCl_4$ (0 08 ml) and stirred at room temp for 1 hr The reaction mixture was diluted with water and extracted with $CHCl_3$ The organic layer was washed with $NaHCO_3$ (satd),

Table 2. ^{13}C NMR data of compound **3a** (20 MHz, $CDCl_3$, TMS as int. standard)

	C	
Glc	1	92 08 *d*
	2	74 83 *d*
	3	75 17 *d*
	4	70.41 *d*
	5	72 69 *d*
	6	62.97 *t*
i-Bu	1	175.31 *s*
	2	33.91 *d*
	3	18.82 *q**
	4	18 30 *q**
Tigl	1	168 89 *s.*
	2	128 16 *s*
	3	138 95 *d*
	4	14 39 *q*
	5	11 99 *q*
Ac	1	170 32 *s*
	2	20.73 *q*

*Assignments interchangeable

dried over Na_2SO_4 and concd. The residue was chromatographed with hexane–EtOAc (9·1) yielding 22 1 mg **5a** and 28 mg **6a**.

Compound **5a**. White crystals from hexane–EtOAc, mp 90–92°. $[\alpha]_D = +154.61°$ ($CHCl_3$; *c* 0.26). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750; CIMS (CH_4) 200 eV, *m/z* (rel. int.): 411 $[M+3]^+$ (8 4), 409 $[M+1]^+$ (19 9), 373 $[M-Cl]^+$ (13), 359 $[411-HOAc]^+$ (13), 349 $[409-HOAc]^+$ (40.4), 309 $[411-RCO_2H]^+$ (8.5), 307 $[409-RCO_2H]^+$ (19.7), 229 $[373-RCO_2H-C_2H_3O]^+$ (90.8), 211 $[373-2HOAc-C_2H_2O]^+$ (100), 169 $[229-HOAc]^+$ (92.7), 109 $[169-HOAc]^+$ (20 1)

Compound **6a** White crystals from hexane–EtOAc, mp 86–88° $[\alpha]_D = -10\,71°$ ($CHCl_3$, *c* 0 28). IR $\nu_{max}^{CHCl_3}$ cm^{-1}· 1760, 1735, EIMS 70 eV, *m/z* (rel int): 373 $[M-C_6H_5O]^+$ (13.7), 211 $[373-RCO_2H-HOAc]^+$ (35.7), 169 $[211-C_2H_2O]^+$ (7.8), 109 $[169-HOAc]^+$ (12.5), 85 $[C_5H_9O]^+$ (81.4), 77 $[C_6H_5]^+$ (2.5), 65 $[C_5H_5]^+$ (2 2), 57 $[C_4H_9]^+$ (48.9), 43 $[C_2H_3O]^+$ (100).

Preparation of **5b–d** and **6b** 800 mg of a mixture of **3a–c** was acetylated with pyridine (4 ml) and Ac_2O (4 ml) for 4 hr at room temp. The reaction mixture was worked-up in the usual manner affording 890 mg of **4a–c** as a crystalline mixture, which was hydrogenated in EtOAc (20 ml) over 120 mg of 5% Pd-C for 24 hr The usual work-up afforded 885 mg of a solid product. 875 mg of this solid and 440 mg of phenol in dry CH_2Cl_2 (8 ml) were treated with $SnCl_4$ (0 3 ml) and stirred at room temp. for 1 hr. The reaction mixture was worked-up in the manner previously described and chromatographed with hexane–Me_2CO (23:2) which was collected as 54 fractions Rechromatography of fractions 5–9 (eluent, hexane, Me_2CO 47.3) afforded 25.6 mg **5a** and 12.9 mg of a mixture of **5b** and **5c**. Fractions 10–24 were rechromatographed and eluted with hexane–Me_2CO (23·2) yielding 15 mg of a mixture of **5a–c**, 36.4 mg of a mixture of **5b** and **5c**, 24 4 mg **5d** and 23.2 mg of **5b–d** as a mixture. Fractions 19–24 were rechromatographed and eluted with hexane–Me_2CO (9·1) yielding 56.3 mg **6a** and 29 6 mg of a mixture of **5d** and **6a**. Rechromatography of fractions 25–40 eluted with hexane–Me_2CO (87 13) yielded 11.5 mg **6a**, 221 1 mg **6b** and 82 mg of **6a** and **6b** as mixture.

Compound **5b** *and* **5c**. White crystals from hexane–EtOAc, mp. 66–69° $[\alpha]_D = +142.75°$ ($CHCl_3$, *c* 0.29). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1755, EIMS 70 eV, *m/z* (rel. int): 373 $[M-C_6H_5O]^+$ (6), 371 $[M-Cl]^+$ (0 5), 211 $[373-RCO_2H-HOAc]^+$ and/or $[371-TiglOH-HOAc]^+$ (9 1), 109 $[211-HOAc-C_2H_2O]^+$ (8.5), 85 $[C_5H_9O]^+$ (83.2), 83 $[C_5H_5O]^+$ (8 4), 57 $[C_4H_9]^+$ (37 5), 55 $[C_4H_7]^+$ (3.4), 43 $[C_2H_3O]^+$ (100)

Compound **5d**. White crystals from hexane–EtOAc, mp 126–135°. $[\alpha]_D = +144°$ ($CHCl_3$, *c* 0.34) IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1738, 1708, 1653; EIMS 70 eV, *m/z* (rel int). 371 $[M-C_6H_5O]^+$ (5.7), 209 $[371-2HOAc-C_2H_2O]^+$ (9 5), 109 $[209-TiglOH]^+$ (4), 83 $[C_5H_7O]^+$ (100), 55 $[C_4H_7]^+$ (13.8), 43 $[C_2H_3O]^+$ (33 5)

Compound **6b** White crystals from hexane–EtOAc, mp 105–107° $[\alpha]_D = -12.5°$ ($CHCl_3$, *c* 0.255) IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1760, 1710, 1650, EIMS 70 eV, *m/z* (rel int.) 371 $[M-C_6H_5O]^+$ (4 4), 209 $[371-2HOAc-C_2H_2O]^+$ (7.4), 109 $[209-TiglOH]^+$ (3.5), 83 $[C_5H_7O]^+$ (100), 55 $[C_4H_7]^+$ (4.2), 43 $[C_2H_3O]^+$ (22.4).

Saponification of **6b**. 48 mg of **6b** and 90 mg of K_2CO_3 in dry MeOH (15 ml) were stirred at room temp. for 90 min under Ar The solvent was blown off by a stream of air and the residue was dissolved in $CHCl_3$ which was washed with H_2O, dried with Na_2SO_4 and concd. The residue was chromatographed and eluted with hexane–Me_2CO (11:9) yielding 12.6 mg **7** from hexane–Me_2CO, mp 137–138°. $[\alpha]_D = -106\,45°$ ($CHCl_3$; *c* 0.31). IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3594, 3438, 1701, 1648; EIMS 70 eV, *m/z* (rel int.)· 245 $[M-C_6H_5O]^+$ (15.3), 227 $[245-H_2O]^+$ (4.2), 109 $[227-TiglOH-H_2O]^+$ (1 5), 83 $[C_5H_7O]^+$ (100), 77 $[C_6H_5]^+$ (4.1), 65 $[C_5H_5]^+$ (2 8), 55 $[C_4H_7]^+$ (30 4), 39 $[C_3H_3]^+$ (3 4)

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