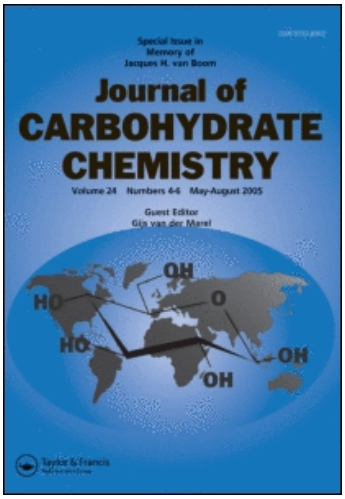

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Kolar, Cenek , Dehmel, Konrad , Moldenhauer, Hans and Gerken, Manfred(1990) 'Semisynthetic β-Rhodomycins: A New Approach to the Synthesis of 4-*O*-Methyl-β-Rhodomycins', Journal of Carbohydrate Chemistry, 9: 6, 873 — 890
To link to this Article: DOI: 10.1080/07328309008543881
URL: http://dx.doi.org/10.1080/07328309008543881

J. CARBOHYDRATE CHEMISTRY, 9(6), 873-890 (1990)

SEMISYNTHETIC β-RHODOMYCINS: A NEW APPROACH TO THE SYNTHESIS OF 4-*O*-METHYL-β-RHODOMYCINS

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Received February 26, 1990 - Final Form August 8, 1990

ABSTRACT

Syntheses of 4-*O*-methyl-β-rhodomycins are described. Glycosylation (trimethylsilyl triflate, dichloromethane-acetone 10:1, -30 °C) of 4-*O*-methyl-10-*O*-*p*-nitrobenzoyl-β-rhodomycinone, obtained from β-rhodomycinone (β-RMN) in a 6-step synthesis, with 1-*O*-*tert*-butyl(dimethyl)silylated derivatives of 4-*O*-acetyl- or 4-*O*-*p*-nitrobenzoyl-2,3,6-trideoxy-3-trifluoroacetylamino-β-L-*arabino*- and *lyxo*-hexopyranoses or 2,6-di-*O*-acetyl-2,6-dideoxy-β-L-*lyxo*-hexopyranose afforded 7-*O*-α-L-glycosyl-β-rhodomycinones. Removal of the *O*- and *N*-acyl groups with 0.1M and 1M NaOH gave the 7-*O*-(3-amino-2,3,6-trideoxy-α-L-*arabino*- and *lyxo*-hexopyranosyl)-4-*O*-methyl-β-rhodomycinones and 7-*O*-(2,6-dideoxy-α-L-*lyxo*-hexopyranosyl)-4-*O*-methyl-β-rhodomycinone.

INTRODUCTION

An important aspect in the structure-activity relationships of anthracyclines is the correlation between their substituents in position 4 and cytotoxicity. Anthracyclines having a methoxy group at C-4 are less cytotoxic than their 4-hydroxy analogues.[1,2] Recently a similar correlation was observed for microbial oxaunomycin and the semisynthetic 4-*O*-methyl analogue 7-*O*-(3-amino-2,3,6-trideoxy-α-L-*lyxo*-hexopyranosyl)-4-*O*-methyl-β-rhodomycinone.[3]

In the synthesis of 4-*O*-methyl-β-rhodomycins, 4-*O*-methyl-10-*O*-trifluoroacetyl-β-rhodomycinone[3] was found to be a suitable glycosyl acceptor. However, problems in the methylation step and the handling of trifluoroacetylated derivatives limited the accessi-

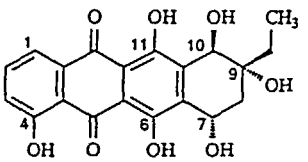
bility of the aglycone. Disadvantage of the glycosyl donor is that the 3-amino-2,3,6-trideoxy-α-L-*lyxo*-hexopyranose (daunosamine)[4,5,6] and its functionalization for coupling[1,7] require multistep synthesis.

We now report on a new approach for the syntheses of 4-*O*-methyl-β-RMN, 1-*O*-*tert*-butyl(dimethyl)silyl-2,6-dideoxy-β-*arabino*- and *lyxo*-hexopyranoses, and their use as glycosylation components in the preparation of 4-*O*-methyl-β-rhodomycins.

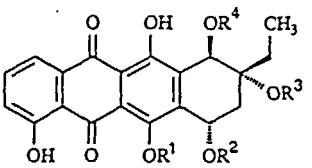
RESULTS AND DISCUSSION

In our efforts to gain access to glycosyl acceptor of 4-*O*-methyl-β-rhodomycinone **8**, an alternative pathway for the protection of β-rhodomycinone (β-RMN) **1** was developed based on 1,1,3,3-tetraisopropyldisiloxane-1,3-diyl (TIPS) group.[8]

Treatment of β-RMN **1** with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane in 1,2-dichloroethane-pyridine afforded mainly the 6,7-*O*-TIPS-β-RMN **2** and 7,9-*O*-TIPS isomer **3** in a ratio 10:1. After regioselective silylation (chlorotrimethylsilane, pyridine-dichloromethane) of the 10-hydroxy group in **2** and **3**, both isomers were isolated by chromatography to give **4** (58%) and **5** (8%). The following methylation (MeI, K_2CO_3 in acetone/chloroform) of **4** occurred mainly[9] at the phenolic hydroxy group OH-4 as in the methylation of 7,10-bis-*O*-trimethylsilyl-β-RMN.[3] The reaction yielded the 4-*O*-methyl- **6** (61%) and 4,11-di-*O*-methyl-ethers **7** (19%). In the ^1H NMR spectrum of **6** a significant one-proton singlet was observed at δ 13.22 ppm, indicating the unsubstituted hydroxy group at C-11. Cleavage of the trimethylsilyl group with aqueous 0.1M HCl in dichloromethane-methanol and of the TIPS group with 1M Bu_4NF in THF[8] in **6** afforded the reported 4-*O*-methyl-β-RMN **8** in a yield of 67%.[3] In the same manner, deprotection of **7** gave the 4,11-di-*O*-methyl-β-RMN **9**.



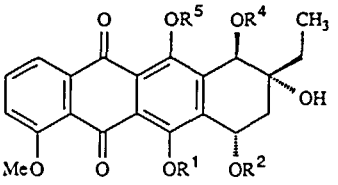
1 ß-RMN



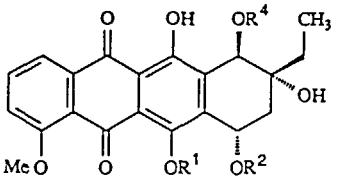
2 R^1+R^2=TIPS $R^3=R^4$=H
3 R^1=H R^2+R^3=TIPS R^4=H
4 R^1+R^2=TIPS R^3=H R^4=Me_3Si
5 R^1=H R^2+R^3=TIPS R^4=Me_3Si

TIPS = -$Si(iPr)_2OSi(iPr)_2$-

The regioselective glycosylation of 4-*O*-methyl-β-RMN **8** in position 7 requires protection of the hydroxy group at C-10. The tertiary hydroxy group at C-9 is less reactive than OH-7 or OH-10. Nevertheless, glycosylation of this position is reported.[10] Thus, the deprotection (0.1M HCl) of the TMS group in **6** afforded intermediate **10**, which was



6 R^1+R^2=TIPS R^4=Me_3Si R^5=H
7 R^1+R^2=TIPS R^4=Me_3Si R^5=Me
8 R^1=R^2=R^3=R^4=R^5=H
9 R^1=R^2=R^3=R^4=H R^5=Me



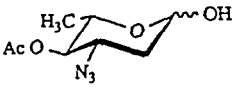
10 R^1+R^2=TIPS R^4=H
11 R^1+R^2=TIPS R^4=pNBz
12 R^1=R^2=H R^4=pNBz

acylated at OH-10 by treatment with *p*-nitrobenzoyl chloride/pyridine followed by cleavage of the TIPS group in **11** with 1M Bu_4NF in THF. The resulting 10-*O*-*p*-nitrobenzoate **12**, obtained after the three steps in ~70% yield, proved to be more stable than the trifluoroacetylated analogue[3] and was easily separated by column chromatography on silica gel.

The most important step in the synthesis of anthracyclines is glycosylation. The glycosyl donors of the 3-amino-2,3,6-trideoxy-L-hexopyranose type used in the condensation step are typical 4-*O*-*p*-nitrobenzoyl or 4-*O*-trifluoroacetyl and 3-*N*-trifluoroacetyl derivatives. The amino sugar is activated for coupling either via the glycosyl halide,[1,11] glycal[1,12] or *p*-nitrobenzoate.[7] The use of these known glycosyl donors in the glycosylation of rhodomycinones, however, results in mono- and bis-glycosylated products.[13,14]

An alternative route for the synthesis of the *arabino*- and *lyxo*-hexopyranosyl donors, based on the readily accessible 4-*O*-acetyl-3-azido-2,3,6-trideoxy-L-*arabino*-hexopyranose[15] **13**, has now been developed. Thus, silylation of **13** with $^tBuMe_2SiCl$ gave in the presence of imidazole and dichloroethane the β-anomer **14β** selectively. Use of DMF as solvent[16] led to the α- and β-anomers **14α** and **14β** in a ratio 1:4 (^1H NMR). After deacetylation of **14α** and **14β**, both anomers **15α** and **15β** can be separated by chromatography. Hydrogenolysis of the azido group in **14β** in the presence of ammonia, in which the acetyl group was cleaved simultaneously, gave the amino sugar **16**. *N*-Acylation of **16** with trifluoroacetic anhydride in dichloromethane-ethanol-triethylamine followed by *O*-acetylation of **17** afforded the *arabino*-pyranosyl donor **18** in high yield.

The new *lyxo*-pyranosyl donor was readily obtained from the 3-azido-*arabino* derivative **14β**. After deacetylation of **14β** by the method of Zemplén, compound **15β** was obtained and then treated with trifluoromethanesulfonic anhydride in pyridine-dichloromethane at -30° to give the triflate **19**. The C-4 epimerization[17] of **19** by treatment with cesium acetate/sodium acetate in DMF gave the *lyxo* compound **20**, which was subsequently deacetylated to **21**. As in the preparation of **18**, the hydrogenolysis of the azide **21** gave the amine **22**, which was *N*-trifluoroacetylated to **23**, followed by *O*-acylation of **23** to the acetate **24** or *p*-nitrobenzoate **25**.



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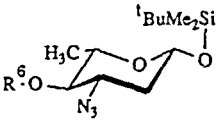
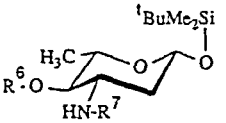
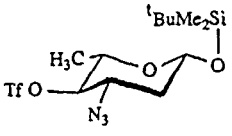


14 R^6=Ac
15 R^6=H

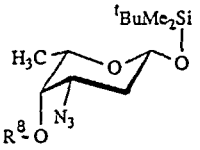


16 R^6=R^7=H
17 R^6=H R^7=F_3CCO
18 R^6=Ac R^7=F_3CCO

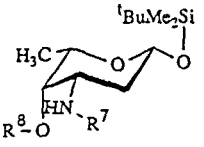


19

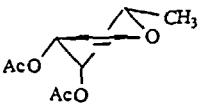
pNBz = 4-O_2N-PhCO
Tf = CF_3SO_2



20 R^8=Ac
21 R^8=H



22 R^7=R^8=H
23 R^7=F_3CCO R^8=H
24 R^7=F_3CCO R^8=Ac
25 R^7=F_3CCO R^8=pNBz



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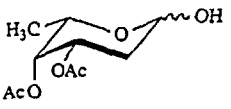

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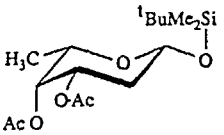


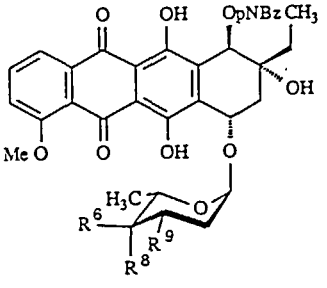
28

The synthesis of α- and β-glycosyloxy-trimethylsilanes and their use for the preparation of acetal-glycosides have been extensively described in the literature.[18-20] It has been suggested that the anomeric oxygen of the glycosyloxy-trimethylsilane is involved in the formation of the glycosidic linkage.[19] Most interesting is the fact that, in the presence of a *tert*-butyl(dimethyl)silyl group, the formation of the glycoside takes place at the anomeric carbon of the glycosyloxysilane. In this case the *tert*-butyl(dimethyl)silyloxy group is the leaving group.[21]

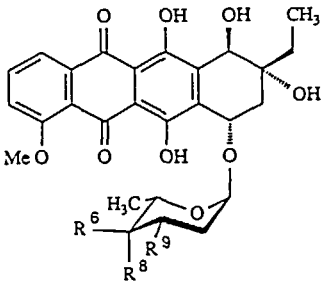
Glycosylation of the aglycone **12** with the acetates **18** or **24**, using trimethylsilyl triflate, in 10:1 dichloromethane-acetone at -30 °C afforded the 7-*O*-α-glycosyl-β-RMNs **29** and **30** in excellent yield. Condensation of the *p*-nitrobenzoate **18** with **12** under similar conditions gave mainly the α-glycoside **31** and a trace of the 7,9-bis-*O*-glycosylated by-product.[3]

We also succeeded in applying the new glycosylation procedure for the synthesis of 7-*O*-(2,6-dideoxy-α-L-*lyxo*-hexopyranosyl)-4-*O*-methyl-β-RMN. This type of compound is of interest for establishing the structure-activity relationships of anthracyclines.[1,22,23] Starting with 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-L-*lyxo*-hex-1-enitol[24] **26**, the glycosyl donor **28** was obtained in two reaction steps. Treatment[24,25] of **26** with 30% trifluoroacetic acid afforded 3,4-di-*O*-acetyl-2,6-dideoxy-β-L-*lyxo*-hexopyranose **27**, which

was silylated with $^{t}BuMe_2SiCl$ in the presence of pyridine-dichloroethane at 60 °C to obtain the glycosyl donor **28** as β-anomer. Condensation (trimethylsilyl triflate, 10:1 dichloromethane-acetone, -30 °C) of **12** with **28** afforded the α-glycoside **32** in high yield.



29 R^6=OAc R^8=H R^9=F_3CCONH
30 R^6=H R^8=OAc R^9=F_3CCONH
31 R^6=OpNBz R^8=H R^9=F_3CCONH
32 R^6=H R^8=R^9=OAc



33 R^6=OH R^8=H R^9=NH_2
34 R^6=H R^8=OH R^9=NH_2
35 R^6=H R^8=R^9=OH

The *O*- and *N*-acylated rhodomycins can be deprotected either partially by removing the *p*-nitrobenzoyl and acetyl groups with 0.1M NaOH or completety using 1M NaOH or by the Zemplén method.[26] In order to avoid difficulties in the purification of the rhodomycins, deprotection of **29**, **30**, **31** and **32** was effected first by *O*- then by *N*-deacylation, to afford the 4-*O*-methyl-β-rhodomycins **33**, **34** and **35**. The analyses of the compounds by NMR spectroscopy at 300 and 400 MHz and by mass spectroscopy were in full agreement with the proposed stuctures.

The α-*O*-linked 2-deoxy-sugars frequently occur in microbial anthracyclines as well in many other antibiotics. For this reason, the reported glycosylation method, which proved to be more effective than other glycosylation techniques, seems to be of particular interest for the preparation of mono- or even oligosaccharide conjugates.

EXPERIMENTAL

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

the standard pulse sequences of the Bruker Aspect-3000 or Jeol software. Specific optical rotations were determined with a Perkin-Elmer 241 polarimeter equipped with 10 cm cuvettes, for solutions in $CHCl_3$ at 24 °C, unless noted otherwise. Reactions were monitored by TLC on silica gel 60 F 254 (Merck) with detection by UV light or by charring with sulfuric acid. Preparative chromatography was performed on Kieselgel 60 (Merck, 0.04-0.063 mm). The glycosylations were performed under argon or nitrogen.

General procedures:

(*a*) *Glycosylation of the aglycone* **12** *with glycosyl donors* **18**, **25** *and* **28**. - To a mixture of aglycone **12** (3.0 mmol), 1-*O*-^{t}BuMe$_2$Si-β-L-*arabino*- or *lyxo*-hexopyranose donor (4.0 mmol) and molecular sieves 4 Å (4.5 g) in 10:1 dichloromethane-acetone (50 mL) at -50 °C was added trimethylsilyl trifluoromethanesulfonate (1.5 eq). After stirring for 14 h at -30 °C, triethylamine (7 mL) and dichloromethane (30 mL) were added and the mixture was filtered off. The filtrate was washed with phosphate buffer (20 mL, pH 9) and citrate buffer (20 mL x 2, pH 5), and concentrated *in vacuo*. Column chromatography of the residue on silica gel (130 g) with 20:1 dichloromethane-acetone gave the α-glycoside.

(*b*) *Deprotection of 4-O-methyl-*β*-rhodomycins* **29**, **30**, **31** *and* **32**. - To a stirred solution of the *O*- and *N*-acylated β-rhodomycin (0.64 mmol) in 3:1 methanol-chloroform (10 mL) was added aqueous 1M NaOH (10 mL) and methanol to homogenize the organic and aqueous layers. After 1 h stirring at room temperature, the mixture was neutralized with 0.1M HCl (~2 mL) and concentrated *in vacuo*. Column chromatography of the residue on silica gel (70 g) with 10:5:2:1:0.5:0.05 chloroform-acetone-methanol-acetic acid-water-triethylamine and/or on aminated silica gel (25 g) with 10:1 methanol-chloroform gave the completely deacylated product.

6,7-*O*-(1,1,3,3-Tetraisopropyldisiloxan-1,3-diyl)-β-rhodomycinone (**2**) and **7,9-*O*-(1,1,3,3-Tetraisopropyldisiloxan-1,3-diyl)-β-rhodomycinone** (**3**). To a solution of β-rhodomycinone **1** (10.00 g, 25.88 mmol) in 1:1 pyridine-1,2-dichloroethane (200 mL) was added a solution of 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (12.2 mL, 38.72 mmol) in 1,2-dichloroethane at 0 °C. The reaction mixture was stirred at 0 °C to room temperature for 24 h and then at 60 °C for 72 h, diluted with methanol (50 mL) and concentrated *in vacuo*. After co-evaporation *in vacuo* with toluene (50 mL x 3), the residue was chromatographed on a column of silica gel (600 g) with 19:1 dichloromethane-ethyl acetate to give a mixture (14.62 g) of compounds **2** and **3**, which was used in the subsequent step without further purification. A part of the residue was separated by preparative TLC in 95:15:1:0.25:0.1 chloroform-acetone-acetic acid-water-triethylamine to give **2** and **3**.

Compound **2** had mp 115-117 °C; $[\alpha]_D$ +425° (*c* 0.2); ^{1}H NMR (200 MHz) δ 13.91 and 13.07 (2 s, 2H, OH-4,11), 7.82 (br d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 7.65 (dd, 1H, $J_{2,3}$ = 8.4 Hz, H-2), 7.30 (br d, 1H, H-3), 5.28 (br s, 1H, H-7), 4.96 (s, 1H, H-10), 4.75 (s, 1H, OH-9), 1.10-1.00 (m, 28H, SiCHMe$_2$).

Anal. Calcd for $C_{32}H_{44}O_9Si_2$ (628.87): C, 61.12; H, 7.05. Found: C, 61.15; H, 7.07.

Compound **3** had mp 62-65 °C; $[\alpha]_D$ +234.3° (*c* 0.055); ^1H NMR (300 MHz) δ 13.58, 12.91 and 12.09 (3 s, 3H, OH-4,6,10), 7.83 (dd, 1H, $J_{1,2}$ = 7.5, $J_{1,3}$ = 1.0 Hz, H-1), 7.67 (dd, 1H, $J_{2,3}$ = 8.5 Hz, H-2), 7.28 (dd, 1H, H-3), 5.25 (dd, 1H, $J_{7,8A}$ = 1.4, $J_{7,8B}$ = 3.6 Hz, H-7), 4.88 (d, 1H, $J_{10,OH}$ = 4.0 Hz, H-10), 2.81 (d, 1H, OH-10), 2.18 (dd, 1H, $J_{8A,8B}$ = 14.5 Hz, H-8A), 2.04 (dd, 1H, H-8B), 1.87 (m, 1H, $J_{13,14}$ = 7.3, $J_{13A,13B}$ = 14.6 Hz, H-13A), 1.72 (m, 1H, H-13B), 1.17 (t, 3H, H-14), 1.10-1.00 (m, 28H, $SiCHMe_2$).

Anal. Calcd for $C_{32}H_{44}O_9Si_2$ (628.87): C, 61.12; H, 7.05. Found: C, 61.33; H, 7.06.

6,7-*O*-(1,1,3,3-Tetraisopropyldisiloxan-1,3-diyl)-10-*O*-trimethylsilyl-β-rhodomycinone (4) and **7,9-*O*-(1,1,3,3-Tetraisopropyldisiloxan-1,3-diyl)-10-*O*-trimethylsilyl-β-rhodomycinone (5)**. To a solution of the crude mixture of products **2** and **3** (14.62 g) in 1:1 dichloromethane-pyridine (400 mL) was added chlorotrimethylsilane (5.6 g, 51.54 mmol) at 0 °C. The reaction mixture was stirred at 0 °C to room temperature for 1 h, diluted with methanol (50 mL) and concentrated *in vacuo*. A solution of the residue in dichloromethane (200 mL) was washed with phosphate-buffer (pH 8.5, 70 mL x 2) and aqueous NaCl solution successively, dried (Na_2SO_4), and concentrated *in vacuo*. Column chromatography of the residue on silica gel (350 g) with 7:3 dichloromethane-light petroleum afforded **4** (10.59 g, 58%) and **5** (1.56 g, 8%).

Compound **4** had mp 194-196 °C; $[\alpha]_D$ +564° (*c* 0.05); ^1H NMR (300 MHz) δ 13.87 and 13.12 (2 s, 2H, OH-6,11), 7.79 (dd, 1H, $J_{1,2}$ = 7.5, $J_{1,3}$ = 1.5 Hz, H-1), 7.61 (dd, 1H, $J_{2,3}$ = 8.5 Hz, H-2), 7.25 (dd, 1H, H-3), 5.28 (dd, 1H, $J_{7,8A}$ = 2.5, $J_{7,8B}$ 4.2 Hz, H-7), 4.86 (br s, 1H, H-10), 2.13 (dd, 1H, $J_{8A,8B}$ = 14.2 Hz, H-8A), 2.06 (dd, 1H, H-8B), 1.64 (q, 2H, $J_{13,14}$ = 7.5 Hz, H-13A and H-13B), 1.30-1.21 (m, 28H, $SiCHMe_2$), 1.02 (t, 3H, H-14), 0.2 (s, 9H, $SiMe_3$).

Anal. Calcd for $C_{35}H_{52}O_9Si_3$ (701.06): C, 59.97; H, 7.48. Found: C, 60.21; H, 7.50.

Compound **5** had mp 174 °C; $[\alpha]_D$ +515.8° (*c* 0.06); ^1H NMR (200 MHz), δ 13.93 (s, 1H, OH-11), 13.18 (s, 1H, OH-4), 7.86 (dd, 1H, $J_{1,2}$ = 7.5, $J_{1,3}$ = 1.2 Hz, H-1), 7.66 (dd, 1H, $J_{2,3}$ = 8.3 Hz, H-2), 7.31 (dd, 1H, H-3), 5.34 (dd, 1H, $J_{7,8A}$ = 2.2, $J_{7,8B}$ = 3.5 Hz, H-7), 4.92 (s, 1H, H-10), 4.48 (s, 1H, OH-9), 2.19 (dd, 1H, $J_{8A,8B}$ 14.7 Hz, H-8A), 2.09 (dd, 1H, H-8B), 1.68 (q, 2H, $J_{13,14}$ = 7.5 Hz, H-13A and H-13B), 1.30-0.93 (m, 28H, $SiCHMe_2$), 1.02 (t, 3H, H-14), 0.13 (br s, 9H, $SiMe_3$).

Anal. Calcd for $C_{35}H_{52}O_9Si_3$ (701.06): C, 59.97; H, 7.48. Found: C, 60.12; H, 7.45.

4-*O*-Methyl-6,7-*O*-(1,1,3,3-tetraisopropyldisiloxan-1,3-diyl)-10-*O*-trimethylsilyl-β-rhodomycinone (6) and **4,11-Di-*O*-methyl-6,7-*O*-(1,1,3,3-tetraisopropyldisiloxan-1,3-diyl)-10-*O*-trimethylsilyl-β-rhodomycinone (7)**. To a solution of compound **4** (6.00 g, 8.55 mmol) in 4:1 acetone-chloroform (300 mL) were added K_2CO_3 (36 g) and iodomethane (80 mL). The reaction mixture was stirred for 5 d at room temperature, filtered and concentrated *in vacuo*. The residue was dissolved in dichloromethane, washed with water, dried over sodium sulfate and concentrated *in vacuo*. Column chromatography of

the residue on silica gel (300 g) with 7:3 dichloromethane-light petroleum gave compound **6** (3.74 g, 61%), compound **7** (1.22 g, 19%) and starting compound **8** (0.65 g, 11%).

Compound **6** had mp 213-214 °C; $[\alpha]_D$ +472.4° (*c* 0.05); ^{1}H NMR (400 MHz) δ 13.22 (s, 1H, OH-11), 7.89 (dd, 1H, $J_{1,2}$ = 8.0, $J_{1,3}$ = 1.1 Hz, H-1), 7.65 (dd, 1H, $J_{2,3}$ = 8.5 Hz, H-2), 7.29 (dd, 1H, H-3), 5.35 (dd, 1H, $J_{7,8A}$ = 3.5, $J_{7,8B}$ = 1.6 Hz, H-7), 4.89 (d, 1H, $J_{8B,10}$ = 1.5 Hz, H-10), 4.45 (s, 1H, OH-9), 3.96 (s, 3H, MeO), 2.17 (dd, 1H, $J_{8A,8B}$ = 14.8 Hz, H-8A), 2.07 (ddd, 1H, H-8B), 1.39 (m, 1H, $J_{13,14}$ = 7.2, $J_{13A,13B}$ = 14.5 Hz, H-13A), 1.33-1.18 (m, 28H, $SiCHMe_2$), 1.15 (m, 1H, H-13B), 1.05 (t, 3H, H-14), 0.1 (s, 9H, $SiMe_3$).

Anal. Calcd for $C_{36}H_{54}O_9Si_3$ (715.08): C, 60.47; H, 7.61. Found: C, 60.58; H, 7.65.

Compound **7** had mp 103-105 °C; $[\alpha]_D$ +124° (*c* 0.05); ^{1}H NMR (400 MHz) δ 7.72 (dd, 1H, $J_{1,2}$ = 7.5, $J_{1,3}$ = 1.2 Hz, H-1), 7.59 (dd, 1H, $J_{2,3}$ = 8.5 Hz, H-2), 7.21 (dd, 1H, H-3), 5.34 (dd, 1H, $J_{7,8A}$ = 3.8, $J_{7,8B}$ = 1.8 Hz, H-7), 4.70 (d, 1H, $J_{8B,10}$ = 1.5 Hz, H-10), 4.50 (s, 1H, OH-9), 3.93 (s, 3H, MeO), 3.91 (s, 3H, MeO), 2.17 (dd, 1H, $J_{8A,8B}$ 14.5 Hz, H-8A), 2.05 (ddd, 1H, H-8B), 1.40 (m, 1H, $J_{13,14}$ = 7.2, $J_{13A,13B}$ = 14.5 Hz, H-13A), 1.31 (m, 1H, H-13B), 1.3-0.9 (m, 28H, $SiCHMe_2$), 0.1 (s, 9H, $SiMe_3$).

Anal. Calcd for $C_{37}H_{56}O_9Si_3$ (729.11): C, 60.95; H, 7.74. Found: C, 61.18; H, 7.78.

4-*O*-Methyl-β-rhodomycinone (8). To a solution of **6** (60 mg, 0.08 mmol) in dry THF (3 mL) was added at 0 °C a 1M solution of tetrabutylammonium fluoride in THF (0.2 mL). After 30 min stirring at 0 °C the mixture was poured into aqueous 0.1M HCl (6 mL) and extracted with chloroform. The organic layer was dried (sodium sulfate) and concentrated *in vacuo*. Column chromatography of the residue on silica gel (10 g) with 7:1 toluene-methanol gave **8** (21 mg, 67%): mp 141-143 °C; $[\alpha]_D$ +73° (*c* 0.018). Lit.[3] mp 141 °C; $[\alpha]_D$ +73° (*c* 0.02).

4,11-Di-*O*-methyl-β-rhodomycinone (9). Treatment of compound **7** (60 mg, 0.08 mmol) as described for preparation of compound **8** afforded **9** (24 mg, 81%): mp 138 °C; $[\alpha]_D$ -214° (*c* 0.1); ^{1}H NMR (300 MHz) δ 14.02 (s, 1H, OH-6), 7.92 (dd, 1H, $J_{1,2}$ = 7.7, $J_{1,3}$ = 1.2 Hz, H-1), 7.77 (dd, 1H, $J_{2,3}$ = 8.4 Hz, H-2), 7.34 (dd, 1H, H-3), 5.24 (br s, 1H, H-7), 7.43 (s, 1H, H-7), 4.08 (s, 3H, MeO), 3.98 (s, 3H, MeO), 3.52 (br s, 1H, OH-10), 2.65 (br s, 1H, OH-7), 2.22 (dd, 1H, $J_{7,8A}$ = 2.5, $J_{8A,8B}$ = 14.8 Hz, H-8A), 2.12 (dd, 1H, $J_{7,8B}$ = 4.5 Hz, H-8B), 1.83 (m, 1H, $J_{13,14}$ = 7.5, $J_{13A,13B}$ = 15.0 Hz, H-13A), 1.77 (m, 1H, H-13B), 1.12 (t, 1H, H-14).

Anal. Calcd for $C_{22}H_{22}O_8$ (414.42): C, 63.76; H, 5.35. Found: C, 63,84; H, 5.37.

4-*O*-Methyl-6,7-*O*-(1,1,3,3-tetraisopropyldisiloxan-1,3-diyl)-β-rhodomycinone (10). To a solution of compound **6** (3.00 g, 4.19 mmol) in 1:1 dichloromethane-methanol (160 mL) was added aqueous 0.1M HCl solution (16 mL). After 30 min stirring, the mixture was diluted with dichloromethane (400 mL), washed with aqueous NaOH (pH 8.5, 200 mL x 3) and with water (150 mL), dried over sodium sulfate, and concentrated *in vacuo*. Column chromatography of the residue on silica gel (100 g) with 20:1 dichloro-

methane-acetone gave **10** (2.56 g, 95%): mp 166-168 °C; $[\alpha]_D$ +386° (*c* 0.005).

Anal. Calcd for $C_{33}H_{46}O_9Si_2$ (642.90): C, 61.65; H, 7.21. Found: C, 61,74; H, 7.24.

4-*O*-Methyl-10-*O*-*p*-nitrobenzoyl-6,7-*O*-(1,1,3,3-tetraisopropyldisiloxan-1,3-diyl)-β-rhodomycinone (11). To a solution of **10** (2.5 g, 3.88 mmol) in 2:1 chloroform-pyridine (170 mL) was added *p*-nitrobenzoyl chloride (1.11 g, 5.98 mmol) at 0 °C. The reaction mixture was stirred for 16 h at 10 °C, diluted with chloroform (100 mL) and washed successively with water, aqueous 0.1M HCl and water. The organic layer was dried over sodium sulfate and concentrated *in vacuo*. Column chromatography of the residue on silica gel (200 g) with 2:1:0.1 light petroleum-dichloromethane-acetone gave compound **11** (2.49 g, 81%) and 200 mg (5%) of 10,11-di-*O*-*p*-nitrobenzoyl-4-*O*-methyl-6,7-*O*-(1,1,3,3-tetraisopropyldisiloxan-1,3-diyl)-β-rhodomycinone. *Compound* **11** had mp 114-116 °C; $[\alpha]_D$ +384° (*c* 0.05); ^{1}H NMR (300 MHz) δ 13.02 (s, 1H, OH-11), 8.22-8.08 (d, 4H, nitroarom. H), 7.84 (dd, 1H, $J_{1,2}$ = 7.5, $J_{1,3}$ = 1.1 Hz, H-1), 7.65 (dd, 1H, $J_{2,3}$ = 8.2 Hz, H-2), 7.32 (dd, 1H, H-3), 5.51 (dd, 1H, $J_{7,8A}$ = 2.0, $J_{7,8B}$ = 4.6 Hz, H-7), 6.56 (d, 1H, $J_{8A,10}$ = 1.0 Hz, H-10), 3.98 (s, 3H, MeO), 2.38 (ddd, 1H, $J_{8A,8B}$ 14.5 Hz, H-8A), 2.07 (dd, 1H, H-8B), 1.83 (m, 1H, $J_{13,14}$ = 7.4, $J_{13A,13B}$ = 14.6 Hz, H-13A), 1.50 (m, 1H, H-13B), 1.07 (t, 3H, H-14), 1.10-0.95 (m, 28H, $SiCHMe_2$).

Anal. Calcd for $C_{40}H_{49}NO_{12}Si_2$ (792.01): C, 60.66; H, 6.24; N, 1.77. Found: C, 60.76; H, 6.27; N, 1.63.

4-*O*-Methyl-10-*O*-p-nitrobenzoyl-β-rhodomycinone (12). To a solution of **11** (2.40 g, 3.03 mmol) in dry THF (120 mL) was added a 1M tetrabutylammonium fluoride solution in THF (4 mL) at 0 °C. The reaction mixture was poured into ice-cool aqueous 0.1M HCl (120 mL) and extracted with chloroform. The organic layer was dried over sodium sulfate and concentrated *in vacuo*. Column chromatography of the residue on silica gel (150 g) with 5:1 dichloromethane-acetone gave **12** (1.51 g, 91%): mp 153-155 °C; $[\alpha]_D$ +275° (*c* 0.02); ^{1}H NMR (300 MHz) δ 13.81 and 13.11 (2 s, 2H, OH-6,11), 8.18-8.08 (m, 4H, nitroarom. H), 7.90 (dd, 1H, $J_{1,2}$ = 7.5, $J_{1,3}$ = 1.1 Hz, H-1), 7.71 (dd, 1H, $J_{2,3}$ = 8.1 Hz, H-2), 7.34 (dd, 1H, H-3), 6.47 (d, 1H, $J_{8A,10}$ = 1.5 Hz, H-10), 5.35 (ddd, 1H, $J_{7,8A}$ = 1.0, $J_{7,8B}$ = 5.0, $J_{7,OH}$ 3.5 Hz, H-7), 4.04 (s, 3H, MeO), 3.75 (s, 1H, OH-9), 3.60 (dd, 1H, OH-7), 2.38 (dd, 1H, $J_{8A,8B}$ = 14.5 Hz, H-8A), 2.08 (ddd, 1H, H-8B), 1.77 (m, 1H, $J_{13,14}$ = 7.2, $J_{13A,13B}$ = 14.4 Hz, H-13A), 1.50 (m, 1H, H-13B), 1.04 (t, 1H, H-14).

Anal. Calcd for $C_{28}H_{23}NO_{11}$ (549.50): C, 61.20; H, 4.22; N, 2.55. Found: C, 61.13, H, 4.22; N, 2.38.

4-*O*-Acetyl-3-azido-2,3,6-trideoxy-L-*arabino*-hexopyranose (13). Conversion of 1,5-anhydro-3,4-di-*O*-acetyl-2,6-dideoxy-L-*arabino*-hex-1-enitol (80 g, 37.34 mmol) with water at 80 °C, followed by treatment of the intermediate with sodium azide in acetic acid, according to the described procedure,[13] gave crude **13**. Column chromatography (10:1 dichloromethane-ethyl acetate) of the product gave a syrup, which after crystallization from diethyl ether-light petroleum afforded **13** (38.6 g, 48%): mp 87-89 °C; $[\alpha]_D$ -131° (*c* 1); ^{1}H

NMR (200 MHz) δ 5.30 (br s, 1H, H-1), 4.61 (dd, 1H, $J_{3,4}$ = 9.6, $J_{4,5}$ = 9.6 Hz, H-4), 3.98 (qd, 1H, $J_{5,6}$ = 6.3 Hz, H-5), 3.86 (ddd, 1H, $J_{2ax,3}$ = 12.5, $J_{2eq,3}$ = 5.0 Hz, H-3), 2.83 (br s, 1H, OH-1), 2.13 (ddd, 1H, $J_{1,2eq}$ = 1.2, $J_{2ax,2eq}$ = 13.0 Hz, H-2eq), 2.08 (s, 3H, Ac), 1.67 (dddd, 1H, $J_{1,2ax}$ = 3.2, $J_{2ax,OH}$ = 1.1 Hz, H-2ax), 1.09 (d, 3H, H-6),

Anal. Calcd for $C_8H_{13}N_3O_4$ (215.21): C, 44.65; H, 6.09; N,19.53. Found: C, 44.57; H, 6.09; N,19.48.

4-*O*-Acetyl-3-azido-1-*O*-*tert*-butyl(dimethyl)silyl-2,3,6-trideoxy-β-L-*arabino*-hexopyranose (14β). To a solution of **13** (15.0 g, 69.70 mmol) in dichloroethane (120 mL) was added *tert*-butyl(dimethyl)silyl chloride (15.0 g, 99.51 mmol) and imidazole (13.75 g). The mixture was stirred for 6 h at room temperature, diluted with 10:1 light petroleum-ethyl acetate (250 mL), washed with phosphate buffer (pH 7.5, 80 mL x 2) and water, dried over sodium sulfate, and concentrated *in vacuo*. Column chromatography of the residue on silica gel (150 g) with 10:1 light petroleum-ethyl acetate gave **14β** (20.90 g, 91.0 %) as a syrup: $[\alpha]_D$ +2° (*c* 1); ^{1}H NMR (200 MHz) δ 4.82 (dd, 1H, $J_{1,2ax}$ = 9.2, $J_{1,2eq}$ = 2.0 Hz, H-1), 4.67 (dd, 1H, $J_{3,4}$ = 10.0, $J_{4,5}$ = 9.6 Hz, H-4), 3.50 (ddd, 1H, $J_{2ax,3}$ = 12.8, $J_{2eq,3}$ = 5.0 Hz, H-3), 3.44 (qd, 1H, $J_{5,6}$ = 6.2 Hz, H-5), 2.20 (ddd, 1H, $J_{2ax,2eq}$ = 13.0 Hz, H-2eq), 2.11 (s, 3H, Ac), 1.68 (ddd, 1H, H-2ax), 1.20 (d, 1H, H-6), 0.90 (s, 9H, $SiCMe_3$), 0.12 and 0.11 (2 s, 6H, $SiMe_2$).

Anal. Calcd for $C_{14}H_{27}N_3O_4Si$ (329.47): C, 51.04; H, 8.26; N, 12.75. Found: C, 51.00; H, 8.26; N, 12.71.

4-*O*-Acetyl-3-azido-1-*O*-*tert*-butyl(dimethyl)silyl-2,3,6-trideoxy-α-L-*arabino*-hexopyranose (14α) and **4-*O*-Acetyl-3-azido-1-*O*-*tert*-butyl(dimethyl)silyl-2,3,6-trideoxy-β-L-*arabino*-hexopyranose (14β).** Treatment of compound **13** (1.50 g, 6.97 mmol) with *tert*-butyl(dimethyl)silyl chloride (1.50 g, 9.95 mmol) and imidazole (1.37 g) in DMF (12 mL), as described for preparation of **14β**, gave a mixture (1.75 g, 76%) of **14α** and **14β** in a ratio 1:4, which was used in the next step without separation of the α- and β-anomers.

Compound **14α** had ^{1}H NMR (200 MHz) δ 5.26 (dd, 1H, $J_{1,2ax}$ = 3.2, $J_{1,2eq}$ = 1.3 Hz, H-1), 4.67 (dd, 1H, $J_{3,4}$ = 10.0, $J_{4,5}$ = 9.6 Hz, H-4), 3.95 (qd, 1H, $J_{5,6}$ = 6.3 Hz, H-5), 3.89 (ddd, 1H, $J_{2ax,3}$ = 12.3, $J_{2eq,3}$ = 5.0 Hz, H-3), 2.14 (s, 3H, Ac), 2.06 (ddd, 1H, $J_{2ax,2eq}$ = 12.8 Hz, H-2eq), 1.74 (ddd, 1H, H-2ax), 1.12 (d, 1H, H-6), 0.91 (s, 9H, $SiCMe_3$), 0.12 and 0.11 (2 s, 6H, $SiMe_2$).

3-Azido-1-*O*-*tert*-butyl(dimethyl)silyl-2,3,6-trideoxy-β-L-*arabino*-hexopyranose (15β). A solution of **14β** (15.46 g, 46.92 mmol) in methanol (200 mL) was adjusted with methanolic 1M sodium methylate solution to pH 11. After 5 h stirring at room temperature, the mixture was adjusted with methanolic 0.1M HCl to pH 8 and concentrated *in vacuo*. A solution of the residue in chloroform (240 mL) was washed with phosphate buffer (pH 7.5, 100 mL), dried over sodium sulfate, and concentrated *in vacuo*. Column chromatography of the crude product on silica gel with 15:1 light petroleum-ethyl acetate gave **15β** (12.40 g, 92 %) as a syrup: $[\alpha]_D$ +23.5° (*c* 1); ^{1}H NMR (200 MHz) δ 4.74 (dd, 1H, $J_{1,2ax}$ = 9.6,

$J_{1,2eq}$ = 2.5 Hz, H-1), 3.44 (ddd, 1H, $J_{2ax,3}$ = 12.5, $J_{2eq,3}$ = 5.0, $J_{3,4}$ = 9.5 Hz, H-3), 3.36 (dq, 1H, $J_{4,5}$ = 9.2, $J_{5,6}$ = 6.5 Hz, H-5), 3.17 (ddd, 1H, $J_{4,OH}$ = 3.5 Hz, H-4), 2.21 (d, 1H, OH-4), 2.21 (ddd, 1H, $J_{2ax,2eq}$ = 12.7 Hz, H-2eq), 1.67 (ddd, 1H, H-2ax), 1.34 (d, 3H, H-6), 0.92 (s, 9H, $SiCMe_3$), 0.14 and 0.13 (2 s, 2H, $SiMe_2$).

Anal. Calcd for $C_{12}H_{25}N_3O_3Si$ (287.44): C, 50.14; H, 8.77; N, 14.62. Found: C, 50.06; H, 8.76; N, 14.52.

3-Azido-1-*O-tert*-butyl(dimethyl)silyl-2,3,6-trideoxy-α-L-*arabino*-hexopyranose (15α) and **3-Azido-1-*O-tert*-butyl(dimethyl)silyl-2,3,6-trideoxy-β-L-*arabino*-hexopyranose (15β)**. Deacetylation of the mixture **14α** and **14β** (1.75 g, 5.31 mmol), as described for preparation of **15β**, afforded **15α** (0.28 g, 19%) and **15β** (1.15 g, 75%) as syrups.

Compound **15α** had $[\alpha]_D$ -68.6° (*c* 0.76); ^1H NMR (200 MHz) δ 5.02 (br s, 1H, H-1), 3.84 (dq, 1H, $J_{4,5}$ = 9.2, $J_{5,6}$ = 6.5 Hz, H-5), 3.78 (ddd, 1H, $J_{2ax,3}$ = 12.7, $J_{2eq,3}$ = 5.0, $J_{3,4}$ = 9.5 Hz, H-3), 3.15 (ddd, 1H, $J_{4,OH}$ = 4.0 Hz, H-4), 2.20 (d, 1H, HO-4), 2.07 (ddd, 1H, $J_{1,2ax}$ = 1.6, $J_{2ax,2eq}$ = 12.7 Hz, H-2eq), 1.73 (ddd, 1H, H-2ax), 1.27 (d, 3H, H-6), 0.92 (s, 9H, $SiCMe_3$), 0.14 and 0.13 (2 s, 2H, $SiMe_2$).

Anal. Found: C, 50.11; H, 8.77; N, 14.57.

3-Amino-1-*O-tert*-butyl(dimethyl)silyl-2,3,6-trideoxy-β-L-*arabino*-hexopyranose (16). A mixture of **15β** (3.43 g, 11.96 mmol) and 10% Pd/C (3.6 g) in methanol (60 mL) and concd NH_3 (0.5 mL) was stirred under hydrogen for 2 h at room temperature, then filtered through Celite, and concentrated *in vacuo* to afford a crude compound **16** (3.04 g, 97%), which was used in the next step without further purification.

1-*O-tert*-Butyl(dimethyl)silyl-2,3,6-trideoxy-3-trifluoroacetylamino-β-L-*arabino*-hexopyranose (17). To a solution of the crude compound **16** (3.04 g) in 1:1 ethanol-dichloromethane (70 mL) was added triethylamine (14 mL) and trifluoroacetic anhydride (3.2 mL) at 0 °C. The mixture was stirred for 2 h at 0 °C and then for 20 h at room temperature, diluted with dichloromethane (70 mL), washed with phosphate buffer (pH 8, 30 mL x 2) and concentrated *in vacuo*. After co-evaporation with toluene, the residue was chromatographed on a column of silica gel with 10:1 chloroform-ethanol to give **17** (3.02 g, 73%): mp 142 °C; $[\alpha]_D$ -7.8° (*c* 1); ^1H NMR (200 MHz) δ 6.59 (br d, 1H, NH), 4.99 (dd, 1H, $J_{1,2ax}$ 8.7, $J_{1,2eq}$ = 2.1 Hz, H-1), 4.08 (m, 1H, H-3), 3.50 (qd, 1H, $J_{4,5}$ = 9.1, $J_{5,6}$ = 6.2 Hz, H-5), 3.29 (ddd, 1H, $J_{3,4}$ = 10.0, $J_{4,OH}$ = 6.0 Hz, H-4), 2.78 (d, 1H, HO-4), 2.34 (ddd, 1H, $J_{2ax,2eq}$ = 12.7 Hz, H-2eq), 1.75 (ddd, 1H, H-2ax), 1.45 (d, 3H, H-6), 0.96 (s, 9H, $SiCMe_3$), 0.12 and 0.11 (2 s, 6H, $SiMe_2$).

Anal. Calcd for $C_{14}H_{26}F_3NO_4Si$ (357.45): C, 47.04; H, 7.33; N, 3.92. Found: C, 47.11; H, 7.34; N, 3.84.

4-*O*-Acetyl-1-*O-tert*-butyl(dimethyl)silyl-2,3,6-trideoxy-3-trifluoroacetylamino-β-L-*arabino*-hexopyranose (18). To a solution of **17** (2.80 g, 7.83 mmol) in 7:1 dichloromethane-pyridine (24 mL) was added a solution of acetic anhydride (3.0 mL) in dichloromethane (15 mL). After 10 h stirring, the mixture was diluted with chloroform (30 mL)

and washed with phosphate buffer (pH 8, 25 mL x 3). The organic layer was dried over sodium sulfate and concentrated *in vacuo*. After co-evaporation with toluene (30 mL x 2), the residue was chromatographed on a column of silica gel with light petroleum-ethyl acetate to give **18** (2.86 g, 91%): mp 78 °C; $[\alpha]_D$ -17° (*c* 1); ^{1}H NMR (200 MHz) δ 6.98 (br d, 1H, NH-3), 4.89 (dd, 1H, $J_{1,2ax}$ = 9.2, $J_{1,2eq}$ = 2.1 Hz, H-1), 4.59 (dd, 1H, $J_{3,4}$ = 10.0, $J_{4,5}$ = 9.5 Hz, H-4), 4.17 (m, 1H, H-3), 3.60 (qd, 1H, $J_{5,6}$ 6.4 Hz, H-5), 2.31 (ddd, 1H, $J_{2ax,2eq}$ = 13.0 Hz, H-2eq), 2.10 (s, 3H, Ac), 1.64 (ddd, 1H, H-2ax), 1.24 (d, 1H, H-6), 0.90 (s, 9H, $SiCMe_3$), 0.13 and 0.12 (2 s, 6H, $SiMe_2$).

Anal. Calcd for $C_{16}H_{28}F_3NO_5Si$ (399.49): C, 48.11; H, 7.06; N, 3.51. Found: C, 48.15; H, 7.07; N, 3.45.

3-Azido-1-*O*-*tert*-butyl(dimethyl)silyl-2,3,6-trideoxy-4-*O*-trifluoromethanesulfonyl-β-L-*arabino*-hexopyranose (19). To a solution of **15β** (6.30 g, 21.91 mmol) in dichloromethane (200 mL) and pyridine (13 mL) was added a solution of trifluoromethanesulfonic anhydride (13 mL) in dichloromethane (100 mL) at -30 °C. The mixture was stirred for 48 h at -30 °C, then diluted with dichloromethane (50 mL) and washed with an aqueous 10% sodium acetate solution (100 mL x 3) and phosphate buffer (pH 9, 50 mL x 2). The organic phase was dried over sodium sulfate and concentrated *in vacuo*. The crude product **19** (9.0 g, 97%) was used in the next step without futher purification.

4-*O*-Acetyl-3-azido-1-*O*-*tert*-butyl(dimethyl)silyl-2,3,6-tri-deoxy-β-L-*lyxo*-hexopyranose (20). To a solution of the crude product **19** (9.0 g) in 3:1 dichloromethane-DMF (80 mL) was added sodium acetate (1.8 g) and cesium acetate (2.1 g) at room temperature. The mixture was stirred for 16 h, then diluted with 2:1 light petroleum-ethyl acetate (120 mL) and washed with phosphate buffer (pH 8, 50 mL) and water, and concentrated *in vacuo*. Column chromatography of the residue on silica gel with 10:1 light petroleum-ethyl acetate afforded **20** (5.23 g, 72%) as a syrup: $[\alpha]_D$ +20.5° (*c* 1); ^{1}H NMR (200 MHz) δ 5.07 (dd, 1H, $J_{3,4}$ = 3.2, $J_{4,5}$ = 1.2 Hz, H-4), 4.80 (dd, 1H, $J_{1,2ax}$ = 8.2, $J_{1,2eq}$ = 3.5 Hz, H-1), 3.61 (dq, 1H, $J_{5,6}$ = 6.4 Hz, H-5), 3.44 (ddd, 1H, $J_{2ax,3}$ = 12.0, $J_{2eq,3}$ = 5.0 Hz, H-3), 2.20 (s, 3H, Ac), 2.03 (ddd, 1H, H-2eq), 1.95 (ddd, 1H, $J_{2ax,2eq}$ = 12.0 Hz, H-2ax), 1.20 (d, 3H, H-6), 1.93 (br s, 9H, $SiCMe_3$), 0.12 and 0.12 (2 s, 6H, $SiMe_2$).

Anal. Calcd for $C_{14}H_{27}N_3O_4Si$ (329.47): C, 51.04; H, 8.26; N, 12.75. Found: C, 51.07; H, 8.26; N, 12.72.

3-Azido-1-*O*-*tert*-butyl(dimethyl)silyl-2,3,6-trideoxy-β-L-*lyxo*-hexopyranose (21). Compound **20** (5.0 g, 15.17 mmol) was deacetylated, according to the procedure described for **15**, to give **21** (4.11 g, 94%): mp 72 °C; $[\alpha]_D$ -2.2° (*c* 1); ^{1}H NMR (200 MHz) δ 4.74 (dd, 1H, $J_{1,2ax}$ = 8.9, $J_{1,2eq}$ = 2.7 Hz, H-1), 3.62 (dd, 1H, $J_{3,4}$ = 2.7, $J_{4,5}$ = 0.7, $J_{4,OH}$ = 8.3 Hz, H-4), 3.50 (dq, 1H, $J_{5,6}$ = 6.4 Hz, H-5), 3.31 (ddd, 1H, $J_{2ax,3}$ = 12.5, $J_{2eq,3}$ = 5.1 Hz, H-3), 2.10 (d, 1H, OH-4), 1.99 (ddd, 1H, $J_{2ax,2eq}$ = 12.7 Hz, H-2eq), 1.85 (ddd, 1H, H-2ax), 1.29 (d, 3H, H-6), 0.91 (br s, 9H, $SiCMe_3$), 0.13 and 0.11 (2 s, 2H, $SiMe_2$).

Anal. Calcd for $C_{12}H_{25}N_3O_3Si$ (287.44): C, 50.14; H, 8.77; N, 14.62. Found: C, 50.11; H, 8.78; N, 14.57.

3-Amino-1-*O*-*tert*-butyl(dimethyl)silyl-2,3,6-trideoxy-β-L-*lyxo*-hexopyranose (22). The azido compound **21** (4.0 g, 13.91 mmol) was treated, as described for the preparation of compound **16**, to give **22** (3.80 g), which was used in the next step without futher purification.

1-*O*-*tert*-Butyl(dimethyl)silyl-2,3,6-trideoxy-3-trifluoroacetylamino-β-L-*lyxo*-hexopyranose (23). Crude compound **22** (3.80 g) was *N*-trifluoroacetylated, according to the method described for **17**, to give **23** (4.02 g, 81%): mp 55 °C; $[\alpha]_D$ +14.2° (*c* 1.06); ^{1}H NMR (200 MHz) δ 6.69 (br d, 1H, NH-3), 4.66 (dd, 1H, $J_{1,2ax}$ = 9.2, $J_{1,2eq}$ = 2.3 Hz, H-1), 3.98 (dddd, 1H, $J_{2ax,3}$ = 12.5, $J_{2eq,3}$ = 5.0, $J_{3,4}$ = 2.3, $J_{3,NH}$ = 10.2 Hz, H-3), 3.51 (qd, 1H, $J_{4,5}$ = 1.0, $J_{5,6}$ = 6.3 Hz, H-5), 3.36 (br s, 1H, H-4), 1.87 (ddd, 1H, $J_{2ax,2eq}$ = 12.8 Hz, H-2eq), 1.42 (ddd, 1H, H-2ax), 1.18 (d, 1H, H-6), 0.80 (s, 9H, $SiCMe_3$), 0.12 and 0.11 (2 s, 6H, $SiMe_2$).

Anal. Calcd for $C_{14}H_{26}F_3NO_4Si$ (357.45): C, 47.04; H, 7.33; N, 3.92. Found: C, 47.14; H, 7.35; N, 3.85.

4-*O*-Acetyl-1-*O*-*tert*-butyl(dimethyl)silyl-2,3,6-trideoxy-3-trifluoroacetylamino-β-L-*lyxo*-hexopyranose (24). Compound **23** (3.80 g, 10.63 mmol) was acetylated, according to the method described for **18**, to give **24** (4.07 g, 96%): $[\alpha]_D$ -24° (*c* 1); ^{1}H NMR (200 MHz) δ 6.44 (br d, 1H, NH-3), 5.02 (br s, 1H, H-4), 4.84 (dd, 1H, $J_{1,2ax}$ = 9.2, $J_{1,2eq}$ = 2.3 Hz, H-1), 4.24 (dddd, 1H, $J_{2ax,3}$ = 12.5, $J_{2eq,3}$ = 5.0, $J_{3,4}$ = 2.3, $J_{3,NH}$ = 10.2 Hz, H-3), 3.71 (qd, 1H, $J_{4,5}$ = 1.2, $J_{5,6}$ = 6.3 Hz, H-5), 2.19 (s, 3H, Ac), 2.01 (ddd, 1H, $J_{2ax,2eq}$ = 12.6, $J_{2eq,4}$ = 0.8 Hz, H-2eq), 1.74 (ddd, 1H, H-2ax), 1.20 (d, 1H, H-6), 0.91 (s, 9H, $SiCMe_3$), 0.14 and 0.12 (2 s, 6H, $SiMe_2$).

Anal. Calcd for $C_{16}H_{28}F_3NO_5Si$ (399.49): C, 48.11; H, 7.06; N, 3.51. Found: C, 48.15; H, 7.07; N, 3.45.

1-*O*-*tert*-Butyl(dimethyl)silyl-4-*O*-*p*-nitrobenzoyl-2,3,6-trideoxy-3-trifluoroacetylamino-β-L-*lyxo*-hexopyranose (25). To a solution of **23** (1.2 g, 3.35 mmol) in pyridine (15 mL) was added *p*-nitrobenzoyl chloride (0.65 g) at 0 °C. The mixture was stirred for 1 h at 0 °C, then for 24 h at room temperature. After addition of sodium acetate (0.50 g) and stirring for 1 h, the mixture was diluted with 7:1 light petroleum-ethyl acetate (40 mL) and washed with phosphate buffer (pH 8, 20 mL x 3) and concentrated *in vacuo*. After co-evaporation with toluene (25 mL x 3), the residue was purified by chromatography on a column of silica gel (45 g) with 10:15:1 chloroform-light petroleum-acetone to give **25** (1.48 g, 88%): mp 75 °C; $[\alpha]_D$ -92° (*c* 1); R_F (10:10:1 chloroform-light petroleum-acetone); ^{1}H NMR (200 MHz) δ 8.36-8.25 (m, 4 H, nitroarom. H), 6.40 (d, 1 H, $J_{3,NH}$ = 7.5 Hz, NH-3), 5.34 (br s, 1H, H-4), 4.94 (dd, 1H, $J_{1,2ax}$ = 7.7, $J_{1,2eq}$ = 2.0 Hz, H-1), 4.37 (m, 1H, H-3), 3.85 (dq, 1H, $J_{4,5}$ = 1.0, $J_{5,6}$ = 6.5 Hz, H-5), 2.08 (ddd, 1H, $J_{2eq,3}$ = 4.5, $J_{2ax,2eq}$ = 12.3 Hz, H-2eq), 1.84 (ddd, 1H, $J_{2ax,3}$ = 12.2 Hz, H-2ax), 1.24 (d, 3H, H-6), 0.94 (s, 9H, $SiCMe_3$), 0.18 and 0.16 (2 s, 6H, $SiMe_2$).

Anal. Calcd for $C_{21}H_{29}F_3N_2O_7Si$ (506.56): C, 49.79; H, 5.77; N, 5.53; Found: C, 49.81; H, 5.78; N, 5.45.

3,4-Di-*O*-acetyl-2,6-dideoxy-L-*lyxo*-hexopyranose (27). A solution of 1,5-anhydro-3,4-di-*O*-acetyl-2,6-dideoxy-L-*lyxo*-hex-1-enitol **26** (20.0 g, 93.36 mmol) in an aqueous 30% trifluoroacetic acid (200 mL) was stirred for 30 min at room temperature. After addition of sodium acetate (10 g), the mixture was neutralized with sodium phosphate and washed with light petroleum (50 mL x 2). The aqueous phase was diluted with ethanol and concentrated *in vacuo*. A solution of the residue in ethyl acetate (150 mL) was stirred with sodium sulfate (15 g) for 20 min, filtered and concentrated *in vacuo*. Column chromatography of the residue on silica gel (200 g) with 6:1 dichloromethane-ethyl acetate gave **27** (18.21 g, 84%): a syrup; $[\alpha]_D$ -99.3° (*c* 1); ^{1}H NMR (200 MHz) α-anomer: δ 5.47 (br s, 1H, H-4), 5.36 (ddd, 1H, $J_{2ax,3}$ = 12.5, $J_{2eq,3}$ = 5.5, $J_{3,4}$ = 3.3 Hz, H-3), 5.20 (s, 1H, H-1), 4.34 (dq, 1H, $J_{4,5}$ = 0.8, $J_{5,6}$ = 6.4 Hz, H-5), 2.91 (s, 1H, OH-1), 2.27 and 2.00 (2 s, 6H, 2 Ac), 2.12-1.82 (m, 2H, H-2ax and H-2eq), 1.14 (d, 3H, H-6), β-anomer: δ 5.11 (br s, 1H, H-4), 5.00 (ddd, 1H, $J_{2ax,3}$ = 12.5, $J_{2eq,3}$ = 5.5, $J_{3,4}$ = 3.2 Hz, H-3), 4.88 (ddd, 1H, $J_{1,OH}$ = 6.5, $J_{1,2ax}$ = 8.9, $J_{1,2eq}$ = 2.2 Hz, H-1), 3.74 (dq, 1H, $J_{4,5}$ = 0.8, $J_{5,6}$ = 6.4 Hz, H-5), 3.56 (d, 1H, OH-1), 2.17 and 2.12 (2 s, 6H, 2 Ac), 2.12-1.82 (m, 2H, H-2ax and H-2eq), 1.22 (d, 3H, H-6).

Anal. Calcd for $C_{10}H_{16}O_6$ (232.24): C, 51.72; H, 6.94. Found: C, 51.68; H, 6.96..

1-*O*-*tert*-Butyl(dimethyl)silyl-3,4-di-*O*-acetyl-2,6-dideoxy-β-L-*lyxo*-hexopyranose (28). Compound **27** (18.0 g, 77.52 mmol) was silylated, according to the method described for **14**, to give **28** (22.02 g, 87%): $[\alpha]_D$ -17.2° (*c* 1.02); ^{1}H NMR (200 MHz, C_6D_6) δ 5.08 (d, 1H, $J_{3,4}$ = 3.1 Hz, H-4), 4.74 (ddd, 1H, $J_{2ax,3}$ 12.5, $J_{2eq,3}$ = 5.2 Hz, H-3), 4.41 (dd, 1H, $J_{1,2ax}$ = 9.2, $J_{1,2eq}$ = 2.5 Hz, H-1), 2.82 (dd, 1H, $J_{4,5}$ = 1.3, $J_{5,6}$ = 6.4 Hz, H-5), 2.05 (ddd, 1H, $J_{2ax,2eq}$ = 11.7 Hz, H-2ax), 1.72 (dddd, 1H, $J_{2eq,4}$ = 1.0 Hz, H-2eq), 1.59 and 1.55 (2s, 6H, 2 Ac), 0.98 (s, 9H, $SiCMe_3$), 0.15 and 0.11 (2s, 6H, $SiMe_2$).

Anal. Calcd for $C_{16}H_{30}O_6Si$ (346.50): C, 55.46; H, 8.73. Found: C, 55.48; H, 8.74.

7-*O*-(4-*O*-Acetyl-2,3,6-trideoxy-3-trifluoroacetylamino-α-L-*arabino*-hexopyranosyl)-4-*O*-methyl-10-*O*-*p*-nitrobenzoyl-β-rhodomycinone (29). Condensation of **12** (0.40 g, 0.72 mmol) with **18** (0.32 g, 0.94 mmol), as described in the general procedure (*a*), afforded **29** (0.50 g, 86%): mp 250 °C; $[\alpha]_D$ +362° (*c* 0.032); ^{1}H NMR (400 MHz) δ 13.88 and 13.25 (2 s, 2H, OH-6,11), 8.26-8.12 (m, 4H, nitroarom. H), 8.01 (dd, 1H, $J_{1,2}$ = 7.6, $J_{2,3}$ = 1.3 Hz, H-1), 7.78 (dd, 1H, $J_{2,3}$ = 8.5 Hz, H-2), 7.40 (dd, 1H, H-3), 6.58 (d, 1H, $J_{8A,10}$ = 1.0 Hz, H-10), 6.57 (d, 1H, $J_{3',NH}$ = 8.2 Hz, NH-3'), 5.52 (d, 1H, $J_{1',2'ax}$ = 3.6 Hz, H-1'), 5.30 (dd, 1H, $J_{7,8A}$ = 1.5, $J_{7,8B}$ = 4.0 Hz, H-7), 4.61 (dd, 1H, $J_{3',4'}$ = 10.1, $J_{4',5'}$ = 9.8 Hz, H-4'), 4.22 (dq, 1H, H-5'), 4.20 (dddd, 1H, $J_{2'ax,3'}$ = 12.8, $J_{2'eq,3'}$ = 4.4 Hz, H-3'), 4.09 (s, 3H, MeO-4), 3.77 (d, 1H, $J_{8A,OH-9}$ = 1.0 Hz, OH-9), 2.49 (ddd, 1H, $J_{8A,8B}$ = 14.1 Hz, H-8A), 2.39 (dd, 1H, $J_{2'ax,2'eq}$ = 12.8, H-2'eq), 2.15 (dd, 1H, H-8B), 2.10 (s, 3H, Ac), 1.87 (m, 1H, $J_{13A,14}$ = 7.3, $J_{13A,13B}$ = 15.0 Hz, H-13A), 1.59 (ddd, 1H, H-2'ax), 1.54 (m, 1H, $J_{13B,14}$ = 7.3 Hz, H-13B), 1.38 (d, 3H, H-6'), 1.09 (t, 3H, H-14).

Anal. Calcd for $C_{38}H_{35}F_3N_2O_{15}$ (816.70): C, 55.89; H, 4.32; N, 3.43. Found: C, 55.76; H, 4.44; N, 3.35.

7-*O*-(4-*O*-Acetyl-2,3,6-trideoxy-3-trifluoroacetylamino-α-L-*lyxo*-hexopyranosyl)-4-*O*-methyl-10-*O*-*p*-nitrobenzoyl-β-rhodomycinone (30). Condensation of **12** (0.40 g, 0.72 mmol) with **24** (0.36 0.91 mmol) as described in general procedure (*a*) afforded **30** (0.47 g, 81%): mp 194 °C; $[\alpha]_D$ +347° (*c* 0.042); ^{1}H NMR (400 MHz) δ 13.88 and 13.23 (2 s, 2H, OH-6,11), 8.24-8.12 (m, 4H, nitroarom. H), 7.98 (dd, 1H, $J_{1,2}$ = 7.9, $J_{1,3}$ = 1.0 Hz, H-1), 7.77 (dd, 1H $J_{2,3}$ = 8.2 Hz, H-2), 7.39 (dd, 1H, H-3), 6.57 (d, 1H, $J_{8A,10}$ = 0.9 Hz, H-10), 6.32 (d, 1H, $J_{3',NH}$ = 7.2 Hz, NH-3'), 5.60 (d, 1H, $J_{1',2'ax}$ = 3.2 Hz, H-1'), 5.32 (dd, 1H, $J_{7,8A}$ = 4.0, $J_{7,8B}$ = 1.2 Hz, H-7), 5.18 (br s, 1H, H-4'), 4.36 (q, 1H, H-5'), 4.32 (m, 1H, H-3'), 4.08 (s, 3H, MeO-4), 3.71 (s, 1H, OH-9), 2.47 (d, 1H, $J_{8A,8B}$ = 15.2 Hz, H-8A), 2.23 (s, 3H, Ac), 2.17 (dd, 1H, H-8B), 2.02 (dd, 1H, $J_{2'eq,3'}$ = 5.1, $J_{2'ax,2'eq}$ = 13.1 Hz, H-2'eq), 1.97 (ddd, 1H, $J_{2'ax,3'}$ = 12.8 Hz, H-2'ax), 1.87 (m, 1H, $J_{13A,14}$ = 7.3, $J_{13A,13B}$ = 14.7 Hz, H-13A), 1.54 (m, 1H, H-13B), 1.23 (d, 3H, $J_{5',6'}$ = 6.3 Hz, H-6'), 1.08 (t, 3H, H-14).

Anal. Calcd for $C_{38}H_{35}F_3N_2O_{15}$ (816.70): C, 55.89; H, 4.32; N, 3.43. Found: C, 55.78; H, 4.42; N, 3.36.

4-*O*-Methyl-10-*O*-p-nitrobenzoyl-7-*O*-(4-*O*-*p*-nitrobenzoyl-2,3,6-trideoxy-3-trifluoroacetylamino-α-L-*lyxo*-hexopyranosyl)-β-rhodomycinone (31). Condensation of **12** (0.20 g, 0.36 mmol) with **25** (0.21 g, 0.41 mmol) as described in general procedure (*a*) afforded **31** (0.25 g, 76%); mp 154 °C; $[\alpha]_D$ +119° (*c* 0.06); ^{1}H NMR (300 MHz) δ 13.92 and 13.23 (2 s, 2H, OH-6,11), 8.36-8.11 (m, 8H, nitroarom. H), 8.01 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 7.79 (dd, 1H, $J_{2,3}$ = 9 Hz, H-2), 7.40 (d, 1H, H-3), 6.58 (s, 1H, H-10), 6.26 (d, 1H, $J_{3',NH}$ = 8.0 Hz, NH-3'), 5.71 (s, 1H, H-1'), 5.36 (d, 1H, $J_{7,8B}$ = 3.5 Hz, H-7), 5.05 (d, 1H, $J_{3',4'}$ = 2.0 Hz, H-4'), 4.49 (q, 1H, $J_{5',6'}$ = 6.5 Hz, H-5'), 4.48 (m, 1H, H-3'), 4.09 (s, 3H, MeO), 3.66 (s, 1H, OH-9), 2.50 (ddd, 1H, $J_{7,8A}$ = 1.5, $J_{8A,10}$ = 1.0, $J_{8A,8B}$ = 15.0 Hz, H-8A), 2.20 (dd, 1H, $J_{7,8B}$ = 3.5 Hz, H-8B), 2.10 (m, 2H, H-2'ax and H-2'eq), 1.88 (m, 1H, $J_{13,14}$ = 7.5, $J_{13A,13B}$ = 14.2 Hz, H-13A), 1.54 (m, 1H, H-13B), 1.27 (d, 3H, H-6'), 1.00 (t, 3H, H-14); ^{1}H NMR (300 MHz, 1:1 C_6D_6-$CDCl_3$) δ 5.49 (d, 1H, $J_{1',2'ax}$ = 3.5 Hz, H-1'), 1.85 (dd, 1H, $J_{2'eq,3'}$ = 5.0, $J_{2'ax,2'eq}$ 13.0 Hz, H-2'eq), 1.69 (ddd, 1H, $J_{2'ax,3'}$ = 13.0 Hz, H-2'ax).

Anal. Calcd for $C_{43}H_{36}F_3N_3O_{17}$ (923.77): C, 55.91; H, 3.93; N, 4.55. Found: C, 55.98; H, 3.96; N, 4.43.

7-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-α-L-*lyxo*-hexopyranosyl)-4-*O*-methyl-10-*O*-*p*-nitrobenzoyl-β-rhodomycinone (32). Condensation of **12** (0.40 g, 0.72 mmol) with **28** (0.32 g, 0.94 mmol) as described in general procedure (*a*) afforded **32** (0.46 g, 83%): mp 140 °C; $[\alpha]_D$ +366° (*c* 0.027); ^{1}H NMR (400 MHz) δ 13.88 and 13.24 (2 s, 2H, OH-6,11), 8.25-8.11 (m, 4H, nitroarom. H), 8.00 (dd, 1H, $J_{1,2}$ = 7.6, $J_{1,3}$ = 1.0 Hz, H-1), 7.78 (dd, 1H, $J_{2,3}$ = 8.5 Hz, H-2), 7.40 (dd, 1H, H-3), 6.56 (d, 1H, $J_{8A,10}$ = 0.9 Hz, H-10), 5.63 (d, 1H, $J_{1',2'ax}$ = 3.8 Hz, H-1'), 5.31 (dd, 1H, $J_{7,8A}$ = 4.1, $J_{7,8B}$ = 1.2 Hz, H-7), 5.24 (d, 1H, $J_{3',4'}$ = 3.1 Hz, H-4'), 5.06 (ddd, 1H, $J_{2'ax,3'}$ = 12.6, $J_{2'eq,3'}$ = 5.4 Hz, H-3'), 4.32 (q, 1H, $J_{5',6'}$ = 6.4 Hz, H-5'), 4.09 (s, 3H, MeO-4), 3.81 (s, 1H, OH-9), 2.47 (d, 1H, $J_{8A,8B}$ = 15.2 Hz,

H-8A), 2.19 (s, 3H, Ac), 2.17 (dd, 1H, H-8B), 2.12 (ddd, 1H, $J_{2'ax,2'eq}$ = 13.1 Hz, H-2'ax), 1.94 (s, 3H, Ac), 1.93 (dd, 1H, H-2'eq), 1.85 (m, 1H, $J_{13A,14}$ = 7.4, $J_{13A,13B}$ = 14.2 Hz, H-13A), 1.51 (m, 1H, 13B), 1.23 (d, 3H, H-6'), 1.07 (t, 1H, H-14).

Anal. Calcd for $C_{38}H_{37}NO_{16}$ (763.72): C, 59.76; H,4.88; N, 1.83. Found: C, 59.74; H,4.88; N, 1.78.

7-*O*-(3-Amino-2,3,6-trideoxy-α-L-*arabino*-hexopyranosyl)-4-*O*-methyl-β-rhodomycinone (33). Treatment of compound **29** (0.40 g, 0.49 mmol) with 1M NaOH, as described in general procedure (*b*), gave **33** (0.26 g, 78%): mp 196 °C; $[\alpha]_D$ +252° (*c* 0.054, MeOH); ^1H NMR (200 MHz, 3:1 $CDCl_3$-MeOD, H→D) δ 8.03 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 7.83 (dd, 1H, $J_{2,3}$ = 8.8 Hz, H-2), 7.45 (d, 1H, H-3), 5.49 (br s, 1H, H-1'), 5.13 (br s, 1H, H-7), 4.86 (s, 1H, H-10), 4.08 (s, 3H, MeO-4), 3.95 (dq, 1H, $J_{4',5'}$ = 9.3, $J_{5',6'}$ = 6.2 Hz, H-5'), 3.27 (dd, 1H, $J_{3',4'}$ = 9.6 Hz, H-4'), 3.18 (ddd, 1H, $J_{2'ax,3'}$ = 11.3, $J_{2'eq,3'}$ = 4.6 Hz, H-3'), 2.18 (m, 2H, H-8A and H-8B), 1.92 1.95 (dd, 1H, $J_{2'ax,2'eq}$ = 13.0 Hz, H-2'eq), 1.84 (m, 1H, $J_{13A,13B}$ = 14.6, $J_{13,14}$ = 7.5 Hz, H-13A), 1.78 (m, 1H, H-13B), 1.60 (ddd, 1H, H-2'ax), 1.37 (d, 3H, H-6'), 1.10 (t, 3H, H-14). FAB-MS, m/s = 530 ($M+H^+$), 399, 383, 365.

Anal. Calcd for $C_{27}H_{31}NO_{10}$ (529.55): C, 61.24; H, 5.90; N, 2.65. Found: C, 61.16; H, 5.92; N, 2.55.

7-*O*-(3-Amino-2,3,6-trideoxy-α-L-*lyxo*-hexopyranosyl)-4-*O*-methyl-β-rhodomycinone (34). Treatment of compound **30** (0.40 g, 0.49 mmol) with 1M NaOH, as described in general procedure (*b*), gave **34** (0.19 g, 73%): mp 192-194 °C; $[\alpha]_D$ +273° (c 0.01, MeOH); FAB-MS, m/s = 530 ($M+H^+$), 399, 383, 365. Lit.[3] mp 192-194 °C; $[\alpha]_D$ +270° (c 0.01, MeOH).

7-*O*-(2,6-Dideoxy-α-L-*lyxo*-hexopyranosyl)-4-*O*-methyl-β-rhodomycinone (35). Treatment of compound **32** (320 mg, 0.42 mmol) with 1M NaOH, as described in general procedure (*b*), gave crude product **35**, which was purified by column chromatography on silica gel (40 g) with 15:1 chloroform-methanol to give **32** (120 mg, 63%): mp 242 °C; $[\alpha]_D$ 238° (*c* 0.05; 20:1 $CHCl_3$-MeOH); ^1H NMR (300 MHz, 5:1 $CDCl_3$-CD_3OD) δ 7.96 (dd, 1H, $J_{1,2}$ = 7.5, $J_{1,3}$ = 1.1 Hz, H-1), 7.73 (dd, 1H, $J_{2,3}$ = 8.2 Hz, H-2), 7.36 (dd, 1H, H-3), 5.42 (d, 1H, $J_{1',2'ax}$ = 3.8 Hz, H-1'), 5.07 (dd, 1H, $J_{7,8A}$ = 2.0, $J_{7,8B}$ = 3.7 Hz, H-7), 4.76 (s, 1H, H-10), 4.02 (q, 1H, $J_{5',6'}$ = 6.5 Hz, H-5'), 4.00 (s, 3H, MeO), 3.67 (ddd, 1H, $J_{2'ax,3'}$ =12.0, $J_{2'eq,3'}$ = 5.5, $J_{3',4'}$ = 2.6 Hz, H-3'), 3.53 (d, 1H, H-4'), 2.13 (ddd, 1H, $J_{8B,10}$ = 1.0, $J_{8A,8B}$ = 15.0 Hz, H-8A), 2.05 (dd, 1H, H-8B), 1.82 (ddd, 1H, $J_{2'ax,2'eq}$ = 12.5 Hz, H-2'ax), 1.74 (m, 1H, $J_{13,14}$ = 7.5, $J_{13A,13B}$= 15.0 Hz, H-13A), 1.72 (dd, 1H, H-2'eq), 1.68 (m, 1H, H-13B), 1.25 (d, 3H, H-6'), 1.00 (t, 3H, H-14).

Anal. Calcd for $C_{27}H_{30}O_{11}$ (530.53): C, 61.13; H, 5.70. Found: C, 61.02; H, 5.73.

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