Carbohydrate Research, 208 (1990) 67–81
Elsevier Science Publishers B.V., Amsterdam

Synthesis of 4-*O*-methyl-β-rhodomycins using derivatives of 4-amino-4-deoxy- and 3,4-diamino-3,4-dideoxy sugars

Cenek Kolar*, Konrad Dehmel, and Hans Moldenhauer
Research Laboratories of Behringwerke AG, P.O.Box 1140, D-3550 Marburg (F.R.G.)

(Received February 28th, 1990; accepted for publication, April 9th, 1990)

ABSTRACT

Synthesis of 7-*O*-(4-amino-2,4,6-trideoxy- and 7-*O*-(3,4-diamino-2,3,4,6-tetradeoxy-α-L-*lyxo*-hexopyranosyl)-4-*O*-methyl-β-rhodomycinones (**31** and **33**) are described. The glycosyl donors 2,4,6-trideoxy-1,3-di-*O*-*p*-nitrobenzoyl-4-trifluoroacetamido-β-L-*lyxo*-hexopyranose (**14β**) and 2,3,4,6-tetradeoxy-1-*O*-*p*-nitrobenzoyl-3,4-bis(trifluoroacetamido)-β-L-*lyxo*-hexopyranose (**23β**) were suitable for the glycosylation of 4-*O*-methyl-10-*O*-*p*-nitrobenzoyl-β-rhodomycinone by the trimethylsilyl triflate method. Saponification of the resulting 7-*O*-α-glycosyl-4-*O*-methyl-β-rhodomycinones gave **31** and **33**.

INTRODUCTION

Recently, we have explored a novel route of synthesis to 7-*O*-(3-amino-2,3,6-trideoxy-α-L-*lyxo*-hexopyranosyl)-4-*O*-methylrhodomycinone[1,2]. Since this semi-synthetic rhodomycin had reduced cytotoxicity compared to that of natural oxaunomycin[3], further analogues were prepared that had 4-amino-4-deoxy- and 3,4-diamino-3,4-dideoxy-*lyxo*-pyranose moieties in order to establish structure–activity relationships for 4-*O*-methyl-β-rhodomycins.

As shown by Hadfield *et al.*[4], 4-amino-4-deoxy derivatives can be prepared from 3-*O*-benzoyl-2,6-dideoxy-4-*O*-mesyl-L-*arabino*-hexopyranoside by treatment with sodium azide in hexamethylphosphoric triamide followed by hydrogenolysis of the azido group in the *lyxo* intermediate. Martin *et al.*[5] applied this procedure to synthesise the 1-*O*-acetyl-3-*O*-benzoyl-4-deoxy-4-trifluoroacetamido derivative, which was used to glycosylate daunomycinone. The synthesis of the 4-amino-4-deoxy and 3,4-diamino-3,4-dideoxy sugar units and the use of their glycosyl chlorides in the glycosylation of anthracyclinones have been described[6,7].

We now describe routes for the synthesis of 4-amino-4-deoxy- and 3,4-diamino-3,4-dideoxy-*lyxo*-hexopyranoses, and their use for the glycosylation of 4-*O*-methyl-β-rhodomycinone.

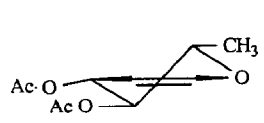
RESULTS AND DISCUSSION

Synthesis of 4-amino-4-deoxy and 3,4-diamino-3,4-dideoxy sugars and their glycosyl donors. — The 4-amino-4-deoxy sugar derivative **11** was synthesised from 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-L-*arabino*-hex-enitol (**1**) as reported[4,8], but using the

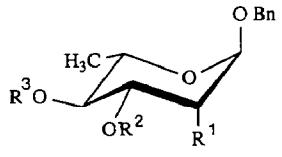
0008-6215/90/$ 03.50

the benzyl glycoside instead of the methyl glycoside. Condensation[9] of **1** with benzyl alcohol in the presence of *N*-iodosuccinimide gave benzyl 3,4-di-*O*-acetyl-2,6-dideoxy-2-iodo-α-L-mannopyranoside (**2**, 89%). Hydrogenolysis (10% Pd–C, ethyl acetate, triethylamine) of **2** yielded the 2-deoxy derivative **3** (92%); under these conditions, the benzyl group was not cleaved[10]. Zemplén *O*-deacetylation of **3** gave **4** which, with benzoyl chloride, gave mainly the desired 3-benzoate **5** (77%) together with the 4-benzoate **6** (1.5%) and the 3,4-dibenzoate **7** (18.7%), which could be *O*-deacylated (M NaOH) to regenerate **4**. The tosylate (**8**) of **5** was converted into the 4-azido-4-deoxy-*lyxo* compound **9** by heating with sodium azide in hexamethylphosphoric triamide for 2 h at 110°. Removal (M NaOH in 2:1 methanol–chloroform) of the benzoyl group from **9** followed by hydrogenolysis (10% Pd–C, methanol, triethylamine) of the azido group in the product **10** gave the 4-amino-4-deoxy intermediate **11**, which was *N*-trifluoroacetylated to obtain **12** (72%). Hydrogenolysis (10% Pd–C, aqueous 30% trifluoroacetic acid) of the benzyl group in **12** gave **13**, which was treated with *p*-nitrobenzoyl chloride in 1:1 dichloromethane–triethylamine at 0° to give **14αβ**. Column chromatography afforded the pure anomers only in small yields, but **14β** was obtained by crystallisation.

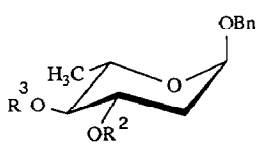
The 3,4-diamino-3,4-dideoxy sugar derivative was synthesised from benzyl 3-azido-2,3,6-trideoxy-α-L-*arabino*-hexopyranoside[11] (**15**). Following the above route, **15** was mesylated, and product **16** was treated with sodium azide to afford the diazido-*lyxo* compound **18**. Isolation of **18** and its hydrogenolysis (10% Pd–C in 20:1 EtOH–Et_3N) to give the diamine **19** were associated with possible explosive decomposition ($T_{Decomp.}$ ~170°). In order to avoid these difficulties, **15** was converted into the triflate **17** by treatment with trifluoromethanesulfonic anhydride in pyridine–dichloromethane at 0°. Reaction of **17** with chloroform saturated with ammonia (−75°) at ~7 atm for 7 h gave the amine **20**. Hydrogenation (Pd–C, MeOH) of **20** then afforded the diamine **19**,



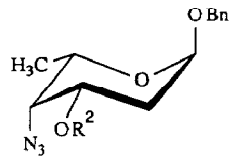
1



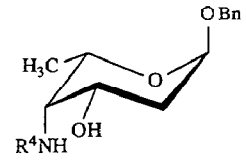
2 R^1=I, R^2=R^3=Ac
3 R^1=H, R^2=R^3=Ac
4 R^1=H, R^2=R^3=H



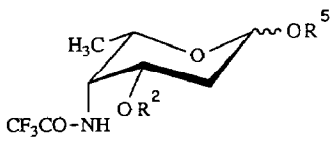
5 R^2=Bz, R^3=H
6 R^2=H, R^3=Bz
7 R^2=R^3=Bz
8 R^2=Bz, R^3=Ts



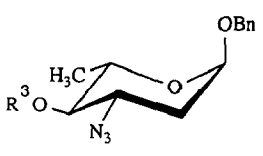
9 R^2=Bz
10 R^2=H



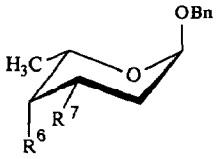
11 R^4=H
12 R^4=CF_3CO



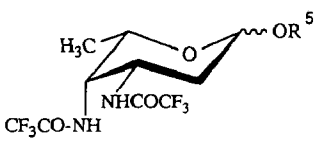
13αβ R^2=R^5=H
14αβ R^2=R^5=pNO_2Bz



15 R^3=H
16 R^3=Ms
17 R^3=CF_3SO_2



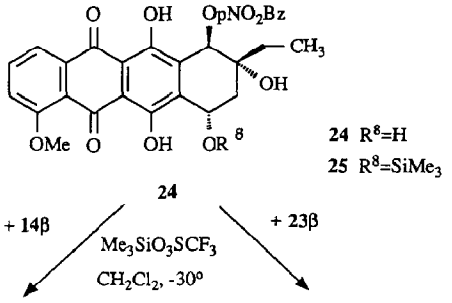
18 R^6=R^7=N_3
19 R^6=R^7=NH_2
20 R^6=NH_2, R^7=N_3
21 R^6=R^7=$NHCOCF_3$



22αβ R^5=H
23αβ R^5=pNBz

trifluoroacetylation of which (→**21**) followed by hydrogenolysis gave the 2,3,4,6-tetradeoxy-3,4-bis(trifluoroacetamido)-pyranose **22** (85%). Treatment of **22** with *p*-nitrobenzoyl chloride in dichloromethane–triethylamine at −10° gave **23αβ** from which the *β*-anomer **23β** (45%) and an *αβ*-mixture (22%) were isolated by chromatography.

Glycosylations. — The suitability of the 4-amino-4-deoxy derivatives **14αβ** and **14β** and the 3,4-diamino-3,4-dideoxy derivatives **23αβ** and **23β** for the glycosylation of 4-*O*-methyl-10-*O*-*p*-nitrobenzoyl-*β*-rhodomycinone[2] **24**, using trimethylsilyl triflate as promoter, was examined. Glycosylation[12,13] (trimethylsilyl triflate, CH_2Cl_2, −30°) of **29** with **14β** afforded the α-glycoside **26** (74%) and the 7,9-di-*O*-α-glycosylated by-product **27** (5.5%). However, the reaction in 10:1 dichloromethane–tetrahydrofuran gave **26**



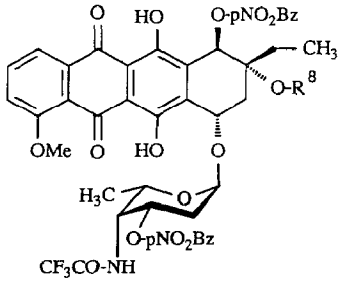
24 R^8=H
25 R^8=$SiMe_3$

24

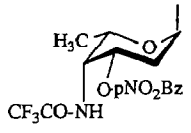
+ **14β**

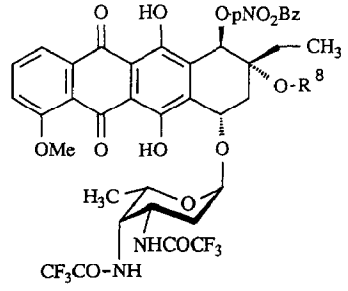
$Me_3SiO_3SCF_3$
CH_2Cl_2, -30°

+ **23β**

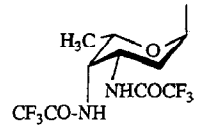


26 R^8=H
27 R^8=





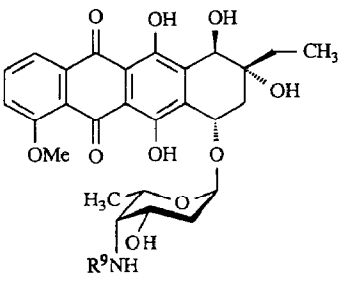
28 R^8=H
29 R^8=



exclusively. On glycosylation of **24** with **14αβ**, **14β** reacted first and **14α** reacted at higher temperatures ($> -10°$) to give the α-glycoside **26** together with the by-product **27**. Glycosylation (trimethylsilyl triflate, 10:1 CH_2Cl_2–tetrahydrofuran, $-30°$) of **24** with **23β** or **23αβ** afforded exclusively the α-glycoside **28** (84%). When **24** and **23β** were reacted in dichloromethane, mainly **28** was obtained, but further glycosylation occurred to give **29**. During these glycosylations, the aglycon **24** was temporarily trimethylsilylated to give **25** as detected by t.l.c. The structure of **25** was confirmed by synthesis.

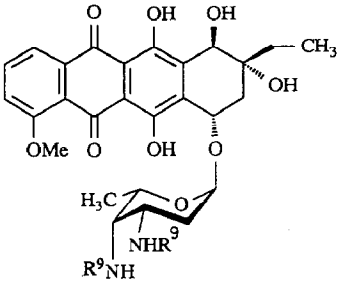
Deprotection reactions[1,13]. — The 7-*O*-glycosyl-β-rhodomycinone derivatives **26** and **28** could be deprotected either partially by cleaving the *p*-nitrobenzoyl groups with 0.1M NaOH to provide **30** and **32**, or completely using M NaOH to provide 7-*O*-(4-amino-2,4,6-trideoxy- (**31**) and 7-*O*-(3,4-diamino-2,3,4,6-tetradeoxy-α-L-*lyxo*-hexopyranosyl)-4-*O*-methyl-β-rhodomycinone (**33**). In order to obtain pure **31** and **33**, the *N*-trifluoroacetylated intermediates **30** and **32** were separated from the *p*-nitrobenzoate salts on silica gel; after *N*-deacylation, **31** and **33** were purified by chromatography on cellulose.

^{1}H,^{1}H-COSY experiments were used to assign the sugar and rhodomycinone ring D protons in the ^{1}H-n.m.r. spectra of **31** and **33**. As expected, the *lyxo*-hexopyranosyl moieties in **31** and **33** were in the $^1C_4$ conformation, as in the daunosaminyl moiety in related analogues[1]. The constitutions of **31** and **33** were confirmed by f.a.b.-mass spectrometry.



30 R^9=CF_3CO

31 R^9=H



32 R^9=CF_3CO

33 R^9=H

EXPERIMENTAL

General. — Reactions were carried out at ambient temperature unless otherwise stated. Solutions were concentrated under reduced pressure at $<40°$ (bath). Organic solutions were washed with 0.1M potassium dihydrogen phosphate or 0.1M sodium citrate adjusted to the appropriate pH using 0.1M NaOH or 0.1M HCl. Melting points, determined on a Büchi apparatus, are uncorrected. ^{1}H-N.m.r. spectra were recorded with a Bruker AC-200, AC-300, or Jeol GX-400 spectrometer on solutions in $CDCl_3$ (internal Me_4Si) unless stated otherwise. The ^{1}H resonances were assigned by ^{1}H,^{1}H-COSY experiments, using the standard pulse sequences of the Bruker Aspect-3000

software. Specific optical rotations were determined with a Perkin–Elmer 241 polarimeter equipped with 10-cm cuvettes, for solutions in $CHCl_3$ at 24°, unless noted otherwise. Reactions were monitored by t.l.c. on Silica Gel 60 F_{254} (Merck) with detection by u.v. light or by charring with sulphuric acid. Preparative chromatography was performed on Kieselgel 60 (Merck, 0.015–0.040 mm). Glycosylations were performed under argon or nitrogen. Extracts and washings were dried over sodium sulfate.

*Benzyl 3,4-di-*O*-acetyl-2,6-dideoxy-2-iodo-α-*L*-mannopyranoside* (**2**). — To a solution of 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-L-*arabino*-hex-1-enitol[14] (**1**; 129.0 g, 0.60 mol) and benzyl alcohol (80 mL, 0.78 mol) in dry acetonitrile (750 mL) was added *N*-iodosuccinimide (162 g, 0.72 mol), and the mixture was stirred for 2 h at room temperature. After the addition of ice–water (1000 mL), the mixture was extracted with ether (300 mL × 3), and the combined extracts were washed with aqueous 10% sodium thiosulfate (200 mL × 2) and water, dried, and concentrated *in vacuo*. Crystallisation of the residue (304.0 g) from ether–hexane afforded **2** (145.32 g, 54.2%). Column chromatography (3:1 light petroleum–diethyl ether) of the remaining crude product on silica gel (1200 g) gave more **2** (93.32 g, 34.7%), m.p. 116°, $[\alpha]_D$ −45.5° (*c* 1). ^{1}H-N.m.r. data (200 MHz): δ 7.32–7.36 (m, 5 H, Ph), 5.18 (s, 1 H, H-1), 5.15 (dd, 1 H, $J_{3,4}$ 8.8, $J_{4,5}$ 10.0 Hz, H-4), 4.70 (d, 1 H, $J_{A,B}$ 11.9 Hz, PhCH_A), 4.62 (dd, 1 H, $J_{2,3}$ 4.5 Hz, H-3), 4.57 (d, 1 H, H-2), 4.53 (d, 1 H, PhCH_B), 3.96 (dq, 1 H, $J_{5,6}$ 6.2 Hz, H-5), 2.08 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 1.22 (d, 3 H, H-6,6,6).

Anal. Calc. for $C_{17}H_{21}IO_6$ (448.28): C, 45.55; H, 4.72. Found: C, 45.64; H, 4.74.

*Benzyl 3,4-di-*O*-acetyl-2,6-dideoxy-α-*L*-*arabino*-hexopyranoside* (**3**). — A mixture of 10% Pd–C (10 g) in ethyl acetate (500 mL) was stirred for 10 min under hydrogen. After the addition of triethylamine (37 mL) and **2** (100.0 g, 0.223 mol), the mixture was stirred under hydrogen for 2 h at room temperature, then filtered, and successively washed with cooled aqueous 10% sodium thiosulfate (200 mL × 2) and ice–water (200 mL × 2), dried, and concentrated *in vacuo*. The crude **3** (66.5 g, 92%), used in the next step without further purification, had $[\alpha]_D$ −132° (*c* 1), R_F 0.35 (10:10:1 chloroform–light petroleum–ethyl acetate). ^{1}H-N.m.r. data (200 MHz): δ 7.30–7.38 (m, 5 H, Ph), 5.31 (ddd, 1 H, $J_{2a,3}$ 11.6, $J_{2e,3}$ 5.4, $J_{3,4}$ 9.5 Hz, H-3), 4.96 (dd, 2 H, $J_{1,2a}$ 3.7, $J_{1,2e}$ 1.1 Hz, H-1), 4.76 (dd, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 4.68 (d, 1 H, $J_{A,B}$ 12.1 Hz, PhCH_A), 4.48 (d, 1 H, PhCH_B), 3.90 (dq, 1 H, $J_{5,6}$ 6.3 Hz, H-5), 2.28 (ddd, 1 H, $J_{2a,2e}$ 12.9 Hz, H-2*e*), 2.05 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 1.81 (ddd, 1 H, H-2*a*), 1.17 (d, 3 H, H-6,6,6).

*Benzyl 2,6-dideoxy-α-*L*-arabino-hexopyranoside* (**4**). — The pH of a solution of crude **3** (66.5 g) in dry methanol (260 mL) was adjusted with methanolic M NaOMe to 12. After the usual work-up, the product was crystallised from ether–light petroleum to give **4** (54.05 g, 92%), m.p. 117°, $[\alpha]_D$ −120° (*c* 1).

Anal. Calc. for $C_{13}H_{18}O_6$ (238.29): C, 65.53; H, 7.61. Found: C, 65.26; H, 7.67.

Benzyl 3- (**5**) *and 4-*O*-benzoyl-2,6-dideoxy-α-*L*-arabino-hexopyranoside* (**6**) *and benzyl 3,4-di-*O*-benzoyl-2,6-dideoxy-α-*L*-arabino-hexopyranoside* (**7**). — To a solution of **4** (15.00 g, 62.94 mmol) in pyridine (45 mL) was added a solution of benzoyl chloride (9.73 g, 69.25 mmol) in dichloromethane (45 mL) at −10°, After stirring for 2 h at 0°, the mixture was diluted with methanol (25 mL), then concentrated *in vacuo*, and toluene

was evaporated from the residue. A solution of the residue in dichloromethane (400 mL) was washed with water (200 mL × 3), dried, and concentrated *in vacuo*. Column chromatography (10:5:0.5→1 light petroleum–chloroform–ethyl acetate) of the residue on silica gel (500 g) gave **5** (16.58 g, 76.9%), **6** (0.32 g, 1.48%), and **7** (5.28 g, 18.7%).

Compound **5** had m.p. 83°, $[\alpha]_D$ −106° (*c* 0.7). ^{1}H-N.m.r. data (200 MHz): δ 8.01–8.07 and 7.30–7.60 (2 m, 10 H, 2 Ph), 5.40 (ddd, 1 H, $J_{2a,3}$ 11.5, $J_{2e,3}$ 5.3, $J_{3,4}$ 9.3 Hz, H-3), 5.01 (d, 1 H, $J_{1,2a}$ 3.7 Hz, H-1), 4.72 (d, 1 H, $J_{A,B}$ 12.0 Hz, PhCH_A), 4.49 (d, 1 H, PhCH_B), 3.85 (dq, 1 H, $J_{5,6}$ 6.2 Hz, H-5), 3.43 (dd, 1 H, H-4), 2.77 (bs, 1 H, HO-4), 2.36 (ddd, 1 H, $J_{1,2e}$ 1.2, $J_{A,B}$ 12.8 Hz, H-2*e*), 1.93 (ddd, 1 H, H-2*a*), 1.35 (d, 3 H, H-6,6,6).

Anal. Calc. for $C_{20}H_{22}O_5$ (342.40): C, 70.16; H, 6.48. Found: C, 70.23; H, 6.45.

Compound **6** had $[\alpha]_D$ −101° (*c* 1). ^{1}H-N.m.r. data (200 MHz): δ 8.02–7.64 (m, 10 H, 2 Ph), 5.02 (d, 1 H, $J_{1,2a}$ 3.8 Hz, H-1), 4.80 (dd, 1 H, $J_{3,4}$ 9.2, $J_{4,5}$ 9.6 Hz, H-4), 4.71 (d, 1 H, $J_{A,B}$ 12.0 Hz, PhCH_A), 4.50 (d, 1 H, PhCH_B), 4.24 (ddd, 1 H, $J_{2a,3}$ 11.5, $J_{2e,3}$ 5.3 Hz, H-3), 4.00 (dq, 1 H, $J_{5,6}$ 6.3 Hz, H-5), 2.33 (ddd, 1 H, $J_{1,2e}$ 1.1, $J_{2a,2e}$ 13.1 Hz, H-2*e*), 1.85 (ddd, 1 H, H-2*a*), 1.26 (d, 3 H, H-6,6,6).

Compound **7** had $[\alpha]_D$ −9.8° (*c* 0.9). ^{1}H-N.m.r. data (200 MHz): δ 7.92–7.58 (m, 10 H, 2 Ph), 5.70 (ddd, 1 H, $J_{2a,3}$ 11.4, $J_{2e,3}$ 5.3, $J_{3,4}$ 9.5 Hz, H-3), 5.25 (dd, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 5.07 (d, $J_{1,2a}$ 3.7 Hz, H-1), 4.76 (d, 1 H, $J_{A,B}$ 12.2 Hz, PhCH_A), 4.56 (d, 1 H, PhCH_B), 4.14 (dq, 1 H, $J_{5,6}$ 6.5 Hz, H-5), 2.55 (ddd, 1 H, $J_{1,2e}$ 1.2, $J_{2a,2e}$ 12.8 Hz, H-2*e*), 1.99 (ddd, 1 H, H-2*a*), 1.28 (d, 3 H, H-6,6,6).

Deacylation (M NaOH) of **6** and **7** gave **4**.

Benzyl 3-O-benzoyl-2,6-dideoxy-4-O-tosyl-α-L-arabino-hexopyranoside (**8**). — A solution of **5** (16.15 g, 47.16 mmol) and tosyl chloride (15.90 g, 83.5 mmol) in 1:1 pyridine–1,2-dichloroethane (160 mL) was stirred for 5 h at room temperature, then for 65 h at 70°, and concentrated *in vacuo*. Toluene was evaporated from the residue, a solution of which in dichloromethane (240 mL) was washed with phosphate buffer (pH 7.5, 50 mL × 2) and water, dried, and concentrated *in vacuo*. Column chromatography (dichloromethane) of the residue on silica gel (400 g) and crystallisation from ether–light petroleum gave **8** (18.1 g, 77%), m.p. 124°, $[\alpha]_D$ −11.5° (*c* 0.4). ^{1}H-N.m.r. data (200 MHz): δ 7.91–6.91 (m, 14 H, 2 Ph and Me*Ph*), 5.70 (ddd, 1 H, $J_{2a,3}$ 11.6, $J_{2e,3}$ 5.4, $J_{3,4}$ 9.3 Hz, H-3), 4.97 (bs, 1 H, H-1), 4.68 (d, 1 H, $J_{A,B}$ 12.1 Hz, PhCH_A), 4.65 (dd, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 4.49 (d, 1 H, PhCH_B), 4.03 (dq, 1 H, $J_{5,6}$ 6.4 Hz, H-5), 2.39 (ddd, 1 H, $J_{1,2e}$ 1.7, $J_{2a,2e}$ 13.3 Hz, H-2*e*), 2.17 (s, 3 H, *Me*Ph), 1.87 (ddd, 1 H, H-2*a*), 1.36 (d, 3 H, H-6,6,6).

Anal. Calc. for $C_{27}H_{28}O_7S$ (496.58): C, 65.31; H, 5.68; S, 6.46. Found: C, 65.37; H, 5.66.

Benzyl 4-azido-3-O-benzoyl-2,4,6-trideoxy-α-L-lyxo-hexopyranoside (**9**). — A mixture of **8** (17.58 g, 35.40 mmol) and sodium azide (4.61 g, 70.9 mmol) in hexamethylphosphoric triamide (100 mL) was heated for 2 h at 110°, then cooled, diluted with 1:1 light petroleum–ethyl acetate (350 mL), filtered, washed with saturated aqueous NaCl (200 mL × 2) and water (250 mL × 3), dried, and concentrated *in vacuo*. Column chromatography (20:1 light petroleum–ethyl acetate) of the residue on silica gel (200 g) gave **9** (12.52 g, 96%), as a syrup, $[\alpha]_D$ −37° (*c* 1). ^{1}H-N.m.r. data (200 MHz): δ 8.05–7.60 (m, 10 H, 2 Ph), 5.65 (ddd, 1 H, $J_{2a,3}$ 11.8, $J_{2e,3}$ 5.2, $J_{3,4}$ 3.3 Hz, H-3), 5.07 (d, 1 H, $J_{1,2a}$ 3.7

Hz, H-1), 4.68 (d, 1 H, $J_{A,B}$ 12.0 Hz, PhCH_A), 4.51 (d, 1 H, PhCH_B), 4.12 (dq, 1 H, $J_{4,5}$ 1.1, $J_{5,6}$ 6.5 Hz, H-5), 3.88 (bs, 1 H, H-4), 2.25 (ddd, 1 H, $J_{1,2a}$ 3.7, $J_{2a,2e}$ 12.6 Hz, H-2*a*), 2.09 (ddd, 1 H, $J_{1,2e}$ 1.1 Hz, H-2*e*), 1.29 (d, 3 H, H-6,6,6).

Anal. Calc. for $C_{20}H_{21}N_3O_4$ (367.41): C, 65.38; H, 5.76; N, 11.44. Found: C, 65.42; H, 5.75; N, 11.35.

*Benzyl 4-azido-2,4,6-trideoxy-α-*L-lyxo-*hexopyranoside* (**10**). — To a solution of **9** (12.5 g, 34.02 mmol) in 2:1 methanol–chloroform (120 mL) was added M NaOH. The mixture was stirred for 15 min, diluted with 2:1 ether–light petroleum (200 mL), and then washed with saturated aqueous NaCl (70 mL × 2) and water. The washings were re-extracted with 1:1 light petroleum–ether, and the combined extracts and organic layer were dried and concentrated *in vacuo*. Elution of the residue from a column of silica gel (80 g) with 2:1 ether–light petroleum followed by crystallisation from ether–light petroleum gave **10** (7.76 g, 86.6%), m.p. 108°, $[\alpha]_D$ −141° (*c* 1). ^{1}H-N.m.r. data (300 MHz): δ 7.30–7.40 (m, 5 H, Ph), 5.02 (dd, 1 H, $J_{1,2a}$ 3.7, $J_{1,2e}$ 1.0 Hz, H-1), 4.66 (d, 1 H, $J_{A,B}$ 12.0 Hz, PhCH_A), 4.50 (d, 1 H, PhCH_B), 4.29 (dddd, 1 H, $J_{2a,3}$ 12.0, $J_{2e,3}$ 5.0, $J_{3,4}$ 3.1, $J_{3,OH}$ 8.5 Hz, H-3), 4.04 (q, 1 H, $J_{5,6}$ 6.6 Hz, H-5), 3.64 (d, 1 H, H-4), 1.99 (ddd, 1 H, $J_{2a,2e}$ 13.0 Hz, H-2*e*), 1.97 (d, 1 H, HO-3), 1.89 (ddd, 1 H, H-2*a*), 1.34 (d, 3 H, H-6,6,6).

Anal. Calc. for $C_{13}H_{17}N_3O_3$ (263.30): C, 59.30; H, 6.51; N, 15.96. Found: C, 59.33; H, 6.53; N,15.86.

*Benzyl 4-amino-2,4,6-trideoxy-α-*L-lyxo-*hexopyranoside* (**11**). — A mixture of **10** (7.60 g, 28.86 mmol), 10% Pd–C (4.2 g), and triethylamine (4 mL) in methanol (200 mL) was stirred under hydrogen for 1.5 h, then filtered, and concentrated *in vacuo*, and toluene (70 mL × 2) was evaporated from the residue, which was dried in high vacuum to yield crude**11** (6.86 g), R_F (3:1 chloroform–methanol) 0.42, which was used directly in the next step.

*Benzyl 2,4,6-trideoxy-4-trifluoroacetamido-α-*L-lyxo-*hexopyranoside* (**12**). — To a solution of the crude product **11** (6.86 g) in 1:1 dichloromethane–ethanol (90 mL) at 0° was added triethylamine (48 mL) and, dropwise during 4 h, a cold solution of trifluoroacetic anhydride (24.11 mL, 174.4 mmol) in 1:1 dichloromethane–ethanol. After stirring for 3 days at 4°, the mixture was diluted with toluene (60 mL) and concentrated *in vacuo*. The residue was eluted from a column of silica gel with 5:1 dichloromethane–methanol. Addition of ether–light petroleum precipitated **12** (6.94 g, 72.1%), m.p. 121°, $[\alpha]_D$ −85° (*c* 1). ^{1}H-N.m.r. data (200 MHz, H→D): δ 7.30–7.40 (m, 5 H, Ph), 6.55 (d, 1 H, $J_{4,NH}$ 8.9 Hz, NH), 5.00 (d, 1 H, $J_{1,2a}$ 3.8 Hz, H-1), 4.64 (d, 1 H, $J_{A,B}$ 12.1 Hz, PhCH_A), 4.48 (d, 1 H, PhCH_B), 4.33 (d, 1 H, $J_{2a,3}$ 12.0, $J_{2e,3}$ 5.2, $J_{3,4}$ 4.0 Hz, H-3), 4.18 (dd, 1 H, $J_{4,5}$ 1.2 Hz, H-4), 4.15 (dq, 1 H, $J_{5,6}$ 6.5 Hz, H-5), 2.40 (bs, 1 H, HO-3), 2.04 (bs, 1 H, $J_{2a,2e}$ 13.7 Hz, H-2*e*), 1.61 (ddd, 1 H, H-2*a*), 1.14 (d, 3 H, H-6,6,6).

Anal. Calc. for $C_{15}H_{18}F_3NO_4$ (333.31): C, 54.05; H, 5.44; N, 4.20. Found: C, 54.08; H, 5.47; N, 4.10.

*2,4,6-Trideoxy-4-trifluoroacetamido-*L-lyxo-*hexopyranose* (**13**). — A mixture of **12** (6.52 g, 19.58 mmol), 10% Pd–C (6.5 g), and aqueous 30% trifluoroacetic acid (0.05 mL) in methanol (100 mL) was stirred under hydrogen (1 atm) for 16 h, then filtered, and concentrated *in vacuo*, and 2:1 methanol–toluene (50 mL × 2) was evaporated from the

residue, which was dried in high vacuum. The resulting amorphous product **13** (6.26 g) was used directly in the next step. Column chromatography (10:1 dichloromethane–MeOH) of a part of the product on silica gel afforded pure **13**, $[\alpha]_D$ −30° (*c* 1, 9:1 chloroform–methanol). ^{1}H-N.m.r. data (400 MHz). α anomer, δ 5.32 (d, 1 H, $J_{1,2a}$ 3.2 Hz, H-1), 4.35 (q, 1 H, $J_{5,6}$ 6.5 Hz, H-5), 4.30 (d, 1 H, $J_{2a,3}$ 12.5 Hz, H-3), 4.18 (s, 1 H, H-4), 1.92 (bd, 1 H, $J_{2a,2e}$ 13.2, $J_{2e,3}$ 3.3 Hz, H-2*e*), 1.66 (ddd, 1 H, H-2*a*), 1.13 (d, 3 H, H-6,6,6); β anomer, δ 4.76 (d, 1 H, $J_{1,2a}$ 9.1 Hz, H-1), 4.13 (s, 1 H, H-4), 3.97 (bd, 1 H, $J_{2a,3}$ 12.6 Hz, H-3), 3.68 (q, 1 H, $J_{5,6}$ 6.4 Hz, H-5), 2.07 (bd, 1 H, $J_{2a,2e}$ 13.0 Hz, H-2*e*), 1.44 (ddd, 1 H, H-2*a*), 1.19 (d, 3 H, H-6,6,6).

Anal. Calc. for $C_8H_{12}F_3NO_4$ (243.18): C, 39.51; H, 4.97; N, 5.76. Found: C, 39.24; H, 5.02; N, 5.62.

2,4,6-Trideoxy-1,3-di-O-p-*nitrobenzoyl-4-trifluoroacetamido*-α- (**14α**) *and* -β-L-lyxo-*hexopyranose* (**14β**). — To a solution of crude **13** (5.20 g) in 1:1 dichloromethane–triethylamine (50 mL) at 0° was added a solution of *p*-nitrobenzoyl chloride (9.10 g, 48.96 mmol) in dichloromethane (25 mL). The mixture was stirred for 2.5 h at 0°, diluted with dichloromethane (50 mL), filtered, washed with 0.2M HCl (40 mL × 5) and citrate buffer (pH 6.5, 25 mL × 2), dried, and concentrated *in vacuo*. The residue was eluted from a column of silica gel (40 g) with dichloromethane–ethyl acetate. Crystallisation from ether–light petroleum gave **14β** (4.90 g, 46.2%), **14αβ** (1.56 g, 14.7%), and **14α** (0.65 g, 6.2%).

Compound **14α** had m.p. 170°, $[\alpha]_D$ −73° (*c* 0.5, 18:1 chloroform–acetone). ^{1}H-N.m.r. data (200 MHz): δ 8.40–8.10 (m, 8 H, aromatic), 6.63 (d, 1 H, NH-4), 6.62 (s, 1 H, H-1), 5.72 (ddd, 1 H, $J_{2a,3}$ 11.8, $J_{2e,3}$ 5.5, $J_{3,4}$ 3.8 Hz, H-3), 4.67 (dd, 1 H, $J_{4,NH}$ 9.2 Hz, H-4), 4.52 (dq, 1 H, $J_{4,5}$ 1.0, $J_{5,6}$ 6.5 Hz, H-5), 2.42 (dd, 1 H, $J_{2a,2e}$ 13.3 Hz, H-2*e*), 2.24 (ddd, 1 H, H-2*a*), 1.29 (d, 3 H, H-6,6,6).

Anal. Calc. for $C_{22}H_{18}F_3N_3O_{10}$ (541.40): C, 48.81; H, 3.35; N, 7.76. Found: C, 48.97; H, 3.38; N, 7.64.

Compound **14β** had m.p. 177°, $[\alpha]_D$ −11° (*c* 1). ^{1}H-N.m.r. data (300 MHz): δ 8.17–7.91 (m, 8 H, aromatic), 5.92 (dd, 1 H, $J_{1,2a}$ 9.8, $J_{1,2e}$ 2.5 Hz, H-1), 5.27 (ddd, 1 H, $J_{2a,3}$ 12.5, $J_{2e,3}$ 5.0, $J_{3,4}$ 3.5 Hz, H-3), 4.39 (dd, 1 H, $J_{4,5}$ 1.5 Hz, H-4), 3.93 (dq, 1 H, $J_{5,6}$ 6.5 Hz, H-5), 2.26 (ddd, 1 H, $J_{2a,2e}$ 12.0 Hz, H-2*e*), 2.06 (ddd, 1 H, H-2*a*), 1.13 (d, 3 H, H-6,6,6).

Anal. Found: C, 48.94; H, 3.36; N, 7.67.

Benzyl 3-azido-2,3,6-trideoxy-4-O-*methanesulfonyl*-α-L-arabino-*hexopyranoside* (**16**). — To a solution of benzyl 3-azido-2,3,6-trideoxy-α-L-*arabino*-hexopyranoside[11] (**15**; 7.54 g, 28.63 mmol) in 1:1 dichloromethane–pyridine (50 mL) at 0° was added methanesulfonyl chloride (2.92 mL, 37.18 mmol). The mixture was stirred for 16 h at room temperature, then poured into ice-cold aqueous 5% $NaHCO_3$ (150 mL) and extracted with dichloromethane (70 mL × 5). The combined extracts were washed with citrate buffer (pH 5.0, 100 mL × 2), dried, and concentrated *in vacuo*. The residue was eluted from a column of silica gel (50 g) with 20:1 dichloromethane–acetone to give **16** (9.57 g, 97.9%), as a syrup, $[\alpha]_D$ −119° (*c* 1). ^{1}H-N.m.r. data (200 MHz), δ 7.40–7.30 (m, 5 H, Ph), 4.98 (d, 1 H, $J_{1,2a}$ 3.6 Hz, H-1), 4.67 (d, 1 H, $J_{A,B}$ 11.8 Hz, PhCH_A), 4.48 (d, 1 H,

PhCH_B), 4.18 (dd, 1 H, $J_{3,4}$ 9.6, $J_{4,5}$ 9.6 Hz, H-4), 4.01 (ddd, 1 H, $J_{2a,3}$ 12.0, $J_{2e,3}$ 5.0, $J_{3,4}$ 9.6 Hz, H-3), 3.90 (dd, 1 H, $J_{5,6}$ 6.2 Hz, H-5), 3.18 (s, 1 H, Ms), 2.33 (dd, 1 H, $J_{1,2e}$ 1.1, $J_{2a,2e}$ 13.1 Hz, H-2*e*), 1.83 (ddd, 1 H, H-2*a*), 1.35 (d, 3 H, H-6,6,6).

Anal. Calc. for $C_{14}H_{19}N_3O_5S$ (341.39): C, 49.26; H, 5.61; N, 12.31. Found: C, 49.16; H, 5.61; N, 12.23.

*Benzyl 3-azido-2,3,6-trideoxy-4-*O*-trifluoromethanesulfonyl-α-*L-arabino-*hexopyranoside* (**17**). — To a solution of **15** (2.0 g, 7.59 mmol) in dichloromethane (50 mL) and pyridine (0.72 g) at −30° was added a solution of trifluoromethanesulfonic anhydride (2.35 g) in dichloromethane (20 mL). After stirring for 2 h at room temperature, the mixture was diluted with toluene (30 mL) and concentrated *in vacuo*, and toluene (30 mL × 3) was evaporated from the residue (3.1 g), to leave **17**, R_F (dichloromethane–light petroleum–ethyl acetate) 0.64, which was used in the next step without further purification.

*Benzyl 3,4-diazido-2,3,4,6-tetradeoxy-α-*L*-*lyxo*-hexopyranoside* (**18**). — A mixture of **16** (9.50 g, 27.82 mmol) and sodium azide (4.35 g) in hexamethylphosphoric triamide (80 mL) was heated for 16 h at 130°, then cooled, diluted with 2:1 ether–light petroleum, washed with ice–water (70 mL × 3), dried, and concentrated *in vacuo*. Column chromatography (5:5:1 dichloromethane–light petroleum–ethyl acetate) of the residue on silica gel (250 g) gave **18** (6.5 g, 81.0%), as a syrup, $[\alpha]_D$ −92° (*c* 1). ^{1}H-N.m.r. data (300 MHz): δ 7.30–7.40 (m, 5 H, pH), 5.02 (bs, 1 H, H-1), 4.64 (d, 1 H, $J_{A,B}$ 12.0 Hz, PhCH_A), 4.49 (d, 1 H, PhCH_B), 4.04 (ddd, 1 H, $J_{2a,3}$ 12.1, $J_{2e,3}$ 5.0, $J_{3,4}$ 3.5 Hz, H-3), 4.00 (dq, 1 H, $J_{4,5}$ 1.5, $J_{5,6}$ 6.5 Hz, H-5), 3.52 (dd, 1 H, H-4), 2.07 (ddd, 1 H, $J_{1,2a}$ 3.5, $J_{2a,2e}$ 12.5 Hz, H-2*a*), 1.97 (ddd, 1 H, $J_{1,2e}$ 1.5, $J_{2e,4}$ 1.0 Hz, H-2*e*), 1.29 (d, 3 H, H-6,6,6).

On differential thermoanalysis on a Mettler TA3000 instrument, decomposition began at 170° and was a maximum at 225° at a thermal gradient of 3°.min^{-1}. The energy of decomposition, ΔH, was −1870 kJ.kg^{-1}. Sensitivity to impact: there was no reaction on impact to a weight of 10 kg falling from 1.0 m.

Anal. Calc. for $C_{13}H_{16}N_6O_2$ (288.31): C, 54.16; H, 5.59; N, 29.15. Found: C, 54.24; H, 5.62; N, 29.05.

*Benzyl 3,4-diamino-2,3,4,6-tetradeoxy-α-*L*-*lyxo*-hexopyranoside* (**19**). — (*a*) A solution of **18** (6.50 g, 22.54 mmol) in ethanol (65 mL) was stirred for 8 h under hydrogen (1 atm.) in the presence of 10% Pd–C (8.5 g) and triethylamine (3.13 mL), then filtered, and concentrated *in vacuo*, and 2:1 methanol–toluene (50 mL × 2) was evaporated from the residue, which was dried in high vacuum to afford crude **19** (4.34 g) that was used directly in the next step. Preparative t.l.c. (20:40:3 chloroform–methanol–conc NH_3) of a part of the product afforded pure **19**, $[\alpha]_D$ −110° (*c* 1, methanol), R_F (40:20:3 methanol–chloroform–conc. NH_3) 0.68.

(*b*) Hydrogenolysis of crude **20** (2.1 g), as described in (*a*), afforded crude **19** (1.9 g), which was used in the next step without further purification.

*Benzyl 4-amino-3-azido-2,3,4,6-tetradeoxy-α-*L*-*lyxo*-hexopyranoside* (**20**). — A solution of crude **17** (3.1 g) in chloroform (50 mL) at −75° was saturated with ammonia, and stirred in an autoclave for 2 h at room temperature, then for 9 h at 60°. After cooling to −20°, the mixture was diluted with methanol (20 mL), the pH was adjusted to 9 with

M NaOH, and the solution was filtered and concentrated *in vacuo*. The residue (2.1 g) that contained **20**, R_F (4:1 dichloromethane–acetone) 0.12, was used in the next step without further purification.

Benzyl 2,3,4,6-tetradeoxy-3,4-bis(trifluoroacetamido)-α-L-lyxo-*hexopyranoside* (**21**). — To a stirred solution of crude **19** (4.20 g) in dichloromethane (80 mL) at 0° was added triethylamine (7.4 mL) and trifluoroacetic anhydride (6.16 mL). The mixture was stirred for 16 h at 4°, then poured into ice-cooled, saturated aqueous $NaHCO_3$ (45 mL), and extracted with dichloromethane (50 mL). The extract was washed with water (60 mL × 2), dried ($MgSO_4$), and concentrated *in vacuo*. Column chromatography (5:1 light petroleum–ethyl acetate) of the residue on silica gel (200 g) gave **21** (6.6 g, 68.36%), as a syrup, $[\alpha]_D$ −76° (*c* 1). ^{1}H-N.m.r. (300 MHz): δ 7.25–7.35 (m, 5 H, Ph), 6.87 (bd, 1 H, $J_{3,NH}$ 6.5 Hz, NH-3), 6.63 (d, 1 H, $J_{4,NH}$ 8.5 Hz, NH-4), 5.00 (bd, 1 H $J_{1,2a}$ 3.5, $J_{1,2e}$ 1.0 Hz, H-1), 4.66, (d, H, $J_{A,B}$ 12.0 Hz, PhCH_A), 4.57 (m, 1 H, H-3), 4.48 (d, H, PhCH_B), 4.28 (bd, 1 H, $J_{3,4}$ 3.5, $J_{4,5}$ 1.0 Hz, H-4), 4.26 (dq, 1 H, $J_{5,6}$ 6.5 Hz, H-5), 2.12 (ddd, 1 H, $J_{2e,3}$ 5.0, $J_{2e,4}$ 1.0, $J_{2a,2e}$ 12.5 Hz, H-2*e*), 1.72 (ddd, 1 H, $J_{2a,3}$ 12.0 Hz, H-2*a*), 1.10 (d, 3 H, H-6,6,6).

Anal. Calc. for $C_{17}H_{18}F_6N_2O_4$ (428.33): C, 47.67; H, 4.24; N, 6.54. Found: C, 47.69; H, 4.24; N, 6.47.

2,3,4,6-Tetradeoxy-3,4-bis(trifluoroacetamido)-L-lyxo-*hexopyranose* (**22**). — The pH of a solution of **21** (6.50 g, 15.17 mmol) in methanol (50 mL) was adjusted with aqueous 30% trifluoroacetic acid to 4. The solution was then stirred under hydrogen (1 atm.) in the presence of 10% Pd–C (6.50 g) for 24 h, filtered, and concentrated *in vacuo*, and 2:1 methanol–toluene (50 mL × 2) was evaporated from the residue, which was dried in high vacuum. Column chromatography (3:1 dichloromethane–methanol) of the crude product on silica gel (120 g) gave **22** (4.39 g, 85.5%), as a syrup, $[\alpha]_D$ −63° (*c* 1, ethyl acetate). ^{1}H-N.m.r. data (300 MHz): α anomer, δ 7.35 (d, 1 H, $J_{3,NH}$ 6.5 Hz, NH-3), 6.68 (d, 1 H, $J_{4,NH}$ 8.5 Hz, NH-4), 5.34 (bs, 1 H, H-1), 4.57 (m, 1 H, H-3), 4.27 (d, 1 H, H-4), 3.78 (dq, 1 H, $J_{4,5}$ 1.0, $J_{5,6}$ 6.5 Hz, H-5), 3.67 (s, 1 H, HO-1), 1.99 (dd, 1 H, $J_{2e,3}$ 5.0, $J_{2e,2a}$ 13.0 Hz, H-2*e*), 1.77 (ddd, 1 H, $J_{1,2a}$ 3.5, $J_{2a,3}$ 12.8 Hz, H-2*a*), 1.15 (d, 3 H, H-6,6,6); β anomer, δ 7.54 (d, 1 H, $J_{3,NH}$ 6.5 Hz, NH-3), 6.85 (d, 1 H, $J_{4,NH}$ 9.0 Hz, NH-4), 4.87 (d, 1 H, $J_{1,2a}$ 9.5 Hz, H-1), 4.61 (s, 1 H, HO-1), 4.47 (dq, 1 H, $J_{4,5}$ 1.2, $J_{5,6}$ 6.5 Hz, H-5), 4.23 (d, 1 H, H-4), 4.22 (m, 1 H, H-3), 2.12 (dddd, 1 H, $J_{1,2e}$ 3.0, $J_{2e,3}$ 5.0, $J_{2e,4}$ 1.0, $J_{2a,2e}$ 13.0 Hz, H-2*e*), 1.61 (ddd, 1 H, $J_{2a,3}$ 12.8 Hz, H-2*a*), 1.08 (d, 3 H, H-6,6,6).

Anal. Calc. for $C_{10}H_{12}F_6N_2O_4$ (338.21): C, 35.51; H, 3.58; N, 8.28. Found: C, 35.57; H, 3.59; N, 8.18.

2,3,4,6-Tetradeoxy-1-O-p-*nitrobenzoyl-3,4-bis(trifluoroacetamido)*-α- (**23α**) *and* -β-L-lyxo-*hexopyranose* (**23β**). — To a solution of **22** (2.21 g, 6.53 mmol) in dichloromethane (20 mL) at −10° was added triethylamine (1.09 mL) and *p*-nitrobenzoyl chloride (1.22 g, 6.53 mmol). The mixture was stirred for 1.5 h at 0°, then diluted with dichloromethane (25 mL), washed with water (40 mL × 2), dried, and concentrated *in vacuo*. Column chromatography of the residue on silica gel (150 g) gave **23β** (2.0 g, 62.8%), **23αβ** (0.92 g, 30%; αβ-ratio ~1:1), and **23α** (0.14 g, 4.4%).

Compound **23α** had m.p. 170°, $[\alpha]_D$ −59° (*c* 1). ^{1}H-N.m.r. data (200 MHz, 8:1 $CDCl_3$–MeOD): δ 8.25–8.38 (m, 4 H, aromatic), 6.50 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.66 (ddd,

1 H, $J_{2a,3}$ 12.9, $J_{2e,3}$ 5.1, $J_{3,4}$ 3.4 Hz, H-3), 4.54 (bs, 1 H, H-4), 4.42 (dq, 1 H, $J_{4,5}$ 1.6, $J_{5,6}$ 6.5 Hz, H-5), 2.24 (ddd, 1 H, $J_{2a,2e}$ 14.1 Hz, H-2*a*), 2.04 (dddd, 1 H, $J_{1,2e}$ 1.4, $J_{2e,4}$ 1.1 Hz, H-2*e*), 1.18 (d, 3 H, H-6,6,6).

Compound **23β** had m.p. 109°, $[\alpha]_D$ +33° (*c* 1, ethyl acetate). ^{1}H-N.m.r. data (200 MHz): δ 8.20–8.34 (m, 4 H, aromatic), 7.21 (d, 1 H, $J_{3,NH}$ 5.5 Hz, NH-3), 6.82 (d, 1 H, $J_{4,NH}$ 8.3 Hz, NH-4), 6.05 (dd, 1 H, $J_{1,2a}$ 10.0, $J_{1,2e}$ 2.6 Hz, H-1), 4.41 (m, 1 H, H-3), 4.37 (bd, 1 H, NH-4), 4.08 (dq, 1 H, $J_{4,5}$ 1.2, $J_{5,6}$ 6.6 Hz, H-5), 2.45 (dddd, 1 H, $J_{2e,3}$ 4.1, $J_{2e,4}$ 1.2, $J_{2a,2e}$ 12.8 Hz, H-2*e*), 1.92 (ddd, 1 H, $J_{2a,3}$ 12.8 Hz, H-2*a*), 1.31 (d, 3 H, H-6,6,6).

Anal. Calc. for $C_{17}H_{15}F_6N_3O_7$ (487.32): C, 41.98; H, 3.10; N, 8.62. Found: C, 41.92; H, 3.13; N, 8.55.

4-O-Methyl-10-O-p-nitrobenzoyl-7-O-trimethylsilyl-β-rhodomycinone (**25**). — To a solution of **24** (100 mg, 0.16 mmol) in 1:1 dichloromethane–pyridine (8 mL) at 4° was added chlorotrimethylsilane (70 mg). After stirring for 0.3 h, the mixture was diluted with dichloromethane (200 mL), washed with phosphate buffer (pH 7, 15 mL × 2), dried, and concentrated *in vacuo*. Crystallisation from chloroform–light petroleum afforded a mixture (95 mg) of the unstable **25** and **24** in the ratio 5:1. ^{1}H-N.m.r. data: (200 MHz): **25**, δ 13.87 and 13.29 (2 s, 2 H, HO-6,11), 8.27–8.07 (m, 4 H, aromatic), 7.98 (dd, 1 H, $J_{1,2}$ 1.0, $J_{1,3}$ 7.8 Hz, H-1), 7.75 (dd, 1 H, $J_{2,3}$ 8.4 Hz, H-2), 7.38 (dd, 1 H, H-3), 6.55 (s, 1 H, H-10), 5.55 (bs, 1 H, H-7), 4.09 (s, 3 H, MeO-4), 2.27 (bd, 1 H, $J_{7,8A}$ 1.2, $J_{8A,10}$ 1.0, $J_{8A,8B}$ 14.5 Hz, H-8A) 2.05 (dd, 1 H, $J_{7,8B}$ 3.7 Hz, H-8B), 1.81 (m, 1 H, $J_{13A,13B}$ 14.6, $J_{13,14}$ 7.2 Hz, H-13A), 1.58 (m, 1 H, H-13B), 1.07 (t, 3 H, H-14,14,14), 0.27 (bs, 9 H, $SiMe_3$).

Glycosylation of **24** *with glycosyl donors* **14β**, **14αβ**, **23β**, *or* **23αβ**. — To a mixture of **24** (1.80 mmol), glycosyl donor (2.28 mmol), and molecular sieves 4 Å (3.0 g) in 10:1 dichloromethane–tetrahydrofuran (100 mL) at −50° was added trimethylsilyl trifluoromethanesulfonate (0.5 mL). After stirring the mixture for 4 h at −30°, triethylamine (1.0 mL) was added, and the mixture was filtered, washed with water (50 mL), dried, and concentrated *in vacuo*. Column chromatography of the residue on silica gel (130 g), with a solvent as specified, gave the α-glycoside and the diglycosylated by-product, respectively.

4-O-Methyl-10-O-p-nitrobenzoyl-7-O-(2,4,6-trideoxy-3-O-p-nitrobenzoyl-4-trifluoroacetamido-α-L-lyxo-hexopyranosyl)-β-rhodomycinone (**26**) *and 4-O-methyl-10-O-p-nitrobenzoyl-7,9-di-O-(2,4,6-trideoxy-3-O-p-nitrobenzoyl-4-trifluoroacetamido-α-L-lyxo-hexopyranosyl-β-rhodomycinone* (**27**). — Condensation of **24** (2.00 g, 3.63 mmol) with **14β** (3.00 g, 4.54 mmol), as described above, gave, after column chromatography (15:5:1 dichloromethane–light petroleum–ethyl acetate) on silica gel (130 g), **26** (2.62 g, 78%), m.p. 218°, $[\alpha]_D$ +310° (*c* 0.046). ^{1}H-N.m.r. data (300 MHz): δ 13.87 and 13.74 (2 s, 2 H, HO-6,11), 8.20–7.96 (m, 8 H, aromatic), 7.94 (dd, 1 H, $J_{1,2}$ 7.5, $J_{1,3}$ 1.1 Hz, H-1), 7.72 (dd, 1 H, $J_{2,3}$ 8.2 Hz, H-2), 7.34 (dd, 1 H, H-3), 6.53 (s, 1 H, H-10), 6.53 (d, 1 H, $J_{4',NH}$ 8.5 Hz, NH-4'), 5.62 (d, 1 H, $J_{1',2'a}$ 4.4 Hz, H-1'), 5.32 (ddd, 1 H, $J_{2',3'a}$ 12.5, $J_{2'e,3'}$ 5.5, $J_{3',4'}$ 3.5 Hz, H-3'), 5.27 (d, 1 H, $J_{7,8b}$ 4.0 Hz, H-7), 4.53 (dd, 1 H, H-4'), 4.50 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5'), 4.02 (s, 3 H, MeO-4), 2.38 (d, 1 H, $J_{8A,8B}$ 15.0 Hz, H-8A), 2.21 (dd, 1 H, $J_{2'e,3'}$ 5.5, $J_{2'a,2'e}$ 13.0 Hz, H-2'*e*), 2.15 (dd, 1 H, H-8B), 1.93 (ddd, 1 H, H-2'*a*), 1.83 (m, 1 H, $J_{13,14}$ 7.4, $J_{13A,13B}$ 15.0 Hz, H-13A), 1.48 (m, 1 H, H-13B), 1.25 (d, 3 H, H-6',6',6'), 1.04 (t, 3 H, H-14,14,14).

Anal. Calc. for $C_{43}H_{36}F_3N_3O_{17}$ (923.77): C, 55.91; H, 3.93; N, 4.55. Found: C, 55.97; H, 3.97; N, 4.34.

Condensation of **24** (0.20 g, 0.36 mmol) with **14β** (0.45 g, 0.77 mmol) in dichloromethane (25 mL), as described above, gave, after column chromatography (15:5:1 dichloromethane–light petroleum–ethyl acetate) on silica gel (20 g), **26** (248 mg, 74.8%) and **27** (25 mg, 5.5%).

Compound **27** had m.p. 198°, $[\alpha]_D$ +77.5° (*c* 0.0413). ^{1}H-N.m.r. data (400 MHz): δ 13.89 and 13.23 (2 s, 2 H, HO-6,11), 8.18–7.72 (m, 12 H, aromatic), 7.93 (dd, 1 H, $J_{1,2}$ 7.6, $J_{1,3}$ 1.3 Hz, H-1), 7.73 (dd, 1 H, $J_{2,3}$ 8.7 Hz, H-2), 7.34 (dd, 1 H, H-3), 7.00 (d, 1 H, $J_{8A,10}$ 1.3 Hz, H-10), 6.62 and 6.51 (2 d, 2 H, $J_{4',NH}$ 9.5, $J_{4'',NH}$ 9.5 Hz, NH-4′,4″), 5.61 (d, 1 H, $J_{1',2'a}$ 3.8 Hz, H-1′), 5.58 (d, 1 H, $J_{1'',2''a}$ 3.8 Hz, H-1″), 5.48 (ddd, 1 H, $J_{2'a,3'}$ 12.6, $J_{2'e,3'}$ 5.0, $J_{3',4'}$ 3.5 Hz, H-3′), 5.44 (ddd, 1 H, $J_{2''a,3''}$ 12.6, $J_{2''e,3''}$ 5.0, $J_{3'',4''}$ 3.5 Hz, H-3″), 5.06 (d, 1 H, $J_{7,8B}$ 5.1 Hz, H-7), 4.77 (dq, 1 H, $J_{4',5'}$ 1.2, $J_{5',6'}$ 6.5 Hz, H-5′), 4.66 (dd, 1 H, H-4″), 4.42 (dd, 1 H, H-4′), 4.02 (s, 3 H, MeO-4), 3.98 (q, 1 H, $J_{5'',6''}$ 6.5 Hz, H-5″), 2.59 (d, 1 H, $J_{8A,8B}$ 15.0 Hz, H-8A), 2.27 (dd, 1 H, $J_{2'a,2'e}$ 13.2 Hz, H-2′*e*), 2.22 (dd, 1 H, $J_{2''a,2''e}$ 13.2 Hz, H-2″*e*), 2.18 (m, 1 H, $J_{13,14}$ 7.6, $J_{13A,13B}$ 15.2 Hz, H-13A), 2.07 (dd, 1 H, H-8B), 1.91 (ddd, 1 H, H-2′*a*), 1.87 (ddd, 1 H, H-2″*a*), 1.44 (m, 1 H, H-13B), 1.30 (d, 3 H, H-6′,6′,6′), 0.99 (t, 3 H, H-14,14,14), 0.51 (d, 1 H, H-6″,6″,6″).

Anal. Calc. for $C_{58}H_{49}F_6N_5O_{25}$ (1298.05): C, 53.67; H, 3.80; N, 5.40. Found: C, 53.87; H, 3.84; N, 5.34.

*4-*O*-Methyl-10-*O*-*p*-nitrobenzoyl-7-*O*-(2,3,4,6-tetradeoxy-3,4-bis(trifluoroacetamido)-*α*-*L*-lyxo-hexopyranosyl)-β-rhodomycinone* (**28**) and *4-*O*-methyl-10-*O*-*p*-nitrobenzoyl-7,9-di-*O*-[2,3,4,6-tetradeoxy-3,4-bis(trifluoroacetamido)-*α*-*L*-lyxo-hexopyranosyl]-β-rhodomycinone* (**29**). — Condensation of **24** (1.20 g, 2.18 mmol) and **23β** (1.38 g, 2.83 mmol) in 10:1 dichloromethane–tetrahydrofuran, as described above, gave, after column chromatography (5:5:1 dichloromethane–ether–light petroleum), **28β** (1.59 g, 84%), m.p. 220–223°, $[\alpha]_D$ +406° (*c* 0.05). ^{1}H-N.m.r. data (300 MHz): δ 13.89 and 13.21 (2 s, 2 H, HO-6,11), 8.24–8.13 (m, 8 H, aromatic), 7.96 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 7.76 (dd, 1 H, $J_{2,3}$ 8.1 Hz, H-2), 7.39 (d, 1 H, H-3), 6.78 (d, 1 H, $J_{4',NH}$ 6.0 Hz, NH-4′), 6.68 (d, 1 H, $J_{3',NH}$ 8.5 Hz, NH-3′), 6.57 (s, 1 H, H-10), 5.58 (d, 1 H, $J_{1',2'a}$ 3.5 Hz, H-1′), 5.30 (d, 1 H, $J_{7,8b}$ 4.0 Hz, H-7), 4.53 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 4.36 (d, 1 H, H-4′), 4.32 (m, 1 H, H-3′), 4.08 (s, 3 H, MeO-4), 3.57 (s, 1 H, HO-9), 2.41 (d, 1 H, $J_{8A,8B}$ 15.0 Hz, H-8A), 2.23 (dd, 1 H, $J_{2'a,2'e}$ 13.0 Hz, H-2′*e*), 2.20 (dd, 1 H, H-8B), 1.87 (m, 1 H, $J_{13,14}$ 7.2 Hz, H-13A), 1.76 (ddd, 1 H, H-2′*a*), 1.54 (m, 1 H, H-13B), 1.28 (d, 3 H, H-6′,6′,6′), 1.09 (t, 3 H, H-14,14,14).

Anal. Calc. for $C_{38}H_{33}F_6N_3O_{14}$ (869.69): C, 52.48; H, 3.82; N, 4.83. Found: C, 52.67; H, 3.92; N, 4.67.

Condensation of **24** (0.60 g, 1.09 mmol) and **23β** (0.69 g, 1.41 mmol) in dichloromethane (75 mL), as described above, gave, after column chromatography (5:5:1 dichloromethane–ether–light petroleum), **28** (0.58 g, 62%) and **29** (0.28 g, 22%).

Compound **29** had m.p. 194°, $[\alpha]_D$ +39° (*c* 0.058). ^{1}H-N.m.r. data (400 MHz): δ 13.86 and 13.18 (2 s, 2 H, HO-6,11), 8.18–8.05 (m, 4 H, aromatic), 7.91 (dd, 1 H, $J_{1,2}$ 7.6, $J_{1,3}$ 1.2 Hz, H-1), 7.82 (d, 1 H, $J_{3'',NH}$ 6.0 Hz, NH-3″), 7.72 (dd, 1 H, $J_{2,3}$ 8.2 Hz, H-2), 7.54 (d, 1 H, $J_{3',NH}$ 6.5 Hz, NH-3′), 7.35 (dd, 1 H, H-3), 6.93 (d, 1 H, $J_{8A,10}$ 1.3 Hz, H-10), 6.67

(d, 1 H, $J_{4',NH}$ 7.6 Hz, NH-4'), 6.57 (d, 1 H, $J_{4',NH}$ 7.6 Hz, NH-4''), 5.49 (bs, 2 H, H-1',1''), 5.01 (d, 1 H, $J_{7,8B}$ 5.2 Hz, H-7), 4.68 (q, 1 H, $J_{5',6'}$ 6.3 Hz, H-5'), 4.41 (m, 1 H, H-3''), 4.33 (m, 1 H, H-3'), 4.19 (d, 1 H, H-4'), 4.07 (d, 1 H, H-4''), 4.03 (s, 3 H, MeO-4), 3.87 (q, 1 H, $J_{5'',6''}$ 6.4 Hz, H-5''), 2.49 (d, 1 H, $J_{8A,8B}$ 15.1 Hz, H-8A), 2.21 (dd, 1 H, $J_{2'e,3'}$ 3.8, $J_{2'a,2'e}$ 13.5 Hz, H-2'*e*), 2.14 (m, 1 H, $J_{13,14}$ 7.6, $J_{13A,13B}$ 15.2 Hz, H-13A), 2.14 (dd, 1 H, $J_{2''e,3''}$ 3.6, $J_{2''a,2''e}$ 13.0 Hz, H-2''*e*), 2.04 (dd, 1 H, $J_{7,8B}$ 5.4 Hz, H-8B), 1.69 (ddd, 1 H, $J_{1'',2''a}$ 3.8, $J_{2''a,3''}$ 12.7 Hz, H-2''*a*), 1.65 (ddd, 1 H, $J_{1',2'a}$ 3.8, $J_{2'a,3'}$ 13.2 Hz, H-2'*a*), 1.43 (m, 1 H, H-13B), 1.25 (d, 3 H, H-6',6',6'), 0.93 (t, 3 H, H-14,14,14), 0.45 (d, 3 H, H-6'',6'',6'').

Anal. Calc. for $C_{48}H_{43}F_{12}N_5O_{17}$ (1189.88): C, 48.45, H, 3.64. Found: C, 48.52, H, 3.66.

*4-O-Methyl-7-O-(2,4,6-trideoxy-4-trifluoroacetamido-α-*L*-lyxo-hexopyranosyl)-β-rhodomycinone* (**30**). — To a stirred mixture of **26** (2.28 g, 2.47 mmol) in 2:1 chloroform–methanol (30 mL) was added 0.1M NaOH (32 mL) at room temperature. After 1 h, the mixture was neutralised with aqueous 0.1M HCl (~30 mL), and concentrated *in vacuo*. A suspension of the residue in 5:1 chloroform–methanol (80 mL) was washed with 0.1M phosphate buffer (pH 7.5, 50 mL × 3) and saturated aqueous NaCl (20 mL), and the organic layer was dried and concentrated *in vacuo*. Column chromatography (8:1 dichloromethane–acetone) of the residue on silica gel (120 g) gave **30** (1.42 g, 92.4%), m.p. 260°, $[\alpha]_D$ +172° (*c* 0.05). ^{1}H-N.m.r. data (300 MHz): δ 13.82 and 13.35 (2 s, 2 H, HO-6,11), 7.97 (dd, 1 H, $J_{1,2}$ 7.5, $J_{1,3}$ 1.1 Hz, H-1), 7.73 (dd, 1 H, $J_{2,3}$ 8.5 Hz, H-2), 7.35 (dd, 1 H, H-3), 6.43 (d, 1 H, $J_{4',NH}$ 9.0 Hz, NH-4'), 5.47 (d, 1 H, $J_{1',2'a}$ 3.9 Hz, H-1'), 5.07 (dd, 1 H, $J_{7,8A}$ 2.5, $J_{7,8B}$ 3.5 Hz, H-7), 4.86 (d, 1 H, $J_{10,OH}$ 3.0 Hz, H-10), 4.31 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5'), 4.15 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, H-4'), 4.06 (m, 1 H, H-3'), 4.03 (s, 3 H, MeO-4), 3.60 (s, 1 H, HO-9), 2.74 (d, 1 H, HO-10), 2.08 (dd, 1 H, $J_{8A,8B}$ 15.0 Hz, H-8A), 2.02 (dd, 1 H, H-8B), 1.93 (dd, 1 H, $J_{2'e,3'}$ 5.5 Hz, H-2'*e*), 1.82 (m, 1 H, $J_{13A,13B}$ 15.0 Hz, H-13A), 1.67 (m, 1 H, H-13B), 1.56 (ddd, 1 H, H-2'*a*), 1.20 (d, 3 H, H-6',6',6'), 1.04 (t, 3 H, H-14,14,14).

Anal. Calc. for $C_{29}H_{30}F_3NO_{11}$ (625.56): C, 55.68; H, 4.83; N, 2.24. Found: C, 55.76; H, 4.86; N, 2.11.

*7-O-(4-Amino-2,4,6-trideoxy-α-*L*-lyxo-hexopyranosyl)-4-O-methyl-β-rhodomycinone* (**31**). — To a stirred solution of **30** (1.35 g, 2.16 mmol) in 1:1 chloroform–methanol (60 mL) was added M NaOH (14 mL). After stirring for 2 h, the mixture was neutralised with M HCl (~14 mL), diluted with 1:1 chloroform–1-butanol (70 mL), washed with saturated aqueous NaCl (20 mL), dried ($MgSO_4$), and concentrated *in vacuo*. Column chromatography of the residue on RP-2 silica gel (35 g, Li-Chroprep 25–40 μm, Merck), with 20:1 chloroform–methanol, and on aminated silica gel (60 g, Li-Chroprep NH_2 40–63 μm, Merck) gave **31** (0.85 g, 74.3%), m.p. 189° (dec.), $[\alpha]_D$ +445° (*c* 0.05). ^{1}H-N.m.r. data (300 MHz, 5:1 $CDCl_3$–MeOD): δ 7.82 (dd, 1 H, $J_{1,2}$ 7.5, $J_{1,3}$ 1.1 Hz, H-1), 7.64 (dd, 1 H, $J_{2,3}$ 8.1 Hz, H-2), 7.26 (dd, 1 H, H-3), 5.35 (d, 1 H, $J_{1',2'a}$ 3.7 Hz, H-1'), 4.98 (bs, 1 H, $J_{7,8A}$ 2.0, $J_{7,8B}$ 3.8 Hz, H-7), 4.74 (s, 1 H, H-10), 4.12 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5'), 3.95 (s, 3 H, MeO-4), 3.77 (ddd, 1 H, $J_{2'a,3'}$ 13.0, $J_{2'e,3'}$ 4.0, $J_{3',4'}$ 3.5 Hz, H-3'), 2.82 (d, 1 H, H-4'), 2.11 (dd, 1 H, $J_{8A,8B}$ 15.0 Hz, H-8A), 2.04 (dd, 1 H, H-8B), 1.78 (dd, 1 H, $J_{2'a,2'e}$ 13.0 Hz, H-2'*e*), 1.76 (m, 1 H, $J_{13,14}$ 7.5, $J_{13A,13B}$ 15 Hz H-13A), 1.69 (m, 1 H, H-13B), 1.61 (ddd, 1 H, H-2'*a*), 1.23 (d, 3 H, H-6',6',6'), 1.01 (t, 3 H, H-14,14,14).

Anal. Calc. for $C_{27}H_{31}NO_{10}$ (529.55): C, 61.24; H, 5.90; N, 2.65. Found: C, 61.31; H, 5.93; N, 2.47.

*4-O-Methyl-7-O-[2,3,4,6-tetradeoxy-3,4-bis(trifluoroacetamido)-α-*L*-lyxo-hexopyranosyl]-β-*rhodomycinone (**32**). — Treatment of **28** (1.40 g, 1.27 mmol) with 0.1M NaOH, as described for the preparation of **30**, gave **32** (0.80 g, 87.6%), m.p. 160°, $[\alpha]_D$ +254° (*c* 0.05). ^{1}H-N.m.r. data (400 MHz): δ 13.80 and 13.31 (2 s, 2 H, HO-6,11), 7.94 (dd, 1 H, $J_{1,2}$ 7.0, $J_{1,3}$ 1.1 Hz, H-1), 7.72 (dd, 1 H, $J_{2,3}$ 8.6 Hz, H-2), 7.32 (dd, 1 H, H-3), 6.66 (d, 1 H, $J_{3',NH}$ 6.3 Hz, NH-3'), 6.58 (d, 1 H, $J_{4',NH}$ 8.2 Hz, NH-4'), 5.46 (d, 1 H, $J_{1',2'a}$ 3.8 Hz, H-1'), 5.05 (bs, 1 H, H-7), 4.85 (s, 1 H, H-10), 4.45 (dq, 1 H, $J_{4',5'}$ 1.0, $J_{5',6'}$ 6.4 Hz, H-5'), 4.24 (m, 2 H, H-3',4'), 4.00 (s, 3 H, MeO-4), 3.32 (s, 1 H, HO-9), 2.67 (bs, 1 H, HO-10), 2.10 (dd, 1 H, $J_{7,8A}$ 4.4, $J_{8A,8B}$ 8.0 Hz, H-8A), 2.05 (bd, 1 H, H-8B), 1.81 (m, 1 H, $J_{13,14}$ 6.3, $J_{13A,13B}$ 17.5 Hz, H-13A), 1.67 (m, 1 H, H-13B), 1.63 (ddd, 1 H, $J_{2'a,3'}$ 8.9, $J_{2'a,2'e}$ 10.0 Hz, H-2'*a*), 1.56 (m, 1 H, H-2'*e*), 1.19 (d, 3 H, H-6',6',6'), 1.05 (t, 3 H, H-14,14,14). F.a.b.-mass spectrum: *m/z* 530 (M + H$^+$).

Anal. Calc. for $C_{31}H_{30}F_6N_2O_{11}$ (720.58): C, 51.67; H, 4.20; N, 3.89. Found: C, 51.34; H, 4.22; N, 3.74.

*7-O-(3,4-Diamino-2,3,4,6-tetradeoxy-α-*L*-lyxo-hexopyranosyl)-4-O-methyl-β-rhodomycinone* (**33**). — Treatment of **32** (0.50 g, 0.69 mmol) with M NaOH, as for the preparation of **31**, followed by column chromatography (65:35:1 chloroform–methanol–conc. NH_3) on silica gel (60 g), yielded **33** (0.29 g, 78.8%), m.p. 160° (dec.), $[\alpha]_D$ +355° (*c* 0.2, methanol). ^{1}H-N.m.r. data (300 MHz, MeOD): δ 7.50 (dd, 1 H, $J_{1,2}$ 7.5, $J_{1,3}$ 1.1 Hz, H-1), 7.44 (dd, 1 H, $J_{2,3}$ 8.5 Hz, H-2), 7.15 (dd, 1 H, H-3), 5.32 (d, 1 H, $J_{1',2'a}$ 3.0 Hz, H-1'), 4.93 (dd, 1 H, $J_{7,8A}$ 1.5 $J_{7,8B}$ 4.0 Hz, H-7), 4.68 (s, 1 H, H-10), 4.22 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5'), 3.78 (s, 3 H, MeO-4), 3.06 (ddd, 1 H, $J_{2'a,3'}$ 13.0, $J_{2'e,3'}$ 4.0, $J_{3',4'}$ 2.6 Hz, H-3'), 2.66 (d, 1 H, H-4'), 2.14 (dd, 1 H, $J_{8A,8B}$ 15.0 Hz, H-8A), 2.06 (dd, 1 H, H-8B), 1.76 (dd, 1 H, $J_{2'a,2'e}$ 13.0 Hz, H-2'*e*), 1.74 (m, 1 H, $J_{13,14}$ 7.5, $J_{13A,13B}$ 15.0 Hz, H-13A), 1.68 (m, 1 H, H-13B), 1.64 (ddd, 1 H, H-2'*a*), 1.22 (d, 3 H, H-6',6',6'), 1.06 (t, 3 H, H-14,14,14). F.a.b.-mass spectrum: *m/z* 529 (M+ H$^+$).

Anal. Calc. for $C_{27}H_{32}N_2O_9$ (528.56): C, 61.36; H, 6.10; N, 5.30. Found: C, 61.48; H, 6.12; N, 5.24.

ACKNOWLEDGMENTS

We thank Dr. S. Berger and Dr. T. Kämpchen (University of Marburg) for measuring the n.m.r. spectra, Dr. H.-W. Fehlhaber (Hoechst AG, Frankfurt) for performing the mass spectrometry, and Dr. T. Grewer (Hoechst AG, Frankfurt) for performing the differential thermoanalysis.

REFERENCES

1 C. Kolar, M. Gerken, H.-P. Kraemer, K. Krohn, and H. Linoh, *J. Carbohydr. Chem.*, in press.
2 C. Kolar, K. Dehmel, and H. Moldenhauer, *J. Carbohydr. Chem.*, in press.
3 A. Yoshimoto, S. Fujii, O. Johdo, K. Kubo, T. Ishikura, H. Naganawa, T. Sawa, T. Takeuchi, and H. Umezawa, *J. Antibiot.*, 39 (1986) 902–907.

4 A. F. Hadfield, L. Cunningham, and A. C. Sartorelli, *Carbohydr. Res.*, 72 (1979) 93–104.
5 A. Martin, C. Monneret, and M. Pais, *Carbohydr. Res.*, 166 (1987) 59–70.
6 A. Bargiotti, G, Cassinelli, S. Penco, F. Arcamone, and A. M. Casazza, Eur. Pat. Appl. 51279 (1982); *Chem. Abstr.*, 97 (1982) 145229u.
7 A. Bargiotti, G. Cassinelli, S. Penco, F. Arcamone, and A. M. Casazza, Eur. Pat. Appl. 51280 (1982); *Chem. Abstr.*, 97 (1982) 145228t.
8 K. Takiura and S. Honda, *Carbohydr. Res.*, 21 (1972) 379–391.
9 J. Thiem, H. Karl, and J. Schwentner, *Synthesis*, (1978) 696–698.
10 C. Kolar, U. Knödler, F. R. Seiler, H.-W. Fehlhaber, V. Sinnwell, M. Schulz, and H. Paulsen, *Justus Liebigs Ann. Chem.*, (1987) 577–581.
11 J.-C. Florent and C. Monneret, *J. Chem. Soc., Chem. Commun.*, 15 (1987) 1171–1172.
12 Y. Kimura, M. Suzuki, T. Matsumoto, R. Abe, and S. Terashima, *Chem. Lett.*, (1984) 501–504.
13 C. Kolar, K. Dehmel, U. Knödler, M. Paal, P. Hermentin, and M. Gerken, *J. Carbohydr. Chem.*, 8 (1989) 295–305.
14 B. Iserlin and T. Reichstein, *Helv. Chim. Acta*, 27 (1944) 1146–1149.