Pergamon

Tetrahedron: Asymmetry Vol. 5, No. 11, pp. 2283-2290, 1994
Elsevier Science Ltd
Printed in Great Britain
0957-4166/94 $7.00+0.00

0957-4166(94)00309-2

Studies on Carbohydrates XVIII. Synthesis of Tetrasaccharide Corresponding to Biological Repeat Units of *Serratia marcescens* O18 Polysaccharide

Jian Zhang, Jianmin Mao, Hongming Chen, Mengshen Cai*

Department of Organic Chemistry, School of Pharmaceutical Sciences, Beijing Medical University, Beijing 100083, China

ABSTRACT: The synthesis of a blocked tetrasaccharide portion of the biological repeat unit, [→2)L-Rha*p*α(1→2)L-Rha*p*α(1→2)L-Rha*p*α(1→6)D-GlcNAc*p*α(1→], of the *Serratia marcescens* O18 polysaccharide was described. The key intermediate compounds was 3,4-blocked -L-rhamnose. All compounds were confirmed by use of high resolution NMR and FAB-MS techniques.

Introduction

Molecular recognition processes that are mediated by carbohydrate recognition markers are widespread and range from antigen-antibody interaction to cell-cell recognition and development. We chose the study of antigen-antibody interactions using bacterial antigens with which to probe such recognition process. *Serratia marcescens*, once thought to be a kind of harmless gram-negative bacteria, are widely distributed in soil, water, and on plant surfaces. In the last two decades, however, it has frequently been reported as a pathogen in urinary tract infection and in septicaemia as well as an opportunist organism colonizing the upper respiratory tract[1].

Result

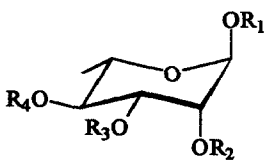
The biological repeating unit of the lipopolysaccharide O-antigen of the bacterium *Serratia marcescens* has the following structure[2]:

$$[\rightarrow 2)\text{-}\alpha\text{-L-Rha}p(1\rightarrow 2)\text{-}\alpha\text{-L-Rha}p(1\rightarrow 2)\text{-}\alpha\text{-L-Rha}p(1\rightarrow 6)\text{-}\alpha\text{-D-GlcNAc}p(1\rightarrow]$$
$$\quad A \qquad\qquad B \qquad\qquad C \qquad\qquad D$$

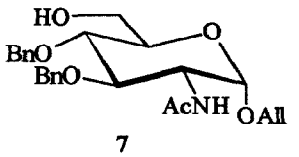
Thus far, we have described the synthesis of disaccharides[3] and trisaccharide[4]. Retrosynthetic analysis indicated that the most advantageous disconnection would be at the *B*—*C* junction since this would yield the disaccharides donor *A*—*B* and acceptor *C*—*D*.

Starting from L-rhamnose, compound **1** was obtained in the yield of 92% by treatment of dried allyl alcohol and L-rhamnose monohydrate with concentrated H_2SO_4 as catalyst[5]. Compound **1** reacted with acetone in the presence of 4AMS and *p*-TsOH to give compound **2** in 86% yield[6]. Compounds **3** and **4** were obtained

according to reference[7]. With the procedure by Gigg[6], we prepared **5** and **6** in the overall yields of 54.5% and 80%, respectively. Compound **7** was prepared from 2-deoxyl-2-acetylamino-D-glucose in four steps according to reference [8,9].



	R_1	R_2	R_3	R_4
1	All	H	H	H
2	All	$>CMe_2$		H
3	All	$>CMe_2$		Bn
4	All	H	H	Bn
5	All	H	Bn	Bn
6	H	Ac	Bn	Bn



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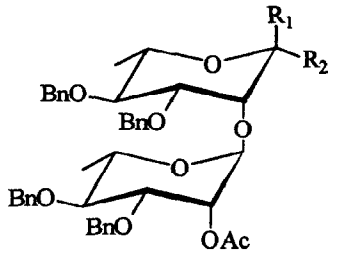
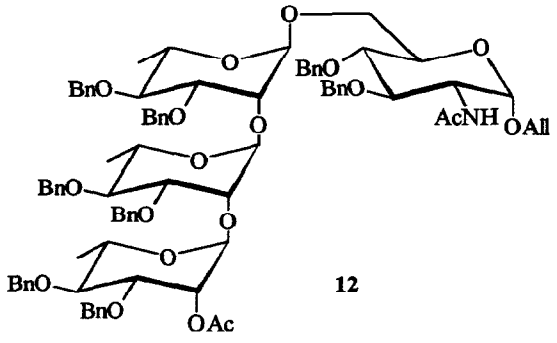


8 **9**

R_1	OAll	H,OH
R_2	H	



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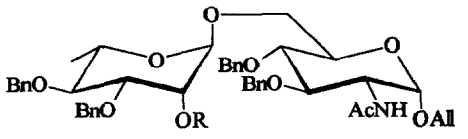

	10	**11**
R	Ac	H

The crucial glycosylation of compound **5** with 2-O-acetyl-3,4-O-dibenzyl-α-L-rhamnopyranosyl trichloroacetimidate in dried dichloromethane in the presence of TMSOTf and 4AMS according to the method of Schmidt[10] afforded a 60.0% yield of compound **8**. The ^{1}HNMR spectrum of compound **8** showed that the pure α anomer was obtained[11]. With similar method, 76.2% yield of compound **10** was prepared by treatment of compound **7** with 2-O-acetyl-3,4-O-dibenzyl-α-L-rhamnopyranosyl trichloroacetimidate in the presence of boron trifluoride. Compound **9** was prepared directly from compound **8** in three steps according to Gigg[6]. Treatment of compound **10** with K_2CO_3 in dried MeOH afforded compound **11** in the yield of 94.7%. Compound **9** was converted to the corresponding imidate ester with similar procedure of compound **6** The

glycosylation of compound **11** with the imidate ester of cmpound **9** in dried dichloromethane in the presence of TMSOTf and 4AMS afforded a 60.5% yield of compound **12**. The ^{1}HNMR and 2D NMR spectrum of compound **12** showed it is a pure α anomer[11].

Experimental

General. — Melting points were determined with a X_4 micromelting-point apparatus and are uncorrected. Optical rotations were determined with a Perkin-Elmer Model 241 MC polarimeter, for solution in $CHCl_3$ at 20°C. VLC[12] was performed on columns of silica gel H (Qingdao). TLC was performed on silica gel G_{F254} (Qingdao). IR spectra were recorded with a Perkin-Elmer Model 983 spectrophotometer, using KBr pellets for the crystalline samples and films for the syrup samples. ^{1}H NMR and ^{1}H-^{1}H COSY spectra were recorded with either a JEOL-GX-400 or a JEOL-GX-90 NMR spectrometer. ^{13}C NMR spectra were recorded with either a JEOL-GX-400 or a JEOL-GX-90 NMR spectrometer operated at either 100 MHz or 22.5 MHz(Me_4Si as an internal standard in $CDCl_3$). Fast-atom-bombardment mass spectra were recorded with a VG ZAB-2F model spectrometer.

Allyl α-L-rhamnopyranoside(**1**)

A solution of L-rhamnopyranose monohydrate (2.0 g, 11 mmol) in dried allyl alcohol (25 ml) and concentrated H_2SO_4 (0.2 ml) was stirred 1 hr. at 100°C, then K_2CO_3 (0.2 g) was added to neutralize the solution. After removing allyl alcohol *in vacuo*, the crude syrup was chromatographed with VLC to afford compound 1 (1.84 g, 92.0%).

Allyl 2,3-isopropylidene-α-L-rhamnopyranoside (**2**)

p-TsOH (0.1 g) and 4AMS (1.2 g) were added to a stirred solution of compound **1** (2.0 g, 9.8 mmol) in dried acetone (20 ml). After refluxing for 1.5 hr, K_2CO_3 (0.1 g) was added to neutralize the solution, and then evaporated to a syrup, which was chromatographed to give compound **2** (2.1 g, 86.0%).

Allyl 2,3-O-isopropylidene-4-O-benzyl-α-L-rhamnopyranoside (**3**)

NaH (80%, 0.8 g, 27 mmol) was added to a stirred solution of compound **2** (2.5 g, 10.2 mol) in dried DMF (20 ml) with a ice bath. Then, benzyl bromide (1.5 ml) were added drowise. After 1 hr at room temperature, water (20 ml) were added. The mixture was extracted with ether (10 ml ×3). The organic layer was dried over $MgSO_4$ and concentrated to a syrup which was purified by VLC to give compound **3** (2.6 g, 80%). IR (ν_{max} cm^{-1}): 3060, 3027 (C=C); 2981 (C-H); 1599, 1499 (C=C). NMR: δ_H (90 MHz, ppm): 1.03, 1.30 (3H×2, s, C*H*$_3$×2), 1.12 (3H, d, $J_{5,6}$ 6.35 Hz, H-6), 3.04-3.94 (4H, m, sugar ring H), 3.92-4.10 (2H, m, C*H*$_2$-CH=CH$_2$), 4.69-4.87 (2H, m, Ph-C*H*$_2$), 4.70 (1H, s, H-1), 5.10-5.20 (2H, m, CH$_2$-CH=C*H*$_2$), 5.55-5.85 (1H, m, CH$_2$-C*H*=CH$_2$), 7.10-7.21 (5H, m, Ar-*H*); δ_C (22.5 MHz, ppm): 17.2 (C-6), 26.0, 27.8 (*C*H$_3$×2), 64.8-75.7 (sugar ring C, Ph-*C*H$_2$), 67 8 (*C*H$_2$-CH=CH$_2$), 96.1 (C-1), 98.6 (>*C*<), 117 6 (CH$_2$-CH=*C*H$_2$), 133.5 (CH$_2$-*C*H=CH$_2$), 126.8-138.2 (Ar).

Allyl 4-O-benzyl-α-L-rhamnopyranoside (**4**)

2N H_2SO_4 (3.0 ml) was added drowise to a stirred solution of compound **3** (2.0 g, 6.0 mmol) in MeOH (30 ml). The solution was maintained for 1.5 hr at 70°C, TLC showed that most compound **3** was converted. The mixture was allowed to cool to the room temperature, then, $NaHCO_3$ was added to the mixture. After removing 25 ml MeOH, $CHCl_3$ (20 ml) was added to the mixture. The organic layer was washed with water, dried over $MgSO_4$ and concentrated to a syrup which was purified to give crystalline compound **4** (1.48g, 84%). m.p. 53-4°C, $[\alpha]_D^{20}$ -60.2 (c 1.2, $CHCl_3$). IR (ν_{max} cm^{-1}): 3355 (s, OH); 3060, 3029 (m, C=C); 2899 (s, C-H); 1644,1450 (m, C=C). NMR: δ_H (400 MHz, ppm): 1.35 (3H, d, $J_{5,6}$ 6.34 Hz, H-6), 2 68 (2H, s, O*H*), 3.34 (1H, m, $J_{4,5}$ 9.28 Hz, $J_{3,4}$ 11.72 Hz, H-4), 3.74 (1H, m, $J_{4,5}$ 9.28 Hz, $J_{5,6}$ 6.35 Hz, H-5), 3.91-3 96 (2H, m, H-2, H-3), 3 96-4.17 (2H, m, *CH*$_2$-CH=CH$_2$), 4.69-4.87 (2H, m, Ph-C*H*$_2$), 4 78 (1H, s, H-1), 5.16-5.92 (2H, m, CH$_2$-CH=C*H*$_2$), 5.82-5.92 (1H, m, CH$_2$-C*H*=CH$_2$), 7.25-7.36 (5H, m, Ar-*H*); δc (100 MHz, ppm): 17.90 (C-6), 67.20 (C-5), 67.80 (C-2), 71.0 (*C*H$_2$-CH=CH$_2$), 71 50 (C-3), 74 90 (Ph-*C*H$_2$), 81.57 (C-4), 98.45 (C-1), 117.28 (CH$_2$-CH=*C*H$_2$), 133.6 (CH$_2$-*C*H=CH$_2$), 127.8, 128.0, 128.5, 138.2 (Ar).

Allyl 3,4-O-dibenzyl-α-L-rhamnopyranoside (**5**)

Compound **5** was prepared with the method of Gigg[6]. $[\alpha]_D^{20}$ -47.2 (c 1 4, $CHCl_3$). Anal. for $C_{23}H_{28}O_5$: Found (calc.) C 71.59 (71.87), H 7.30 (7.29). FAB-MS (%): 383 (7) $[M-1]^+$, 327 (8) $[M\text{-}OAll]^+$, 181(58), 131(18), 91(100). IR (ν_{max} cm^{-1}): 3457 (bs, OH); 3062, 3029(m); 2973, 2910(m); 1493, 1449(s) NMR· δ_H (90 MHz, ppm): 1.35 (3H, d, $J_{5,6}$ 6.34 Hz, H-6), 4.75 (1H, s, H-1), 5.85 (1H, m, CH$_2$-C*H*=CH$_2$), 7.3-7.5 (10H, m, Ar-*H*); δc (22.5 MHz, ppm): 16.43 (C-6), 96.68 (C-1).

2-O-Acetyl-3,4-O-dibenzyl-α-L-rhamnopyranose (**6**)

t-BuOK (4.0 g, 35.7 mmol) were added to a stirred solution of compound **5** (4.0 g, 10.42 mmol) in dried DMSO (40 ml). After 2 hrs at 50°C, ice-water (40 ml) were added and extracted with ether (20 ml ×3). The ether layer was dried over $MgSO_4$, and evaporated to a syrup, then, pyridine (15 ml) and acetic anhydride (10 ml) were added to the crude syrup. After stirring for 2.5 hrs, ice-water (30 ml) was added, then the mixture was extracted with $CHCl_3$ (15 ml ×3) The organic layer was washed with water and concentrated to a syrup. To the solution of the syrup in acetone (36 ml) and water (4 0 ml), HgO (4 0 g) and $HgCl_2$ (4 0 g) were added. After stirring for 2.5 hrs, TLC showed the reaction was completed. Removal of acetone *in vacuo* gave a syrup, then, $CHCl_3$ (40 ml) was added. The mixture was washed with saturated NaI solution and water, dried over $MgSO_4$. Evaporated and chromatographed to afford a syrup compound **6** (3.20 g, 80%). $[\alpha]_D^{20}$ -23.5 (c 1.2, $CHCl_3$). Anal. for $C_{22}H_{26}O_6$ Found (calc): C68 36 (68.39), H 6.94 (6.74). IR (ν_{max} cm^{-1}): 3405 (s); 3086, 3061, 3029(s); 2975, 2932(m); 1739 (s, C=O), 1604. FAB-MS (%): 409(70) [M+Na], 385 (8) [M-1], 369 (48), 279(30), 261 (15), 181(91), 107(18), 91(100). NMR: δ_H (90 MHz, ppm): 1.19 (3H, d, $J_{5,6}$ 6.34 Hz, H-6), 2.05 (3H, s, C*H*$_3$CO) 5.01 (1H, d, J 1 45 H-1), 7.2-7.4 (10H, m, Ar-*H*); δc (22 5 MHz, ppm)· 16 50 (C-6), 19.60 (*C*H$_3$CO), 90.77 (C-1), 169.07 (CH$_3$*C*O).

Allyl 2-acetylamino-2-deoxy-3,4-dibenzyl-α-D-glucopyranoside (7)

To a stirred solution of allyl 2-acetylamino-2-deoxy-3,4-O-dibenzyl-6-O-trityl-α-D-glucopyranoside[8] (3.0 g, 4.6 mmol) in dried acetonitrile (25 ml), Me_3SiCl (1.5 ml) and NaI (1.5 g) were added. After 15 min., water (25 ml) were added. The mixture was stirred for 15 min and extracted with $CHCl_3$ (15 ml ×3). The organic layer was washed with 10% $Na_2S_2O_3$ solution and water, dried over $MgSO_4$, concentrated to a solid which was purified with VLC to give a white solid compound 7 (1.45 g, 74.2%). m.p. 146-8°C, $[\alpha]_D^{20}$ +56.7 (c 1.3, $CHCl_3$). IR (ν_{max} cm^{-1}): 3297 (s, OH, NH); 3064, 3031 (m, =C-H); 2922 (s, C-H); 1645(s, C=O), 1548, 1494, 1450 (m, C=C). NMR: δ_H (400 MHz, ppm): 1.84 (3H, s, C*H*$_3$CONH), 2.05 (1H, s, O*H*), 3.67-3.83 (4H, m, H-3, H-4, H-5, H-6), 3.89-4.14 (2H, m, C*H*$_2$-CH=CH$_2$), 4.18-4.24 (1H, m, $J_{1,2}$ 3.41 Hz, $J_{2,NH}$ 9.26 Hz, $J_{2,3}$ 9.77 Hz, H-2), 4.64-4.88 (4H, m, Ph-C*H*$_2$), 4.81 (1H, d, $J_{1,2}$ 3.41 Hz, H-1), 5.18-5.25 (2H, m, CH$_2$-CH=C*H*$_2$), 5.33 (1H, d, $J_{2,NH}$ 9.28 Hz, N*H*), 5.81-5.89 (1H, m, CH$_2$-C*H*=CH$_2$), 7.26-7.37 (10H, m, Ar-*H*); δc (100 MHz, ppm): 23.32 (*C*H$_3$CONH), 52.53(C-2), 61.59 (C-6), 68.12 (*C*H$_2$-CH=CH$_2$), 71.60 (C-3), 74.78, 75.10 (Ph-*C*H$_2$), 78.10 (C-4), 79.9 (C-5) 96.77 (C-1), 117.63 (CH$_2$-CH=*C*H$_2$), 133.46 (CH$_2$-*C*H=CH$_2$), 127.79-138.3 (Ar), 169.87 (CH$_3$*C*ONH)

Allyl 2-O-(2-O-Acetyl-3,4-O-dibenzyl-α-L-rhamnopyranosyl)-3,4-O-dibenzyl-α-L-rhamnopyranoside (8)

To a stirred solution of 2-O-(2-O-acetyl-3,4-dibenzyl-α-L-rhamnopyranose (6) (650 mg, 1.70 mmol) in dried dichloromethane (20 ml), trichloroacetonitrile (0.8 ml), NaH (80%, 20 mg), and 4AMS (1.0 g) were added. After 40 min at room temprature, the mixture was filtered with silica gel and evaporated to give a crude syrup. Then dried dichloromethane (15 ml), compound 5 (620 mg, 1.61 mmol) and 4AMS (1.0 g) were added. After stirring for 10 min, 3 drops of TMSOTf were added to the mixture. The mixture was filtered after 1 hr, and washed with water, dried over $MgSO_4$, evaporated to a syrup which was chromatographed to give a syrup compound 8 (730 mg, 60.1%). $[\alpha]_D^{20}$ -19.3 (c 1.2, $CHCl_3$). Anal. for $C_{45}H_{52}O_{10}$ Found (calc.): C71.58 (71.81), H 6.85 (6.91). FAB-MS (%): 775(3) [M+Na]; 751(1.2) [M-1], 695(1), 499(5), 475(2.3), 369(68), 261(38), 181(98), 107(70), 91(100). IR (ν_{max} cm^{-1}): 3059, 3027(m); 2973, 2910(m); 1739(s, C=O), 1493, 1449. NMR: δ_H (400 MHz, ppm): 1.34 (6H, d, $J_{5,6}$ 6.35 Hz, H-6,6'), 2.15 (3H, s, C*H*$_3$CO), 3.53-3.96 (7H, m, sugar-ring H), 3.96-4.15 (2H, m, C*H*$_2$-CH=CH$_2$), 4.72 (1H, s, H-1), 4.83 (1H, d, $J_{1',2'}$ 1.46 Hz H-1'), 5.12-5.28 (CH$_2$-CH=C*H*$_2$), 5.38 (1H, m, $J_{1',2'}$ 1.47 Hz, H-2'); 5.79-5.91 (1H, m, CH$_2$-C*H*=CH$_2$), 7.26-7.60 (20H, m, Ar-*H*) δc (100 MHz, ppm): 17.51, 17.94 (C-6,6'), 21.04 (*C*H$_3$CO), 67.90-80.0 (sugar-ring C, Ph-*C*H$_2$, *C*H$_2$-CH=CH$_2$) 98.22 (C-1), 97.80 (C-1'), 117.40(CH$_2$-CH=*C*H$_2$) 127.28-138.4 (Ar-*C*, CH$_2$-*C*H=CH$_2$), 170.40 (CH$_3$*C*O).

2-O-(2-O-Acetyl-3,4-O-dibenzyl-α-L-rhamnopyranosyl)-3,4-O-dibenzyl-α-L-rhamnopyranose (9)

t-BuOK (2.5 g, 20.5 mmol) were added to a stirred solution of 8 (1.0 g, 1.33 mmol) in dried DMSO (25 ml). After 2 hrs at 50°C, ice-water (40 ml) was added, and the mixture was extracted with ether (20 ml ×3). The ether layer was dried over $MgSO_4$, and concentrated to a syrup. Pyridine (10 ml) and acetic anhydride (7 ml) were added to the crude syrup. After stirring for 2.5 hrs, ice-water (30 ml) was added, then the mixture was

extracted with CHCl3. The organic layer was washed with water and evaporated to a syrup. To the solution of the syrup in acetone (9 ml) and water (1 ml), HgO (1.0g) and $HgCl_2$ (1.0 g) were added. After stirring for 2.5 hrs, TLC showed the reaction was completed. Removal of acetone *in vacuo* gave a syrup. $CHCl_3$ (20 ml) were added to the syrup. The $CHCl_3$ layer was washed with saturated NaI solution and water, dried over $MgSO_4$ and concentrated to a syrup which was purified to afford a syrup compound **9** (620 mg, 65%). $[\alpha]_D^{20}$ -11 (c 1.0, $CHCl_3$). FAB-MS: 711(1) [M-1], 605(2), 369(20), 279(8), 261(31), 181(80), 91(100). IR (ν_{max} cm^{-1}): 3395 (s, OH), 3059, 3027(m); 2973, 2929 (m); 1738 (s, Ac C=O), 1600(w) 1492, 1450. NMR: δ_H (400 MHz, ppm): 1.32 (6H, d, $J_{5',6'}$ 6.32 Hz, H-6,6'), 2.15 (3H, s, C*H*$_3$CO), 2.21 (1H, s, O*H*), 3.37-4.01, (7H, m, H-2,3,3',4,4',5,5'), 4.49-4.93 (8H, m, Ph-C*H*$_2$), 4.80 (1H, s, H-1'), 5.14 (1H, d, $J_{1,2}$ 1.46 Hz, H-1), 5.39 (1H, m, $J_{1',2'}$ 1.47 Hz, H-2'), 7.25-7.38 (20H, m, Ar-*H*); δc (100 MHz, ppm): 17.98 (C-6,6'), 21.10 (*C*H$_3$CO), 67.78-79.98 (sugar-ring C, Ph*C*H2), 92.41 (C-1), 97.89(C-1'), 127.44-138.36 (Ar), 170.50 (CH$_3$*C*O)

Allyl 2-acetylamino-2-deoxy-3,4-dibenzyl-6-O-(2-O-Acetyl-3,4-O-dibenzyl-α-L-rhamnopyranosyl)-α-D-glucopyranoside (**10**)

To a stirred solution of 2-O-(2-O-acetyl-3,4-dibenzyl-α-L-rhamnopyranose (**6**) (200 mg, 0.52mmol) in dried dichloromethane (10 ml), trichloroacetonitrile (0.5 ml), NaH (80%, 20 mg), and 4AMS (1.0g) were added. After 40 min at room temprature, the mixture was filtered with silica gel and the the filtered solution was concentrated to give a crude syrup. Then, dried dichloromethane (15 ml), compound **7** (230 mg, 0.52 mmol) and 1.0 g 4AMS were added. After stirring for 10 min, 1 drops of BF_3·Et_2O was added to the mixture. The mixture was filtered after 2 hrs, and washed with water, dried over $MgSO_4$, evaporated to a syrup which was chromatographed to give a white crystal compound **10** (320 mg, 76 1%). m.p. 112-114°C, $[\alpha]_D^{20}$ +43.7 (c 1.2, $CHCl_3$). Anal. for $C_{47}H_{55}NO_{11}$ Found (calc.): 69.94 (69.72), H 7.02 (6.81), N 1.84 (1.74). FAB-MS: 810 [M+1] (10), 752(5), 369(17), 181(100), 107(38), 91(56). IR (ν_{max} cm^{-1}): 3317 (s, NH), 3060, 3027(m); 2912(m); 1739 (s, Ac C=O), 1644(s, AcNH C=O), 1539, 1490, 1450. NMR: δ_H (400 MHz, ppm): 1.29 (3H, d, $J_{5',6'}$ 6.35 Hz, H-6'), 1.86 (3H, s, C*H*$_3$CONH), 2.14 (3H, s, C*H*$_3$CO), 3.40-3.94, (8H, m, H-3,3',4,4',5,5', 6), 3.94-4.12 (2H, m, C*H*$_2$-CH=CH$_2$), 4.23-4.28 (1H, m, $J_{1,2}$ 3.42 Hz, $J_{2,NH}$ 9.77 Hz, $J_{2,3}$ 10 25 Hz, H-2), 4.53-4.94 (8H, m, Ph-C*H*$_2$), 4.75 (1H, d, $J_{1,2}$ 3.42 Hz, H-1), 4.71 (1H, s, H-1'), 5.16-5.21 (2H, m, CH$_2$-CH=C*H*$_2$), 5.31 (1H, dd, $J_{1',2'}$ 1.47 Hz, $J_{2',3'}$ 3.42 Hz, H-2'), 5.36 (1H, d, $J_{2,NH}$ 9.77 Hz, N*H*), 5.81-5.88 (1H, m, CH$_2$-C*H*=CH$_2$), 7.25-7.34 (20H, m, Ar-*H*); δc (100 MHz, ppm): 17.89 (C-6'), 21.08 (*C*H$_3$CO), 23.43 (*C*H$_3$CONH), 52.40 (C-2), 65.9-80.54 (sugar-ring C, Ph*C*H2, *C*H$_2$-CH=CH$_2$) 96.67 (C-1), 97.71(C-1'), 117.74 (CH$_2$-CH=*C*H$_2$), 127.64-138.47 (Ar, CH$_2$-*C*H=CH$_2$), 169.76 (CH$_3$*C*ONH), 170.25 (CH$_3$*C*O).

Allyl 2-acetylamino-2-deoxy-3,4-dibenzyl-6-O-(3,4-O-dibenzyl-α-L-rhamnopyranosyl)-α-D-glucopyranoside (**11**)

K_2CO_3 (40 mg, 0.28 mmol) were added to a stirred solution of allyl 2-acetylamino-2-deoxy-3,4-dibenzyl-6-O-(2-O-Acetyl-3,4-O-dibenzyl-α-L-rhamnopyranosyl)-α-D-glucopyranoside (**10**) (200 mg, 0.25 mmol) in MeOH

(20 ml). After 1 hr at room temprature, TLC showed the reaction was completed The mixture was filtered and concentrated to a syrup which was chramatographed to give a white solid compound **11** (180 mg,, 94.7%). m.p. 149-150°C $[\alpha]_D^{20}$ +34.7 (c 1.2, $CHCl_3$). Anal. for $C_{45}H_{53}NO_{10}$ Found (calc.): C70.60 (70.40), H 6.91 (6.91), N 1.74 (1.82). FAB-MS: 768(4) [M+1], 710(1), 442(20), 384(51), 243(25), 181(91), 91(100). IR (ν_{max} cm^{-1}): 3468 (s, OH), 3319 (s, NH), 3059, 3027(m); 2912(m); 1644(s, Ac C=O), 1538, 1450. NMR: δ_H (400 MHz, ppm): 1.27 (3H, d, $J_{5',6'}$ 6.35 Hz, H-6'), 1.87 (3H, s, C*H*$_3$CONH), 3.40-3.94, (9H, m, H-2',3,3',4,4',5,5',6), 3.92-4.12 (2H, m, C*H*$_2$-CH=CH$_2$), 4.23-4.29 (1H, m, $J_{1,2}$ 3.42 Hz, $J_{2,NH}$ 9.76 Hz, $J_{2,3}$ 10.25 Hz, H-2), 4.52-4.91 (8H, m, Ph-C*H*$_2$), 4.75 (1H, d, $J_{1,2}$ 3.42 Hz, H-1), 4.71 (1H, s, H-1'), 5.17-5.25 (2H, m, CH$_2$-CH=C*H*$_2$), 5.36 (1H, d, $J_{2,NH}$ 9.77 Hz, NH), 5.82-5.88 (1H, m, CH$_2$-C*H*=CH$_2$), 7.25-7.37 (20H, m, Ar-*H*); δc (100 MHz, ppm: 17.84 (C-6'), 23.49 (*C*H$_3$CONH), 52.40 (C-2), 65.61-80.65 (sugar-ring C, *C*H$_2$-CH=CH$_2$, Ph*C*H$_2$), 96.80 (C-1), 98.97 (C-1'), 117.80 (CH$_2$-CH=*C*H$_2$), 133.55 (CH$_2$-*C*H=CH$_2$), 127.67-138.42 (Ar), 169.74 (CH$_3$*C*ONH).

Allyl 2-acetylamino-2-deoxy-3,4-dibenzyl-6-O-{2-O-[2-O-(2-O-acetyl-3,4-O-dibenzyl-α-L-rhamnopyranosyl)-3,4-O-dibenzyl-α-L-rhamnopyranosyl]-3,4-O-dibenzyl-α-L-rhamnopyranosyl}-α-D-glucopyranoside (**12**)

To a solution of 2-O-(2-O-Acetyl-3,4-O-dibenzyl-α-L-rhamnopyranosyl)-3,4-O-dibenzyl-α-L-rhamnopyranose (**9**) (200 mg, 0.28 mmol) in dried dichloromethane (20 ml), trichloroacetonitrile (0.3 ml), NaH (80%, 10 mg), and 4AMS (1.0 g) were added. After stirring for 40 min at room temprature, the mixture was filtered with silica gel. and evaporated to give a crude syrup. To the crude syrup in flask, dried dichloromethane (15 ml), compound **11** (200mg, 0.26 mmlo) and 4AMS (1.0 g) were added. After stirring for 10 min, 3 drops of TMSOTf were added to the mixture. The mixture was filtered after 2 hrs and washed with water, dried over $MgSO_4$, evaporated to a syrup which was purified with VLC to give a white solid compound **12** (230 mg, 60.5%). $[\alpha]_D^{20}$ +34.7 (c 1.4, $CHCl_3$). Anal. for $C_{87}H_{99}NO_{19}$ Found (calc.): C 71.19 (71.42), H 6.75 (6.45), N 1.08 (0.96). FAB-MS: 1500(10) [M+K], 1174(18), 369(48), 261(62), 181(100). IR (ν_{max} cm^{-1}): 3298 (s, NH), 3059, 3027(m); 2922(m); 1740 (s, Ac C=O), 1650 (s, AcNH C=O), 1544, 1493, 1450. NMR: δ_H (400 MHz, ppm): 1.20, 1.25 (9H, dd, J 6.35Hz, H-6',6",6'"), 1.86 (3H, s, C*H*$_3$CONH), 2.12 (3H, s, C*H*$_3$CO), 3.36-3.97, (16H, m, sugar-ring H), 3.68 (1H, d, $J_{2,3}$ 10.27 Hz, H-3), 3.94-4.11 (2H, m, C*H*$_2$-CH=CH$_2$), 4.22-4.28 (1H, m, $J_{1,2}$ 3.42 Hz, $J_{2,NH}$ 9.76 Hz, $J_{2,3}$ 10.25 Hz, H-2), 4.47-4.92 (16H, m, Ph-C*H*$_2$), 4.76 (1H, d, $J_{1,2}$ 3.42 Hz, H-1), 4.65, 4.70 (2H, s, H-1',1"), 4.98 (1H, s, H-1'"), 5.16-5.24 (2H, m, CH$_2$-CH=C*H*$_2$), 5.35 (1H, d, $J_{2,NH}$ 9.77 Hz, N*H*), 5.54 (1H, s, H-2'"), 5.80-5.87 (1H, m, CH$_2$-C*H*=CH$_2$), 7.23-7.35 (40H, m, Ar-*H*); δc (100 MHz, ppm: 17.94 (C-6',6",6'"), 21.10 (*C*H$_3$CO), 23.45 (*C*H$_3$CONH), 52.42 (C-2), 65.61-80.48 (suga-ring C, Ph*C*H$_2$, *C*H$_2$-CH=CH$_2$), 96.71 (C-1), 98.77 (C-1', 1"), 99.20 (C-1'"), 117.82 (CH$_2$-CH=*C*H$_2$), 127.50-138.40 (Ar, CH$_2$-*C*H=CH$_2$), 169.76 (CH$_3$*C*ONH), 170.02 (CH$_3$*C*O).

Acknowlegement

The project was supported by National Natural Sciences Foundation of China.

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(*Received* 16 *September* 1994)