Convenient Synthesis of Alcohol *O*-Hemiesters using Isopropenyl Esters as Acylating Reagents: Synthesis of Hydrophilic Oxaunomycin 10-*O*-Hemiester Derivatives

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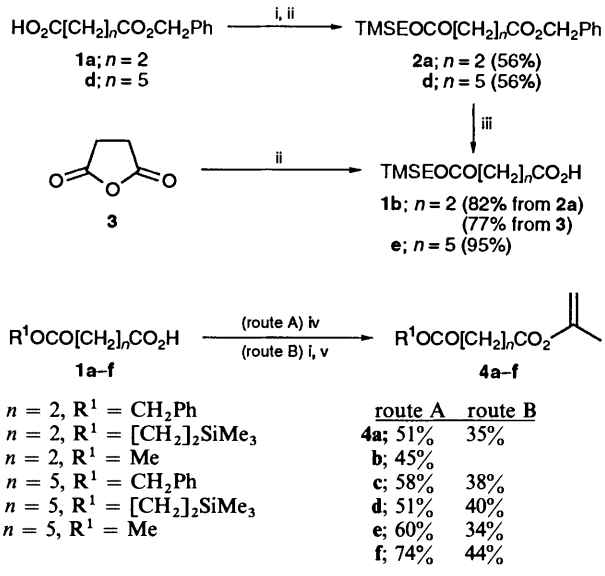
Various types of alcohol *O*-hemiesters **7a–m** were synthesized conveniently in good yield by reaction with isopropenyl esters **4a–f** in the presence of a catalytic amount of conc. H_2SO_4 or toluene-*p*-sulfonic acid followed by selective deprotection of the terminal esters. This method was applied to a preparation of hydrophilic oxaunomycin 10-*O*-hemiester derivatives **14a, b** and **19a–c**.

Considerable efforts have been devoted to the synthesis of hydrophilic *O*-hemiester derivatives of various clinically efficacious drugs, notably in the fields of steroids,[1] tocopherols,[2] anthracycline antibiotics[3] and taxol.[4] Currently, they are prepared by (i) treatment of alcohols with cyclic acid anhydrides, (ii) treatment of alcohols with acid chlorides in the presence of a base, followed by deprotection of the terminal esters which are prepared by method (i) or from only simple alcohols and dicarboxylic acids, or (iii) conversion of alcohols into halogeno compounds followed by nucleophilic substitution with dicarboxylic monoanions, and are used to create less toxic drugs. These methods, however, have several restrictions: (i) medium to large unstable anhydrides[5] cannot be employed in the direct acylation of alcohols, (ii) bulky secondary or tertiary alcohols do not react easily with acid anhydrides or acid chlorides, (iii) alcohols bearing some base-sensitive functional groups cannot be allowed to react with acid anhydrides or acid halides in the presence of the base and (iv) bulky alcohols may be troublesome to transform into the halogeno compounds. In a previous communication, we reported a novel and convenient method for the acylation of bulky alcohols using isopropenyl esters and selective deprotection of the terminal ester leading to the monoesters.[6] We now report a full account of these studies and their applications to hydrophilic oxaunomycin 10-*O*-hemiesters and related derivatives.



Scheme 1 *Reagents:* i, $(COCl)_2$, CH_2Cl_2; ii, 2-(trimethylsilyl)-ethanol, pyridine; iii, H_2/Pd, 1,4-dioxane; iv, isopropenyl acetate, cat. BF_3·Et_2O, cat. $Hg(OAc)_2$; v, acetone, KH, DME

Results and Discussion

The isopropenyl esters **4a–f**[7] were prepared from the half-esters **1a–f** bearing terminal esters as the protecting groups (Scheme 1). The known half-esters **1a**,[8] **1c**,[9] **1d**[10] and **1f**[11] were prepared by standard methods. The unknown half-esters **1b, e** bearing 2-(trimethylsilyl)ethyl (TMSE) ester groupings were synthesized from the benzyl esters **1a, d** or from succinic anhydride **3**. Thus, the half-esters **1a, d** were converted into the diesters **2a, d** by chlorination with oxalyl dichloride at below room temperature† followed by alcoholysis with 2-(trimethylsilyl)ethanol in the presence of pyridine. Catalytic hydrogenation of diesters **2a, d** afforded compounds **1b, e** in good yield. Alternatively, hemiester **1b** was obtained conveniently from succinic anhydride **3** by treatment with 2-(trimethylsilyl)ethanol in the presence of pyridine.

The desired isopropenyl esters **4a–f** were prepared by two different methods. Similarly to the reported methods,[12] half-esters **1a–f** reacted with isopropenyl acetate in the presence of a catalytic amount of BF_3·Et_2O and mercury(II) acetate to give diesters **4a–f** in moderate yield (route A). The esters **4a** and **4c–f** were also prepared by direct acylation of the potassium enolate generated from acetone and potassium hydride in 1,2-dimethoxyethane (DME) with the corresponding acid chloride‡ at 0 °C (route B). Physical data of these isopropenyl esters are summarized in Table 1.

All acylations were performed in the presence of a catalytic amount of acid to give a high yield of diesters **6a–y**. When conc. H_2SO_4 was used as catalyst, the acylation was over in a short time through the use of a slight excess of the reagent (Table 2, runs 1, 5, 7, 9 and 11). Use of *p*-TsOH (PTSA) as catalyst required two mole equivalents of the reagents to consume the alcohol completely (runs 2, 4, 6, 8, 10 and 12). This acylation method is quite useful not only for the bulky alcohols such as tertiary alcohols **5e, f** (runs 22–27), *endo*-trinorborneol **5d** (run 21) and pantolactone **5i** (runs 31–33), but also for phenol **5j** (runs 34–36). Furthermore, olefin and nitrile groups were not affected under these reaction conditions (runs 28–30). In the

† Although the acid chloride could not be obtained from compound **1a** under reflux in $CHCl_3$ in the presence of thionyl dichloride according to ref. 10 because of thermal instability, it was obtained at below room temperature in CH_2Cl_2 in the presence of oxalyl dichloride.

‡ These acid chlorides were prepared according to the preceding footnote.† The acid chloride derived from compound **1b** was unstable and we were unable to isolate it.

Table 1 Physical data of isopropenyl esters **4**

Compound	B.p./°C (mmHg)	$\nu_{max}(CHCl_3)$/cm^{-1} C=O	C=C	$\delta_H(CDCl_3)$	Formula	Found (%) (Required) C	H
4a	165–168 (2.0)	1735	1670	1.89 (3 H, s), 2.72 (4 H, s), 4.67 and 4.69 (1 H each, 2 s), 5.14 (2 H, s), 7.35 (5 H, s)	$C_{14}H_{16}O_4$	67.4 (67.72)	6.45 (6.50)
4b	122–124 (0.60)	1725	1670	0.04 (9 H, s), 0.9–1.1 (2 H, m), 1.93 (3 H, s), 2.5–2.8 (4 H, m), 4.1–4.3 (2 H, m), 4.65–4.75 (2 H, m)	$C_{12}H_{22}O_4Si$	55.6 (55.78)	8.55 (8.58)
4c	104–106 (14)	1735	1670	1.92 (3 H, s), 2.6–2.8 (4 H, m), 3.71 (3 H, s), 4.65–4.75 (2 H, m)	$C_8H_{12}O_4$	55.45 (55.80)	7.15) (7.03)
4d	168–171 (0.30)	1735	1670	1.3–1.5 (2 H, m), 1.5–1.8 (4 H, m), 1.91 (3.H, s), 2.37 (4 H, br t, *J* 7.3), 4.66 and 4.69 (1 H each, 2 s), 5.11 (2 H, s), 7.3–7.5 (5 H, m)	$C_{17}H_{22}O_4$	70.25 (70.32)	7.5 (7.64)
4e	128 (0.38)	1720	1670	0.04 (9 H, s), 0.9–1.1 (2 H, m), 1.3–1.5 (2 H, m), 1.5–1.8 (4 H, m), 1.92 (3 H, s), 2.29 and 2.38 (2 H each, 2 t, *J* 7.3), 4.1–4.3 (2 H, m), 4.65–4.75 (2 H, m)	$C_{15}H_{28}O_4Si$	60.05 (59.96)	9.45 (9.39)
4f	121–123 (2.5)	1730	1670	1.3–1.5 (2 H, m), 1.6–1.8 (4 H, m), 1.92 (3 H, s), 2.25–2.45 (4 H, m), 3.67 (3 H, s), 4.67 and 4.70 (1 H each, 2 s)	$C_{11}H_{18}O_4$	61.5 (61.66)	8.3 (8.47)

work-up of the reaction, an excess of acylating reagent was quenched by treatment with several drops of conc. hydrochloric acid under ice-cooling. All results of the acylation and the physical data of acylation products (diesters) are summarized in Tables 2 and 3, respectively.

For the purpose of obtaining alcohol *O*-hemiesters **7**, a terminal ester of diester **6** must be removed selectively. Three types of deprotection methods were examined with substrates **6m–o** as representative examples (Table 2): (i) catalytic hydrogenation of the benzyl ester **6m** (method A), (ii) desilylative fragmentation of the 2-(trimethylsilyl)ethyl (TMSE) ester **6n** by treatment of tetrabutylammonium fluoride (TBAF)[13] (method B) and (iii) selective saponification of the methyl ester **6o** by treatment with alkali (method C). High yields of the alcohol *O*-hemiester **7f** were obtained in every case. Various other types of alcohol *O*-hemiesters **7a–e** and **7g–m** were prepared from the corresponding diesters by one of the above methods. In the case of the diesters obtained from primary or secondary alcohols and phenol, methods A and B gave satisfactory results. Method B is the best for removal of the terminal ester having an olefin or a nitrile moiety in the molecule. Method C is effective in deprotecting the terminal methyl ester, especially in the case of the bulky esters obtained from tertiary alcohols. All results of deprotections of the terminal esters and physical data of alcohol *O*-hemiesters are summarized in Tables 2 and 4, respectively. In this way, we have developed a quite general and convenient synthesis of alcohol *O*-hemiesters.

Finally, we applied this method to the *O*-hemiesterification of the anthracycline antibiotic, oxaunomycin,[14] which was found to be about 100-fold more active than adriamycin against leukaemic L-1210 cultures.[15] The acylating reagents **4a**, **c**, **f** smoothly reacted with 7,9-*O*-phenylboranediyl-β-rhodomycinone **8**[14] in the presence of a catalytic amount of conc. H_2SO_4 to afford diesters **9a–c** in 80–87% yield without any acylation of phenolic hydroxy groups. The boronate moiety in diesters **9** was removed by treatment with 2-methylpentane-2,4-diol and acetic acid in acetone to give the desired 10-*O*-acyl-β-rhodomycinones **10a–c** in high yield. For the preparation of hemiesters **14a**, **b** glycosidation of 1,3-diols **10a**, **b** with the 1,4-bis-*O*-(*p*-nitrobenzoyl)-L-daunosamine derivative **11** using trimethylsilyl trifluoromethanesulfonate (TMSOTf) and molecular sieves (MS) 4 Å in a mixed solvent of anhydrous dichloromethane and diethyl ether at −15 °C[16] gave the 7-*O*-α-glycosides **12a**, **b** in 79 and 77% yield, respectively. The glycosides **12a**, **b** were deprotected with 1.2 mole equivalents of 0.1 mol dm^{-3} NaOH at 0 °C in dichloromethane–MeOH to afford 4′-hydroxy compounds **13a**, **b**, which were further treated with an excess of 0.1 mol dm^{-3} NaOH at room temperature to give the desired *N*-(trifluoroacetyl)oxaunomycin 10-*O*-hemisuccinate **14a** and 10-*O*-hemipimelate **14b** in 51 and 41% yield, respectively (Scheme 2).

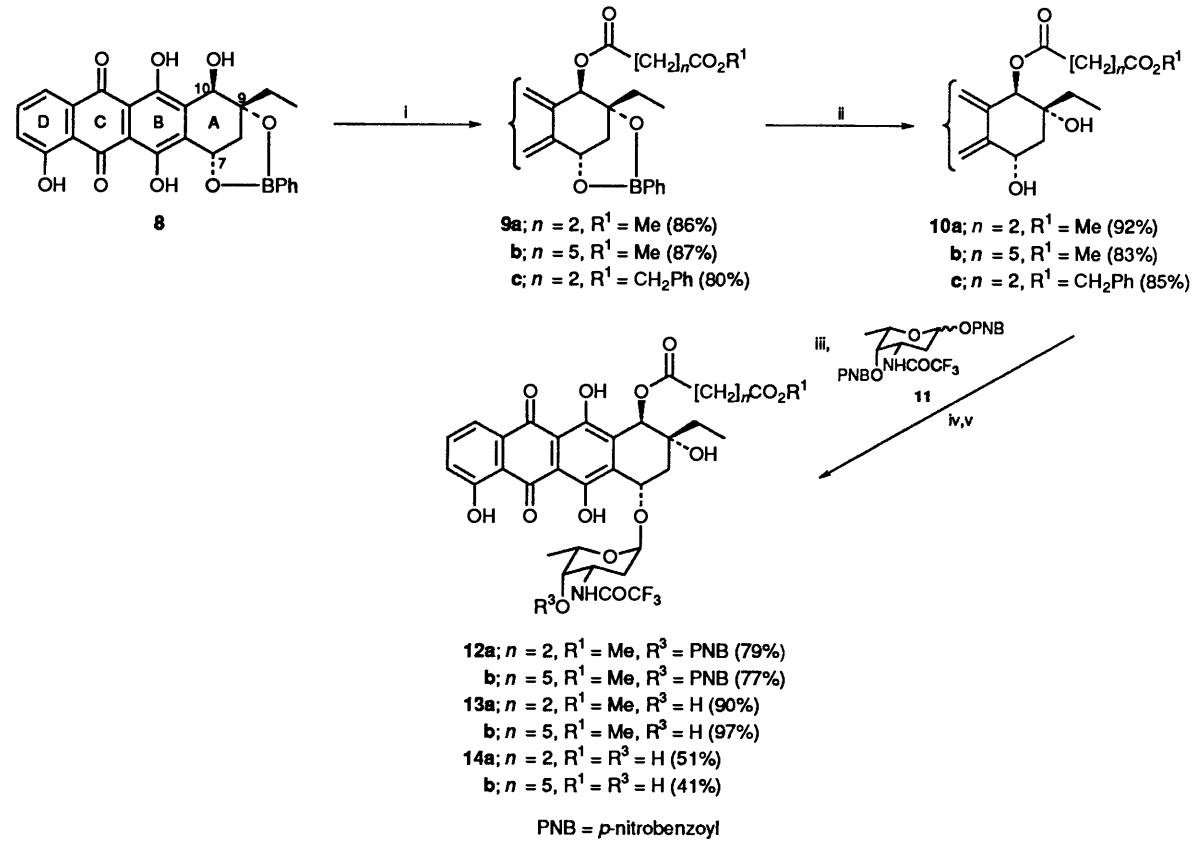
Furthermore, we synthesized the oxaunomycin derivatives **19a–c** in which the L-daunosamine residue was replaced by not only 2-deoxy-D-*erythro*-pentopyranose but also 2,6-dideoxy-2-fluoro-L-talopyranose. This is because of the amount of attention that has been paid to the antitumour activities of anthracycline derivatives containing a sugar which has an axial 2′-fluoro substituent.[17] The glycosidations of compounds **10b**, **c** with the protected sugars **15**[18] and **16** under Koenigs–Knorr conditions afforded the corresponding β-glycosides **17a** and α-glycosides **17b**, **c** in 57–80% yield. These diacetates were deprotected by treatment with 3 mole equivalents of 0.1 mol dm^{-3} NaOH to give the 3′,4′-dihydroxy compounds **18a–c**, which were further treated with an excess of 0.1 mol dm^{-3} NaOH at room temperature to yield the desired derivatives **19a–c** in 56–62% yield from **17a–c** (Scheme 3).

The preparation of other oxaunomycin 10-*O*-hemiester derivatives and biological testing for activity against tumour cells is in progress. The present acylation and deprotection method opens up a potentially useful method for the *O*-hemiesterification of other natural products.

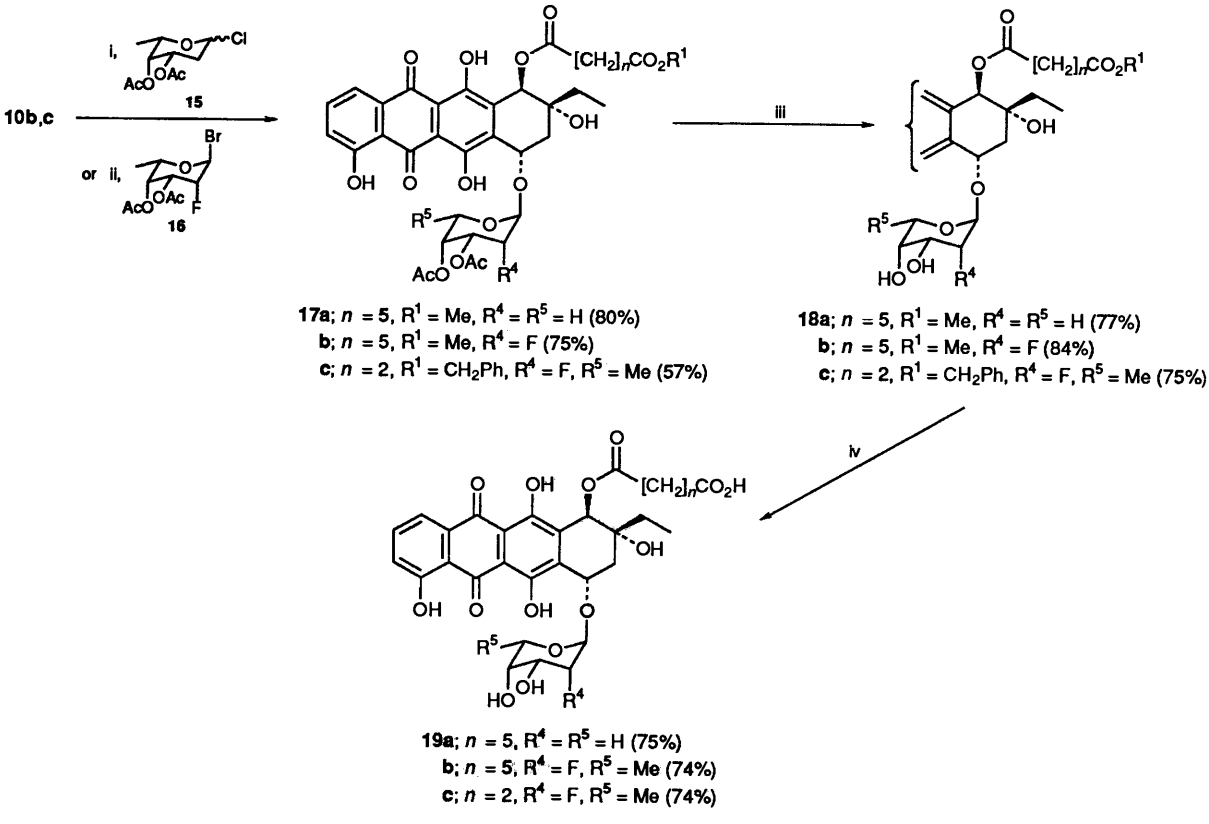
Experimental

All b.p.s and m.p.s are uncorrected; m.p.s were measured on a Yanagimoto micro melting point apparatus. Optical rotations were measured with a Perkin-Elmer 241 polarimeter using a 10 cm cell and are given in 10^{-1} deg cm^2 g^{-1}. IR spectra were recorded on a JASCO HPIR-102 spectrophotometer. ^{1}H NMR spectra were measured on a Varian VXR-200 (200 MHz), a Hitachi R-250HT (250 MHz), or a JEOL JNM-GX500 (500 MHz) spectrometer with Me_4Si as internal standard. *J*- and $w_{\frac{1}{2}}$-values are given in Hz. Mass spectra were obtained on a JEOL JMS-D300 [for electron impact (EI) MS] or a JEOL HX-100 [for fast atom bombardment (FAB) MS] mass spectrometer. E. Merck silica gel 60 (70–230 mesh ASTM) was used for column chromatography and E. Merck precoated TLC plates, silica gel 60 F_{254}, were used for preparative TLC (PLC).

Benzyl 2-(Trimethylsilyl)ethyl Succinate **2a**.—Oxalyl dichloride (9.20 cm^3, 104 mmol) was added to a solution of hemiester **1a**[8] (7.30 g, 35.1 mmol) in dry CH_2Cl_2 (40 cm^3) at 0 °C and the mixture was stirred below 25 °C for 2 h. The reaction mixture was concentrated under reduced pressure to give a residue, which was dissolved in dry CH_2Cl_2 (40 cm^3). A solution of 2-(trimethylsilyl)ethanol (5.00 g, 42.4 mmol) in dry pyridine (50 cm^3) was added to the above solution at −30 °C.



Scheme 2 *Reagents:* i, **4a**, **4c** or **4f**, cat. H_2SO_4, CH_2Cl_2; ii, 2-methylpentane-2,4-diol, AcOH–acetone–CH_2Cl_2; iii, TMSOTf, MS 4 Å, CH_2Cl_2–Et_2O; iv, 0.1 mol dm^{-3} NaOH (1.2 mol equiv.), CH_2Cl_2–MeOH; v, 0.1 mol dm^{-3} NaOH (20 mol equiv.), DME

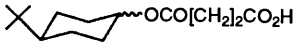
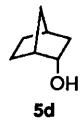
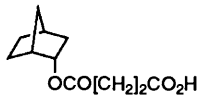
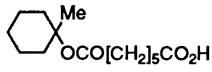
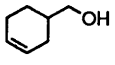
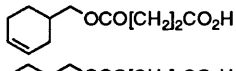
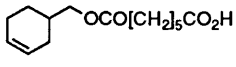
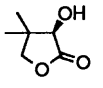
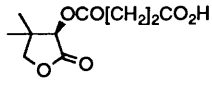


Scheme 3 *Reagents:* i, yellow HgO, $HgBr_2$, MS 4 Å, CH_2Cl_2; ii, yellow HgO, $HgBr_2$, MS 3 Å, CH_2Cl_2; iii, 0.1 mol dm^{-3} NaOH (3 mol equiv.), MeOH; iv, 0.1 mol dm^{-3} NaOH (40 mol equiv.), MeOH

Table 2 Acylation of alcohols **5** with reagents **4** and subsequent deprotection of diesters **6** to *O*-hemiesters **7**

$$R^2OH \xrightarrow{\textbf{4a–f}} R^2OCO[CH_2]_nCO_2R^1 \xrightarrow[\text{method A–C}]{\text{deprotection}} R^2OCO[CH_2]_nCO_2H$$

5a–j **6a–y** **7a–m**

Run	Alcohol	Conditions: 4 (mol equiv.), catalyst, time	Yield[a] of 6 (R^1)[b] (%)	Deprotection method[c]	Structure of *O*-hemiester	Yield[a] of 7 (%)
1	$PhCH_2CH_2OH$	**4a** (1.2), c. H_2SO_4, 0.5 h	**6a** (Bn) (76)	A		**7a** (88)
2	**5a**	(2.0), *p*-TsOH, 4 H	(Bn) (81)		$PhCH_2CH_2OCO[CH_2]_2CO_2H$	
3		**4b** (2.0), c. H_2SO_4, 11 h	**6b** (TMSE) (41)	B		(80)
4		(2.0), *p*-TsOH, 12 h	(TMSE) (75)			
5		**4c** (1.2), c. H_2SO_4, 2 h	**6c** (Me) (72)			
6		(2.0), *p*-TsOH, 7 h	(Me) (80)			
7		**4d** (1.2), c. H_2SO_4, 0.3 h	**6d** (Bn) (93)	A		**7b** (95)
8		(2.0), *p*-TsOH, 1 h	(Bn) (99)		$PhCH_2CH_2OCO[CH_2]_5CO_2H$	
9		**4e** (1.2), c. H_2SO_4, 0.8 h	**6e** (TMSE) (94)	B		(85)
10		(2.0), *p*-TsOH, 1.5 h	(TMSE) (98)			
11		**4f** (1.2), c. H_2SO_4, 1.5 h	**6f** (Me) (78)			
12		(2.0), *p*-TsOH, 7 h	(Me) (89)			
13	$PhCH_2OH$	**4b** (2.0), *p*-TsOH, 10 h[d]	**6g**[e] (TMSE) (67)	B		**7c**[f] (84)
14	**5b**	**4f** (1.2), c. H_2SO_4, 0.7 h	**6h** (Me) (70)		$PhCH_2OCO[CH_2]_2CO_2H$	
15		(2.0), *p*-TsOH, 4 h	(Me) (79)			
16		**4a** (2.0), c. H_2SO_4, 2 h	**6i** (Bn) (72)	A		**7d** (78)
17		(2.0), *p*-TsOH, 9 h	(Bn) (70)			
18		**4b** (2.0), *p*-TsOH, 8 h[d]	**6j** (TMSE) (75)	B		(78)
19	**5c**	**4f** (2.0), H_2SO_4, 0.7h	**6k** (Me) (82)			
20		(2.0), *p*-TsOH, 3 h	(Me) (88)			
21	 **5d**	**4a** (2.0), *p*-TsOH, 4 h	**6l** (Bn) (77)	A		**7e** (98)
22	$PhCH_2CMe_2OH$	**4a** (2.0), *p*-TsOH, 6 h	**6m** (Bn) (86)	A	$PhCH_2CMe_2OCO[CH_2]_2CO_2H$	**7f** (97)
23	**5e**	**4b** (2.0), *p*-TsOH, 13 h[d]	**6n** (TMSE) (73)	B		(88)
24		**4c** (2.0), *p*-TsOH, 3 h	**6o** (Me) (70)	C		(85)
25		**4f** (2.0), *p*-TsOH, 3 h	**6p** (Me) (75)	C	$PhCH_2CMe_2OCO[CH_2]_5CO_2H$	**7g** (81)
26		**4d** (2.0), *p*-TsOH, 4 h[g]	**6q** (Bn) (84)	A		**7h** (92)
27	**5f**	**4f** (2.0), *p*-TsOH, 4 h[g]	**6r** (Me) (79)	C		(92)
28		**4b** (2.0), *p*-TsOH, 8 h[d]	**6s** (TMSE) (65)	B		**7i** (85)
29	**5g**	**4e** (2.0), *p*-TsOH, 1 h	**6t** (TMSE) (92)	B		**7j** (85)
30	$NC[CH_2]_3OH$ **5h**	**4b** (2.0), *p*-TsOH, 8 h[d,g]	**6u** (TMSE) (65)	B	$NC[CH_2]_3OCO[CH_2]_2CO_2H$	**7k** (82)
31	 **5i**	**4a** (2.0), c. H_2SO_4, 1 h	**6v** (Bn) (92)	A		**7l** (95)
32		(2.0), *p*-TsOH, 4 h	(Bn) (94)			
33		**4b** (2.0), *p*-TsOH, 12 h[d]	**6w** (TMSE) (70)	B		(75)
34	PhOH	**4a** (2.0), c. H_2SO_4, 2 h	**6x** (Bn) (81)	A	$PhOCO[CH_2]_2CO_2H$	**7m** (84)
35	**5j**	(2.0), *p*-TsOH, 3 h	(Bn) (82)			
36		**4f** (2.0), *p*-TsOH, 1.3 h	**6y** (Me) (62)			

[a] Isolated yields are given. [b] Abbreviations: Bn = CH_2Ph, TMSE = $Me_3Si[CH_2]_2$. [c] Method A: H_2/Pd, 1,4-dioxane; method B: TBAF, DMF; method C: NaOH, aq. MeOH. [d] Carried out at 40 °C. [e] This compound is identical with **2a**. [f] This compound is identical with **1a**. [g] In the work-up, the treatment with conc. HCl was omitted.

After being stirred for 1 h the mixture was concentrated under reduced pressure. The residue was acidified with 5% aq. HCl and extracted with EtOAc. The extract was washed with saturated aq. $NaHCO_3$, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed on silica gel [hexane–Et_2O (14:1)] to give the *title compound* **2a** (6.0 g, 56%) as an oil. Physical data are shown in Table 3 (**6g** ≡ **2a**).

Benzyl 2-(Trimethylsilyl)ethyl Pimelate **2d**.—*Compound* **2d** (781 mg, 56%) was prepared from half-ester **1d**[10] (1.00 g, 4.00 mmol), oxalyl dichloride (1.52 g, 12.0 mmol), 2-(trimethylsilyl)-ethanol (520 mg, 4.40 mmol) and pyridine (350 mg, 4.40 mmol), as an oil, b.p. 165–175 °C/0.28 mmHg (bath temperature); $\nu_{max}(CHCl_3)/cm^{-1}$ 1720; δ_H(200 MHz; $CDCl_3$) 0.03 (9 H, s, $SiMe_3$), 0.9–1.05 (2 H, m, $SiCH_2$), 1.2–1.5 (2 H, m, CH_2), 1.5–1.8 (4 H, m, CH_2 × 2), 2.26 and 2.36 (2 H each, 2 t, *J*

Table 3 Physical data of diesters **6**

Compound	B.p./°C[a] (mmHg)	$\nu_{max}(CHCl_3)$/cm^{-1} C=O	$\delta_H(CDCl_3)$	Formula	Found (%) (Required) C	H
6a	*b*	1725	2.5–2.75 (4 H, m), 2.91 (2 H, t, *J* 7.0), 4.29 (2 H, t, *J* 7.0), 5.12 (2 H, s), 7.1–7.4 (10 H, m)	$C_{19}H_{20}O_4$	312.1352[c] (312.1359)	
6b	140–150 (0.30)	1720	0.04 (9 H, s), 0.9–1.1 (2 H, m), 2.5–2.7 (4 H, m), 2.94 (2 H, t, *J* 7.0), 4.1–4.3 (2 H, m), 4.31 (2 H, t, *J* 7.0), 7.1–7.4 (5 H, m)	$C_{17}H_{26}O_4Si$	63.45 (63.31)	8.0 (8.13)
6c	150–155 (0.30)	1720	2.61 (4 H, s), 2.94 (2 H, t, *J* 7.0), 3.68 (3 H, s), 4.31 (2 H, t, *J* 7.0), 7.1–7.4 (5 H, m)	$C_{13}H_{16}O_4$	65.85 (66.08)	7.0 (6.83)
6d	155–165 (0.18)	1725	1.2–1.4 (2 H, m), 1.5–1.8 (4 H, m), 2.2–2.4 (4 H, m), 2.92 (2 H, t, *J* 7.0), 4.28 (2 H, t, *J* 7.0), 5.11 (2 H, s), 7.1–7.5 (10 H, m)	$C_{22}H_{26}O_4$	74.3 (74.55)	7.45 (7.39)
6e	135–145 (0.30)	1725	0.04 (9 H, s), 0.9–1.1 (2 H, m), 1.2–1.4 (2 H, m), 1.5–1.7 (4 H, m), 2.2–2.4 (4 H, m), 2.93 (2 H, t, *J* 7.0), 4.1–4.25 (2 H, m), 4.29 (2 H, t, *J* 7.0), 7.1–7.4 (5 H, m)	$C_{20}H_{32}O_4Si$	364.2071[c] (364.2070)	
6f	160–170 (0.40)	1725	1.2–1.4 (2 H, m), 1.5–1.7 (4 H, m), 2.29 (4 H, t, *J* 7.1), 2.93 (2 H, t, *J* 7.0), 3.66 (3 H, s), 4.29 (2 H, t, *J* 6.9), 7.1–7.3 (5 H, m)	$C_{16}H_{22}O_4$	68.95 (69.04)	8.05 (7.97)
6g (≡**2a**)	140–150 (0.45)	1720	0.03 (9 H, s), 0.9–1.1 (2 H, m), 2.5–2.8 (4 H, m), 4.1–4.3 (2 H, m), 5.14 (2 H, s), 7.35 (5 H, s)	$C_{16}H_{24}O_4Si$	62.15 (62.30)	7.75 (7.84)
6h	150–155 (0.35)	1725	1.2–1.4 (2 H, m), 1.5–1.7 (4 H, m), 2.2–2.4 (4 H, m), 3.66 (3 H, s), 5.11 (2 H, s), 7.35 (5 H, s)	$C_{15}H_{20}O_4$	68.05 (68.16)	7.5 (7.63)
6i	180–190 (0.50)	1725	0.85 (9 H, s), 0.9–2.1 (9 H, m), 2.55–2.75 (4 H, m), 4.55–4.70 ($\frac{5}{7}$ H, m), 5.00–5.05 ($\frac{2}{7}$ H, m), 5.13 (2 H, s), 7.3–7.4 (5 H, m)	$C_{21}H_{30}O_4$	72.55 (72.80)	8.7 (8.73)
6j	120–130 (0.30)	1720	0.04 (9 H, s), 0.85 ($\frac{5}{7}$ × 9 H, s), 0.86 ($\frac{2}{7}$ × 9 H, s) 0.9–2.1 (11 H, m), 2.56–2.65 (4 H, m), 4.12–4.24 (2 H, m), 4.55–4.73 ($\frac{5}{7}$ H, m), 4.99–5.07 ($\frac{2}{7}$ H, m)	$C_{19}H_{36}O_4Si$	63.95 (64.00)	10.05 (10.18)
6k	120–130 (0.28)	1720	0.85 ($\frac{5}{7}$ × 9 H, s), 0.86 ($\frac{2}{7}$ × 9 H, s), 0.9–2.1 (15 H, m), 2.2–2.35 (4 H, m), 3.67 (3 H, s), 4.55–4.65 ($\frac{5}{7}$ H, m), 4.96–5.04 ($\frac{2}{7}$ H, m)	$C_{18}H_{32}O_4$	69.05 (69.19)	10.25 (10.32)
6l	180–190 (0.23)	1720	0.85–1.05 (1 H, m), 1.2–1.45 (4 H, m), 1.45–1.80 (2 H, m), 1.85–2.05 (1 H, m), 2.1–2.3 (1 H, m), 2.35–2.5 (1 H, m), 2.65–2.75 (4 H, m), 4.85–5.00 (1 H, m), 5.13 (2 H, s), 7.35 (5 H, s)	$C_{18}H_{22}O_4$	302.1479[c] (302.1518)	
6m	*b*	1720	1.42 (6 H, s), 2.5–2.7 (4 H, m), 3.03 (2 H, s), 5.13 (2 H, s), 7.1–7.4 (10 H, m)	$C_{21}H_{24}O_4$	74.0 (74.09)	7.2 (7.11)
6n	130–140 (0.40)	1715	0.04 (9 H, s), 0.9–1.1 (2 H, m), 1.45 (6 H, s), 2.55 (4 H, s), 3.06 (2 H, s), 4.1–4.3 (2 H, m), 7.1–7.4 (5 H, m)	$C_{19}H_{30}O_4Si$	65.0 (65.10)	8.65 (8.63)
6o	185–190 (0.30)	1715	1.44 (6 H, s), 2.56 (4 H, s), 3.05 (2 H, s), 3.68 (3 H, s), 7.1–7.4 (5 H, m)	$C_{15}H_{20}O_4$	67.95 (68.16)	7.65 (7.63)
6p	150–170 (0.50)	1715	1.2–1.4 (2 H, m), 1.44 (6 H, s), 1.5–1.7 (4 H, m), 2.22 (2 H, t, *J* 7.4), 2.30 (2 H, t, *J* 7.4), 3.05 (2 H, s), 3.66 (3 H, s), 7.15–7.35 (5 H, m)	$C_{18}H_{26}O_4$	70.35 (70.56)	8.45 (8.55)
6q	165–170 (0.20)	1725	1.0–2.0 (14 H, m), 1.45 (3 H, s), 2.05–2.20 (2 H, m), 2.24 (2 H, t, *J* 7.3), 2.37 (2 H, t, *J* 7.3), 5.11 (2 H, s), 7.3–7.4 (5 H, m)	$C_{21}H_{30}O_4$	72.4 (72.80)	8.8[d] (8.73)
6r	140–145 (0.36)	1720	1.2–1.7 (14 H, m), 1.46 (3 H, s), 2.05–2.4 (6 H, m), 3.67 (3 H, s)	$C_{15}H_{26}O_4$	66.5 (66.63)	9.75 (9.69)
6s	125–135 (0.51)	1720	0.04 (9 H, s), 0.9–1.1 (2 H, m), 1.2–2.2 (7 H, m), 2.5–2.7 (4 H, m), 4.00 (2 H, d, *J* 6.4), 4.1–4.3 (2 H, m), 5.6–5.8 (2 H, m)	$C_{16}H_{28}O_4Si$	61.25 (61.50)	9.0 (9.03)
6t	145–150 (0.32)	1720	0.04 (9 H, s), 0.9–1.05 (2 H, m), 1.2–2.4 (13 H, m), 2.28 and 2.32 (2 H each, 2 t, *J* 7.1), 3.97 (2 H, d, *J* 6.4), 4.1–4.3 (2 H, m), 5.6–5.7 (2 H, m)	$C_{19}H_{34}O_4Si$	64.0 (64.36)	9.55 (9.67)
6u	140–145 (0.32)	1725	0.04 (9 H, s), 0.9–1.1 (2 H, m), 1.9–2.2 (2 H, m), 2.47 (2 H, t, *J* 7.1), 2.61 (4 H, s), 4.1–4.3 (2 H, m), 4.23 (2 H, t, *J* 6.0)	$C_{13}H_{23}NO_4Si$	54.5 (54.71)	8.0[e] (8.12)
6v	170–180 (0.50)	1790, 1735	1.09 (3 H, s), 1.18 (3 H, s), 2.6–2.9 (4 H, m), 4.02 (2 H, s), 5.14 (2 H, s), 5.36 (1 H, s), 7.34 (5 H, s)	$C_{17}H_{20}O_6$	63.45 (63.74)	6.3 (6.29)
6w	135–145 (0.35)	1790, 1750, 1725	0.04 (9 H, s), 0.9–1.1 (2 H, m), 1.13 and 1.21 (3 H each, 2 s), 2.6–2.9 (4 H, m), 4.04 (2 H, d), 4.1–4.3 (2 H, m), 5.38 (1 H, s)	$C_{15}H_{26}O_6Si$	54.15 (54.52)	7.8[f] (7.93)
6x	160–170[g] (0.20)	1730	2.7–3.0 (4 H, m), 5.16 (2 H, s), 7.0–7.5 (10 H, m)	$C_{17}H_{16}O_4$	71.8 (71.82)	5.6 (5.67)
6y	140–150 (0.20)	1720	1.35–1.5 (2 H, m), 1.6–1.9 (4 H, m), 2.35 (2 H, t, *J* 7.4), 2.56 (2 H, t, *J* 7.4), 3.67 (3 H, s), 7.07 (2 H, d, *J* 8.6), 7.15–7.30 (1 H, m), 7.37 (2 H, t, *J* 7.9)	$C_{14}H_{18}O_4$	66.9 (67.18)	7.3 (7.25)

[a] Bath temperature. [b] Oil. Partial decomposition occurred on distillation. [c] High-resolution (EI) data. [d] High-resolution (FAB, positive) data (Found: $M^+ + H$, 347.2249. $C_{21}H_{31}O_4$ requires M + H, 347.2222). [e] (Found: N, 4.85. Requires N, 4.91%). [f] High-resolution (EI) data (Found: M^+, 330.1524. $C_{15}H_{26}O_6Si$ requires M, 330.1499). [g] M.p. 47–48 °C.

Table 4 Physical data of alcohol *O*-hemiesters **7**

Compound	B.p./°C (mmHg)[a] or m.p./°C (recrystalln. solvent)	$\nu_{max}(CHCl_3)$/cm^{-1} C=O	$\delta_H(CDCl_3)$	Formula	Found (%) (Required) C	H
7a	70–70.5 (hexane)	1720	2.5–2.7 (4 H, m), 2.94 (2 H, t, *J* 7.0), 4.32 (2 H, t, *J* 7.0), 7.1–7.4 (5 H, m)	$C_{12}H_{14}O_4$	64.4 (64.85)	6.45[b] (6.35)
7b	125–135 (0.22)	1710	1.2–1.4 (2 H, m), 1.5–1.7 (4 H, m), 2.2–2.4 (4 H, m), 2.93 (2 H, t, *J* 7.0), 4.29 (2 H, t, *J* 7.0), 7.1–7.4 (5 H, m)	$C_{15}H_{20}O_4$	67.7 (68.16)	7.35[c] (7.63)
7c (≡**1a**)	57–58[d] (hexane)	1715	2.69 (4 H, s), 5.14 (2 H, s), 7.35 (5 H, s)	$C_{11}H_{12}O_4$		
7d	130–135 (0.30)	1710	0.85 ($\frac{5}{7}$ × 9 H, s), 0.86 ($\frac{2}{7}$ × 9 H, s), 0.9–2.1 (9 H, m), 2.5–2.8 (4 H, m), 4.5–4.8 ($\frac{5}{7}$ H, m), 5.0–5.1 ($\frac{2}{7}$ H, m)	$C_{14}H_{24}O_4$	65.35 (65.60)	9.3 (9.44)
7e	95–105 (0.22)	1720	0.9–1.1 (1 H, m), 1.2–1.5 (4 H, m), 1.5–1.9 (2 H, m), 1.9–2.1 (1 H, m), 2.1–2.3 (1 H, m), 2.4–2.5 (1 H, m), 2.5–2.8 (4 H, m), 4.9–5.1 (1 H, m)	$C_{11}H_{16}O_4$	61.8 (62.25)	7.55[e] (7.60)
7f	65–66 (hexane)	1705	1.44 (6 H, s), 2.5–2.7 (4 H, m), 3.06 (2 H, s), 7.1–7.4 (5 H, m)	$C_{14}H_{18}O_4$	66.95 (67.18)	7.3 (7.25)
7g	185–95 (0.50)	1700	1.2–1.4 (2 H, m), 1.44 (6 H, s), 1.5–1.8 (4 H, m), 2.22 (2 H, t, *J* 7.6), 2.29 (2 H, t, *J* 7.6), 3.05 (2 H, s), 7.1–7.4 (5 H, m)	$C_{17}H_{24}O_4$	292.1655[f] (292.1672)	
7h	*g*	1710	1.1–1.8 (14 H, m), 1.46 (3 H, s), 2.0–2.2 (2 H, m), 2.26 (2 H, t, *J* 7.4), 2.36 (2 H, t, *J* 7.4)	$C_{14}H_{24}O_4$	65.15 (65.59)	9.35[h] (9.44)
7i	140–150 (0.50)	1710	1.15–1.45 (1 H, m), 1.6–2.2 (6 H, m), 2.5–2.8 (4 H, m), 4.01 (2 H, d, *J* 6.4), 5.55–5.8 (2 H, m)	$C_{11}H_{16}O_4$	212.1075[f] (212.1049)	
7j	135–145 (0.30)	1710	1.2–2.2 (13 H, m), 2.33 and 2.36 (2 H each, 2 t, *J* 7.1), 3.98 (2 H, d, *J* 6.2), 5.5–5.8 (2 H, m)	$C_{14}H_{22}O_4$	254.1525[f] (254.1518)	
7k	*g*	1730	1.9–2.1 (2 H, m), 2.47 (2 H, t, *J* 7.1), 2.5–2.8 (4 H, m), 4.24 (2 H, t, *J* 6.0), 6.6–7.4 (1 H, br)	$C_8H_{11}NO_4$	185.0683[f] (185.0685)	
7l	170–180 (0.40)	1790, 1750, 1720	1.11 and 1.20 (3 H each, 2 s), 2.6–2.9 (4 H, m), 4.04 (2 H, d, *J* 1.8), 5.39 (1 H, s)	$C_{10}H_{14}O_6$	230.0780[f] (230.0788)	
7m	96.5–97.5[i] (hexane)	1755, 1715	2.7–3.0 (4 H, m), 7.0–7.5 (5 H, m)	$C_{10}H_{10}O_4$		

[a] Bath temperature. [b] High-resolution (EI) data (Found: M$^+$, 222.0908. $C_{12}H_{14}O_4$ requires M, 222.0892). [c] High-resolution (EI) data (Found: M$^+$, 264.1376. $C_{15}H_{20}O_4$ requires M, 264.1361). [d] Lit.,[8] m.p. 58–59 °C. [e] High-resolution (EI) data (Found: M$^+$, 212.1064. $C_{11}H_{16}O_4$ requires M, 212.1049. [f] High-resolution (EI) data. [g] Oil. Partial decomposition occurred on distillation. [h] High-resolution (FAB, positive) data (Found: M$^+$ + H, 257.1775. $C_{14}H_{25}O_4$ requires M + H, 257.1753). [i] Lit.,[19] 97–98 °C.

7.5, $COCH_2$ × 2), 4.1–4.25 (2 H, m, OCH_2), 5.11 (2 H, s, benzyl CH_2) and 7.3–7.5 (5 H, m, ArH) (Found: C, 65.05; H, 8.65. $C_{19}H_{30}O_4$ requires C, 65.10; H, 8.62%).

2-(*Trimethylsilyl*)*ethyl Hydrogen Succinate* **1b**.—Pd-black (70.0 mg) was added to a solution of compound **2a** (6.00 g, 19.5 mmol) in 1,4-dioxane (40 cm^3), and the mixture was subjected to catalytic hydrogenation under hydrogen for 15 h. The catalyst was filtered off and the filtrate was concentrated under reduced pressure to give an oil, which was distilled to give the *title compound* **1b** (3.30 g, 82%) as an oil, b.p. 132–133 °C/0.6 mmHg; $\nu_{max}(CHCl_3)$/cm^{-1} 1710; δ_H(200 MHz; $CDCl_3$) 0.04 (9 H, s, $SiMe_3$), 0.9–1.1 (2 H, m, $SiCH_2$), 2.5–2.8 (4 H, m, CH_2CH_2) and 4.1–4.3 (2 H, m, OCH_2) [Found: M$^+$ (EI), 218.0975; C, 49.05; H, 8.25. $C_9H_{18}O_4Si$ requires $C_9H_{18}O_4Si$ requires M, 218.0981; C, 49.51; H, 8.31%].

Compound **1b** was also obtained by the following method. A mixture of succinic anhydride **3** (11.5 g, 115 mmol), 2-(trimethylsilyl)ethanol (10.0 g, 84.7 mmol) and pyridine (6.70 g, 84.8 mmol) was heated at 100 °C for 5 h. After concentration of the reaction mixture under reduced pressure, saturated aq. $NaHCO_3$ was added to the residue. The separated oil was acidified to pH 1 with 10% aq. HCl and extracted with EtOAc. The extract was dried ($MgSO_4$), and concentrated under reduced pressure. $CHCl_3$ was added to the residue and the mixture was filtered. The filtrate was concentrated under reduced pressure to give an oil, which was distilled to give the title compound **1b** (14.2 g, 77%) as an oil.

2-(*Trimethylsilyl*)*ethyl Hydrogen Pimelate* **1e**.—*Compound* **1e** (7.90 g, 95%) was prepared from diester **2d** (14.0 g, 40.0 mmol) and Pd-black (550 mg), as an oil, b.p. 170–175 °C/0.30 mmHg; $\nu_{max}(CHCl_3)$/cm^{-1} 1720–1705; δ_H(200 MHz; $CDCl_3$) 0.03 (9 H, s, $SiMe_3$), 0.9–1.05 (2 H, m, $SiCH_2$), 1.25–1.5 (2 H, m, CH_2), 1.55–1.75 (4 H, m, CH_2 × 2), 2.28 and 2.35 (2 H each, 2 t, *J* 7.3, $COCH_2$ × 2) and 4.05–4.25 (2 H, m, OCH_2) [Found: M$^+$ (EI), 260.1438. $C_{12}H_{24}O_4Si$ requires M, 260.1411].

General Procedures for Formation of Isopropenyl Ester: from Half-esters **1a–f** *and Isopropenyl Acetate* (*Route A*).—*Benzyl isopropenyl succinate* **4a**. A mixture of compound **1a** (20.1 g, 96.6 mmol), isopropenyl acetate (53.1 g, 531 mmol), $Hg(OAc)_2$ (920 mg, 2.90 mmol) and BF_3·Et_2O (0.50 cm^3, 4.1 mmol) was stirred at 30 °C for 2 h. The reaction mixture was cooled to 0 °C and Et_3N (0.6 cm^3) was added. After concentration under reduced pressure, the residue was filtered through Florisil (200 cm^3) in a short column with the aid of hexane. After concentration under reduced pressure, the residual oil was distilled to give the *title isopropenyl ester* **4a** (12.3 g, 51%) as an oil. Data are given in Table 1.

Compounds **4c** and **4f** were obtained similarly as described for the preparation of compound **4a**. Compound **4b** was purified by the preceding Florisil short-column chromatography [hexane–Et_2O (2:1)], silical gel column chromatography [hexane–Et_2O (7:1)], and distillation under reduced pressure. Compound **4d** was purified by the preceding Florisil short-column chromatography (hexane), silica gel column chromatography [hexane–Et_2O (10:1)], and distillation under reduced pressure. Compound **4e**

was purified by the preceding Florisil short-column chromatography (hexane), silica gel column chromatography [hexane–Et_2O (5:1)], and distillation under reduced pressure.

From Acid Chlorides of Hemiesters **1a**, **c–f** *and Potassium Enolate of Acetone (Route B).—Isopropenyl methyl succinate* **4c**. Under nitrogen, KH (727 mg, 18.2 mmol) was suspended in dry DME (16 cm^3) below 0 °C. To this stirred suspension was added dropwise a solution of anhydrous acetone (1.33 cm^3, 18.1 mmol) in dry DME (16 cm^3) with cooling below 0 °C. The mixture was stirred at the same temperature for 30 min. A solution of this potassium enolate was added slowly to a solution of the respective acid chloride [prepared from the reaction of compound **1c** (2.26 g, 17.1 mmol) and oxalyl dichloride (3.70 cm^3, 42.4 mmol) in dry CH_2Cl_2 (25 cm^3) below room temperature and successive removal of excess of $(COCl)_2$ and CH_2Cl_2 below 30 °C under reduced pressure] in DME (15 cm^3) with cooling below 0 °C. The reaction mixture was allowed to warm to room temperature during 2 h and was stirred for 7 h. Et_2O and water were added to the mixture and the organic layer was separated, dried ($MgSO_4$), concentrated under reduced pressure, and purified by chromatography on silica gel [hexane–Et_2O (7:1)] to give the *title isopropenyl ester* **4c** (1.12 g, 38%) as an oil.

Compounds **4a, d–f** were purified by column chromatography on silica gel {**4a** [hexane–Et_2O (5:1)], **4d** [hexane–EtOAc (10:1)], **4e** [hexane–Et_2O (7:1)], **4f** [hexane–Et_2O (4:1)]}. Physical data for compounds **4a–f** are summarized in Table 1.

General Procedures for Acylation Reaction: by using a Catalytic Amount of conc. H_2SO_4.—*Benzyl 2-phenylethyl succinate* **6a**. To a solution of compound **4a** (244 mg, 0.980 mmol) and phenethyl alcohol **5a** (100 mg, 0.820 mmol) in dry CH_2Cl_2 (10 cm^3) was added a drop of conc. H_2SO_4 (*d* 1.84 g cm^{-3}) and the mixture was stirred for 30 min at room temperature. After the mixture had been concentrated under reduced pressure, MeCN (0.2 cm^3) and a drop of conc. HCl were added to the residue at 0 °C. The mixture was stirred for 20 min and partitioned between EtOAc and saturated aq. $NaHCO_3$. The organic layer was dried ($MgSO_4$) and evaporated to give a residue, which was purified by column chromatography on silica gel [hexane–Et_2O (3:1)] to give the *title diester* **6a** (194 mg, 76%) as an oil. Physical data for compounds **6** are given in Table 3.

By using a Catalytic Amount of p-*TsOH.—2-Phenylethyl 2-(trimethylsilyl)ethyl succinate* **6b**. To a solution of compound **4b** (550 mg, 2.13 mmol) and the alcohol **5a** (130 mg, 1.07 mmol) in dry CH_2Cl_2 (8 cm^3) was added anhydrous *p*-TsOH (37.0 mg, 0.210 mmol) and the mixture was stirred at 40 °C for 12 h. After the mixture had been concentrated under reduced pressure, MeCN (0.1 cm^3) and three drops of conc. HCl were added to the residue at 0 °C. The mixture was stirred for 30 min and then partitioned between EtOAc and saturated aq. $NaHCO_3$. The organic layer was dried ($MgSO_4$) and evaporated to give a residue, which was purified by column chromatography on silica gel [hexane–Et_2O (8:1)] to give the *title diester* **6b** (256 mg, 75%) as an oil.

Reaction conditions of the synthesis of compounds **6a–y** are shown in Table 2. Products **6c–y** were purified by column chromatography on silica gel {**6c**, **g** (≡**2a**), **i,l** [hexane–Et_2O (5:1)], **6d** [hexane–Et_2O (7:1)], **6e**, **t** [hexane–Et_2O (10:1)], **6f**, **w** [hexane–Et_2O (2:1)], **6h**, **k** [hexane–Et_2O (3:1)], **6j**, **s** [hexane–Et_2O (9:1)], **6m** [hexane–EtOAc (20:1)], **6n** [hexane–Et_2O (11:1)], **6o** [hexane–EtOAc (2:1)], **6p** [hexane–EtOAc (8:1)], **6q** [hexane–EtOAc (15:1)], **6r** [hexane–Et_2O (4:1)], **6u** [hexane–Et_2O (3:2)], **6v** [hexane–Et_2O (2:3)], **6x** [hexane–benzene–Et_2O (8:6:1)], **6y** [hexane–$CHCl_3$ (1:2)]}.

General Procedures for Synthesis of Alcohol O-*Hemiesters: By Catalytic Hydrogenation (Method A).—2-Phenylethyl hydrogen succinate* **7a**. Pd-black (30 mg) was added to a solution of diester **6a** (250 mg, 0.800 mmol) in 1,4-dioxane (2 cm^3), and the mixture was subjected to catalytic hydrogenation under hydrogen for 4 h. The catalyst was filtered off and the filtrate was concentrated under reduced pressure. To the crude product was added a mixture of saturated aq. $NaHCO_3$ and EtOAc. The aqueous layer was separated, acidified with 10% aq. HCl, and extracted with EtOAc. The extract was dried ($MgSO_4$), and concentrated under reduced pressure to give the *title* O-*hemiester* **7a** (156 mg, 88%) as an oil. Physical data for compounds **7** are summarized in Table 4.

By using TBAF (Method B).—2-Phenylethyl hydrogen pimelate **7b**. To a solution of compound **6e** (300 mg, 0.820 mmol) in dimethylformamide (DMF) (4 cm^3) was added TBAF·$3H_2O$ (517 mg, 1.64 mmol) and the mixture was stirred at room temperature for 1.5 h. A mixture of saturated aq. $NaHCO_3$ and EtOAc was added to the reaction mixture. The aqueous layer was separated, acidified with 10% aq. HCl, and extracted with EtOAc. The extract was dried ($MgSO_4$), and concentrated under reduced pressure to give the *title* O-*hemiester* **7b** (185 mg, 85%) as an oil.

By Alkaline Hydrolysis (Method C).—1,1-Dimethyl-2-phenylethyl hydrogen succinate **7f**. To a solution of compound **6o** (150 mg, 0.570 mmol) in MeOH (6 cm^3) at 5 °C was added 0.38 mol dm^{-3} NaOH (3.00 cm^3, 1.14 mmol) and the mixture was stirred at room temperature for 2.5 h. After the reaction mixture had been washed with EtOAc, the aqueous layer was acidified with 10% aq. HCl and extracted with EtOAc. The extract was dried ($MgSO_4$), and concentrated under reduced pressure to give the *title* O-*hemiester* **7f** (120 mg, 85%) as an oil.

Reaction conditions for the synthesis of half-esters **7a–m** are shown in Table 2.

10-O-[3-(*Methoxycarbonyl*)*propionyl*]-7,9-O-*phenylboranediyl*-β-*rhodomycinone* **9a**.—Under nitrogen, a drop of conc. H_2SO_4 (*d* 1.84 g cm^{-3}) was added to a stirred solution of compound **8**[14] (33.0 mg, 0.064 mmol) and diester **4c** (44.0 mg, 0.250 mmol) in dry CH_2Cl_2 (7 cm^3) at room temperature. After being stirred at room temperature for 2 h, the reaction mixture was quenched with saturated aq. $NaHCO_3$ and extracted with CH_2Cl_2. The extract was dried (Na_2SO_4), and concentrated under reduced pressure. The residue was washed with hexane and purified by PLC [CH_2Cl_2–Et_2O (9:1)] to give the *title compound* **9a** (32.0 mg, 86%) as red crystals, m.p. 209–211 °C (from $CHCl_3$–Et_2O); $[\alpha]_D^{25}$ +314 (*c* 0.10, $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 1735 and 1600; δ_H(500 MHz; $CDCl_3$) 1.11 (3 H, t, *J* 7.3, 14-H_3), 1.69 and 2.03 (1 H each, 2 sextet, *J* 7.3, 13-H_2), 2.20 (1 H, dd, *J* 14.5 and 2.4, 8-H), 2.35 (1 H, dd, *J* 14.5 and 1.2, 8-H), 2.55–2.80 (4 H, m, CH_2CH_2), 3.69 (3 H, s, CO_2Me), 5.75 (1 H, br t, *J* 2.5, 7-H), 6.36 (1 H, d, *J* 1.2, 10-H), 7.20–7.45 (4 H, m, 3-H and ArH), 7.70 (1 H, t, *J* 8.0, 2-H), 7.77 (2 H, d, *J* 6.7, ArH), 7.86 (1 H, d, *J* 8.0, 1-H), 12.12 (1 H, s, 4-OH), 12.80 (1 H, s, 6-OH) and 13.38 (1 H, s, 11-OH) (Found: C, 63.3; H, 4.6. $C_{31}H_{27}BO_{11}$ requires C, 63.50; H, 4.64%).

10-O-[6-(*Methoxycarbonyl*)*hexanoyl*]-7,9-O-*phenylboranediyl*-β-*rhodomycinone* **9b**.—*Compound* **9b** (23.0 mg, 87%) was prepared from compound **8** (20.0 mg, 0.0420 mmol), diester **4f** (40.0 mg, 0.187 mmol) and a drop of conc. H_2SO_4, as red crystals, m.p. 70–74 °C (from $CHCl_3$–hexane); $[\alpha]_D^{25}$ +360 (*c* 0.11, $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 1730 and 1600; δ_H(500 MHz; $CDCl_3$) 1.11 (3 H, t, *J* 7.3, 14-H_3), 1.32–1.45 (2 H, m, CH_2), 1.55–1.75 (5 H, m, 13-H and CH_2 × 2), 2.05 (1 H, sextet, *J* 7.3, 13-H), 2.20 (1 H, dd, *J* 14.0 and 1.8, 8-H), 2.25–2.40 (5 H,

m, 8-H and CH_2 × 2), 3.64 (3 H, s, CO_2Me), 5.74 (1 H, br s, $w_{\frac{1}{2}}$ 6.0, 7-H), 6.36 (1 H, s, 10-H), 7.25–7.43 (4 H, m, 3-H and ArH), 7.68 (1 H, t, *J* 8.0, 2-H), 7.78 (2 H, d, *J* 6.7, ArH), 7.84 (1 H, d, *J* 8.0, 1-H), 12.10 (1 H, s, 4-OH), 12.78 (1 H, s, 6-OH) and 13.38 (1 H, s, 11-OH) (Found: C, 64.8; H, 5.2. $C_{34}H_{33}BO_{11}$ requires C, 64.98; H, 5.29%).

10-O-[3-(*Benzyloxycarbonyl*)*propionyl*]-7,9-O-*phenylboranediyl*-β-*rhodomycinone* **9c**.—*Compound* **9c** (28.0 mg, 80%) was prepared from compound **8** (25.0 mg, 0.0530 mmol), diester **4a** (65.0 mg, 0.260 mmol) and a drop of conc. H_2SO_4, as red crystals, m.p. 86–89 °C (from $CHCl_3$–hexane); $[\alpha]_D^{25}$ +181 (*c* 0.097, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1735 and 1600; δ_H(500 MHz; $CDCl_3$) 1.09 (3 H, t, *J* 7.3, 14-H_3), 1.68 and 2.03 (1 H each, 2 sextet, *J* 7.3, 13-H_2), 2.17 (1 H, dd, *J* 14.0 and 2.0, 8-H), 2.32 (1 H, d, *J* 14.0, 8-H), 2.63–2.85 (4 H, m, CH_2CH_2), 5.12 (2 H, br s, benzyl CH_2), 5.72 (1 H, s, $w_{\frac{1}{2}}$ 7.5, 7-H), 6.35 (1 H, s, 10-H), 7.25–7.40 (9 H, m, 3-H and ArH), 7.67 (1 H, t, *J* 8.0, 2-H), 7.77 (2 H, d, *J* 7.3, ArH), 7.81 (1 H, d, *J* 8.0, 1-H), 12.08 (1 H, s, 4-OH), 12.76 (1 H, s, 6-OH) and 13.35 (1 H, s, 11-OH) (Found: C, 67.25; H, 4.7. $C_{37}H_{31}BO_{11}$ requires C, 67.08; H, 4.72%).

10-O-[3-(*Methoxycarbonyl*)*propionyl*]-β-*rhodomycinone* **10a**.—A mixture of boronate **9a** (28.0 mg, 0.0480 mmol), 2-methylpentane-2,4-diol (0.12 cm^3), AcOH (0.06 cm^3), acetone (1.8 cm^3) and CH_2Cl_2 (2.4 cm^3) was stirred at room temperature for 24 h. The reaction mixture was poured into a mixture of EtOAc and saturated aq. $NaHCO_3$. The organic layer was separated, washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was washed with hexane and recrystallized from $CHCl_3$–hexane to give the *title compound* **10a** (22.0 mg, 92%) as red crystals, m.p. 241–243 °C (from $CHCl_3$–hexane); $[\alpha]_D^{25}$ −75.5 (*c* 0.10, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 and 1600; δ_H(500 MHz; $CDCl_3$) 1.08 (3 H, t, *J* 7.3, 14-H_3), 1.57 and 1.75 (1 H each, 2 sextet, *J* 7.3, 13-H_2), 2.02 (1 H, dd, *J* 14.6 and 5.2, 8-H), 2.36 (1 H, d, *J* 14.6, 8-H), 2.50–2.75 (4 H, m, CH_2CH_2), 3.39 (1 H, br s, 9-OH), 3.66 (3 H, s, CO_2Me), 5.27 (1 H, br s, $w_{\frac{1}{2}}$ 10.5, 7-H), 6.29 (1 H, s, 10-H), 7.28 (1 H, d, *J* 8.0, 3-H), 7.69 (1 H, t, *J* 8.0, 2-H), 7.81 (1 H, d, *J* 8.0, 1-H), 12.04 (1 H, s, 4-OH), 12.86 (1 H, s, 6-OH) and 13.32 (1 H, s, 11-OH) (Found: C, 59.65; H, 4.85. $C_{25}H_{24}O_{11}$ requires C, 60.00; H, 4.83%).

10-O-[6-(*Methoxycarbonyl*)*hexanoyl*]-β-*rhodomycinone* **10b**.—*Compound* **10b** (36.0 mg, 83%) was prepared from compound **9b** (50.0 mg, 0.0800 mmol), 2-methylpentane-2,4-diol (0.2 cm^3), AcOH (0.1 cm^3), acetone (3.1 cm^3), and CH_2Cl_2 (4.1 cm^3), as red crystals, m.p. 210–213 °C (from $CHCl_3$–hexane); $[\alpha]_D^{25}$ +124 (*c* 0.043, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1720 and 1600; δ_H(500 MHz; $CDCl_3$) 1.09 (3 H, t, *J* 7.3, 14-H_3), 1.28–1.40 (2 H, m, CH_2), 1.50–1.70 (5 H, m, 13-H and CH_2 × 2), 1.74 (1 H, sextet, *J* 7.3, 13-H), 2.00 (1 H, dd, *J* 14.7 and 4.9, 8-H), 2.20–2.32 (4 H, m, CH_2 × 2), 2.35 (1 H, d, *J* 14.7, 8-H), 3.39 (1 H, s, 9-OH), 3.63 (3 H, s, CO_2Me), 3.66 (1 H, d, *J* 5.5, 7-OH), 5.27 (1 H, t, *J* 4.5, 7-H), 6.29 (1 H, s, 10-H), 7.28 (1 H, d, *J* 8.0, 3-H), 7.69 (1 H, t, *J* 8.0, 2-H), 7.82 (1 H, d, *J* 8.0, 1-H), 12.05 (1 H, s, 4-OH), 12.87 (1 H, s, 6-OH) and 13.34 (1 H, s, 11-OH) (Found: C, 61.65; H, 5.5. $C_{28}H_{30}O_{11}$ requires C, 61.98; H, 5.57%).

10-O-[3-(*Benzyloxycarbonyl*)*propionyl*]-β-*rhodomycinone* **10c**.—*Compound* **10c** (20.0 mg, 85%) was prepared from boronate **9c** (27.0 mg, 0.0410 mmol), 2-methylpentane-2,4-diol (0.1 cm^3), AcOH (0.05 cm^3), acetone (1.6 cm^3), and CH_2Cl_2 (2 cm^3), as red crystals, m.p. 213–215 °C (from $CHCl_3$–hexane); $[\alpha]_D^{25}$ +27.8 (*c* 0.036, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 and 1600; δ_H(500 MHz; $CDCl_3$) 1.06 (3 H, t, *J* 7.3, 14-H_3), 1.55 and 1.74 (1 H each, 2 sextet, *J* 7.3, 13-H_2), 2.00 (1 H, dd, *J* 14.7 and 4.9, 8-H), 2.33 (1 H, d, *J* 14.7, 8-H), 2.55–2.78 (4 H, m, CH_2CH_2), 3.37 (1 H, s, 9-OH), 3.63 (1 H, d, *J* 5.5, 7-OH), 5.09 (2 H, d, *J* 1.8, benzyl CH_2), 5.25 (1 H, t, *J* 4.5, 7-H), 6.28 (1 H, d, *J* 1.2, 10-H), 7.24–7.45 (6 H, m, 3-H and ArH), 7.69 (1 H, t, *J* 8.0, 2-H), 7.82 (1 H, d, *J* 8.0, 1-H), 12.03 (1 H, s, 4-OH), 12.84 (1 H, s, 6-OH) and 13.31 (1 H, s, 11-OH) (Found: C, 64.35; H, 4.8. $C_{31}H_{28}O_{11}$ requires C, 64.58; H, 4.89%).

10-O-[3-(*Methoxycarbonyl*)*propionyl*]-4′-O-(p-*nitrobenzoyl*)-3′-N-(*trifluoroacetyl*)*oxaunomycin* **12a**.—Under nitrogen, TMSOTf (0.023 cm^3, 0.13 mmol) was added to a stirred mixture of compound **11** (35.0 mg, 0.063 mmol) and MS 4 Å in dry CH_2Cl_2 (7 cm^3)–dry Et_2O (2.6 cm^3) at −40 °C. The mixture was stirred at −5 °C for 1 h and was then cooled to −15 °C, and a solution of compound **10a** (25.0 mg, 0.050 mmol) in dry CH_2Cl_2 (7 cm^3) was added. After being stirred for 6 h under the same conditions, the mixture was poured into a vigorously stirred mixture of EtOAc and saturated aq. $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by PLC [CH_2Cl_2–Et_2O (9:1)] gave the *title compound* **12a** (34.5 mg, 79%) as red crystals, m.p. 158–160 °C (from $CHCl_3$–hexane); $[\alpha]_D^{25}$ −79.4 (*c* 0.10, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1735, 1600 and 1530; δ_H(500 MHz; $CDCl_3$) 1.08 (3 H, t, *J* 7.3, 14-H_3), 1.27 (3 H, d, *J* 6.1, 6′-H_3), 1.54 and 1.70 (1 H each, 2 sextet, *J* 7.3, 13-H_2), 2.02–2.20 (3 H, m, 8-H and 2′-H_2), 2.41 (1 H, d, *J* 15.3, 8-H), 2.50–2.75 (4 H, m, CH_2CH_2), 3.49 (1 H, br, 9-OH), 3.67 (3 H, s, CO_2Me), 4.46 (1 H, m, 3′-H), 4.49 (1 H, q, *J* 6.1, 5′-H), 5.24 (1 H, br d, *J* 2.4, 7-H), 5.48 (1 H, br s, 4′-H), 5.65 (1 H, br d, *J* 3.7, 1′-H), 6.26 (1 H, br d, *J* 7.3, 3′-NH), 6.32 (1 H, d, *J* 1.2, 10-H), 7.34 (1 H, d, *J* 8.0, 3-H), 7.74 (1 H, t, *J* 8.0, 2-H), 7.91 (1 H, d, *J* 8.0, 1-H), 8.29 and 8.35 (2 H each, 2 d, *J* 8.8, ArH), 12.09 (1 H, s, 4-OH), 12.90 (1 H, s, 6-OH) and 13.43 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 874.2011. $C_{40}H_{37}F_3N_2O_{17}$ requires M, 874.2045].

10-O-[6-(*Methoxycarbonyl*)*hexanoyl*]-4′-O-(p-*nitrobenzoyl*)-3′-N-(*trifluoroacetyl*)*oxaunomycin* **12b**.—*Compound* **12b** (39.0 mg, 77%) was prepared from compound **11** (38.0 mg, 0.0700 mmol), TMSOTf (0.026 cm^3, 0.14 mmol), and compound **10b** (30.0 mg, 0.0560 mmol) in the presence of MS 4 Å (220 mg), as red crystals, m.p. 144–147 °C (from $CHCl_3$–hexane); $[\alpha]_D^{25}$ −33.0 (*c* 0.10, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1730, 1600 and 1530; δ_H(500 MHz; $CDCl_3$) 1.08 (3 H, t, *J* 7.3, 14-H_3), 1.27 (3 H, d, *J* 6.7, 6′-H_3), 1.25–1.40 (2 H, m, CH_2), 1.49 (1 H, sextet, *J* 7.3, 13-H), 1.55–1.70 (4 H, m, CH_2 × 2), 1.70 (1 H, sextet, *J* 7.3, 13-H), 2.05–2.20 (3 H, m, 8-H and 2′-H_2), 2.27 (4 H, t, *J* 7.3, CH_2 × 2), 2.41 (1 H, d, *J* 15.3, 8-H), 3.48 (1 H, s, 9-OH), 3.62 (3 H, s, CO_2Me), 4.43–4.53 (2 H, m, 3′- and 5′-H), 5.24 (1 H, br d, *J* 2.4, 7-H), 5.48 (1 H, br s, 4′-H), 5.65 (1 H, br d, *J* 3.7, 1′-H), 6.29 (1 H, br d, *J* 7.3, 3′-NH), 6.30 (1 H, s, 10-H), 7.33 (1 H, d, *J* 8.0, 3-H), 7.73 (1 H, t, *J* 8.0, 2-H), 7.90 (1 H, d, *J* 8.0, 1-H), 8.29 and 8.35 (2 H each, 2 d, *J* 8.8, ArH), 12.08 (1 H, s, 4-OH), 12.89 (1 H, s, 6-OH) and 13.43 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 916.2502. $C_{43}H_{43}F_3N_2O_{17}$ requires M, 916.2514].

10-O-[3-(*Methoxycarbonyl*)*propionyl*]-3′-N-(*trifluoroacetyl*)*oxaunomycin* **13a**.—A solution of nitrobenzoate **12a** (23.0 mg, 0.0260 mmol) in CH_2Cl_2 (1.4 cm^3)–MeOH (1.4 cm^3) was treated with 0.1 mol dm^{-3} NaOH (0.310 cm^3, 0.0310 mmol) at 0 °C. The mixture was stirred for 30 min under the same conditions, then a drop of 10% aq. HCl was added. The resulting mixture was partitioned between CH_2Cl_2 and water. The separated organic layer was dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by PLC

[CH_2Cl_2–Et_2O (3:1)] gave the *title compound* **13a** (17.0 mg, 90%) as red crystals, m.p. 142–145 °C (from $CHCl_3$–hexane); $[\alpha]_D^{25}$ +209 (*c* 0.096, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 and 1600; δ_H(500 MHz; $CDCl_3$) 1.05 (3 H, t, *J* 7.3, 14-H_3), 1.32 (3 H, d, *J* 6.7, 6'-H_3), 1.51 and 1.79 (1 H each, 2 sextet, *J* 7.3, 13-H_2), 1.83 (1 H, dt, *J* 13.0 and 3.7, 2'-H), 1.98 (1 H, br d, *J* 9.0, 4'-OH), 2.00–2.10 (2 H, m, 8- and 2'-H), 2.38 (1 H, d, *J* 15.3, 8-H), 2.50–2.75 (4 H, m, CH_2CH_2), 3.61 (1 H, s, 9-OH), 3.65–3.75 (1 H, m, 4'-H), 3.66 (3 H, s, CO_2Me), 4.15–4.25 (1 H, m, 3'-H), 4.30 (1 H, q, *J* 6.7, 5'-H), 5.17 (1 H, br d, *J* 2.4, 7-H), 5.46 (1 H, br d, *J* 3.7, 1'-H), 6.30 (1 H, s, 10-H), 6.65 (1 H, d, *J* 8.6, 3'-NH), 7.33 (1 H, d, *J* 8.0, 3-H), 7.72 (1 H, t, *J* 8.0, 2-H), 7.90 (1 H, d, *J* 8.0, 1-H), 12.08 (1 H, s, 4-OH), 12.84 (1 H, s, 6-OH) and 13.42 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 725.1956. $C_{33}H_{34}F_3NO_{14}$ requires M, 725.1931].

10-O-[6-(*Methoxycarbonyl*)*hexanoyl*]-3'-N-(*trifluoroacetyl*)*oxaunomycin* **13b**.—*Compound* **13b** (19.0 mg, 97%) was prepared from nitrobenzoate **12b** (23.5 mg, 0.0260 mmol) and 0.1 mol dm^{-3} NaOH (0.310 cm^3, 0.0310 mmol), as red crystals, m.p. 108–111 °C (from $CHCl_3$–hexane); $[\alpha]_D^{25}$ +255 (*c* 0.081, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1725 and 1600; δ_H(500 MHz; $CDCl_3$) 1.05 (3 H, t, *J* 7.3, 14-H_3), 1.25–1.40 (2 H, m, CH_2), 1.32 (3 H, d, *J* 6.7, 6'-H_3), 1.45 (1 H, sextet, *J* 7.3, 13-H), 1.55–1.70 (4 H, m, CH_2 × 2), 1.78 (1 H, sextet, *J* 7.3, 13-H), 1.83 (1 H, dt, *J* 13.0 and 3.7, 2'-H), 1.98 (1 H, d, *J* 7.9, 4'-OH), 2.00–2.10 (2 H, m, 8- and 2'-H), 2.27 (4 H, t, *J* 7.3, CH_2 × 2), 2.38 (1 H, d, *J* 14.7, 8-H), 3.59 (1 H, s, 9-OH), 3.63 (3 H, s, CO_2Me), 3.65–3.70 (1 H, m, 4'-H), 4.15–4.25 (1 H, m, 3'-H), 4.31 (1 H, q, *J* 6.7, 5'-H), 5.17 (1 H, br d, *J* 2.4, 7-H), 5.46 (1 H, br d, *J* 3.7, 1'-H), 6.29 (1 H, d, *J* 1.2, 10-H), 6.64 (1 H, d, *J* 8.6, 3'-NH), 7.32 (1 H, d, *J* 8.0, 3-H), 7.72 (1 H, t, *J* 8.0, 2-H), 7.90 (1 H, d, *J* 8.0, 1-H), 12.09 (1 H, s, 4-OH), 12.85 (1 H, s, 6-OH) and 13.44 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 767.2374. $C_{36}H_{40}F_3NO_{14}$ requires M, 767.2401].

10-O-(3-*Carboxypropionyl*)-3'-N-(*trifluoroacetyl*)*oxaunomysin* **14a**.—A solution of ester **13a** (10.0 mg, 0.0140 mmol) in DME (2 cm^3) was treated with a mixture of 0.1 mol dm^{-3} NaOH (2.80 cm^3, 0.280 mmol) and DME (1 cm^3) at 0 °C. The mixture was stirred at room temperature for 30 min, then a drop of 5% aq. AcOH was added. The resulting mixture was partitioned between EtOAc and water. The separated organic layer was dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by PLC [$CHCl_3$–MeOH (95:5)] gave *hemiester* **14a** (5.0 mg, 51%) as red crystals, m.p. 169–172 °C (from $CHCl_3$–MeOH–hexane); $[\alpha]_D^{25}$ +305 (*c* 0.011, acetone); ν_{max}(KBr)/cm^{-1} 1720 and 1600; δ_H[500 MHz; $(CD_3)_2SO$] 0.95 (3 H, t, *J* 7.3, 14-H_3), 1.13 (3 H, d, *J* 6.7, 6'-H_3), 1.40–1.52 (2 H, m, 13- and 2'-H), 1.56 (1 H, sextet, *J* 7.3, 13-H), 1.89 (1 H, dd, *J* 14.7 and 4.9, 8-H), 2.09 (1 H, dt, *J* 13.0 and 3.7, 2'-H), 2.26 (1 H, d, *J* 14.7, 8-H), 2.48–2.55 (4 H, m, CH_2CH_2), 3.51 (1 H, br d, *J* 9.4, 4'-H), 3.95–4.02 (1 H, m, 3'-H), 4.21 (1 H, q, *J* 6.7, 5'-H), 4.39 (1 H, s, 9-OH), 4.97 (1 H, br d, *J* 4.9, 7-H), 5.00 (1 H, d, *J* 2.4, 4'-OH), 5.27 (1 H, br d, *J* 3.1, 1'-H), 6.10 (1 H, s, 10-H), 7.42 (1 H, d, *J* 7.9, 3-H), 7.80–7.90 (2 H, m, 1- and 2-H), 9.06 (1 H, d, *J* 7.3, 3'-NH), 11.96 (1 H, br s, 4-OH), 12.10–12.24 (1 H, br, CO_2H), 12.77 (1 H, br s, 6-OH) and 13.36 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 711.1815. $C_{32}H_{32}F_3NO_{14}$ requires M, 711.1776].

10-O-(6-*Carboxyhexanoyl*)-3'-N-(*trifluoroacetyl*)*oxaunomycin* **14b**.—*Compound* **14b** (2.0 mg, 41%) was prepared from ester **13b** (5.0 mg, 0.0065 mmol) and 0.1 mol dm^{-3} NaOH (1.30 cm^3, 0.130 mmol), as red crystals, m.p. 147–149 °C (from $CHCl_3$–hexane); $[\alpha]_D^{25}$ +250 (*c* 0.010, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1720 and 1605; δ_H[500 MHz; $(CD_3)_2SO$] 0.96 (3 H, t, *J* 7.3, 14-H_3), 1.12 (3 H, d, *J* 6.7, 6'-H_3), 1.20–1.30 (2 H, m, CH_2), 1.38–1.54 (6 H, m, 13-, 2'-H and CH_2 × 2), 1.58 (1 H, sextet, *J* 7.3, 13-H), 1.87 (1 H, dd, *J* 14.8 and 4.6, 8-H), 2.08 (1 H, dt, *J* 13.0 and 3.7, 2'-H), 2.13 (2 H, t, *J* 7.3, CH_2), 2.19–2.21 (3 H, m, 8-H and CH_2), 3.51 (1 H, br d, *J* 3.7, 4'-H), 3.95–4.02 (1 H, m, 3'-H), 4.22 (1 H, q, *J* 6.7, 5'-H), 4.41 (1 H, s, 9-OH), 4.97 (1 H, d, *J* 3.7, 7-H), 5.00 (1 H, d, *J* 5.5, 4'-OH), 5.27 (1 H, br d, *J* 3.1, 1'-H), 6.11 (1 H, s, 10-H), 7.42 (1 H, d, *J* 7.9, 3-H), 7.80–7.90 (2 H, m, 1-and 2-H), 9.05 (1 H, d, *J* 7.3, 3'-NH), 11.83–11.95 (1 H, br, CO_2H), 11.96 (1 H, s, 4-OH), 12.77 (1 H, s, 6-OH) and 13.39 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 753.2274. $C_{35}H_{38}F_3NO_{14}$ requires M, 753.2245].

7-O-(3',4'-*Di*-O-*acetyl*-2'-*deoxy*-β-D-erythro-*pentopyranosyl*)-10-O-[6-(*methoxycarbonyl*)*hexanoyl*]-β-*rhodomycinone* **17a**.—Under nitrogen, a mixture of compound **10b** (42.0 mg, 0.0770 mmol), yellow HgO, (42.0 mg, 0.194 mmol), $HgBr_2$ (34.0 mg, 0.0940 mmol), and MS 4 Å (500 mg) in dry CH_2Cl_2 (20 cm^3) was stirred at room temperature for 1 h. A solution of the chloride **15** (0.231 mmol) [derived from 1,3,4-tri-*O*-acetyl-2-deoxy-D-*erythro*-pentopyranose (60.1 mg, 0.231 mmol) according to the reported method][18] in dry CH_2Cl_2 (10 cm^3) was added, and the mixture was stirred for 24 h in the dark. After filtration with the aid of $CHCl_3$, the organic solution was washed successively with aq. 30% KI and saturated aq. $NaHCO_3$, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by PLC [CH_2Cl_2–Et_2O (9:1)] gave the *title compound* **17a** (46.0 mg, 80%) as red crystals, m.p. 62–65 °C (from $CHCl_3$–hexane); $[\alpha]_D^{25}$ +106 (*c* 0.073, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1740 and 1605; δ_H(500 MHz; $CDCl_3$) 1.06 (3 H, t, *J* 7.3, 14-H_3), 1.25–1.40 (2 H, m, CH_2), 1.46 (1 H, sextet, *J* 7.3, 13-H), 1.50–1.70 (4 H, m, CH_2 × 2), 1.75 (1 H, sextet, *J* 7.3, 13-H), 1.80–1.90 (1 H, m, 2'-H), 1.90–2.20 (2 H, m, 8- and 2'-H), 1.98 and 2.15 (3 H each, 2 s, OAc × 2), 2.20–2.30 (4 H, m, CH_2 × 2), 2.45 (1 H, d, *J* 15.3, 8-H), 3.62 (3 H, s, CO_2Me), 3.89 (1 H, dd, *J* 13.0 and 3.1, 5'-H), 4.16 (1 H, dd, *J* 13.0 and 1.8, 5'-H), 5.05–5.35 (3 H, m, 3'-, 4'- and 7-H), 5.55 (1 H, br t, *J* 2.5, 1'-H), 6.29 (1 H, s, 10-H), 7.33 (1 H, dd, *J* 8.5 and 1.2, 3-H), 7.72 (1 H, t, *J* 8.5, 2-H), 7.90 (1 H, dd, *J* 8.5 and 1.2, 1-H), 12.10 (1 H, s, 4-OH), 12.88 (1 H, s, 6-OH) and 13.43 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 742.2505. $C_{37}H_{42}O_{16}$ requires M, 742.2473].

7-O-(3',4'-*Di*-O-*acetyl*-2',6'-*dideoxy*-2'-*fluoro*-α-L-*talopyranosyl*)-10-O-[6-(*methoxycarbonyl*)*hexanoyl*]-β-*rhodomycinone* **17b**.—Under nitrogen, a mixture of compound **10b** (28.0 mg, 0.0520 mmol), yellow HgO (45.0 mg, 0.208 mmol), $HgBr_2$ (19.0 mg, 0.0520 mmol), and MS 3 Å (260 mg) in dry CH_2Cl_2 (10 cm^3) was stirred at room temperature for 30 min. A solution of the fluoride **16** (0.103 mmol) [derived from 1,3,4-tri-*O*-acetyl-2,6-dideoxy-2-fluoro-α-L-talopyranose (30.1 mg, 0.103 mmol) according to the reported method][17] in dry CH_2Cl_2 (2 cm^3) was added, and the mixture was stirred for 48 h in the dark. After filtration with the aid of $CHCl_3$, the organic solution was washed successively with aq. 30% KI and saturated aq. $NaHCO_3$, dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by PLC [CH_2Cl_2–Et_2O (9:1)] gave the *title compound* **17b** (30.0 mg, 75%) as red crystals, m.p. 109–111 °C (from $CHCl_3$–hexane); $[\alpha]_D^{25}$ +146 (*c* 0.24, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1740 and 1605; δ_H(500 MHz; $CDCl_3$) 1.06 (3 H, t, *J* 7.3, 14-H_3), 1.29 (3 H, d, *J* 6.7, 6'-H_3), 1.25–1.38 (2 H, m, CH_2), 1.47 (1 H, sextet, *J* 7.3, 13-H), 1.55–1.68 (4 H, m, CH_2 × 2), 1.77 (1 H, sextet, *J* 7.3, 13-H), 2.01 and 2.19 (3 H each, 2 s, OAc × 2), 2.07 (1 H, dd, *J* 15.0 and 4.3, 8-H), 2.23–2.30 (4 H, m, CH_2 × 2), 2.43 (1 H, d, *J* 15.0, 8-H), 3.03 (1 H, s, 9-OH), 3.63 (3 H, s, CO_2Me), 4.38 (1 H, q, *J* 6.7, 5'-H), 4.60 (1 H, br d, *J* 49.4, 2'-H), 4.97 (1 H, dt, *J* 32.5 and 3.2, 3'-H), 5.18–5.28 (2 H, m, 7-and 4'-H), 5.61 (1 H, d, *J* 9.7, 1'-H), 6.28

(1 H, d, *J* 1.2, 10-H), 7.34 (1 H, d, *J* 8.0, 3-H), 7.73 (1 H, t, *J* 8.0, 2-H), 7.90 (1 H, d, *J* 8.0, 1-H), 12.08 (1 H, s, 4-OH), 12.87 (1 H, s, 6-OH) and 13.41 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 774.2507. $C_{38}H_{43}FO_{16}$ requires M, 774.2536].

10-O-[3-(*Benzyloxycarbonyl*)*propionyl*)-7-O-(3',4'-*di*-O-*acetyl*-2',6'-*dideoxy*-2'-*fluoro*-α-L-*talopyranosyl*)-β-*rhodomycinone* **17c**.—*Compound* **17c** (20.0 mg, 57%) was prepared from compound **10c** (25.0 mg, 0.0430 mmol), yellow HgO (38.0 mg, 0.176 mmol), $HgBr_2$ (16.0 mg, 0.0440 mmol), MS 3 Å (230 mg), and the fluoride **16** (0.103 mmol), as red crystals, m.p. 118–121 °C (from $CHCl_3$–hexane); $[\alpha]_D^{25}$ +142 (*c* 0.13, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1735 and 1600; δ_H(500 MHz; $CDCl_3$) 1.04 (3 H, t, *J* 7.3, 14-H_3), 1.29 (3 H, d, *J* 6.5, 6'-H_3), 1.52 and 1.76 (1 H each, 2 sextet, *J* 7.3, 13-H_2), 2.03 and 2.19 (3 H, each, 2 s, OAc × 2), 2.04 (1 H, dd, *J* 15.3 and 4.3, 8-H), 2.40 (1 H, d, *J* 15.3, 8-H), 2.52–2.78 (4 H, m, CH_2CH_2), 3.03 (1 H, s, 9-OH), 4.37 (1 H, q, *J* 6.5, 5'-H), 4.59 (1 H, br d, *J* 49.5, 2'-H), 4.96 (1 H, dt, *J* 33.0 and 3.5, 3'-H), 5.09 (2 H, s, benzyl CH_2), 5.19 (1 H, d, *J* 3.1, 4'-H), 5.23 (1 H, d, *J* 3.7, 7-H), 5.60 (1 H, d, *J* 9.2, 1'-H), 6.28 (1 H, s, 10-H), 7.21–7.39 (6 H, m, 3-H and ArH), 7.73 (1 H, t, *J* 8.0, 2-H), 7.89 (1 H, d, *J* 8.0, 1-H), 12.07 (1 H, s, 4-OH), 12.85 (1 H, s, 6-OH) and 13.38 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 808.2402. $C_{41}H_{41}FO_{16}$ requires M, 808.2379].

7-O-(2'-*Deoxy*-β-D-erythro-*pentopyranosyl*)-10-O-[6-(*methoxycarbonyl*)*hexanoyl*]-β-*rhodomycinone* **18a**.—A solution of diacetate **17a** (56.0 mg, 0.0750 mmol) in MeOH (4 cm^3) was treated with 0.1 mol dm^{-3} NaOH (2.25 cm^3, 0.225 mmol) at 10 °C. The mixture was stirred at room temperature for 10 min, then three drops of AcOH were added. The resulting mixture was partitioned between CH_2Cl_2 and water. The separated organic layer was dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by PLC [$CHCl_3$–MeOH (9:1)] gave the *title compound* **18a** (38.0 mg, 77%) as red crystals, m.p. 196–199 °C (from $CHCl_3$–Et_2O); $[\alpha]_D^{25}$ +89.9 (*c* 0.11, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1735 and 1605; δ_H(500 MHz; $CDCl_3$) 1.06 (3 H, t, *J* 7.3, 14-H_3), 1.25–1.40 (2 H, m, CH_2), 1.46 (1 H, sextet, *J* 7.3, 13-H), 1.50–1.70 (4 H, m, CH_2 × 2), 1.87 (1 H, ddd, *J* 13.4, 5.0 and 3.0, 2-H), 1.95–2.05 (2 H, m, 8- and 2'-H), 2.20–2.45 (4 H, m, CH_2 × 2), 2.47 (1 H, d, *J* 15.3, 8-H), 3.62 (3 H, s, CO_2Me), 3.80–4.00 (3 H, m, 3'-, 4'- and 5'-H), 4.07 (1 H, d, *J* 10.4, 5'-H), 5.19 (1 H, dd, *J* 4.0 and 1.8, 7-H), 5.50 (1 H, dd, *J* 3.3 and 3.0, 1'-H), 6.27 (1 H, d, *J* 1.2, 10-H), 7.32 (1 H, dd, *J* 8.0 and 1.2, 3-H), 7.71 (1 H, t, *J* 8.0, 2-H), 7.89 (1 H, dd, *J* 8.0 and 1.2, 1-H), 12.10 (1 H, s, 4-OH), 12.87 (1 H, s, 6-OH) and 13.44 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 658.2286; C, 59.75; H, 5.95. $C_{33}H_{38}O_{14}$ requires M, 658.2262; C, 60.17; H, 5.82%].

7-O-(2',6'-*Dideoxy*-2'-*fluoro*-α-L-*talopyranosyl*)-10-O-[6-(*methoxycarbonyl*)*hexanoyl*]-β-*rhodomycinone* **18b**.—*Compound* **18b** (21.0 mg, 84%) was prepared from compound **17b** (28.0 mg, 0.0360 mmol) and 0.1 mol dm^{-3} NaOH (1.08 cm^3, 0.108 mmol), as red crystals, m.p. 208–210 °C (from $CHCl_3$–Et_2O); $[\alpha]_D^{25}$ +102 (*c* 0.10, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3550, 1730 and 1605; δ_H(500 MHz; $CDCl_3$) 1.06 (3 H, t, *J* 7.3, 14-H_3), 1.25–1.38 (2 H, m, CH_2), 1.40 (3 H, d, *J* 6.7, 6'-H_3), 1.48 (1 H, sextet, *J* 7.3, 13-H), 1.53–1.68 (4 H, m, CH_2 × 2), 1.77 (1 H, sextet, *J* 7.3, 13-H), 1.89 (1 H, dd, *J* 11.3 and 8.0, 4'-OH), 2.06 (1 H, dd, *J* 15.3 and 4.6, 8-H), 2.27 (4 H, br t, *J* 7.3, CH_2 × 2), 2.43 (1 H, d, *J* 15.3, 8-H), 2.88 (1 H, d, *J* 11.0, 3'-OH), 3.16 (1 H, s, 9-OH), 3.63 (3 H, s, CO_2Me), 3.56–3.70 (2 H, m, 3'- and 4'-H), 4.22 (1 H, q, *J* 6.7, 5'-H), 4.62 (1 H, br d, *J* 48.8, 2'-H), 5.23 (1 H, d, *J* 2.4, 7-H), 5.57 (1 H, d, *J* 9.8, 1'-H), 6.27 (1 H, d, *J* 1.2, 10-H), 7.34 (1 H, d, *J* 8.0, 3-H), 7.73 (1 H, t, *J* 8.0, 2-H), 7.90 (1 H, d, *J* 8.0, 1-H), 12.08 (1 H, s, 4-OH), 12.89 (1 H, s, 6-OH) and 13.41 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 690.2298. $C_{34}H_{39}FO_{14}$ requires M, 690.2324].

10-O-[3-(*Benzyloxycarbonyl*)*propionyl*]-7-O-(2',6'-*dideoxy*-2'-*fluoro*-α-L-*talopyranosyl*)-β-*rhodomycinone* **18c**.—*Compound* **18c** (10.0 mg, 75%) was prepared from diacetate **17c** (15.0 mg, 0.019 mmol) and 0.1 mol dm^{-3} NaOH (0.600 cm^3, 0.0600 mmol), as red crystals, m.p. 251–254 °C (from $CHCl_3$–Et_2O); $[\alpha]_D^{25}$ +43.8 (*c* 0.089, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3520, 1730 and 1600; δ_H(500 MHz; $CDCl_3$) 1.03 (3 H, t, *J* 7.3, 14-H_3), 1.40 (3 H, d, *J* 6.7, 6'-H_3), 1.53 and 1.75 (1 H each, 2 sextet, *J* 7.3, 13-H_2), 1.88 (1 H, dd, *J* 11.6 and 7.9, 4'-OH), 2.04 (1 H, dd, *J* 15.3 and 4.3, 8-H), 2.40 (1 H, d, *J* 15.3, 8-H), 2.53–2.79 (4 H, m, CH_2CH_2), 2.87 (1 H, d, *J* 11.0, 3'-OH), 3.15 (1 H, s, 9-OH), 3.55–3.70 (2 H, m, 3'- and 4'-H), 4.21 (1 H, q, *J* 6.7, 5'-H), 4.61 (1 H, br d, *J* 49.4, 2'-H), 5.09 (2 H, s, benzyl CH_2), 5.20 (1 H, br d, *J* 3.1, 7-H), 5.56 (1 H, d, *J* 8.6, 1'-H), 6.27 (1 H, d, *J* 1.2, 10-H), 7.24–7.40 (6 H, m, 3-H and ArH), 7.73 (1 H, t, *J* 8.0, 2-H), 7.90 (1 H, d, *J* 8.0, 1-H), 12.07 (1 H, s, 4-OH), 12.87 (1 H, s, 6-OH) and 13.39 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 724.2192. $C_{37}H_{37}FO_{14}$ requires M, 724.2168].

10-O-(6-*Carboxyhexanoyl*)-7-O-(2'-*deoxy*-β-D-erythro-*pentopyranosyl*)-β-*rhodomycinone* **19a**.—A solution of ester **18a** (8.0 mg, 0.012 mmol) in MeOH (2 cm^3) was treated with 0.1 mol dm^{-3} NaOH (4.80 cm^3, 0.480 mmol) at 10 °C. The mixture was stirred at room temperature for 1 h, then four drops of AcOH were added at 0 °C. The resulting mixutre was partitioned between EtOAc and water. The separated organic layer was dried (Na_2SO_4), and concentrated under reduced pressure. Purification of the residue by PLC [$CHCl_3$–MeOH (9:1)] gave the *title compound* **19a** (6.0 mg, 75%) as red crystals, m.p. 178–181 °C (from $CHCl_3$–Et_2O); $[\alpha]_D^{25}$ +235 [*c* 0.021, $CHCl_3$–MeOH (9:1)]; ν_{max}(KBr)/cm^{-1} 3300, 1735 and 1600; δ_H[500 MHz; $(CD_3)_2SO$] 0.95 (3 H, t, *J* 7.3, 14-H_3), 1.20–1.30 (2 H, m, CH_2), 1.35–1.60 (6 H, m, 13-H_2 and CH_2 × 2), 1.85–1.95 (2 H, m, 8- and 2'-H), 2.12 (2 H, t, *J* 7.3, CH_2), 2.15–2.30 (3 H, m, 2'-H and CH_2), 2.30 (1 H, d, *J* 15.3, 8-H), 3.55–3.65 (2 H, m, 4'- and 5'-H), 3.70 (1 H, ddd, *J* 8.6, 4.0 and 2.5, 3'-H), 3.92 (1 H, dd, *J* 13.1 and 3.4, 5'-H), 5.00 (1 H, dd, *J* 4.0 and 1.0, 7-H), 5.29 (1 H, br t, *J* 3.0, 1'-H), 6.08 (1 H, d, *J* 1.0, 10-H), 7.42 (1 H, dd, *J* 8.0 and 1.2, 3-H), 7.82 (1 H, dd, *J* 8.0 and 1.2, 1-H), 7.86 (1 H, t, *J* 8.0, 2-H), 11.94 (1 H, s, 4-OH), 12.79 (1 H, s, 6-OH) and 13.37 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 644.2081. $C_{32}H_{36}O_{14}$ requires M, 644.2105].

10-O-(6-*Carboxyhexanoyl*)-7-O-(2',6'-*dideoxy*-2'-*fluoro*-α-L-*talopyranosyl*)-β-*rhodomycinone* **19b**.—*Compound* **19b** (6.5 mg, 74%) was prepared from ester **18b** (9.0 mg, 0.013 mmol) and 0.1 mol dm^{-3} NaOH (5.20 cm^3, 0.520 mmol), as red crystals, m.p. 233–236 °C (from $CHCl_3$–Et_2O); $[\alpha]_D^{25}$ +99.3 [*c* 0.028, $CHCl_3$–MeOH (9:1)]; ν_{max}(KBr)/cm^{-1} 3350, 1705 and 1600; δ_H[500 MHz; $(CD_3)_2SO$] 0.95 (3 H, t, *J* 7.3, 14-H_3), 1.19 (3 H, d, *J* 6.7, 6'-H_3), 1.18–1.29 (2 H, m, CH_2), 1.35–1.52 (5 H, m, 13-H and CH_2 × 2), 1.57 (1 H, sextet, *J* 7.3, 13-H), 1.90 (1 H, dd, *J* 15.3 and 4.9, 8-H), 2.12 (2 H, t, *J* 7.3, CH_2), 2.19–2.32 (3 H, m, 8-H and CH_2), 3.45–3.60 (2 H, m, 3'- and 4'-H), 4.21 (1 H, q, *J* 6.7, 5'-H), 4.32 (1 H, br d, *J* 49.4, 2'-H), 4.35 (1 H, s, 9-OH), 5.01 (1 H, d, *J* 4.9, 7-H), 5.32 (1 H, d, *J* 9.2, 1'-H), 6.10 (1 H, s, 10-H), 7.44 (1 H, d, *J* 7.9, 3-H), 7.80–7.90 (2 H, m, 1- and 2-H), 11.97 (1 H, s, 4-OH), 12.79 (1 H, s, 6-OH) and 13.37 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 676.2172. $C_{33}H_{37}FO_{14}$ requires M, 676.2167].

10-O-(3-*Carboxypropionyl*)-7-O-(2',6'-*dideoxy*-2'-*fluoro*-α-L-*talopyranosyl*)-β-*rhodomycinone* **19c**.—*Compound* **19c** (6.5 mg, 74%) was prepared from ester **18c** (7.0 mg, 0.0096 mmol) and

0.1 mol dm^{-3} NaOH (4.0 cm^3, 0.40 mmol), as red crystals, m.p. 264–267 °C (from $CHCl_3$–Et_2O); $[\alpha]_D^{25}$ +90.9 [*c* 0.011, $CHCl_3$–MeOH (9:1)]; ν_{max}(KBr)/cm^{-1} 3480, 1720 and 1595; δ_H[500 MHz; $(CD_3)_2SO$] 0.94 (3 H, t, *J* 7.3, 14-H_3), 1.19 (3 H, d, *J* 6.7, 6'-H_3), 1.48 and 1.58 (1 H each, 2 sextets, *J* 7.3, 13-H_2), 1.91 (1 H, dd, *J* 15.3 and 4.3, 8-H), 2.23 (1 H, d, *J* 15.3, 8-H), 2.40–2.58 (4 H, m, CH_2CH_2), 3.45–3.60 (2 H, m, 3'-and 4'-H), 4.22 (1 H, q, *J* 6.7, 5'-H), 4.32 (1 H, br d, *J* 49.4, 2'-H), 4.33 (1 H, s, 9-OH), 5.02 (1 H, d, *J* 4.3, 7-H), 5.32 (1 H, d, *J* 9.8, 1'-H), 6.09 (1 H, s, 10-H), 7.44 (1 H, d, *J* 8.0, 3-H), 7.80–7.90 (2 H, m, 1- and 2-H), 11.97 (1 H, s, 4-OH), 12.80 (1 H, s, 6-OH) and 13.33 (1 H, s, 11-OH) [Found: M^- (FAB, negative), 634.1678. $C_{30}H_{31}FO_{14}$ requires M, 634.1698].

References

1 R. Yamamoto, S. Fujisawa and M. Kawamura, *Yakugaku Zasshi*, 1971, **91**, 855; H. Minlon, U.S. Pat. 2 656 366, 1953 (*Chem. Abstr.*, 1954, **48**, 10794b).
2 J. G. Baxter, C. D. Robeson, J. D. Taylor and R. W. Lehman, *J. Am. Chem. Soc.*, 1943, **65**, 918.
3 M. Israel, P. G. Potti and R. Seshadri, *J. Med. Chem.*, 1985, **28**, 1223; T. Tsuchiya, Y. Takagi, S. Umezawa, T. Takeuchi, K. Komuro, C. Nosaka, H. Umezawa, S. Fukatsu and T. Yoneta, *J. Antibiot.*, 1988, **41**, 988.
4 N. F. Magri and D. G. I. Kingston, *J. Nat. Prod.*, 1988, **51**, 298; H. M. Deutsch, J. A. Glinski, M. Hernandez, R. D. Haugwitz, V. L. Narayanan, M. Suffness and L. H. Zalkow, *J. Med. Chem.*, 1989, **32**, 788.
5 J. W. Hill and W. H. Carothers, *J. Am. Chem. Soc.*, 1933, **55**, 5023.
6 Y. Kita, H. Maeda, F. Takahashi and S. Fukui, *J. Chem. Soc., Chem. Commun.*, 1993, 410.
7 For similar acylating reagents, see: Y. Tamura, J. Haruta, S. Okuyama and Y. Kita, *Tetrahedron Lett.*, 1978, 3737; Y. Kita, J. Haruta, H. Tagawa and Y. Tamura, *J. Org. Chem.*, 1980, **45**, 4519; Y. Kita, J. Haruta, H. Yasuda, K. Fukunaga, Y. Shirouchi and Y. Tamura, *J. Org. Chem.*, 1982, **47**, 2697; Y. Kita, S. Akai, N. Ajimura, M. Yoshigi, T. Tsugoshi, H. Yasuda and Y. Tamura, *J. Org. Chem.*, 1986, **51**, 4150; Y. Kita, S. Akai, M. Yamamoto, M. Taniguchi and Y. Tamura, *Synthesis*, 1989, 334.
8 R. P. Linstead, B. C. L. Weedon and B. Wlandislaw, *J. Chem. Soc.*, 1955, 1097.
9 J. Cason, *Org. Synth.*, 1955, Coll. Vol. 3, p. 169.
10 J. H. Short and U. Biermacher, *Chim. Ther.*, 1966, 456.
11 G. T. Morgan and E. Walton, *J. Chem. Soc.*, 1935, 290.
12 E. S. Rothman, S. Serota and D. Swern, *J. Org. Chem.*, 1966, **31**, 629.
13 P. Sieber, *Helv. Chim. Acta*, 1977, **60**, 2711; H. Gerlach, *Helv. Chim. Acta*, 1977, **60**, 3039.
14 Y. Kita, H. Maeda, M. Kirihara, Y. Fujii, T. Nakajima, H. Yamamoto and H. Fujioka, *Tetrahedron Lett.*, 1990, **31**, 7173; Y. Kita, H. Maeda, M. Kirihara, Y. Fujii, T. Nakajima, H. Yamamoto, Y. Tamura and H. Fujioka, *Chem. Pharm. Bull.*, 1992, **40**, 61.
15 A. Yoshimoto, S. Fujii, O. Johdo, K. Kubo, T. Ishikura, H. Naganawa, T. Sawa, T. Takeuchi and H. Umezawa, *J. Antibiot.*, 1986, **39**, 902.
16 Y. Kimura, M. Suzuki, T. Matsumoto, R. Abe and S. Terashima, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 423.
17 K.-D. Ok, T. Takagi, T. Tsuchiya, S. Umezawa and H. Umezawa, *Carbohydr. Res.*, 1987, **169**, 69.
18 J. Davoll and B. Lythgoe, *J. Chem. Soc.*, 1949, 2526.
19 F. G. Baddar and L. S. El-Assal, *J. Chem. Soc.*, 1950, 3606.

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