Studies of Tritylated Pentoses and 6-Deoxyhexoses. III. The *O*-Tritylation of Methyl α- and β-D-Xylopyranoside[1)]

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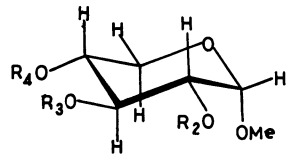
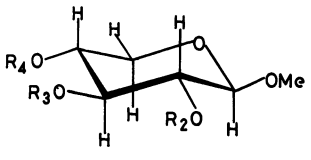
Synopsis. The tritylation of methyl α- and β-D-xylopyranoside afforded three isomeric trityl ethers in both cases. All the ethers were separated by column chromatography in almost pure forms on TLC. Among them, methyl 2-*O*-trityl-α- and methyl 3-*O*-trityl-β-D-xylopyranoside were crystallized from aqueous ethanol. The position of the trityl group in each ether was mainly established by the use of ^{1}H NMR with its diacetyl derivative.

In previous papers of this series, it was shown that methyl α-D-fucopyranoside[2)] and methyl α- and β-L-rhamnopyranoside[3)] readily formed trityl ethers, although they had no primary hydroxyl group in their molecules. In these glycosides, the equatorial hydroxyl groups, each of which is in a *cis*-form with an axial hydroxyl group, seem reactive toward tritylation.

Jackson, Hockett, and Hudson[4-5)] have reported that methyl β-D-xylopyranoside (**2**) reacted with trityl chloride in dry pyridine to give ethers. This glycoside also has no primary hydroxyl group in its molecule. They isolated two crystalline ditrityl ethers and two monotrityl ethers as crystalline di-*O*-acetates. However, they did not describe their structures. Robertson and Speedie[6)] prepared methyl 2,4-di-*O*-methyl-3-*O*-tosyl-β-D-xylopyranoside from a syrupy tritylation product of **2** through crystalline methyl di-*O*-acetyl-β-D-xylopyranoside mononitrate. From the position of the tosyl group in the resulting compound, they assumed that the starting tritylation product consisted mainly of methyl 3-*O*-trityl-β-D-xylopyranoside. They did not describe any physical data of the trityl ether or the presence of other tritylation products of **2**. Also, there has been no report about the tritylation of methyl α-D-xylopyranoside (**1**). This paper will deal with the chromatographic isolation of the three possible trityl ethers from each tritylation product of **1** and **2** and with their structures.





1	$R_2=R_3=R_4=H$	**2**	$R_2=R_3=R_4=H$
3a	$R_2=Tr$, $R_3=R_4=H$	**6a**	$R_2=Tr$, $R_3=R_4=H$
3b	$R_2=Tr$, $R_3=R_4=Ac$	**6b**	$R_2=Tr$, $R_3=R_4=Ac$
4a	$R_3=Tr$, $R_2=R_4=H$	**7a**	$R_3=Tr$, $R_2=R_4=H$
4b	$R_3=Tr$, $R_2=R_4=Ac$	**7b**	$R_3=Tr$, $R_2=R_4=Ac$
5a	$R_4=Tr$, $R_2=R_3=H$	**8a**	$R_4=Tr$, $R_2=R_3=H$
5b	$R_4=Tr$, $R_2=R_3=Ac$	**8b**	$R_4=Tr$, $R_2=R_3=Ac$

Tr : $-C(C_6H_5)_3$

Results and Discussion

The reaction of **1** with 1.5 molar equivalents of trityl chloride in pyridine afforded three monotrityl ethers: the 2-*O*- (**3a**), 3-*O*- (**4a**), and 4-*O*-trityl derivatives (**5a**), in a ratio of 45 : 34 : 21 and in a combined yield of 58%. Among them, **3a** was crystallized from aqueous ethanol. A dark green spot, the R_f value of which was higher than that of triphenylmethanol, was observed on a TLC of the reaction mixture; it was assumed to correspond to the ditrityl ether of **1**. The analogous tritylation of **2** gave a 39 : 34 : 27 mixture of three monotrityl ethers: the 2-*O*- (**6a**), 3-*O*- (**7a**), and 4-*O*-trityl derivatives (**8a**), in a combined yield of 67%. Among them, **7a** was crystallized from aqueous ethanol. Two dark green spots with high R_f values on a TLC of the reaction mixture were assumed to be the di-*O*-trityl derivatives of **2**. All the mono-*O*-trityl-di-*O*-acetyl derivatives (**3b**, **4b**, **5b**, **6b**, **7b**, and **8b**) derived from each monotrityl ether were crystallized from aqueous ethanol. Two acetates, **6b** and **8b**, have almost the same mp's as the compounds reported by Jackson *et al.*;[5)] however the $[\alpha]_D$'s of **6b** and **8b** do not agree with those of the compounds in their report. The ^{1}H NMR spectra of the trityl acetyl derivatives were analyzed with a favorable Cl conformation, aided by the nuclear magnetic double resonance (NMDR) technique, thus confirming the structures. *O*-Trityl-methine proton signals are distinguished by their high-field shifts from signals of acetylmethine protons. The ^{1}H NMR data in the first-order analysis of the trityl acetyl derivatives are summarized in Table 1.

In the reactions of both **1** and **2**, the sequence of the reactivity of the hydroxyl groups toward tritylation was OH-2, OH-3, and OH-4. No considerable difference was recognized in the ratios of the three monotrityl ethers between the tritylation products of **1** and **2**.

Table 1. ^{1}H NMR parameters of methine protons in the trityl acetyl derivatives

	Chemical shifts, δ					
	H-1	H-2	H-3	H-4	H-5ax	H-5eq
3b	3.85(d)	3.38(dd)	5.61(dd)	4.62(ddd)	3.45(dd)	3.57(dd)
4b	4.71(d)	4.93(dd)	3.17(dd)	4.93(ddd)	3.60—3.75(multi)	
irr 4.7	—	d	dd	ddd	multi	
5b	4.64(d)	4.52(dd)	5.60(dd)	2.78(ddd)	3.50(dd)	3.45(dd)
6b	3.90(d)	3.43(dd)	5.24(dd)	4.66(ddd)	3.92(dd)	3.45(dd)
irr 4.7	d	dd	d	—	d	d
7b	4.14(d)	4.89(dd)	3.53(dd)	4.66(ddd)	3.05(dd)	4.09(dd)
irr 3.1	d	dd	dd	dd	—	d
irr 3.5	—	d	—	dd	—	—
8b	4.29(d)	4.65(dd)	5.30(dd)	3.60(ddd)	3.0—3.3(multi)	
	Coupling constants/Hz					
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5ax}$	$J_{4,5eq}$	$J_{5ax,5eq}$
3b	3.9	10.0	10.0	11.0	6.5	11.0
4b	4.0	9.2	*ca.* 10	*ca.* 10	6.0	—
5b	4.0	10.0	8.7	*ca.* 10	*ca.* 6	*ca.* 10
6b	4.4	6.5	6.6	6.0	4.5	12.5
7b	5.1	7.0	7.0	6.5	4.2	12.5
8b	6.7	9.0	9.0	9 0	5 2	—

d: doublet, dd: d of d's, ddd: d of dd's, irr: irradiated at.

Experimental

General Methods. The solutions were evaporated under reduced pressure below 40 °C. The optical rotations were measured with a Japan Spectroscopic DIP-SL polarimeter. The TLC was performed using a DC-Alufolien Kieselgel 60 F_{254} plate, 0.2 mm in thickness (Merck), developed two times with a solvent system of methanol–acetone–pyridine–water–chloroform (1.5 : 1.5 : 0.5 : 0.5 : 96). Preparative column chromatography was achieved using Wakogel C-200 (Wako Junyaku Co., Ltd.), eluted with the same solvent system as that used in the TLC described above. The ^{1}H NMR spectra were recorded with a Varian EM 390 (90 MHz), a Varian XL-100 (100 MHz) or a JEOL XF-200 (200 MHz) spectrometer, chloroform-*d* being used as the solvent and tetramethylsilane as the internal standard.

*Tritylation of Methyl α- (**1**) and β-D-Xylopyranoside (**2**).* Xyloside **1** and **2** were prepared from commercial D-xylose. A mixture of **1** or **2** and trityl chloride in a molar ratio of 1 : 1.5, dissolved in dry pyridine (×5), was allowed to stand for five days at room temperature. Thus, a small amount of water was added to the solution. After concentration, the residue was dissolved in toluene (×5). Triphenylmethanol (TPM) was then filtered from the toluene solution, and the TPM-free concentrate was subjected to recycling column chromatography eight times on silica gel (30 g). In the reaction of **1** (3.28 g), the evaporation of the eluting solvent in the fraction with R_f values of 0.29, 0.57, and 0.39 gave 2.128 g of **3a**, 1.599 g of **4a**, and 1.022 g of **5a** respectively. Compound **3a** was crystallized from 80% ethanol as white prisms: mp 135—136 °C. $[\alpha]_D^{20}$ (*c* 2.0 chloroform): **3a**, +41.3°; **4a**, +5.9°; **5a**, +53.3°. Found: **3a**, C, 73.67; H, 6.49%; **4a**, C, 74.02; H, 6.60%; **5a**, C, 73.86; H, 6.56%. Calcd for $C_{25}H_{26}O_5$: C, 73.86; H, 6.45%.

The TPM-free concentrate of the tritylation product of **2** (3.28 g) was chromatographed on silica gel (30 g) in a recycling manner eight times. The concentration of the fractions with R_f values of 0.71, 0.60, and 0.52 on a TLC gave 2.101 g of **6a**, 1.875 g of **7a**, and 1.500 g of **8a** respectively. Compound **7a** was crystallized from 80% ethanol as white needles: mp 80—81 °C. $[\alpha]_D^{20}$ (*c* 2.0 chloroform): **6a**, +10.4°; **7a**, −48.0°; **8a**, −73.5°. Found: **6a**, C, 73.57; H, 6.48%; **7a**, C, 73.63; H, 6.45%; **8a**, C, 73.58; H, 6.57%. Calcd for $C_{25}H_{25}O_5$: C, 73.86; H, 6.45%.

Acetylation of Methyl O-Tritylxylopyranosides. Each sample was acetylated under standard conditions for 2 d. After chromatographic purification, all the acetates were recrystallized from 80% ethanol in yields of 70—80%. Mp: **3b**:176—177 °C; **4b**, 154 °C; **5b**, 107—108 °C; **6b**, 169—171 °C; **7b**, 162—163 °C; **8b**, 125—126 °C. $[\alpha]_D^{20}$ (*c* 2.0 chloroform): **3b**, +61.8°; **4b**, +65.5°; **5b**, +55.6°; **6b**, −6.4°; **7b**, −27.6°; **8b**, −54.2°. Chemical shifts of methyl protons in ^{1}H NMR δ=**3b**, 1.84, 1.98, 3.24; **4b**, 1.52, 1.59, 3.17; **5b**, 1.87, 2.03, 3.31; **6b**, 1.79, 2.11, 2.99; **7b**, 1.57, 1.73, 3.39; **8b**, 1.70, 2.05, 3.39. Found: **3b**, C, 71.14; H, 6.29%; **4b**, C, 70.83; H, 6.30%; **5b**, C, 70.89; H, 6.30%; **6b**, C, 71.11; H, 6.28%; **7b**, C, 70.86; H, 6.35%; **8b**, C, 70.76; H, 6.37%. Calcd for $C_{29}H_{30}O_7$: C, 71.00; H, 6.16%.

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