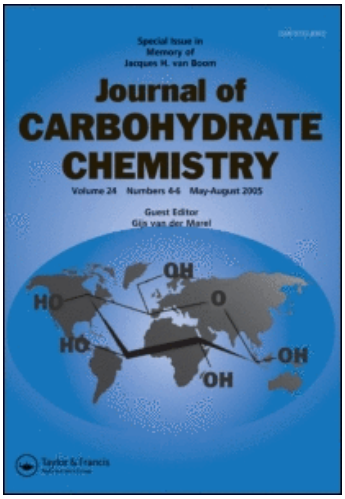

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NOVEL SYNTHESES OF DIPHENYL AND/OR TRIMETHYLENE DITHIOACETALS OF MONO- AND OLIGOSACCHARIDES IN 90% TRIFLUOROACETIC ACID

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ABSTRACT

Dithioacetals of aldopentoses (D-arabinose, D-ribose, D-xylose, and D-lyxose), aldohexoses (D-glucose, D-mannose, D-galactose), and common oligosaccharides (cellobiose, lactose, gentibiose, melibiose, maltose, and maltotriose) were conveniently prepared by reacting the corresponding free sugars respectively with benzenethiol and/or 1,3-propanedithiol at room temperature in 90% trifluoroacetic acid in much better yields than by the conventional methods.

INTRODUCTION

Sugar dithioacetals and their derivatives, typical classes of acyclic carbohydrates, are versatile synthetic intermediates not only because various transformations[1] are possible at the dithioacetal groups, but also because all the sugar hydroxyl groups are potentially available as chiral building blocks for chemical modification or for natural product synthesis through their selective protections.

As part of our programs on utilization of free aldoses as raw starting materials, we are in need of preparing some of the dialkyl or diaryl dithioacetal derivatives of mono- and oligo-saccharides for chain elongation, modification, and so on.

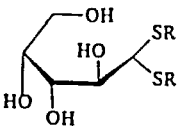
However, the standard methods for preparing aldose dithioacetals, which generally require concentrated hydrochloric acid as the reaction medium, are inappropriate for the synthesis of oligosaccharide dithioacetals, since the interglycosidic linkages usually do not survive during dithioacetalation in such strong acid except for a few examples.[2] At the same time, the reported methods for preparing aldose diphenyldithioacetals of monosaccharides are not always satisfactory and consistent in terms of yield and reaction conditions. Since E. Fischer himself[3] reported the unsuccessful synthesis of D-aldose diphenyldithioacetal by his own method, no reliable papers appeared for more than 50 years until Richtmyer et al.[4] pubished the first synthesis of three aldose diphenyldithioacetals. They isolated D-glucose, D-mannose, and D-galactose diphenyldithioacetal in diverse yields of 71%, 69.5%, and 15.4% respectively at irregular reaction times ranging from 1.5 hours to 11 days at room temperature. Horton and coworkers,[5] on the other hand, obtained diphenyldithioacetals of D-ribose, D-arabinose, D-xylose, D-lyxose, and L-rhamnose in various yields of 42%, 70%, 50%, 30%, and 55% respectively at 0 °C to room temperature employing shorter reaction times. In recent papers, Redlich et al.[6] reported a modified procedure for preparation of several aldose trimethylenedithioacetals using a mixed solvent system such as chloroform/concentrated hydrochloric acid. Though the yields (60~87%) are fairly improved, the physical data (melting points and optical rotations) of D-arabinose, D-lyxose, and D-galactose trimethylenenedithioacetals (**1b**, **4b**, and **7b**) reported by these workers are not consistent with the present data obtained by our procedure.

In this paper, therefore, we wish to describe more versatile and generally applicable procedures both for preparative syntheses of diphenyl- and trimethylenedithioacetals of seven monosaccharides and for facile syntheses of diphenyl dithioacetals of six common oligosaccharides including five disaccharides and one trisaccharide.

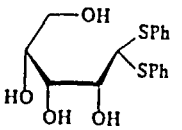
RESULTS AND DISCUSSION

Among various trials done using several acidic organic solvents which might condense free sugars with thiols more smoothly, 90% trifluoroacetic acid was found to be best choice as a reaction medium. Both 50% and 100% trifluoroacetic acid[7] gave no better results, probably because of the lowered solubility of either the thiols or the free sugars.

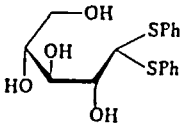
In the case of monosaccharides(four aldopentoses and three aldohexoses), two different reation procedures (A and B) were effectively adopted in 90% trifluoroacetic acid. The first procedure (A) was conducted by mixing the sugar and the thiol at 50-60 °C for 30-50 minutes on a water-bath(~60 °C) to give a clear solution which was concentrated *in vacuo* to yield mostly pure products crystallizable from ethanol in very good yields. The individual yield and physical data (melting points and optical rotations) of the dithioacetals are listed in Table 1. Except for D-lyxose,[8] the physical data from the diphenyldithioacetals (**1a-7a**) of the pentoses (D-arabinose, D-ribose, D-lyxose, D-xylose) and hexoses (D-glucose, D-mannose and D-galactose) were in good accord with the reported data. In the case of 1,3-propanedithiol, our data of trimethylenediothioacetals (**1b**, **4b**, and **7b**) of D-arabinose, D-lyxose, D-glucose, D-galactose and D-mannose showed generally higher melting points than those in the corresponding literature.[6] The second procedure (B) was also effectively applied to the above aldoses by stirring the mixture of sugar and thiol at room temperature for more prolonged reaction time (12-15 hours) to give similar good results as shown in Table 1.



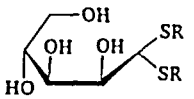
1a,1b



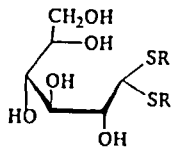
2a



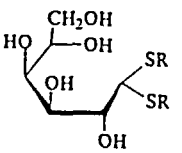
3a



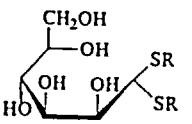
4a,4b



5a,5b



6a,6b



7a,7b

a) R=Ph
b) R=$(CH_2)_3$

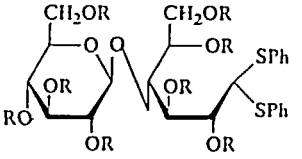
In the case of oligosaccharides, the second procedure (B) was more suitable for avoiding the cleavage of interglycosidic linkages and gave the corresponding dithioacetals of cellobiose, lactose, maltose, melibiose, gentibiose, and maltotriose in fairly good yields around 70%. However, prolonged reaction times (2-7days) caused lowered yields because of the partial cleavage of glycosidic bond. The structures of peracetylated derivatives (**8b**, **9b**, **10b**, **11b**, **12b**, and **13b**)[9] were characterized respectively from ^{1}H NMR(2D) and mass spectral data. ^{1}H NMR chemical shifts and coupling constants of common disaccharide diphenyldithioacetal peracetates are listed in

Table 1. Yields and Physical Data for Dithioacetals of Aldopentoses and Aldohexoses

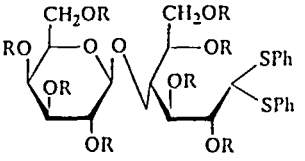
Entry	Aldoses	Thiols	Modes	Products /%	Melting Points/°C	$[\alpha]_D$ (t=20°C)
1	D-Arabinose	PhSH	A	**1a** : 85 (70)[5]	185-186 (186.5-187)[5]	+23° (c 1.1,P) {+24.0° (c1,P)}[5]
		$HS(CH_2)_3SH$	B	**1b** : 79 (70)[6b]	164-165 (134)[6b]	+ 10° (c0.59,W) {+6.1° (c1.0,P)}[6b]
2	D-Ribose	PhSH	A	**2** : 78 (42)[5]	102-103 (101.5-102)[5]	+42° (c1.0,P) {+42.3° (c1.0,P)}[5]
3	D-Xylose	PhSH	A	**3** : 80(50)[5]	100-101 (98-100)[5]	-7.5 (c 1.0,P) {-8.0° (c 0.5,E)}[5]
4	D-Lyxose	PhSH	A	**4a** : 83 (30)[5]	108-109 (63-64)[5]	-29° (c 0.43, P) {-79° (c1.1,E)}[5]
		$HS(CH_2)_3SH$	B	**4b** : 85 (65)[6c]	123-124(116)[6c]	-1.4 (c 0.55,P) {-13.5(c1.0,M)}[6c]
5	D-Glucose	PhSH	A	**5a** : 88 (71)[4]	159-160 (155-157)[4]	+2.0° (c 1.1,P) {+1.5° (c1.0,P)}[4]
		$HS(CH_2)_3SH$	B	**5b** : 85 (75)[6b]	135-136 (130)[6b]	-3.4° (c 0.61,W) {-4.6° (c1.0,M)}[6b]
6	D-Galactose	PhSH	B	**6a** : 94(69.5)[4]	175-176 (173-174)[4]	-32° (c 1.0, P) {-31.5° (c4.4,P)}[4]
		$HS(CH_2)_3SH$	B	**6b** : 88 (77)[6c]	188-189 (157)[6c]	-1.7° (c 0.47,W) {-2.9° (c1.0,M)}[6c]
7	D-Mannose	PhSH	B	**7a** : 81(15.4)[4]	140-141 (138-139)[4]	-30° (c 1.2, P) {-30.0° (c2.6, P)}[4]
		$HS(CH_2)_3SH$	A	**7b** : 92 (73)[6b]	170-171 (165)[6b]	-5.5° (c 0.55,P) {-6.° (c1.0,M)}[6b]

(E=ethanol, M=methanol, P=pyridine, W=distilled water)

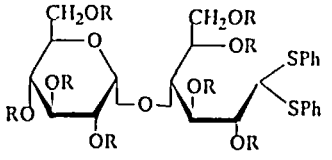
Table 2. The chemical shifts of H-5', H-6'a, and H-6'b protons of melibiose derivative (**12b**) were almost same, and unfortunately unresolved even in a 500 MHz NMR spectrum. All other protons in the oligosaccharide series were easily assigned by first order analysis.



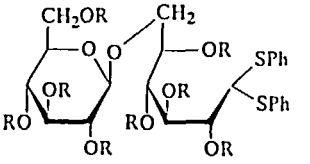
Cellobiose diphenyl dithioacetal (8a,8b)



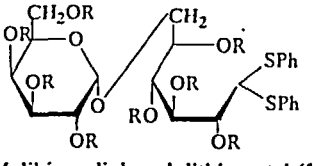
Lactose diphenyl dithioacetal (9a,9b)



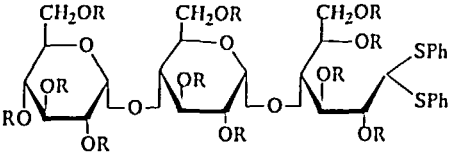
Maltose diphenyl dithioacetal (10a,10b)



Gentibiose diphenyl dithioacetal (11a,11b)



Melibiose diphenyl dithioacetal (12a,12b)



Maltotriose diphenyl dithioacetal (13a,13b)

[a) R=H, b) R=$COCH_3$]

EXPERIMENTAL

General Methods. Melting points were determined on a Yazawa micro melting point apparatus BY-2 and are uncorrected. Optical rotations were determined with a JASCO DIP-140 digital polarimeter. ^1H NMR spectra were recorded with JEOL spectrometers (JNM-GSX 400 and 500MHz) for solutions in $CDCl_3$ containing tetramethylsilane as the internal reference. Mass spectra were measured with a JEOL JMS-HX110 mass pectrometer. TLC was performed on precoated plates of silica gel 60 (Merck) with the following solvent systems: A, 1-butanol-acetic acid-H_2O (8:1:2) for free sugar dithioacetals; B, benzene-ethyl acetate (2:1) for peracetates of the sugar dithioacetals. Compounds were detected with iodine vapor or 5% methanolic sulfuric acid spray followed by heating on a hot plate. Column chromatography was performed by the flash technique on silica gel (Wako-gel C-300) mainly in the case of oligosaccharide diphenyldithioacetals.

Table 2. ^{1}H NMR(400MHz) data of disaccharide diphenyldithioacetal octaacetates

Compounds	H_1	H_2	H_3	H_4	H_5	H_{6a}	H_{6b}	$H_{1'}$	$H_{2'}$	$H_{3'}$	$H_{4'}$	$H_{5'}$	$H_{6'a}$	$H_{6'b}$	$COCH_3$
8b	4.71(d)	5.56(dd)	5.83(dd)	4.24(t)	5.10(m)	4.32(dd)	4.07(dd)	4.70(d)	4.49(dd)	5.12(dd)	4.94(t)	3.54(o)	4.11(q)	3.79(dd)	2.014
	$J_{1,2}$=	$J_{2,3}$=	$J_{3,4}$=	$J_{4,5}$=	$J_{5,6a}$=	$J_{5,6b}$=	$J_{6a,6b}$=	$J_{1',2'}$=	$J_{2',3'}$=	$J_{3',4'}$=	$J_{4',5'}$ =	$J_{5',6'a}$=	$J_{5',6'b}$=	$J_{6'a,6'b}$	2.022
	3.4	6.4	4.0	4.0	2.75	7.0	12.6	8.8	9.4	10.0	10.0	2.4	4.9	=12.4	2.042
															2.048
9b	4.78(d)	5.50(dd)	5.94(t)	4.20(t)	5.13(m)	4.34(dd)	4.11(dd)	4.72(d)	5.20(dd)	5.01(dd)	5.36(t)	3.88(m)	4.29(q)	4.02(q)	1.987
	$J_{1,2}$=	$J_{2,3}$=	$J_{3,4}$=	$J_{4,5}$=	$J_{5,6a}$=	$J_{5,6b}$=	$J_{6a,6b}$=	$J_{1',2'}$=	$J_{2',3'}$=	$J_{3',4'}$=	$J_{4',5'}$ =	$J_{5',6'a}$=	$J_{5',6'b}$=	$J_{6'a,6'b}$	1.993
	4..40	4.7	4.7	4.7	3.38	6.60	12.4	8.24	10.4	3.3	3.3	6.60	6.60	=12.4	2.008
															2.037
															2.047
															2.056
10b	4.63(d)	5.39(dd)	5.83(dd)	4.04(dd)	5.15(m)	4.50(dd)	4.18(dd)	5.20(d)	4.90(dd)	5.34(t)	5.05(t)	4.18(m)	4.29(q)	4.02(q)	2.037
	$J_{1,2}$=	$J_{2,3}$=	$J_{3,4}$=	$J_{4,5}$=	$J_{5,6a}$=	$J_{5,6b}$=	$J_{6a,6b}$=	$J_{1',2'}$=	$J_{2',3'}$=	$J_{3',4'}$=	$J_{4',5'}$=	$J_{5',6'a}$=	$J_{5',6'b}$=	$J_{6'a,6'b}$	2.048
	5.80	2.80	3.10	3.60	3.90	6.70	12.3	3.67	10.4	10.4	10.1	4.27	2.1	=12.5	2.062
															2.089
															2.071
11b	4.48(d)	5.35(dd)	5.76(dd)	5.35(dd)	4.98(m)	3.83(dd)	3.49(dd)	4.42(d)	5.15(dd)	3.64(t)	4.94(t)	3.64(o)	4.24(dd)	4.08(dd)	1.985
	$J_{1,2}$=	$J_{2,3}$=	$J_{3,4}$=	$J_{4,5}$=	$J_{5,6a}$=	$J_{5,6b}$=	$J_{6a,6b}$=	$J_{1',2'}$=	$J_{2',3'}$=	$J_{3',4'}$=	$J_{4',5'}$=	$J_{5',6'a}$ =	$J_{5',6'b}$ =	$J_{6'a,6'b}$	1.990
	3.05	2.5	7.97	4.98	3.57	5.78	11.3	7.97	9.6	9.6	9.6	4.67	2.20	=11.4	2.013
															2.031
															2.039
															1.993
12b	4.49(d)	5.37(dd)	5.75(dd)	5.50(dd)	4.94(m)	3.57(dd)	3.50(dd)	5.46(d)	5.28(dd)	5.02(dd)	5.04(t)	4.06(m)	4.06	4.06	2.026
	$J_{1,2}$=	$J_{2,3}$=	$J_{3,4}$=	$J_{4,5}$=	$J_{5,6a}$=	$J_{5,6b}$=	$J_{6a,6b}$=	$J_{1',2'}$=	$J_{2',3'}$=	$J_{3',4'}$=	$J_{4',5'}$=	not	not	not	2.028
	2.75	8.25	2.20	8.52	9.68	3.03	12.0	3.30	9.9	3.30	3.30	resolved	resolved	resolved	2.041
															2.127
															2.132

Procedure A for monosaccharides; A mixture of the aldose (0.01 mol) and benzenethiol (0.022 mol) or 1,3-propanedithiol (0.011 mol) in 90% trifluoroacetic acid (3-5 mL) was warmed at 50-60 °C for 30-50 min with stirring, the reaction solution was then concentrated *in vacuo* to a crystalline residue, which was then recrystallized mostly from ethanol (ethyl acetate is better for D-lyxose and D-mannnose diphenyldithioacetal) to give the desired dithioacetals (**1-7**) in good yields. The yields and physical data (melting points and optical rotaions) are listed in Table 1.

Procedure B for both mono- and oligosaccharides: A mixture of aldose (0.01 mol) and benzenethiol (0.022 mol) or 1,3-propanedithiol (0.011 mol) in 90% trifluoroacetic acid (3-5 mL) was kept at room temperature with stirring for 12-15 h and the resulting homogeneous reaction solution was then concentrated *in vacuo* to a crystalline residue which was treated as above. In the case of oligosaccharides, the reaction was performed on a 1 mmol scale in 90% trifluoroacetic acid (3-5 mL), and the reaction solution was then carefully poured into ice-water containing sodium carbonate. The aqueous solution was extracted with 1-butanol, the organic layer was then washed with aqueous sodium carbonate and brine successively, and concentrated *in vacuo* to an amorphous or syrupy residue, which was subjected to flash chromatography by successive elution with toluene, ethyl acetate and acetone. From ethyl acetate/acetone (2/1) to acetone fractions was obtained a syrupy or amorphous residue, which was conventionally acetylated with pyridine-acetic anhydride and finally purified again with silica gel column chromatography by successive elution with toluene and ethyl acetate to give the corresponding dithioacetal peracetates (**8d-13b**) from toluene/ethyl acetate (1/1) in reasonable yields. The yields and physical data of the oligosaccahride diphenyldithioacetals are described below respectively.

Cellobiose Diphenyl Dithioacetal Octaacetate (8b). A portion (220 mg) of the syrupy cellobiose diphenyldithioacetal (**8a**, 76%) thus obtained was acetylated with acetic anhydride (3 mL) and pyridine (3 mL) to give the corresponding octaacetate (**8b**) after column chromatography: amorphous powder (72%); $[\alpha]_D^{27}$ +25.2° (*c* 0.33, acetone); FAB-MS *m/z*, 880(M^+), 771(M^+-SPh), 331, 169, 109; EI-MS *m/z*, 881(M^++H).

Anal. Calcd for $C_{40}H_{48}O_{18}S_2$: C, 54.45 ; H, 5.49. Found: C, 54.18 ; H, 5.77.

Lactose Diphenyl Dithioacetal Octaacetate (9b). A portion (250 mg) of the syrupy lactose diphenyl dithioacetal (**9a**, 76%) was acetylated with acetic anhydride (3 mL) and pyridine (3 mL) to give the corresponding octaacetate (**9b**) after column chromatography: amorphous powder (65%); $[\alpha]_D^{27}$ +5.9° (*c* 0.41, acetone); FAB-MS *m/z*, 880(M^+), 771(M^+-SPh), 331, 169, 109; EI-MS ; *m/z*, 881(M^++H)

Anal. Calcd for $C_{40}H_{48}O_{18}S_2$: C, 54.45; H. 5.49. Found: C,54.18 ; H,5.80.

Maltose Diphenyl Dithioacetal (10a): A portion (0.84 g) of amorphous powder(2.25 g,83%) obtaned from maltose (1.8 g,5 mmol) and benzenethiol (1.1 g, 10 mmol), was crystallized from acetonitrile to give pure crystals (0.43g): mp 177-178°C; $[\alpha]_D^{27}$ +40.3° (*c* 0.63, acetone); FAB-MS *m/z*, 567[M+Na]$^+$.

Anal. Calcd for $C_{24}H_{32}O_{10}S_2$: C, 52.92; H, 5.92. Found: C,52.72 ; H,6.20.

Maltose Diphenyl Dithioacetal Octaacetate(10b): A portion (250 mg) of **10b** was acetylated with acetic anhydride(3 mL) and pyridine(3 mL) to give the corresponding octaacetate (**10b**) after column chromatography: clear syrup (75%); $[\alpha]_D^{27}$ +41.2° (*c* 0.17, acetone); FAB-MS *m/z*: 880(M$^+$), 771(M$^+$-SPh), 331, 169, 109.

Anal. Calcd for $C_{40}H_{48}O_{18}S_2$: C, 54.45; H, 5.49. Found : C, 54.15 ; H, 5.77.

Gentibiose Diphenyl Dithioacetal Octaacetate (11b). A portion (220 mg) of the syrupy gentibiose diphenyldithioacetal (**8a**, 66% from acetone fraction) was acetylated with acetic anhydride (3 mL) and pyridine (3 mL) to give the corresponding octaacetate (**11b**) after column chromatography: amorphous powder (76%); $[\alpha]_D^{27}$ -24.9° (*c* 0.33, acetone).

Anal. Calcd for $C_{40}H_{48}O_{18}S_2$: C, 54.45; H, 5.49. Found: C, 54.18 ; H, 5.87.

Melibiose Diphenyl Dithioacetal Octaacetate (12b). A portion (230 mg) of the syrupy melibiose diphenyl dithioacetal (**12a**, 86%) was acetylated with acetic anhydride (3 mL) and pyridine (3 mL) to give the corresponding octaacetate (**12b**) after column chromatography: amorphous powder(72%); $[\alpha]_D^{27}$ +77.7° (*c* 0.53, acetone).

Anal. Calcd for $C_{40}H_{48}O_{18}S_2$: C, 54.45; H, 5.49. Found: C,54.21 ; H,5.83.

Maltotriose Diphenyl Dithioacetal (13a). A mixture of maltotriose (1.1 g, 2 mmol) and benzenethiol (0.45 g, 4 mmol) in 90% trifluoroacetic acid (10 mL) was stirred at room temperature for 20 min. and the resulting solution was kept for 15 h. After workup described above and column chromatography (acetone fractions), product was isolated as a hygroscopic powder (0.94 g, 67%); $[\alpha]_D^{27}$ +65.2° (*c* 0.50, acetone); FAB-MS *m/z*, 729[M+Na]$^+$.

Maltotriose Diphenyl Dithioacetal Undecaacetate (13b). A portion (240 mg) of the syrupy **13a** was acetylated with acetic anhydride (3 mL) and pyridine (3 mL) to give the corresponding undecaacetate (**13b**) after column chromatography (toluene/ethyl acetate: 2/1); amorphous powder (65%); $[\alpha]_D^{27}$ +76.7° (*c* 0.48, acetone); FAB-MS *m/z*, 1191[M+Na]$^+$. ^{1}H NMR (500MHz) δ 2.005, 2.009, 2.032, 2.057, 2.068, 2.078, 2.081, 2.104, 2.143 (33H, 11-$COCH_3$), 3.92(m, 1H, $J_{4',5'}$=10.2,

$J_{5",6"a}$=3.6, $J_{5",6"a}$ =3.3, H-5"), 3.93(dd, 1H, $J_{3',4'}$=10.0, $J_{4',5'}$=8.8, H-4'), 4.02(dd, 1H, $J_{3,4}$=6.87. $J_{4,5}$ =3.6, H-4), 4.04(dd, 1H, $J_{5',6'a}$=2.4, $J_{6'a,6'b}$=11.0, H-6'b), 4.04(m, 1H, $J_{4',5'}$=8.8, $J_{5',6'a}$=2.4, $J_{5',6'b}$ =2.2, H-5') 4.20(dd, 1H, $J_{5",6"a}$=3.3, $J_{6"a,6"b}$=12.3, H-6a), 4.21(dd,1H, $J_{5",6"b}$=3.3, $J_{6"a,6"b}$=12.2, H-6"b) , 4.25(dd,1H, $J_{5",6"a}$=3.3, H-6"a), 4.44(dd, 1H, $J_{5',6'a}$=2.4, H-6'a), 4.48(dd, 1H, $J_{5.6'a}$=3.85, $J_{6a,6b}$=12.3, H-6a), 4.65(d, 2.057, 1H, $J_{1,2}$=5.67, H-1) , 4.79(dd, 1H, $J_{1",2"}$=3.85, $J_{2",3"}$=9.0, H-2"), 5.07(t, 1H, $J_{2",3"}$=$J_{3",4"}$=10, H-3"), 5.08(d, 1H, $J_{1",2"}$=3.85, H-1"), 5.16(m, 1H, $J_{4,5}$=3.58, $J_{5,6a}$=3.85, $J_{5,6b}$=6.6, H-5), 5.36(t, 1H, $J_{3",4"}$=$J_{4",5"}$ =10, H-4"), 5.36(t, 1H, $J_{2',3'}$=$J_{3',4'}$=10, H-3'), 5.41(d, 1H, $J_{1',2'}$=4.13, H-1'),5.39 (dd,1H,$J_{2,3}$=3.0, H-2),5.82 (dd,1H, J3,4=6.87,H-3), 7.26,7.28(m,10H,Ph).

Anal. Calcd for $C_{52}H_{64}O_{26}S_2$: C, 53.42 ; H, 5.52. Found: C,53.23 ; H,5.83.

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8. The ^{1}H NMR spectrum of D-lyxose diphenyl dithioacetal 2,3,4,5-tetraacetate was in good accord with the reported spectrum (ref. 4).
9. Purification of free oligosaccharide diphenyldithioacetals except maltose diphenyl dithioacetal was unexpectedly difficult, because 1-butanol used for extraction could not completely be removed even *in vacuo* from the dithioacetals.