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Ditritylation of Methyl and Benzyl α-D-Gluco-, -Manno-, and -Galactopyranosides and Preparation of Their Partially Benzylated Derivatives[1)]

Shinkiti Koto,* Naohiko Morishima, Toyosaku Yoshida, Masaharu Uchino, and Shonosuke Zen

School of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo 108

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The ditritylation of methyl and benzyl α-D-gluco-, -manno-, and -galactopyranosides with trityl chloride in pyridine at 70 °C proceeds in a regioselective manner to give the 2,6-dityrityl ethers of the glucosides, the 3,6-ones of the mannosides, and both 2,6- and 3,6-ones of the galactosides. The rearrangement of the trityl group from *O*-3 to *O*-2 of the mannosides at 100 °C causes the selective formation of the 2,6-dityrityl ethers. From the 2,6- and the 3,6-dityrityl ethers, the 3,4- and 2,4-dibenzyl ethers of the hexopyranosides are prepared.

Trityl group has been used for the selective protection of the primary hydroxyl group of carbohydrates;[2)] tritylation of the secondary one has also often been carried out.[2,3)] The continuing methodological study of oligosaccharide synthesis[4)] needs efficient synthetic routes to various kinds of partially benzylated monosaccharides. This has made us investigate the ditritylation of methyl and benzyl α-D-gluco-, -manno-, and -galactopyranosides in order to protect the primary hydroxyl group and one of the secondary ones temporarily. To our surprise, no practical synthesis of such dityrityl ethers has been reported.† They are useful precursors of partially benzylated sugars, some of which have been synthesized *via* partial stannylation by Ogawa *et al.*[5)]

Results and Discussion

The ditritylation of the methyl hexosides with three molar amounts of trityl chloride (TrCl) in pyridine (Py) proceeded smoothly at 50 and 70 °C (Table 1). The locations of trityl groups in the dityrityl ethers were determined by analyzing the ^{1}H NMR spectra of their acetates (Table 5). The structures of the dityrityl ethers were further confirmed by their conversion into the dibenzyl ethers through benzylation followed by detritylation as described below. The results of the reactions conducted at 50 and 70 °C in Table 1 indicate that the regioselectivity of the reaction depends on the steric disposition of the hydroxyl group involved. The starting materials were always exhausted and the primary hydroxyl group was completely tritylated. The second trityl group was introduced to *O*-2 of the glucoside, *O*-3 of the mannoside, and both *O*-2 and *O*-3 of the galactoside, preferentially. Small amounts of the 4,6-dityrityl ethers of the glucoside and the mannoside were also isolated, but that of the galactoside was not detected.

Table 1. Yields of dityrityl and monotrityl ethers of hexopyranosides

Starting material	Temp/°C	Time/h	Yield/% 2,6-Dityrityl ether		3,6-Dityrityl ether		4,6-Dityrityl ether		6-Monotrityl ether	
1	50	18	**7**	36	**8**	19	**9**	12	**1t**[a)]	32
	70	18		52		12		12		18
	100	18		34		2		6		39
2	50	18	**13**	3	**14**	62	**15**	9	**2t**[b)]	26
	70	18		6		56		7		16
	100	18		45		5		4		37
3	50	18	**19**	32	**20**	39			**3t**[c)]	27
	70	8[g)]		39		37				19
	100	6[g)]		35		16				41
4	70	18	**10**	53	**11**	4	**12**	7	**4t**[d)]	16
	100	18		43		3		4		38
5	70	18	**16**	4	**17**	46	**18**	6	**5t**[e)]	19
	100	18		28		12		3		38
6	70	8[g)]	**21**	37	**22**	31			**6t**[f)]	19
	100	5[g)]		36		14				42

a) B. Helferich and J. Becker, *Justus Liebigs Ann. Chem.*, **440**, 1 (1924). b) A. J. Watters, R. C. Hockett, and C. S. Hudson, *J. Am. Chem. Soc.*, **61**, 1528 (1939). c) H. H. Baer and S. A. Abbas, *Carbohydr. Res.*, **77**, 117 (1979). d) S. Koto, S. Inada, T. Yoshida, M. Toyama, and S. Zen, *Can. J. Chem.*, **59**, 255 (1981). e) $[\alpha]_D^{20}+16°$ (*c* 0.6, $CHCl_3$). Found: C, 74.56; H, 6.25%. Calcd for $C_{32}H_{32}O_6$: C, 74.98; H, 6.30%. f) Mp 84—87 °C, $[\alpha]_D^{20}+60°$ (*c* 1.0, $CHCl_3$). Found: C, 74.26; H, 6.40%. Calcd for $C_{32}H_{32}O_6$: C, 74.98; H, 6.30%. g) Longer reaction time caused serious coloration of the reaction mixture and significant depression of yields.

† Ogawa *et al.* have synthesized **7** *via* stannylation (Ref. 5d).

Table 2. Results of reaction of ditrityl ethers with pyridinium chloride

Starting material	Time/h	Yield/%			
		2,6-Ditrityl ether	3,6-Ditrityl ether	4,6-Ditrityl ether	6-Trityl ether
7	18	38	2	1	53
8	18	26	9	1	56
9	18	28	4	2	59
13	18	68	0	0	24
14	18	50	9	0	27
15	18	21	17	2	57
19	6	48	2	0	45
20	6	1	23	0	74

Thus, the orders of reactivity of the secondary hydroxyl group to TrCl in Py at 50 to 70 °C are: OH-2≫OH-3≥OH-4 for the glucoside, OH-3≫OH-4≥OH-2 for the mannoside, and OH-2≈OH-3≥OH-4 for the galactoside; in other words, the equatorial hydroxyl groups vicinal to the axial oxygenous substituent are reactive, whereas the axial ones are not.[2b,6] Highly selective introduction of the trityl group to OH-3 of methyl 6-deoxy-α-L-mannopyranoside and fairly high reactivity of not only OH-2 but OH-3 toward tritylation of methyl 6-deoxy-α-L-galactopyranoside were reported by Otake *et al.*[3b] Benzyl α-D-hexopyranosides also exhibited similar trends of the reactivity of secondary hydroxyl groups in the tritylation at 70 °C.

A remarkable change in the regioselectivity occurred in the tritylation of mannosides **2** and **5** at 100 °C. The formation of the 2,6-ditrityl ether **13** predominated and that of the 3,6-isomer **14** was much lower. The ditritylation of the glucosides and the galactosides also raised the selectivity for the 2,6-ditrityl ethers. The increase in the yield of the monotrityl ether in each case at 100 °C suggests that the trityl group at the secondary hydroxyl group is apt to undergo the reverse reaction with pyridinium chloride (Py·HCl) formed during tritylation in Py (Eq. 1).[7] Since Py·HCl always

$$=CHOH + TrCl + Py \rightleftarrows =CHOTr + Py\cdot HCl \quad (1)$$

precipitated during the tritylation at 70 °C, while the reaction at 100 °C was homogeneous, greater solubility of the salt in Py at 100 °C may help the reverse reaction in Eq. 1. The time course of the reaction of **2** at 100 °C shows that the second trityl group enters into OH-3 and then rearranges to OH-2 (Fig. 1). It was further found that the 3,6-ditrityl ether **14** was converted into the 2,6-isomer **13** in the presence of Py·HCl in Py at 100 °C

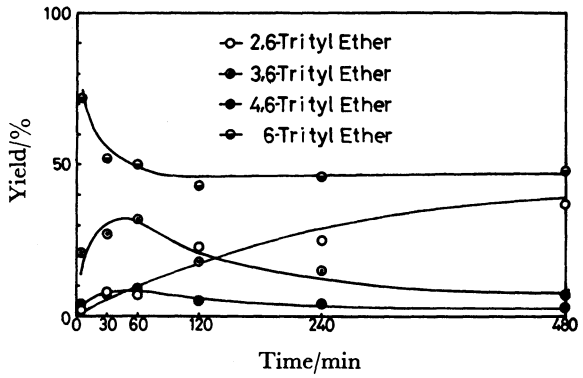
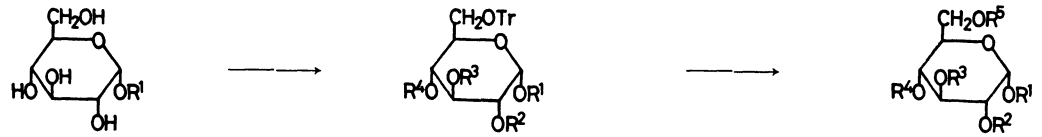


Fig. 1. Time course of tritylation of methyl α-D-mannopyranoside (**2**). Using three molar amount of trityl chloride in pyridine at 100 °C.

(Table 2). The 4,6-isomer **15** behaved in a similar manner. Contrary to these results, the 2,6-isomer **13** did not rearrange. The glucosides exhibited similar trends as shown in Table 2; the 3,6- and the 4,6-ditrityl ethers were converted into the 2,6-isomer but the 2,6-isomer did not change into the 3,6- and the 4,6-isomers. As for the galactosides, although the 3,6-isomer did not rearrange into the 2,6-isomer, the results in Table 2 show that the latter is more resistant to degradation into the monotrityl ether **3t** than the former. Thus, the tritylation of the hexopyranosides with TrCl in Py at 100 °C furnishes a quasi-equilibrium mixture in which the 2,6-ditrityl ether predominates.[8]

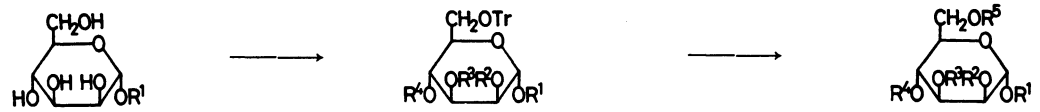
The 2,6- and the 3,6-ditrityl ethers thus obtained afforded the 3,4- and the 2,4-dibenzyl ethers, respectively, with ease through benzylation and subsequent



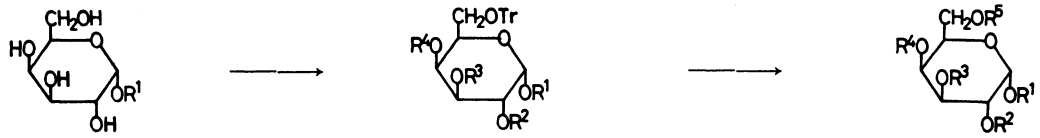
1 (**4**) R^1=Me(Bn)

1t (**4t**) R^1=Me(Bn), R^2=R^3=R^4=H
7 (**10**) R^1=Me(Bn), R^2=Tr, R^3=R^4=H
8 (**11**) R^1=Me(Bn), R^3=Tr, R^2=R^4=H
9 (**12**) R^1=Me(Bn), R^4=Tr, R^2=R^3=H
7a (**10a**) R^1=Me(Bn), R^2=Tr, R^3=R^4=Ac
8a (**11a**) R^1=Me(Bn), R^3=Tr, R^2=R^4=Ac
9a (**12a**) R^1=Me(Bn), R^4=Tr, R^2=R^3=Ac

23 (**25**) R^1=Me(Bn), R^3=R^4=Bn, R^2=R^5=H
24 (**26**) R^1=Me(Bn), R^2=R^4=Bn, R^3=R^5=H
23a (**25a**) R^1=Me(Bn), R^3=R^4=Bn, R^2=R^5=Ac
24a (**26a**) R^1=Me(Bn), R^2=R^4=Bn, R^3=R^5=Ac



2 (**5**) R^1=Me(Bn) **2t** (**5t**) R^1=Me(Bn), R^2=R^3=R^4=H
13 (**16**) R^1=Me(Bn), R^2=Tr, R^3=R^4=H
14 (**17**) R^1=Me(Bn), R^3=Tr, R^2=R^4=H
15 (**18**) R^1=Me(Bn), R^4=Tr, R^2=R^3=H
13a (**16a**) R^1=Me(Bn), R^2=Tr, R^3=R^4=Ac
14a (**17a**) R^1=Me(Bn), R^3=Tr, R^2=R^4=Ac
15a (**18a**) R^1=Me(Bn), R^4=Tr, R^2=R^3=Ac
27 (**29**) R^1=Me (Bn), R^3=R^4=Bn, R^2=R^5=H
28 (**30**) R^1=Me(Bn), R^2=R^4=Bn, R^3=R^5=H
27a (**29a**) R^1=Me(Bn), R^3=R^4=Bn, R^2=R^5=Ac
28a (**30a**) R^1=Me(Bn), R^2=R^4=Bn, R^3=R^5=Ac



3 (**6**) R^1=Me(Bn) **3t** (**6t**) R^1=Me(Bn), R^2=R^3=R^4=H
19 (**21**) R^1=Me(Bn), R^2=Tr, R^3=R^4=H
20 (**22**) R^1=Me(Bn), R^3=Tr, R^2=R^4=H
19a (**21a**) R^1=Me(Bn), R^2=Tr, R^3=R^4=Ac
20a (**22a**) R^1=Me(Bn), R^3=Tr, R^2=R^4=Ac
31 (**33**) R^1=Me(Bn), R^3=R^4=Bn,R^2=R^5=H
32 (**34**) R^1=Me(Bn), R^2=R^4=Bn, R^3=R^5=H
31a (**33a**) R^1=Me(Bn), R^3=R^4=Bn, R^2=R^5=Ac
32a (**34a**) R^1=Me(Bn), R^2=R^4=Bn, R^3=R^5=Ac

Table 3. Physical and Analytical Data of Ditrity Ethers of Methyl and Benzyl α-D-Hexosides

Compound	Mp θ_m/°C	$[\alpha]_D^{20}$/°	(c, $CHCl_3$)	Formula	Calcd (%) C	Calcd (%) H	Found (%) C	Found (%) H	R_f[a] TB	R_f[a] HE	Lit
7	108—109	+36	(1.0)	$C_{45}H_{42}O_6$	79.62	6.24	79.49	6.20	0.26		b)
8	96—99	+49	(1.0)				79.64	6.50	0.54		
9	124—125	+53	(1.0)				79.57	6.48	0.10		
10	104—106	+48	(0.3)	$C_{51}H_{46}O_6$	81.14	6.14	81.02	6.21	0.40		
11	100—101	+40	(0.6)				81.36	6.10	0.70		
12	127—130	+59	(0.3)				80.88	6.13	0.13		
13	99—104	−8	(0.5)	$C_{45}H_{42}O_6$	79.62	6.24	79.58	6.49	0.35		
14	167	+30	(1.0)				78.38	6.55	0.66		
15	112—114	+16	(0.5)				79.48	6.47	0.22		
16	104—105	+12	(1.2)	$C_{51}H_{46}O_6$	81.14	6.14	80.75	6.12	0.42	0.40	
17	85—87	+27	(0.5)				81.10	6.52	0.69	0.64	
18	63—66	+34	(1.4)				80.56	6.10	0.42	0.35	
19	113—118	+36	(0.5)	$C_{45}H_{42}O_6$	79.62	6.24	79.50	6.26	0.63		
20	104	+63	(1.0)				79.61	6.61	0.34		
21	106—107	+30	(1.0)	$C_{51}H_{46}O_6$	81.14	6.14	80.75	6.33	0.62		
22	96—97	+45	(1.0)				81.00	6.09	0.48		

a) TM=Toluene: 2-butanone (10 : 1). HE=Hexane: ethyl acetate (3 : 1). b) Ref. 5d: $[\alpha]_D^{20}$+32.8° (c 0.90 , $CHCl_3$).

detritylation.[9] The structures of the dibenzyl ethers were readily determined through the examination of the ^1H NMR spectra of their acetates (Table 6) and are consistent with that of the starting ditrityl ethers.

Experimental

General. Methyl α-D-glucopyranoside (**1**, Tokyo Kasei) and methyl α-D-mannopyranoside (**2**, Sigma) were used directly. Methyl α-D-galactopyranoside monohydrate (**3**·H_2O, Pfanstiehl) was dehydrated *in vacuo* over P_2O_5 at 80 °C before use. Benzyl α-D-glucopyranoside (**4**) was prepared as before;[4a] benzyl α-D-manno- and -galactopyranoside (**5** and **6**) were synthesized from the respective hexoses in a similar manner. Trityl chloride (TrCl, Tokyo Kasei) was used directly and pyridinium chloride (Py·HCl, Tokyo Kasei) was dried over P_2O_5 *in vacuo* before use. Pyridine (Py) was distilled from BaO. For other items, see the preceeding reports.[4] Acetylation was carried out with excess acetic anhydride in Py at room temperature; chromatographycally pure acetates were obtained through column chromatography on silica gel (Kanto Kagaku) with the mixture of benzene and 2-butanone (gradient elution).

Procedure for Ditritylation. A mixture of a glycoside (2.0 mmol), TrCl (3.0 equiv.) and Py (5.0 ml/g of glycoside) was heated under anhydrous conditions with good stirring. Py·HCl soon precipitated in the reaction at 70 °C, but did not at 50 and 100 °C. After cooling and quenching with iced water, the mixture was extracted with $CHCl_3$. The organic

Table 4. Physical and analytical data of dibenzyl ethers of methyl and benzyl α-D-hexosides

Compound	Mp θ_m/°C	$[\alpha]_D^{20}$/°	(c, $CHCl_3$)	Formula	Calcd (%) C	Calcd (%) H	Found (%) C	Found (%) H	Lit
23	108—109	+106	(1.0)	$C_{21}H_{26}O_6$	67.36	7.00	67.21	7.07	a)
24[e]	74—75	+88	(0.6)				67.10	6.90	
25	—	+94	(2.4)	$C_{27}H_{30}O_6$	71.98	6.71	71.04	6.73	
26[f]	78—79	+123	(0.5)				71.42	6.70	b)
27	—	+14	(0.7)	$C_{21}H_{26}O_6$	67.36	7.00	66.54	7.27	c)
28	—	+31	(0.8)				66.93	7.31	d)
29	—	+35	(1.3)	$C_{27}H_{30}O_6$	71.98	6.71	71.37	6.68	
30	81—83	+34	(0.7)				72.22	6.69	
31	132—133	+98	(1.0)	$C_{21}H_{26}O_6$	67.36	7.00	67.14	6.98	
32	101—102	+59	(0.9)				67.30	7.11	
33	94—95	+66	(0.5)	$C_{27}H_{30}O_6$	71.98	6.71	71.52	6.74	
34	123—124	+94	(0.6)				71.88	6.81	

a) Ref. 5c, mp 105—106 °C, $[\alpha]_D^{20}$+101.3° (c 0.545, $CHCl_3$). b) Ref. 5e, mp 77—78 °C, $[\alpha]_D^{20}$+157.6° (c 1.3, $CHCl_3$). c) Ref. 5b, $[\alpha]_D^{20}$+50.0 (c 0.22, $CHCl_3$). d) Ref. 5a, $[\alpha]_D^{20}$+23.5° (c 0.77, $CHCl_3$). e) Identified with the product obtained from methyl 2,4-di-*O*-benzyl-6-*O*-trityl-α-D-glucopyranoside (Ref. 4a) *via* detritylation. f) Identified with the product obtained from benzyl 2,4-di-*O*-benzyl-α-D-glucopyranoside (Ref. 4a) *via* detritylation.

Table 5. ^{1}H NMR data of acetates of ditrityl ethers of methyl and benzyl α-D-hexosides[a]

Compound	Chemical shifts/ppm[b] H-1	H-2	H-3	H-4	H-5	OAc	OAc	OMe	Coupling constants/Hz J_{12}	J_{23}	J_{34}	J_{45}
7a	3.86	3.36	5.47	4.51	3.71	1.63	1.72	2.31	3.4	9.5	9.5	9.1
8a	4.81	4.89	3.42	4.97	3.54	1.21	1.34	3.31	3.9	10.4	10.4	9.3
9a	4.72	4.24	5.46	2.74	3.16	1.09	1.94	3.64	3.8	9.9	9.6	9.6
10a	4.01	3.45	5.46	4.53	3.82	1.60	1.69	—	3.5	9.9	9.5	9.5
11a	5.00	4.88	3.67	5.03	3.53	1.87	1.96	—	3.8	9.8	9.8	9.8
12a	4.88	4.31	5.54	2.78	4.38	1.11	1.91	—	4.0	9.8	9.8	9.8
13a	3.91	3.71	4.87	5.90	3.71	1.66	1.74	3.07	1.5	3.1	10.2	10.2
14a	4.46	4.05	3.78	5.27	3.46	1.43	2.16	3.23	1.8	3.0	9.9	9.9
15a	4.47	5.00	5.17	2.86	4.26	1.07	1.75	3.59	1.4	3.1	9.2	9.2
16a	4.16	3.84	4.99	5.98	3.85	1.69	1.78	—	1.5	3.6	10.5	10.5
17a	4.73	4.23	3.81	5.37	3.50	1.76	2.21	—	1.5	3.0	9.8	9.8
18a	4.59	5.88	5.28	2.91	4.38	1.09	1.72	—	1.5	3.3	9.3	9.3
19a	3.89	3.63	5.36	5.31	3.88	1.63	1.72	3.32	3.6	9.5	3.2	1.0
20a	4.76	5.13	3.89	4.46	3.28	1.74	1.98	3.18	3.8	10.4	3.1	1.0
21a	4.07	3.67	5.27	5.35	3.90	1.61	1.65	—	3.6	10.0	3.0	1.0
22a	4.90	5.10	3.98	4.63	3.35	1.60	2.01	—	3.6	10.2	3.0	1.0

a) At 90 MHz in CCl_4 with Me_4Si. b) Underlined values are of H–C(–OAc)

Table 6. ^{1}H NMR data of acetates of dibenzyl ethers of methyl and benzyl α-D-hexosides[a]

Compound	Chemical shifts/ppm[b] H-1	H-2	H-3	H-4	H-5	OAc	OAc	OMe	Coupling constants/Hz J_{12}	J_{23}	J_{34}	J_{45}
23a	4.76	4.65	3.87	3.38	3.64	1.83	1.95	3.32	4.0	10.0	10.0	8.6
24a	4.58	3.38	5.42	n	n	1.86	1.96	3.30	4.0	9.5	9.5	n
25a	4.92	4.63	3.91	3.39	n	1.85	1.93	—	3.9	9.8	9.0	9.5
26a	4.74	3.33	5.50	3.37	n	1.87	1.97	—	4.0	9.6	9.6	9.6
27a	4.52	5.23	3.82	n	n	1.94	2.07	3.31	1.5	3.0	8.6	n
28a	n	n	5.03	n	n	1.86	1.97	3.32	n	3.3	9.0	n
29a	4.78	5.29	3.90	n	n	1.97	2.06	—	1.5	3.3	8.7	n
30a	n	n	5.08	n	n	1.86	1.96	—	2.1	3.4	8.5	n
31a	4.84	5.14	3.81	n	n	1.90	1.99	3.29	3.5	11.0	2.9	n
32a	4.59	3.88	5.08	n	n	1.91	1.94	3.30	3.5	10.5	3.0	n
33a	5.05	5.17	n	n	n	1.93	1.96	—	3.5	10.0	n	n
34a	4.81	n	5.15	n	n	1.93	1.95	—	3.5	11.0	3.0	n

a) At 90 MHz in CCl_4 with Me_4Si. b) Underlined values are of H–C(–OAc).

layer was washed with H_2O well, dried over Na_2SO_4, evaporated under reduced pressure at ≈50 °C, and chromatographed on silica gel (Kanto Kagaku, No. 37047, >100 mesh) with toluene–2-butanone system (gradient elution, 100 : 1→1 : 1). This gave the results as summarized in Table 1. Physical and analytical data of the dirityl ethers are summarized in Table 3. The ^1H NMR data of the acetates of the dirityl ethers are listed in Table 5.

Procedure for Rearrangement of Dirityl Ethers. A mixture of dirityl ether (50 mg, 0.074 mmol), Py·HCl (17 mg, 2.0 equiv.), and Py (0.25 ml) was heated at 100 °C under anhydrous conditions. After processing as above, chromatography gave the results in Table 2.

Procedure for Transformation of Dirityl Ethers into Dibenzyl Ethers. A mixture of dirityl ether (1.0 mmol), crushed KOH (7 g/g of dirityl ether), and $PhCH_2Cl$ (20 ml/g of dirityl ether) was heated at ≈110°C for 18 h under good stirring. After filtration and evaporation under reduced pressure on a boiling water bath, the resulting mixture was heated in a mixture (20 ml/g of dirityl ether) of CF_3CO_2H, MeOH, and $CHCl_3$ (1 : 3 : 10, v/v/v) for 2—5 h. After neutralization with triethylamine and evaporation, the residue was chromatographed on silica gel using toluene–2-butanone system to give the dibenzyl ethers (60—75% yield). Physical and analytical data of the dibenzyl ethers are summarized in Table 4. The ^1H NMR spectral data of the acetates of the dibenzyl ethers are listed in Table 6.

References

1) Partly presented at the 44th National Meeting of the Chem. Soc. Jpn. Okayama, Oct. 1981.

2) a) B. Helferich, *Adv. Carbohydr. Chem.*, **3**, 79 (1948); b) A. H. Haines, *ibid.*, **33**, 11 (1976); c) C. B. Reese, "Protective Group in Organic Chemistry," ed by J. F. W. McOmie, Plenum Press, New York (1973), Chap. 3; T. W. Greene, "Protective Groups in Organic Synthesis," John Wiley and Sons, Inc. New York (1981), Chap. 2.

3) a) R. C. Hockett and C. S. Hudson, *J. Am. Chem. Soc.*, **56**, 945 (1934); E. L. Jackson, R. C. Hockett, and C. S. Hudson, *ibid.*, **56**, 947 (1934); R. C. Hockett, H. G. Fletcher, Jr., and J. B. Ames, *ibid.*, **63**, 2516 (1941); R. C. Hockett and D. F. Mowery, Jr., *ibid.*, **65**, 403 (1943); N. C. Yung and J. J. Fox, *ibid.*, **83**, 3060 (1961); A. F. Cook and J. G. Moffatt, *ibid.*, **89**, 2697 (1967); W. W. Zorbach, S. L. de Bernardo, and K. V. Baht, *Carbohydr. Res.*, **11**, 413 (1969); K. Koizumi and T. Utamura, *Chem. Pharm. Bull.*, **29**, 3118 (1981); b) T. Otake and T. Sonobe, *Bull. Chem. Soc. Jpn.*, **49**, 1050 (1978); T. Otake, T. Sonobe, and T. Suami, *ibid.*, **52**, 3109 (1979).

4) a) S. Koto, S. Inada, T. Yoshida, M. Toyama, and S. Zen, *Can. J. Chem.*, **59**, 255 (1981); b) S. Koto, N. Morishima, C. Kusuhara, S. Sekido, T. Yoshida, and S. Zen, *Bull. Chem. Soc. Jpn.*, **55**, 2995 (1982); N. Morishima, S. Koto, and S. Zen, *Chem. Lett.*, **1982**, 1039.

5) a) T. Ogawa and M. Matsui, *Carbohydr. Res.*, **62**, Cl (1978); b) T. Ogawa and K. Sasajima, *ibid.*, **93**, 67 (1981); c) T. Ogawa, Y. Takahashi, and M. Matsui, *ibid.*, **102**, 207 (1982); d) T. Ogawa, T. Nukada, and M. Matsui, *ibid.*, **102**, 263 (1982); e) T. Ogawa and T. Kaburagi, *ibid.*, **103**, 53 (1982).

6) J. M. Williams and A. C. Richardson, *Tetrahedron*, **23**, 1369 (1967).

7) B. Helferich, P. Speidel, and W. Toeldte, *Chem. Ber.*, **56**, 766 (1927); C. D. Hurd, C. O. Mack, E. M. Filachione, and J. C. Sowden, *J. Am. Chem. Soc.*, **59**, 1952 (1937); M. L. Wolfrom, W. J. Burke, and S. W. Waisbrot, *ibid.*, **61**, 1827 (1939).

8) The stability of the 2,6-dirityl ethers might be, at least in part, attributable to the inductive effect of the anomeric center. The effect may slightly decrease the electronegativity of the oxygen at C-2 to depress effectively its affinity to the proton of the acid PyH^+ in the competing basic medium Py, as in the following equation:

$$\mathrm{ROTr} + \mathrm{PyH^+ \cdot Cl^-} \rightarrow \overset{\mathrm{H}}{[\mathrm{ROTr}]^+}\mathrm{Cl^-} + \mathrm{Py} \rightarrow \mathrm{ROH} + \mathrm{TrCl} + \mathrm{Py}$$

9) In the case of the glucosides, however, the monotrityl ether, **1t** and **4t**, are practically better precursors of the 2,4-dibenzyl ethers, **24** and **26**, respectively, because they are readily prepared through detritylation of methyl and benzyl-2,4-di-*O*-benzyl-6-*O*-trityl-α-D-glucopyranoside (Ref. 4a) prepared directly from **1t** and **4t**.