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Stereoselective Synthesis of α-L-Rhamnopyranosyl Phosphonates via α-L-Rhamnopyranosyl Trifluoroacetate

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STEREOSELECTIVE SYNTHESIS OF α -L-RHAMNOPYRANOSYL PHOSPHONATES VIA α -L-RHAMNOPYRANOSYL TRIFLUOROACETATE

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ABSTRACT: α-L-Rhamnopyranosyl phosphates 8a-b~12a-b were obtained in high yield and high stereoselectivity from α-L-rhamnopyranosyl trifluoroacetate 2a-b and phosphoric acid diesters in the presence of a Lewis acid.

Glycosyl phosphates are of importance as cell wall materials and as intermediates in biological glycosyl transfer 1 . The preparation of these compounds is usually based on the condensation of haloglycose with phosphoric acid diesters, but , low yields and α,β -selectivities are often observed 2 . Recently, major advances in this field have been made by the use of trichloroacetimidate method 3 .

In this paper, we report the synthesis α -L-rhamnopyranosyl phosphate using the trifluoroacetoxyl group as the anomeric leaving group. The method is easy to operate and the reaction proceeds under mild conditions.

2,3,4-Tri-O-acetyl or benzyl- α -L-rhamnopyranose **1a-b** was treated with trifluoroacetic anhydride ⁴⁻⁹ to give 1-O-trifluoroacetyl-2,3,4-tri-O-acetyl or benzyl- α -L-rhamnopyranose **2a-b**. When **2a** or **2b** was reacted with some

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2546 LI, LI, AND LI

phosphoric acid diesters 3-7 in the presence of boron trifluoride etherate in dichloromethane, the compounds 8a-b~12a-b were obtained in high yields (84~96%).

a: R=Acetyl 8: $R_2=R_3=Ethyl$ 9: $R_2=R_3=Propyl$ 10: $R_2=R_3=Isopropyl$ b: R=Benzyl 11: $R_2=R_3=n$ -Butyl 12: $R_2=R_3=Benzyl$

Scheme 1

EXPERIMENTAL

The NMR spectra were recorded as CDCl₃ solutions on a Varian XL 300 spectrometer. Mass spectroscopic analyses were performed with a Perkin-Elmer 240c mass spectrometer. Column chromatography was performed on silica-gel H (Qing Dao Chem. Co.).

Preparation of 1-O-trifluoroacetyl-2,3,4-tri-O-acetyl or benzyl- α -L-rhamnopyranose 2a-b

2,3,4-Tri-O-acetyl or benzyl- α -L-rhamnopyranose 1a-b (1.0mmoL) was added to trifluoroacetic anhydride (6mL) with stirring at room temperature for 5 mins, then sodium trifluoroacetate (1.0mmoL) was added. The reaction was monitored by TLC (CHCl₃: CH₃OH=10: 1). Dichloromethane (10mL) was added to the mixture after 40 mins. Then the product was subjected to silica gel column chromatography using dichloromethane (20mL) as eluant. The solvent was removed in vacuo to give a syrup, 2a or 2b, yields 95% and 98%, respectively.

Preparation of α-L-rhamnopyranosyl phosphates 8a-b~12a-b: General procedure.

A solution of 2a or 2b (1mmoL), phosphonic acid diesters 3-7 (1.5mmoL) and boron trifluoride etherate (3 drops) in dichloromethane (5mL) was stirred at room

temperature for 1-3 hrs. When TLC (CHCl₃: CH₃OH=10: 1) showed the absence of substrate and the presence of new product, the solvent was evaporated to give a syrup. Compounds 8a-b~12a-b were obtained as colorless needles or syrups after silica gel column chromatography. The reaction time, melting point, and yields are indicated in Table 1. The data of spectra and analysis are follows:

8a: ^{1}H NMR: δ 5.97 (d ,1H , J $_{1,2}$ =1.3Hz , H-1) ; 5.30-5.10 (m , 3H , H-2 ,3 , and 4) ; 3.90(m ,1H, H-5) ;3.35 (m,4H ,OCH $_{2}$ -) ;2.20-2.01(3s,9H ,-COCH $_{3}$) ; 1.22 (d ,3H , J $_{5,6}$ =5.8Hz , Rha-CH $_{3}$) ; 0.93 (t ,6H ,-C-CH $_{3}$) . Mass spectrum : m/z 426 (M $^{+}$). Anal Calcd for $C_{16}H_{27}O_{11}P$ (426) : C , 45.07 ; H , 6.38. Found : C , 45.09 ; H , 6.40.

9a: $^1\mathrm{H}$ NMR: δ 6.01(d ,1H, $J_{1,2}{=}1.0\mathrm{Hz}$,H-1) ; 5.35 (dd ,1H, $J_{2,3}{=}3.0\mathrm{Hz}$,H-2) ; 5.20 (dd , 1H , $J_{4,5}{=}10\mathrm{Hz}$,H-4) ;5.10 (dd ,1H , $J_{3,4}{=}9.5\mathrm{Hz}$,H-3) ;3.86 (m ,1H , H-5) ; 3.33 (m ,4H ,OCH_2-) ; 2.25-2.01 (3s ,9H ,-COCH_3) ; 1.25 (d ,3H , $J_{5,6}{=}6.0\mathrm{Hz}$, Rha-CH_3) ;1.10 (m ,4H ,-C-CH_2-Me) ; 0.90 (t ,6H ,-C-CH_3) . Mass spectrum : m/z 454 (M $^+$). Anal Calcd for $C_{18}H_{31}O_{11}P$ (454) : C ,47.57 ; H , 6.88. Found : C , 47.45 ; H , 6.59.

10a: 1H NMR: δ 5.90 (d , 1H , $J_{1,2}{=}1.5Hz$, H-1) ; 5.34-5.08 (m,3H, H-2 ,3,and 4) ; 3.94 (m ,1H , H-5) ; 3.41(m , 2H ,OCHMe) ; 2.28-2.10 (3s,9H,-COCH_3) ; 1.19 (d , 3H , $J_{5,6}{=}6.2Hz$, Rha-CH_3) ; 0.98 (t , 6H , isopropyl-CH_3) . Mass spectrum : m/z 454 (M^+). Anal Calcd for $C_{18}H_{31}O_{11}P$ (454) : C , 47.57 ; H , 6.88. Found : C , 45.89 ; H , 6.50.

11a: 1H NMR: δ 5.96 (d , 1H , $J_{1,2}{=}1.1Hz$, $H{-}1$) ; 5.38 (dd ,1H , $J_{2,3}{=}3.0Hz$, $H{-}2$) ; 5.20-5.05 (m , 2H , H- 3 and 4) ; 3.99 (m , 1H , H-5) ; 3.54 (m , 4H , OCH_2-) ; 2.23-2.05 (3s , 9H , -COCH_3) ; 1.25 (d , 3H, $J_{5,6}{=}5.8Hz$, Rha-CH_3) ; 1.15 (m , 8H , -C-CH_2-CH_2-Me) ; 0.97 (m , 6H , -C-CH_3) . Mass spectrum : m/z 482 (M $^+$). Anal Calcd for $C_{20}H_{35}O_{11}P$ (482) : C , 49.79 ; H , 7.31 . Found : C , 49.38 ; H , 6.99.

12a: 1H NMR: δ 7.40–7.20 (m , 10H , Ph-H) ; 6.05 (d,1H , $J_{1,2}$ =1.3Hz , H-1) ; 5.35-5.05 (m , 3H , H-2 ,3 ,and 4) ; 4.45 (m , 4H, Ph-CH $_2$) ; 3.89(m,1H ,H-5) ; 2.20-2.01 (3s , 9H , -COCH $_3$) ; 1.19 (d , 3H , $J_{5,6}$ =5.9Hz , Rha-CH $_3$) . Mass spectrum : m/z 550 (M^+). Anal Calcd for $C_{26}H_{31}O_{11}P$ (550) : C , 56.73 ; H , 5.68. Found : C , 56.25 ; H , 5.48.

2548 LI, LI, AND LI

Table 1 Data of reaction conditions, melting points, and yields of 8a-b~12a-b

Products	Reaction time ^a (h)	m. p. (C)	Yield ^b (%)
Me → OCH ₂ C	•		
8a OAc OAc OCH ₂ CH ₂ C		104-106	85
9a OAC OAC OAC		oil	88
10a OAC OAC OCH2CH2CH	3 1 ₂ cH ₃	84-86	93
Aco Me OAc OAc OAC	3	oil	84
Me OAc OAc	2	oil	92

8b: ^{1}H NMR: δ 7.50–7.20 (m , 15H , Ph-H) ; 5.88 (d ,1H , $J_{1,2}$ =1.0Hz , H-1) ; 4.48 (m , 6H , Ph-CH $_2$) ; 4.20-3.60 (m, 3H , H-2 ,3 ,and 4) ;3.50-3.30 (m ,5H , H-5 and -OCH $_2$ -Me) ;1.29 (d ,3H , $J_{5,6}$ =5.9Hz ,Rha-CH $_3$) ;1.05 (t,6H ,-C-CH $_3$). Mass spectrum : m/z 570 (M $^+$). Anal Calcd for $C_{31}H_{39}O_8P$ (570): C , 65.25 ; H , 6.89. Found : C , 65.09 ; H , 6.54.

9b: 1H NMR: δ 7.55–7.10 (m , 15H , Ph-H) ; 5.85 (d ,1H , $J_{1,2}$ =1.0Hz , H-1) ; 4.60-4.45 (m , 6H , Ph-CH $_2$) ; 4.30-3.60 (m ,3H, H-2 ,3 ,and 4) ;3.45-3.30 (m ,

Table 1. Continued

Products	Reaction time ^a (h)	m. p. (C)	Yield ^b (%)
ا ا	∕осн ₂ сн ₃ ∼осн ₂ сн ₃		
	2 сн ₂ сн ₂ сн ₃ сн ₂ сн ₂ сн ₃	oil	86
9b OBn OBn	2 ·осн ^{(сн₃)₂ ·осн(сн₃)₂}	79-81	93
0P	2 .ch ₂ ch ₂ ch ₂ ch ₃ .ch ₂ ch ₂ ch ₂ ch ₃	oil	89
11b OBn OBn	2 •och ₂ ph •och ₂ ph	oil	91
Me OBn OBn	3	oil	96

a: All reactions were carried out in dichloromethane.

b: Isolated yield.

2550 LI, LI, AND LI

5H , H-5 and -OCH₂-Me) ; 1.25 (d , 3H , $J_{5,6}$ =5.9Hz , Rha-CH₃) ;1.10 (m,4H , -C-CH₂-Me) ; 0.90 (t , 6H , -C-CH₃). Mass spectrum : m/z 598 (M⁺). Anal Calcd for $C_{33}H_{43}O_8P$ (598) : C , 66.21 ; H , 7.26. Found : C , 66.20 ; H , 7.14.

10b: 1H NMR: δ 7.50–7.10 (m , 15H , Ph-H) ; 5.95 (d ,1H, $J_{1,2}$ =1.0Hz , H-1) ; 4.70-4.38 (m , 6H , Ph-CH $_2$) ; 4.20-3.50 (m, 3H, H-2 ,3 ,and 4) ;3.40-3.20 (m , 3H , H-5 and -OCH-Me) ; 1.20 (d, 3H , $J_{5,6}$ =5.9Hz , Rha-CH $_3$) ;1.00 (m ,12H , isopropyl-CH $_3$). Mass spectrum : m/z 598 (M^+). Anal Calcd for $C_{33}H_{43}O_8P$ (598) : C , 66.21 ; H , 7.26. Found : C , 66.15 ; H , 7.08.

11b: 1H NMR: δ 7.56–7.10 (m , 15H , Ph-H) ; 5.85 (d,1H , $J_{1,2}$ =1.0Hz , H-1) ; 4.58-4.40 (m , 6H , Ph-CH $_2$) ; 4.25-3.50 (m,3H , H-2 ,3 ,and 4) ;3.40-3.28 (m , 5H , H-5 and -OCH $_2$ -Me) ; 1.20 (d, 3H , $J_{5,6}$ =5.9Hz , Rha-CH $_3$) ;1.10 (m, 8H , -C-CH $_2$ -CH $_2$ -Me) ; 0.94 (m , 6H , -C-CH $_3$). Mass spectrum : m/z 626 (M^+). Anal Calcd for $C_{35}H_{47}O_8P$ (626) : C , 67.07 ; H , 7.56. Found : C , 67.01 ; H , 7.50.

12b: 1H NMR: δ 7.50–7.18 (m ,15H , Ph-H) ; 5.94 (d ,1H , $J_{1,2}$ =1.0Hz , H-1) ; 4.65-4.38 (m ,10H , Ph-CH $_2$) ; 4.20-3.60 (m ,3H ,H-2 ,3 ,and 4) ; 3.40 (m ,1H , H-5) ; 1.18 (d , 3H , $J_{5,6}$ =5.9Hz , Rha-CH $_3$) . Mass spectrum : m/z 694 (M^+). Anal Calcd for $C_{41}H_{43}O_8P$ (694) : C , 70.88 ; H , 6.24. Found : C , 70.60 ; H , 6.05.

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