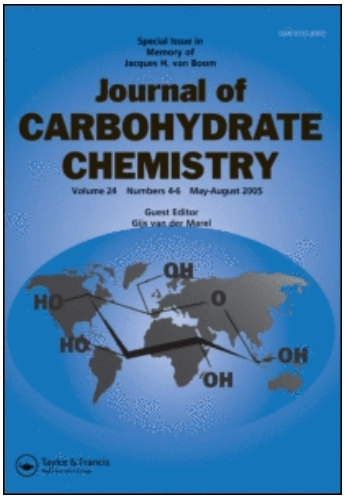

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Trimethylsilyl Triflate - Catalysid Acetal Formation Between Silylated Hexopyranosides and Methyl Pyruvate[1]

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TRIMETHYLSILYL TRIFLATE - CATALYSED ACETAL FORMATION BETWEEN SILYLATED HEXOPYRANOSIDES AND METHYL PYRUVATE[1]

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ABSTRACT

Trimethylsilyl ethers of 2,3-di-O-substituted glycopyranosides or their thioglycopyranoside analogues were reacted with methyl pyruvate in the presence of trimethylsilyl triflate to give pyruvylated hexopyranosides in yields of 60-75 %, and the ratio of the diastereoisomers was found to be ca. 1:1. The reaction can also be applied for cellobioside derivatives, providing suitable building blocks for the preparation of pyruvate-containing oligosaccharides.

INTRODUCTION

Many polysaccharides contain pyruvic acetal, linked as a cyclic acetal to a glycosyl residue. The occurence of such type of structures in agar, in which the pyruvic acetal is bonded to O-4 and O-6 of β-D-galactopyranosyl residues was published by Hirase.[2] In polysaccharides the hexopyranosyl building blocks are mainly pyruvylated at O-4 and O-6 as 4,6-O-acetals, but dioxolane-type acetals can also be formed between either cis-axial/equatorial,[3,4] or trans-diequatorial[5] hydroxyl groups. Most recently pyruvylated oligosaccharides have also been isolated from C-mycosidic glycopeptidolipide antigens of the Mycobacte-

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Dedicated to Professor Hildebert Wagner in celebration of his 60th birthday.

rium avium - Mycobacterium intracellulare - Mycobacterium scrofulaceum complex,[6] and from the glycolipids of Mycobacterium smegmatis[7] having the following structures:

A:[6] 4,6-O-(1'-carboxy)ethylidene-3-O-Me-β-D-Glcp-(1→3)-α-L-Rhap-(1→2)-6-deoxy-LTalp,

B:[7] 4,6-O-(1'-carboxy)ethylidene-3-O-Me-β-D-Glcp-(1→3)-4,6-O-(1'-carboxy)ethylidene-β-D-Glcp-(1→4)-β-D-Glcp-(1→6)-α-D-Glcp-(1→1)-α-D-Glcp,

C:[7] 3-O-Me-β-D-Glcp-(1→3)-4,6-O-(1'-carboxy)ethylidene-β-D-Glcp-(1→4)-β-D-Glcp-(1→6)-α-D-Glcp-(1→1)-α-D-Glcp,

D:[7] 4,6-O-(1'-carboxy)ethylidene-β-D-Glcp-(1→4)-β-D-Glcp-(1→6)-α-D-Glcp-(1→1)-α-D-Glcp.

These pyruvylated oligosaccharides are antigens of these bacteria, and their immunological properties may depend on the pyruvate content and on the absolute configuration of the acetals. Recent interest in mycobacteria arises from their occurence as opportunistic pathogens in many patients with acquired immunodeficiency syndrome (AIDS).[8-11]

To determine the absolute configuration of the pyruvate-containing natural products synthetic model compounds were used. Three papers[5,12,13] from two groups have dealt with the synthesis of pyruvate acetals using the following route: hexopyranosides were treated with 1-acetoxy-2-propanone and the isomers of the acetals formed were separated. These acetals were transformed into hydroxyisopropylidene derivatives by saponification. The methyleneoxy groups were oxidized with the platinium-oxygen system and the formed carboxyl groups were methylated with diazomethane. The yields are generally rather low; the highest published yield was 8 %, but in most cases it was below 1 %. This route provided suitable quantities of the desired compounds for spectroscopic measurements without satisfying preparative purposes. Our interest in synthesizing some oligosaccharides of mycobacteria antigens[14,15] prompted us to investigate the synthesis of the pyruvate acetals of carbohydrates in detail.

RESULTS AND DISCUSSION

Our efforts to condense methyl pyruvate with suitably protected carbohydrate diols in the presence of protic or Lewis acids failed; not even traces of condensation products could be detected. The acetal exchange reactions resulted only in mixed acetals,[16] and we were unable to force the ring closure and produce full acetals.

Recently the Yoshimura group[17,18] successfully synthesized glycosylideneglycoses, a type of spiro-cyclic orthoester compounds, by using aldonolactones and trimethylsilyl ethers of diols in the presence of trimethylsilyl triflate as the condensing agent. On the other hand, the 1-O-trimethylsilyl aldoses have been found to serve as glycosyl donors in various glycoside syntheses,[19-23] and these condensations liberate hexamethyldisiloxane instead of water.

On the basis of these observations we chose methyl 2,3-di-O-benzyl-4,6-bis-O-(trimethylsilyl)-α-D-glucopyranoside[18] and phenyl 2,3-di-O-benzyl-4,6-bis-O-(trimethylsilyl)-β-D-galactopyranoside (1) as diol components. Compound 1 was prepared by conventional silylation of phenyl 2,3-di-O-benzyl-β-D-galactopyranoside[24] using hexamethyldisilazane in dry dichloromethane in the presence of a catalytic amount of trifluoroacetic acid. The two disilylated compounds were treated with 2 equivalents of methyl pyruvate in dichloromethane solution in the presence of 0.1 equivalent of trimethylsilyl triflate. The reactions required 16-18 hours at room temperature, and the ratio of the isomers was nearly 1:1. The diastereoisomeric acetals /2(R); 2(S) and 3(R); 3(S)/ were separated by silica gel column chromatography.

These two reactions showed that the pyruvate acetal formation can be achieved by this method both in the gluco- and galacto-pyranoside series in the presence of benzyl protective groups. To get more insight into the compatibility of different blocking groups with this procedure, methyl 4,6-O-benzylidene-α-D-glucopyranoside[25] was benzoylated and the benzylidene group was removed from compound 4 to afford methyl 2,3-di-O-benzoyl-α-D-glucopyranoside (5). Compound 5 was silylated using the general procedure to obtain compound 6. Treatment of 6 with methyl pyruvate resulted in two diastereomeric isomers /7(R) and 7(S)/ which were separated by chromatography.

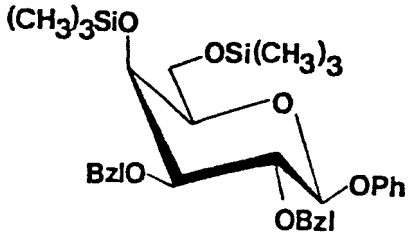
It was also interesting to explore whether this method could be applied in the case of thioglycosides since these compounds are sensitive against strong Lewis acids, and also whether the pyruvylated thioglycosides could serve as glycosyl donors in the synthesis of the target oligosaccharides. To answer these questions the following experiments were carried out. Methyl 4,6-O-benzylidene-1-thio-β-D-glucopyranoside[26] was benzoylated to yield methyl 2,3-di-O-benzoyl-4,6-O-benzylidene-1-thio-β-D-glucopyranoside (8). Acid hydrolysis of the benzylidene group resulted in the diol 9 and this was treated with hexamethyldisilazane to yield 10.

The acetal formation was conducted at -20 °C for 2 hours and the temperature was allowed to reach room temperature which was then maintained for 18 hours. Two isomers were formed in favour of the 11(S) isomer, but 11(R) could also be isolated in a yield of 20 %.

Additional target compounds were the pyruvate acetals of 3-O-methyl-D-glucose, being the terminal residues of the trisaccharide A and that of the pentasaccharide B. Using the Schneider procedure[27,28] 2,4,6-tri-O-acetyl-3-O-methyl-α-D-glucopyranosyl bromide[29] was converted into methyl 2,4,6-tri-O-acetyl-3-O-methyl-1-thio-β-D-glucopyranoside (12). Conventional Zemplén[30] deacetylation resulted in 94 % mono-O-acetyl derivative, which was proved to be methyl 2-O-acetyl-3-O-methyl-1-thio-β-D-glucopyranoside (13). Our first observation[31] that the C-2 O-acyl groups of 3-O-substituted galactopyranoside derivatives can not be removed by catalytic amount of $NaOCH_3$ was found to be a common feature for 3-O-substituted hexopyranosides.[32-36] However, upon forced conditions methyl 3-O-methyl-1-thio-β-D-glucopyranoside (14) was obtained.

Compound 13 was silylated and 15 was obtained in excellent yield. A similar treatment of 15, as described for 10, resulted in two isomeric compounds; the major product was proved to be the S-isomer /16(S)/ and the minor component was 16(R).

In the tetrasaccharides C and D pyruvylated cellobiosyl units are present. For this reason the pyruvylation reaction of methyl 1-thio-β-cellobioside[37] was studied by treatment with 2,2-dimethoxy propane and the formed mono-isopropylidene derivative was directly benzoylated and methyl 2,3,6,2',3'-penta-O-benzoyl-4',6'-O-iso-



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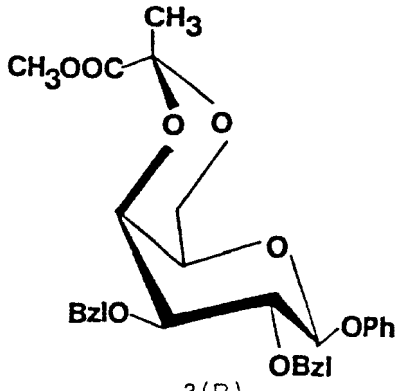
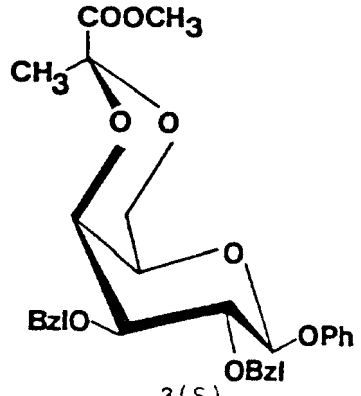
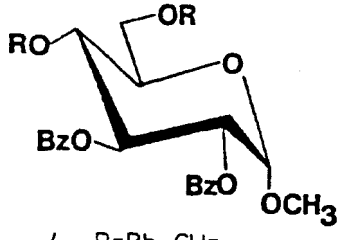


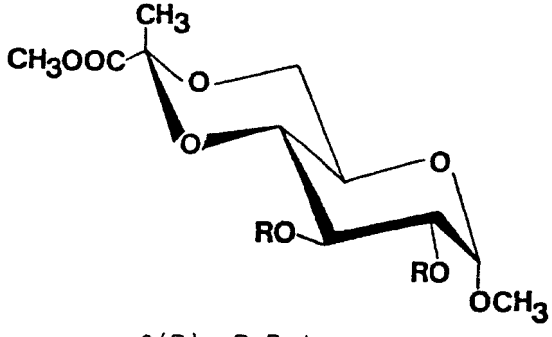
3(R)



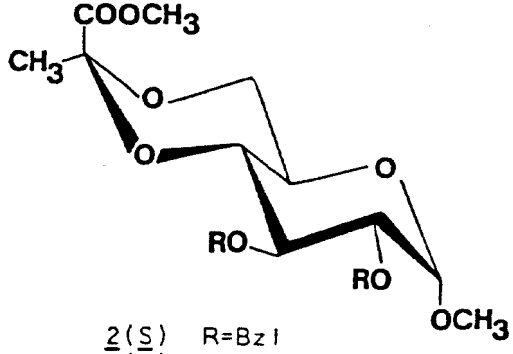
3(S)



4 R=Ph-CH=
5 R=H
6 R=Si(CH3)3

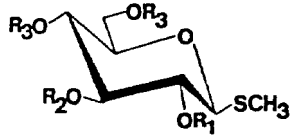


2(R) R=Bzl
7(R) R=Bz



2(S) R=Bzl
7(S) R=Bz

SCHEME 1.



8 R_1=R_2=Bz; R_3= Ph-CH=

9 R_1=R_2=Bz; R_3=H

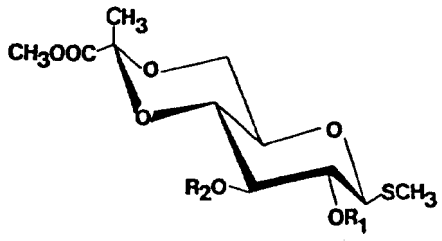
10 R_1=R_2=Bz; R_3=$Si(CH_3)_3$

12 R_1=R_3=Ac; R_2=CH_3

13 R_1=Ac; R_2=CH_3; R_3=H

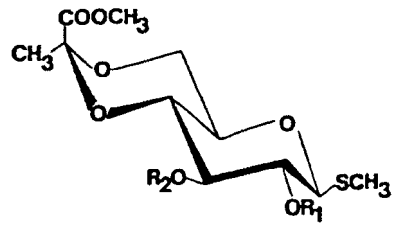
14 R_1=R_3=H; R_2=CH_3

15 R_1=Ac; R_2=CH_3; R_3=$Si(CH_3)_3$



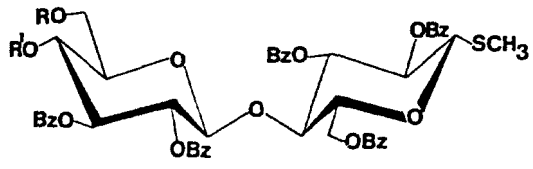
11(R) R_1=R_2=Bz

16(R) R_1=Ac; R_2=CH_3



11(S)

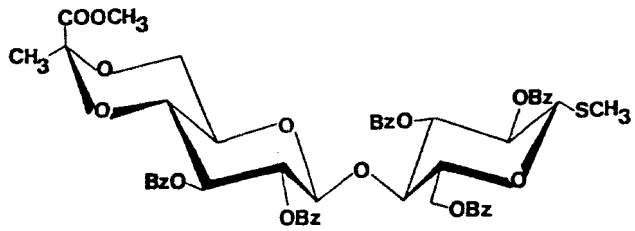
16(S)



17 R R'=CMe_2

18 R=R'=H

19 R=R'=$SiMe_3$



20(S)

SCHEME 2.

TABLE. ^{13}C NMR Data of the Pyruvate Acetals[a]

	C-1	C-2	C-3	C-4	C-5	C-6	C_a	CH_3	C=O	O=C-OCH_3	OCH_3/SCH_3
2(R)	99.35	79.04	78.38	74.70	62.68	63.24	97.78	17.79	168.78	52.72	55.26
2(S)	99.29	78.91	78.57	78.28	61.74	65.58	99.00	25.50	170.26	52.53	55.31
7(R)	97.87	69.52	72.57	71.66	62.05	63.19	98.16	18.11	168.35	52.59	55.38
7(S)	97.79	69.47	72.35	75.26	62.00	65.35	99.30	25.09	169.86	52.37	55.40
3(R)	102.53	78.82	78.25	68.82	65.74	65.49	93.10	25.92	168.31	52.31	-
3(S)	102.22	79.38	78.47	67.48	66.78	64.87	97.28	23.03	169.90	52.27	-
11(R)	83.99	70.41	71.84	71.09	73.20	63.15	98.21	18.65	168.46	52.79	11.65
11(S)	83.91	70.21	70.57	74.77	73.19	65.01	99.32	25.12	169.80	52.60	11.51
16(R)	83.76	70.61	81.79	73.42	71.40	63.03	97.91	18.44	168.30	52.65	11.15
16(S)	83.63	70.30	81.32	76.58	70.01	64.89	98.95	25.30	169.88	52.57	11.06
20(S)[b]	101.80	72.04	69.84	74.30	72.51	64.14	99.08	25.01	169.43	52.50	-

a. in $CDCl_3$.
b. Data of the nonreducing end.

propylidene-1-thio-β-cellobioside (17) was isolated and characterized. Hydrolysis of the isopropylidene group of 17 gave 18 which was silylated to obtain 19. Compound 19 was treated with methyl pyruvate at -20 °C and later on at room temperature. In the kinetic phase of the reaction both isomers were formed in a similar ratio, but after complete conversion the amount of the S-isomer /20(S)/ increased to 90 % and only this isomer was isolated.

In all pyruvylated thioglycosides participating groups are present so they are suitable glycosyl donors for the preparation of 1,2-trans-glycosides. These results will be published separately.[38]

The configuration of the newly formed acetalic chiral centers was assigned on the basis of the ^{13}C NMR chemical shift values of methyl groups. It was shown earlier that the ^{13}C NMR chemical shift value of the methyl group in the 4,6-O-isopropylidene-,[39] 4,6-O-(1'-methyl)-benzylidene-[40] or 4,6-O-(1'-carboxymethyl)ethylidene[5,12,13] derivatives of hexopyranosides is strongly dependent on the steric arrangement. The axial methyl groups resonate at higher magnetic field than the equatorial ones, and the difference may be as high as 10 ppm. The occurence of the high field resonance can be rationalized on the basis of the general gauche effect.[41] As a consequence of the gauche effect, the C-6 and C-4 of all R-isomers also resonated at high field, thus the acetalysation shifts ($\Delta\delta = \delta_{C-4}$ or δ_{C-6} of acetals- δ_{C-4} or δ_{C-6} of diols) have very low values. The chemical shift values of acetalic carbons are also characteristic; these carbons of the R-isomers resonated at higher magnetic field, and the difference is nearly 1 ppm. In the case of the galactopyranoside derivatives the ^{13}C NMR shift values are reversed. The complete ^{13}C NMR spectroscopic assignments are given in the Table.

It is also to be noted that the chromatographic mobilities are also characteristic for the isomers; in the gluco-series the S-isomers are the faster moving compounds.

EXPERIMENTAL

Melting points were determined on a Kofler apparatus and are uncorrected. Optical rotations were determined with a Perkin-Elmer 241

polarimeter. NMR spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Bruker WP-200 spectrometer at room temperature. TLC was performed on Kieselgel 60 F_{254} (Merck) with detection by charring with sulphuric acid. Short-column chromatography was effected on Kieselgel G (Reanal) adsorbent.

Methyl 2,3-Di-O-benzoyl-4,6-O-benzylidene-α-D-glucopyranoside (4). A solution of methyl 4,6-O-benzylidene-α-D-glucopyranoside (2.82 g, 1 mmol) in abs pyridine (10 mL) was treated with benzoyl chloride (4.2 g, 3 mmol) at 0 °C for 24 h. The reaction mixture was poured onto crushed ice (100 g) and the precipitated solid was washed with cold water. The crude product was crystallized from ethanol (95 mL) to give 4 (4.20 g, 85.6%), mp 156-157 °C, $[\alpha]_D$ +85.9° (c 0.7 chloroform), R_f 0.52 (dichloromethane-acetone, 95:5).

Anal. Calcd for $C_{28}H_{26}O_8$: C, 68.56; H, 5.34. Found: C, 68.65; H, 5.40.

Methyl 2,3-Di-O-benzoyl-α-D-glucopyranoside (5). Compound 4 (2.5 g) was dissolved in dichloromethane (25 mL) and treated with trifluoroacetic acid (2.5 mL) in the presence of water (0.05 mL) at room temperature. After 3 min complete hydrolysis occurred and the reaction mixture was diluted with dichloromethane (75 mL), washed with saturated $NaHCO_3$ solution and with water to neutral. The solution was dried (Na_2SO_4) and concentrated to give syrupy 5 (1.96 g, 95.5%), $[\alpha]_D$ +142.6° (c 0.57, chloroform), R_f 0.27 (dichloromethane-acetone, 9:1). ^{13}C NMR ($CDCl_3$): δ 97.03 (C-1), 71.75 (C-2), 73.78 (C-3), 69.38 (C-4), 71.41 (C-5), 61.72 (C-6), 55.26 (O-CH_3), 166.96 and 165.97 (2 CO).

Anal. Calcd for $C_{21}H_{22}O_8$: C, 62.67; H, 5.51. Found: C, 62.86; H, 5.60.

Methyl 2,3-Di-O-benzoyl-4,6-O-benzylidene-1-thio-β-D-glucopyranoside (8). Methyl 4,6-O-benzylidene-1-thio-β-D-glucopyranoside (1.49 g, 0.5 mmol) was benzoylated in abs pyridine (10 mL) with benzoyl chloride (2.31 g, 1.66 mmol) as described for compound 4. The crystalline crude product was recrystallized from ethanol to give 8 (1.80 g, 71.2%) mp 170 °C, $[\alpha]_D$ +17.3° (c 0.7863, chloroform), R_f 0.68 (n-hexane-ethyl acetate, 6:4).

Anal. Calcd for $C_{28}H_{26}O_7S$: C, 66.38; H, 5.17; S, 6.32. Found: C, 66.45; H, 5.21; S, 6.39.

Methyl 2,3-Di-O-benzoyl-1-thio-β-D-glucopyranoside (9). Compound 8 (1.8 g) was dissolved in dichloromethane (20 mL) and hydrolyzed with trifluoroacetic acid (2 mL) in the presence of water (0.04 mL) for 10 min, and worked-up as described in the case of compound 5. The syrupy compound 9 (1.46 g, 98.1%) proved to be homogenous. $[\alpha]_D$ +59.5° (c 0.40, chloroform), R_f 0.50 (dichloromethane-acetone, 8:2).

Anal. Calcd for $C_{21}H_{22}O_7S$: C, 60.27; H, 5.30; S, 7.66. Found: C, 60.39; H, 5.39; S, 7.70.

Methyl 2,4,6-Tri-O-acetyl-3-O-methyl-1-thio-β-D-glucopyranoside (12). 2,4,6-Tri-O-acetyl-3-O-methyl-α-D-glucopyranosyl bromide (7.0 g) 1.83 mmol) and 4.45 g of thiourea in 50 mL dry acetone were heated 60 min at the boiling point. The reaction mixture was concentrated and the solid residue was dissolved in dichloromethane (100 mL) and water (100 mL). The well stirred solution was treated with sodium carbonate (6.36 g) and sodium sulphite (3.57 g) for 1 h at room temperature. The organic layer was separated, dried and treated with iodomethane (4.3 mL) in the presence of triethylamine (5.8 mL) at room temperature. After 1 h the solution was washed with water, dried ($MgSO_4$), filtered, and concentrated to give 12 (4.05 g, 63.7%), mp 66 °C (from ether-n-hexane), $[\alpha]_D$ -7.9° (c 1.4, chloroform); ^{13}C NMR ($CDCl_3$): δ 83.01 (C-1), 70.17 (C-2), 82.73 (C-3), 69.32 (C-4), 76.17 (C-5), 62.42 (C-6), 11.04 ($S-CH_3$), 59.16 ($O-CH_3$).

Anal. Calcd for $C_{14}H_{22}O_8S$: C, 47.98; H, 6.32; S, 9.15. Found: C, 48.10; H, 6.28; S, 9.10.

Methyl 2-O-Acetyl-3-O-methyl-1-thio-β-D-glucopyranoside (13). To a solution of 12 (3.82 g) in dry methanol (30 mL) was added sodium methoxide (3 mg). After 24 h at room temperature, the mixture was neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. The crystalline residue (2.9 g) was recrystallised from ethyl acetate (5 mL) and cyclohexane (20 mL) mixture, to yield 13 (2.84 g, 97.8%), mp 100 °C, $[\alpha]_D$ -25.3° (c 0.9, chloroform), R_f 0.44 (dichloromethane-acetone, 7:3). ^1H NMR ($CDCl_3$): δ 4.88 (dd, 1H, $J_{1,2}$ = 9.8 Hz, $J_{2,3}$ = 9.1 Hz, H-2), 4.25 (d, 1H, H-1), 3.49 (s, 3H, CH_3-O), 2.12 (s, 3H, CH_3-S), 2.08 (s, 3H, AcO-2).

Anal. Calcd for $C_{10}H_{18}O_6S$: C, 45.09; H, 6.81; S, 12.03. Found: C, 45.12; H, 6.88; S, 12.10.

Methyl 3-O-Methyl-1-thio-β-D-glucopyranoside (14). Compound 12 (300 mg) in dry methanol (5 mL) was treated with sodium methoxide (40 mg). After 24 h at room temperature the solution was heated to 50 °C for 1 h. The usual workup resulted in a solid residue which was recrystallised from ethyl acetate (6 mL) to give 14 (185 mg, 96.3%), mp 138-139 °C, $[\alpha]_D$ -38.8 (c 0.7 methanol), R_f 0.35 (dichloromethane-methanol, 9:1).

Anal. Calcd for $C_8H_{16}O_5S$: C, 42.84; H, 7.19; S, 14.29. Found: C, 42.91; H, 7.22; S, 14.23.

Methyl 2,3,6,2',3'-Penta-O-benzoyl-4',6'-O-isopropylidene-1-thio-β-cellobioside (17). Methyl 1-thio-β-cellobioside (2.3 g) was suspended in 2,2-dimethoxypropane (15 mL) in the presence of toluene-p-sulphonic acid (250 mg) and stirred for 1 h. After 20 min complete dissolution occurred and the starting compound disappeared. The reaction mixture was diluted with dry pyridine (50 mL), cooled in ice bath and treated with benzoyl chloride (5.2 g) for 24 h. The reaction mixture was poured into ice-water (200 g) and the precipitated syrup was dissolved in dichloromethane (200 mL), washed with 1M H_2SO_4 (3x50 mL), with saturated $NaHCO_3$ solution (5x100 mL) and with water (3x100 mL), dried ($MgSO_4$) and evaporated to the syrupy 17. The crude product was purified by column chromatography to give glassy 17 (4.8 g, 84.7%), $[\alpha]_D$ +62.8° (c 1.2, chloroform), R_f 0.67 (dichloromethane-acetone, 95:5). ^1H NMR ($CDCl_3$): δ 2.11 (s, 3H, S-CH_3), 1.61 and 1.38 (2s, 6H, 2 CH_3).

Anal. Calcd for $C_{51}H_{48}O_{15}S$: C, 65.65; H, 5.18; S, 3.43. Found: C, 66.00; H, 5.28; S, 3.40.

Methyl 2,3,6,2',3'-Penta-O-benzoyl-1-thio-β-cellobioside (18). Compound 17 (1.75 g) was dissolved in dichloromethane (10 mL) and treated with trifluoroacetic acid (1 mL) in the presence of water (0.02 ml) for 15 min at room temperature. Workup procedure was followed as described for compound 5 to give syrupy 18 (1.15 g, 68.6%), $[\alpha]_D$ +77.7° (c 1.1, chloroform), R_f 0.73 (dichloromethane-acetone, 85:15).

Anal. Calcd for $C_{48}H_{44}O_{15}S$: C, 64.56; H, 4.96; S, 3.59. Found: C, 64.60; H, 5.06; S, 3.65.

Trimethylsilylation of diols: To a solution of diol (2 mmol) and hexamethyldisilazane (16 mmol) in dichloromethane (3 mL) were added one drop of trifluoroacetic acid at 0 °C, and the mixture was stirred

overnight at room temperature. After the reaction was complete, the mixture was concentrated. Purification of the residue was achieved by crystallization or by column chromatography.

Phenyl 2,3-Di-O-benzyl-4,6-bis-O-(trimethylsilyl)-β-D-galacto-pyranoside (1). Yield: 78%, mp 86-88 °C (from n-hexane), $[\alpha]_D$ -16.25° (c 1.6, chloroform). ^{13}C NMR ($CDCl_3$): δ 101.59 (C-1), 82.21 (C-2), 84.59 (C-3), 70.84 (C-4), 76.61 (C-5), 61.99 (C-6), 75.37 and 74.92 ($2xCH_2$-Ph), 0.49 (Me_3Si).

Anal. Calcd for $C_{32}H_{44}O_6Si_2$: C, 66.17; H, 7.63. Found: C, 66.08; H, 7.59.

Methyl 2,3-Di-O-benzoyl-4,6-bis-O-(trimethylsilyl)-α-D-gluco-pyranoside (6). Yield: 82%, mp 76-78 °C (from n-hexane), $[\alpha]_D$ 126.9° (c 0.36, chloroform), R_f 0.86 (dichloromethane-ethyl acetate, 95:5). ^{13}C NMR ($CDCl_3$): δ 96.90 (C-1), 69.39 (C-2), 72.34 (C-3), 72.24 (C-4), 73.78 (C-5), 61.35 (C-6), 55.26 (MeO-1), 0.165 and -0.36 ($2Me_3Si$).

Anal. Calcd for $C_{27}H_{38}O_8Si_2$: C, 59.31; H, 7.00. Found: C, 59.40; H, 7.06.

Methyl 2,3-Di-O-benzoyl-1-thio-4,6-bis-O-(trimethylsilyl)-β-D-glucopyranoside (10). Yield: 78%, mp 58-60 °C (from n-hexane), $[\alpha]_D$ +69.6° (c 0.32, chloroform), R_f 0.67 (dichloromethane-ethyl acetate, 95:5).

Anal. Calcd for $C_{27}H_{38}O_7SSi_2$: C, 57.62; H, 6.80; S, 5.69. Found: C, 57.70; H, 6.91; S, 5.75.

Methyl 2-O-Acetyl-3-O-methyl-1-thio-4,6-bis-O-(trimethylsilyl)-β-D-glucopyranoside (15). Yield: 91.8%, syrup, $[\alpha]_D$ -34.26° (c 1.8, chloroform), R_f 0.65 (dichloromethane-acetone, 98:2). ^{13}C NMR ($CDCl_3$): δ 83.06 (C-1), 70.54 (C-2), 86.09 (C-3), 80.78 (C-4), 71.46 (C-5), 61.81 (C-6), 169.39 (C=O), 60.65 (O-CH_3), 20.85 (CH_3-CO), 11.18 (S-CH_3), 0.26 ($Si(CH_3)_3$).

Anal. Calcd for $C_{16}H_{34}O_6SSi_2$: C, 46.79; H, 8.34; S, 7.81. Found: C, 47.00; H, 8.39; S, 7.90.

Methyl 2,3,6,2',3'-Penta-O-benzoyl-1-thio-4',6'-bis-O-(trimethyl-silyl)-β-cellobioside (19). Yield: 89%, foam, $[\alpha]_D$ +70.4° (c 1.2, chloroform), R_f 0.62 (n-hexane-ethyl acetate, 6:4).

Anal. Calcd for $C_{54}H_{62}O_{15}S\,Si_2$: C, 62.40; H, 6.01; S, 3.08. Found: C, 62.60; H, 6.06; S, 3.00.

Reaction of trimethylsilylated diols with methyl pyruvate:

Trimethylsilylated diols (1 mmol) were dissolved in dry dichloromethane (5 mL) and were treated with methyl pyruvate (2 mmol). The catalyst, trimethylsilyl triflate (0.1 mmol), was added to the reaction mixture at room temperature (in the case of the O-glycosides) or at -20 °C using thioglycoside derivatives. After 2 h the temperature was allowed to reach room temperature for 18-24 h. The reaction mixture was diluted with dichloromethane (50 mL) and immediately neutralized with saturated $NaHCO_3$ solution. The organic layer was washed with water, dried, concentrated and the isomers were separated by silica gel column chromatography.

Methyl 2,3-di-O-benzyl-4,6-O-(1'-methoxycarbonyl)ethylidene-α-D-glucopyranoside /2(R) and 2(S)/. 2(R): Yield: 27.1%, mp 104-106 °C (from cyclohexane), $[\alpha]_D$ -7.84° (c 0.6, chloroform), R_f 0.50 (n-hexane-ethyl acetate, 6:4).

Anal. Calcd for $C_{25}H_{30}O_8$: C, 65.48; H, 6.59. Found: C, 65.52; H, 6.62.

2(S). Yield: 32.8%, mp 104-106 °C (from cyclo hexane), $[\alpha]_D$ +43.4° (c 1.0, chloroform), R_f 0.70 (n-hexane-ethyl acetate, 6:4).

Anal. Found: C, 65.56; H, 6.54.

Phenyl 2,3-Di-O-benzyl-4,6-O-(1'-methoxycarbonyl)ethylidene-β-D-galactopyranoside /3(R) and 3(S)/. 3(R): Yield: 28%, amorphous powder, $[\alpha]_D$ -33.1° (c 1.5, chloroform), R_f 0.61 (dichloromethane-ethyl acetate, 93:7).

Anal. Calcd for $C_{30}H_{32}O_8$: C, 69.21; H, 6.19. Found: C, 69.40; H, 6.24.

3(S): Yield: 31.6%, foam, $[\alpha]_D$ -7.7° (c 1.4, chloroform), R_f 0.68 (dichloromethane-ethyl acetate, 93:7).

Anal. Found: C, 69.35; H, 6.30.

Methyl 2,3-Di-O-benzoyl-4,6-O-(1'-methoxycarbonyl)ethylidene-α-D-glucopyranoside /7(R) and 7(S)/. 7(R): Yield: 20.5%, mp 117 °C, $[\alpha]_D$ +88.3° (c 0.9, chloroform), R_f 0.17 (n-hexane-ethyl acetate, 65:35).

Anal. Calcd for $C_{25}H_{26}O_{10}$: C, 61.72; H, 5.38. Found: C, 61.91; H, 5.45.

7(S): Yield: 48%, syrup, $[\alpha]_D$ +124.4° (c 0.8 chloroform), R_f 0.24 (n-hexane-ethyl acetate, 65:35).

Anal. Found: C, 61.47; H, 5.39.

Methyl 2,3-Di-O-benzoyl-4,6-O-(1'-methoxycarbonyl)ethylidene-1-thio-β-D-glucopyranoside /11(R) and 11(S)/. 11(R): Yield: 19%, syrup, $[\alpha]_D$ +75° (c 0.7, chloroform), R_f 0.34 (n-hexane-ethyl acetate, 65:35).

Anal. Calcd for $C_{25}H_{26}O_9S$: C, 59.75; H, 5.21; S, 6.38. Found: C, 60.01; H, 5.26; S, 6.42.

11(S): Yield: 28.9%, syrup, $[\alpha]_D$ +23.9° (c 0.8, chloroform), R_f 0.52 (n-hexane-ethyl acetate, 65:35).

Anal. Found: C, 59.92; H, 5.19; S, 6.46.

Methyl 2-O-Acetyl-4,6-O-(1'-methoxycarbonyl)ethylidene-3-O-methyl-1-thio-β-D-glucopyranoside /16(R) and 16(S)/. 16(R): Yield: 35.1%, foam, $[\alpha]_D$ +31.6° (c 1.4, chloroform), R_f 0.54 (n-hexane-ethyl acetate, 7:3).

Anal. Calcd for $C_{14}H_{22}O_8S$: C, 47.99; H, 6.32; S, 9.15. Found: C, 48.10; H, 6.40; S, 9.26.

16(S): Yield: 40.3%, foam, $[\alpha]_D$ +81.6° (c 1.2, chloroform), R_f 0.62 (n-hexane-ethyl acetate, 7:3).

Anal. Found: C, 48.02; H, 6.31; S, 9.18.

Methyl 2,3,6,2',3'-Penta-O-benzoyl-4',6'-O-(1'-methoxycarbonyl)-ethylidene-1-thio- -cellobioside /20(S)/. Yield: 35.2%, solid powder, $[\alpha]_D$ +59.35° (c 1.4, chloroform), R_f 0.61 (n-hexane-ethyl acetate, 6:4).

Anal. Calcd for $C_{52}H_{48}O_{17}S$: C, 63.92; H, 4.95; S, 3.28. Found: C, 64.08; H, 5.03; S, 3.31.

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