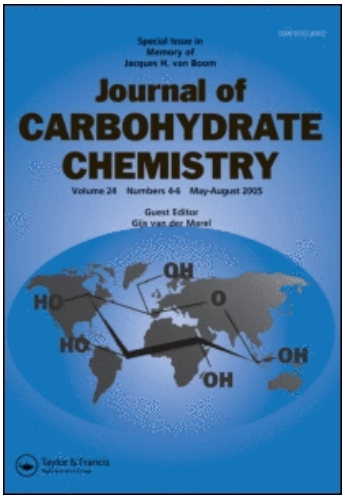

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Synthesis of 1-*O*-(Methylthio)thiocarbonyl Sugar Derivatives Bearing Acyl Protective Groups Using Phase Transfer Catalysis Methods

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SYNTHESIS OF 1-*O*-(METHYLTHIO)THIOCARBONYL SUGAR DERIVATIVES BEARING ACYL PROTECTIVE GROUPS USING PHASE TRANSFER CATALYSIS METHODS

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ABSTRACT

2,3,4,6-Tetra-*O*-acetyl-D-glucopyranose (**1**) was successfully transformed to an anomeric mixture of 2,3,4,6-tetra-*O*-acetyl-1-*O*-(methylthio)thiocarbonyl-D-glucopyranose (**2**) by liquid - liquid and solid - liquid phase transfer methods. Similar anomeric free sugar derivatives bearing acetyl or benzoyl protective groups were also smoothly converted to the corresponding 1-*O*-(methylthio)thiocarbonyl derivatives. Thermal rearrangement of 1-*O*-(methylthio)thiocarbonylfuranose derivatives proceeded well to give 1-*S*-methylthiocarbonyl-1-thiofuranose derivatives.

INTRODUCTION

Synthetic utility of non-anomeric *O*-(methylthio)thiocarbonyl sugar derivatives is widely recognized through the syntheses of deoxy sugars,[1-5] branched chain sugars,[6,7] unsaturated sugars,[8,9] thiosugars,[10,11] halogeno-sugars[12] and deoxydeuterio sugars.[13] Anomeric *O*-(methylthio)thiocarbonyl sugar derivatives are expected to have potential utility for organic transformations of sugar derivatives. Pougny has shown that anomeric *O*-(methylthio)thiocarbonyl sugars effectively gave glycosides and disaccharides by the treatment with alcohols or sugars in the presence of boron trifluoride diethyl etherate.[14]

There are, however, only three anomeric *O*-(methylthio)thiocarbonyl sugar derivatives in the literature, that is, 2,3:5,6-di-*O*-isopropylidene-1-*O*-(methylthio)thiocarbonyl-α-D-mannofuranose,[15-17] 2,3,4,6-tetra-*O*-benzyl-1-*O*-(methylthio)thiocarbonyl-α-D-glucopyranose[14,15] and -galactopyranose.[14] These three compounds and almost all of the known non-anomeric *O*-(methylthio)thiocarbonyl sugar derivatives contain only base insensitive protective groups such as isopropylidene and benzyl groups.[18] They can be synthesized using simple and inexpensive preparative methods by treatment of the corresponding sugar derivatives bearing one or two free hydroxyl groups with strong base and carbon disulfide, and then with iodomethane. In the case of sugar derivatives with base sensitive protective groups, however, an *O*-imidazolylthiocarbonyl or *O*-(phenyloxy)thiocarbonyl group is recommended and was used in the place of the *O*-(methylthio)thiocarbonyl group for the similar synthetic purposes.[4,6,19-21]

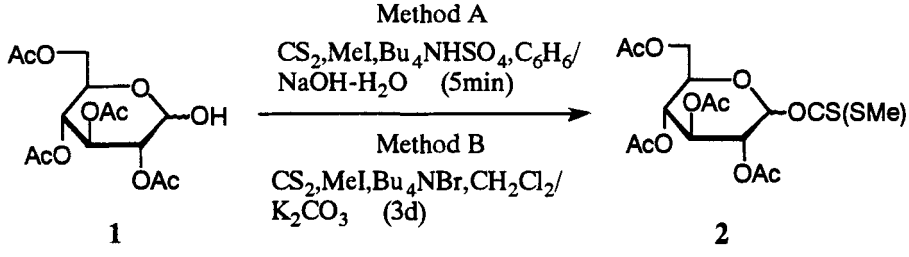
In the course of our synthetic investigation on *C*-glycosyl compounds, 2,3,4,6-tetra-*O*-acetyl-1-*O*-(methylthio)thiocarbonyl-D-glucopyranose (**2**)[22] and 5-*O*-benzoyl-2,3-*O*-isopropylidene-1-*O*-(methylthio)thiocarbonyl-D-ribofuranose (**4**)[23] or their equivalents were needed. Both the attempted *O*-imidazolylthiocarbonylation and *O*-(phenyloxy)thiocarbonylation of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**1**) gave complex mixtures and the desired products could not be isolated.[24] Phase transfer catalyzed reactions using aqueous basic media are well known to proceed effectively even if the substrates have base sensitive substituents.[25] Thus we next examined the liquid - liquid two phase method similar to that of Di Cesare and Gross[15] and also a solid - liquid two phase method,[26] and were able to obtain the desired 1-*O*-(methylthio)thiocarbonyl derivative in good yield. In the present paper we describe in detail the synthesis of a new class of 1-*O*-(methylthio)thiocarbonyl sugar derivatives bearing acetyl or benzoyl protective groups using phase transfer catalysis methods.

RESULTS AND DISCUSSION

According to the method of Di Cesare and Gross,[15] designated here as method A, 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**1**)[27] was converted to an anomeric mixture of 2,3,4,6-tetra-*O*-acetyl-1-*O*-(methylthio)thiocarbonyl-D-glucopyranose (**2**) (α/β = 1:3) in 64% yield. Similar treatment of 5-*O*-benzoyl-2,3-*O*-isopropylidene-D-ribofuranose (**3**)[28] gave 5-*O*-benzoyl-2,3-*O*-isopropylidene-1-*O*-(methylthio)thiocarbonyl-α- and -β-D-ribofuranose (**4α** and **4β**) in 67 % and 13 % yields. However, in the case of 2,3,5-tri-*O*-benzoyl-D-ribofuranose (**5**),[27] the resulting reaction mixture turned yellow, TLC examination of which suggested formation of a complex mixture. Consequently, chromatographic separation of the mixture was abandoned. Moreover, the reaction of 2,3,5-

tri-*O*-acetyl-D-ribofuranose (**6**)[27] gave a deep yellow and more complex mixture, which produced a mercaptan-like odor. In the reaction of **3**, trace amounts of a crude by-product were also obtained besides the desired products **4α** and **4β**. The structure of the by-product was assumed to be 2,3-*O*-isopropylidene-1,5-di-*O*-(methylthio)thiocarbonyl-D-ribofuranose from its ^{1}H NMR spectrum,[29] suggesting the debenzoylation of **3**, **4α** or **4β** in the course of the reaction. In addition, all the 1-*O*-(methylthio)thiocarbonylfuranose derivatives obtained in the present work tend to decompose during silica gel column chromatography and during storage for a few weeks at room temperature. These observations suggest that in the case of more base labile derivatives such as **5** and **6**, deacylation of the starting material and/or of the corresponding product and decomposition of the corresponding product probably occurs in the course of the reaction.

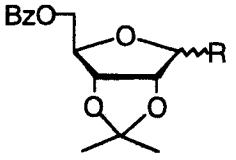
Then we attempted to utilize a solid - liquid two phase method for the 1-*O*-(methylthio)thiocarbonylation of **1**. Mixtures of **1**, carbon disulfide, iodomethane, solvent such as dichloromethane, benzene and tetrahydrofuran, phase transfer catalyst such as tetrabutylammonium bromide or tetrabutylammonium hydrogen sulphate, and a solid base such as potassium carbonate or lithium carbonate were stirred at room temperature for 40 h. TLC examinations of the time-course of each reaction revealed that dichloromethane was the most suitable solvent, tetrabutylammonium bromide the more effective phase transfer catalyst, and potassium carbonate the more effective base.



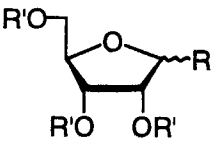
1 **2**

A mixture of **1**, carbon disulfide, iodomethane, tetrabutylammonium bromide, potassium carbonate and dichloromethane was vigorously stirred at ambient temperature for three days (designated as method B). Although the reaction needed a long reaction time, it gave a clear colourless reaction mixture, thin-layer chromatography of which indicated no formation of by-products or decomposed materials; the chromatogram had only one spot (α- and β-isomers have nearly the same Rf values). The desired product **2** was obtained in high yield (85%; α/β = 1.6:1). In the similar reaction of **3**, only the α-anomer of the desired product **4α** was obtained (86% yield). Anomerization of **2β** to **2α** was confirmed by a treatment of a mixture of **2α** and **2β** (α/β = 1:2.4) under the same conditions as method B for three days giving a mixture of **2α** and **2β** (α/β = 1:1.2).[30]

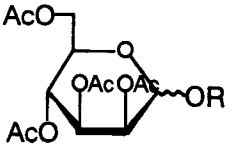
Thus the α-anomeric selectivity of these reactions compared with the above method A probably arose from the long reaction time enabling the reaction to equilibrate to some extent. In the reaction of **5**, a large amount of unreacted starting material **5** (about 45%) remained and 2,3,5-tri-*O*-benzoyl-1-*S*-methylthiocarbonyl-1-thio-β-D-ribofuranose(**7**) (about 30%), which was considered to arise from rearrangement of the initially formed 1-*O*-(methylthio)thiocarbonyl derivatives, was formed after a reaction time of 3 d. Longer reaction time (7d) gave only **7** in 58% yield. The structure of **7** was determined from



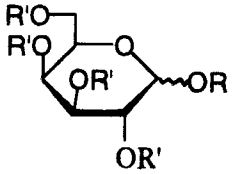
3 : R = OH
4 : R = OCS(SMe)
24 : R = SCO(SMe)



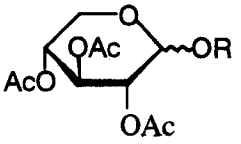
5 : R' = Bz, R = OH
6 : R' = Ac, R = OH
7 : R' = Bz, R = SCO(SMe)



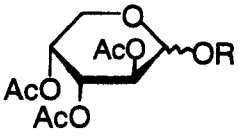
8 : R = H
9 : R = CS(SMe)



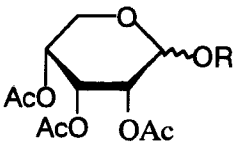
10 : R' = Ac,R = H
11 : R' = Ac,R = CS(SMe)
23 : R' = Bn, R = H



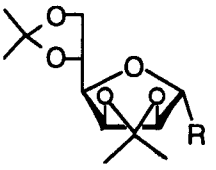
12 : R = H
13 : R = CS(SMe)



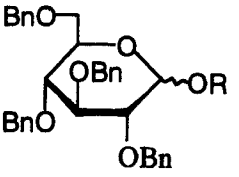
14 : R = H
15 : R = CS(SMe)



16 : R = H
17 : R = CS(SMe)



18 : R = OR
20 : R = OCS(SMe)
21 : R = SCO(SMe)



19 : R = H
22 : R = CS(SMe)

the chemical shift of the dithiocarbonate carbon signal in its ^{13}C NMR spectrum (187.1 ppm); all the dithiocarbonate carbon signals of 1-*S*-methylthiocarbonates of thermal rearranged products appeared at about 187 ppm, while the corresponding signals of 1-*O*-(methylthio)thiocarbonates appeared at about 214 ppm (see experimental section). Murai

Table 1. 1-*O*-(Methylthio)thiocarbonylation of 1-OH sugar derivatives

1-OH Sugar	Method	Reaction time	Product	Yield (α/β)
1	A	5 min	**2α,2β**	65 % (1:3)
1	B	3 d	**2α,2β**	85 % (1.6:1)
3	A	10 min	**4α,4β**	80 % (6:1)
3	B	7 d	**4 α**	86 %
5	B	7 d	**7** *	58 %
8	B	3 d	**9**	86 %
10	B	3 d	**11α,11β**	78 % (2.5:1)
12	B	3 d	**13α,13β**	66 % (1.6:1)
14	B	2 d	**15α,15β**	62 % (1:2.1)
16	B	3 d	**17**	80 %
18	B	4 d	**20 + 21***	82 % (**20/21** = 8:1)

* Rearranged product

et al. recently reported a similar observation in the ^{13}C NMR spectra of methyl monothiobenzoates; carbonyl carbon resonates at 185.0 ppm and thiocarbonyl carbons at 212.2 ppm.[31]

An attempted 1-*O*-(methylthio)thiocarbonylation of 2,3,5-tri-*O*-acetyl-D-ribofuranose (**6**)[27] resulted in crude products (about 50%; α/β = 1:1), which were highly unstable and decomposed through silica-gel column chromatography.

From these results we decided that a solid - liquid phase transfer catalysis method (method B) is milder than and superior to a liquid - liquid one (method A) for 1-*O*-(methylthio)thiocarbonylation of more base unstable sugar derivatives. Therefore, several other tri- or tetra-*O*-acetyl-D-pyranoses were used as substrates for 1-*O*-(methylthio)thiocarbonylation using method B. The results obtained are summarized in Table 1. The α/β ratios were determined from intensities of the corresponding signals of anomeric protons and/or methyl protons of methylthio groups in their ^1H NMR spectra.

In order to determine the limitation of method B, 1-*O*-(methylthio)thiocarbonylation of 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose (**18**),[32] and 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**19**)[33] was carried out using method B. The reaction of **18** gave the desired product, 2,3:5,6-di-*O*-isopropylidene-1-*O*-(methylthio)thiocarbonyl-α-D-

mannofuranose (**20**), and the rearranged product, 2,3:5,6-di-*O*-isopropylidene-1-*S*-methylthiocarbonyl-1-thio-α-D-mannofuranose (**21**), in 82% yield (**20**:**21** = 8:1). Tetra-*O*-benzylpyranose **19** was unreactive and gave no desired product. Starting material was recovered in over 90% yield. Di Cesare and Gross obtained the corresponding 1-*O*-(methylthio)thiocarbonyl derivatives **20** and 2,3,4,6-tetra-*O*-benzyl-1-*O*-(methylthio)thiocarbonyl-α-D-glucopyranose (**22**) in 72% and 56% yields, respectively, using their liquid - liquid two phase method.[15] The earlier papers[16,17] did not describe the yields of **20**. The sodium hydride - imidazole method[14] gave a high yield (95%) of **22**. Thus, for sugar derivatives bearing no base sensitive groups, the imidazole catalyzed strong base method is the most suitable, but for sugar derivatives bearing base sensitive protective groups, the solid - liquid two phase method (method B) is the most suitable . Di Cesare and Gross's method (method A) is a simple and suitable one applicable to both sugar derivatives bearing no and a few base sensitive groups.

Isolation of compounds **7** and **21** in method B suggested that thermal rearrangement of 1-*O*-(methylthio)thiocarbonyl groups to 1-*S*-methylthiocarbonyl groups occurred in the course of the reaction. Thermal and acid rearrangements of anomeric dithiocarbonate 2,3,4,6-tetra-*O*-benzyl-1-*O*-(methylthio)thiocarbonyl-α-D-glucopyranose (**22**) and -galactopyranose (**23**) to the corresponding 1-*S*-methylthiocarbonyl derivatives are known.[14] Thermal rearrangement of non-anomeric dithiocarbonate 1,2:5,6-di-*O*-isopropylidene-3-*O*-(methylthio)thiocarbonyl-α-D-glucofuranose to the corresponding 3-*S*-methylthiocarbonyl-3-thio-α-D-glucofuranose is also known.[16] The rearrangement was considered to proceed through SNi type process.[14] Refluxing of a solution of **20** in benzene for 24 h gave **21** in 97% yield. Similar treatment of **4α** gave 5-*O*-benzoyl-2,3-*O*-isopropylidene-1-*S*-methylthiocarbonyl-1-thio-β-D-ribofuranose (**24**) in 81% yield, and **4β** gave similarly the same rearranged product **24** together with the starting material **4β** in 76% yield (**24**/**4β** = 1:1). The fact that both the rearrangements of anomeric pair **4α** and **4β** gave the same product **24** shows the present rearrangement proceeds not through the SNi but through the SN1 process. An attempted rearrangement of pyranose type 1-*O*-(methylthio)thiocarbonyl sugar derivative **2** gave no rearranged products. It is thus suggested that furanose type 1-*O*-(methylthio)thiocarbonyl sugar derivatives are more reactive or unstable than pyranose derivatives.

Thermal rearrangements of **20**, **22**[14] and **23**[14] to the corresponding 1-*S*-methylthiocarbonyl-1-thiosugar derivatives, glycosidations of **22** and **23**,[14] glycosidations of similar anomeric *S*-ethyloxythiocarbonyl derivatives[34] and a *C*-glycosylation of **4α**[23,35] indicate the versatile utility of these 1-*O*-(methylthio)thiocarbonyl sugar derivatives for organic transformations.

CONCLUSION

In this paper, we have synthesized a new class of compound, 1-*O*-(methylthio)thiocarbonyl sugar derivatives bearing acetyl or benzoyl groups using a solid - liquid phase transfer catalysis method.

EXPERIMENTAL

General Methods. Melting points were determined on a Laboratory Device MEL-TEMP and are uncorrected. Elemental analyses were carried out with a Perkin-Elmer 2400 instrument. ^1H and ^{13}C NMR spectra were recorded with JEOL GSX-270 (270 MHz) instrument for solutions in chloroform-d with tetramethylsilane as an internal standard. Specific rotations were determined with JASCO DIP-SL instrument. TLC was performed on Merck silica gel 60 F_{254} precoated plates (thickness 0.25 mm). Column chromatography was performed on Wakogel C-300.

2,3,4,6-Tetra-*O*-acetyl-1-*O*-(methylthio)thiocarbonyl-D-glucopyranose (2) (method A). To a mixture of a solution of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**1**) (2.23 g, 6.4 mmol), carbon disulfide (3.2 mL, 53 mmol), iodomethane (3.2 mL, 51 mmol), tetrabutylammonium hydrogen sulphate (2.2 g, 6.5 mmol) and benzene (60 mL), was added 50% aqueous sodium hydroxide (60 mL) with vigorous stirring at room temperature. After 5 min, benzene and water were added to the mixture. The organic layer was washed with water and dried with sodium sulphate and concentrated *in vacuo*. Column chromatography (acetone/benzene) of the residue gave an anomeric mixture of **2** (α/β = 1:3); Yield 1.84 g (65%). Crystallization of the fractions of the chromatography from 2-propanol gave pure α- and β-isomers (**2**α and **2**β). Compound **2**α: mp 112-114 °C; $[\alpha]_D$ +41.4° (*c* 1.01, $CHCl_3$); ^1H NMR δ 2.03, 2.04, 2.05, 2.08 (4s, 12H, OAc), 2.57 (s, 3H, SMe), 3.38 (ddd, 1H, $J_{5,6}$ = 4.8 Hz, $J_{5,6'}$ = 2.2 Hz, H-5), 4.12 (dd, 1H, H-6'), 4.28 (dd, 1H, $J_{6,6'}$ = 12.5 Hz, H-6), 5.16 (m, 1H, H-4), 5.26 - 5.35 (m, 2H, H-2,3), 6.32 (m [virtual coupling, signal width 9.3 Hz], 1H, H-1); ^{13}C NMR δ 214.3, 170.5, 170.0, 169.3, 169.1, 96.5, 72.62, 72.55, 70.0, 67.8, 61.4, 20.7, 20.5, 19.2.

Anal. Calcd for $C_{12}H_{22}O_{10}S_2$: C, 43.83; H, 5.06; S, 14.63. Found: C, 44.03; H, 5.04; S, 14.42.

Compound **2**β: mp 62-64 °C; $[\alpha]_D$ +104.9° (*c* 0.84, $CHCl_3$); ^1H NMR δ 2.03, 2.04, 2.05, 2.09 (4s, 12H, OAc), 2.63 (s, 3H, SMe), 4.06-4.14 (m, 2H, H-5,6'), 4.30 (dd, 1H, $J_{5.6}$ = 4.0 Hz, $J_{6,6'}$ = 12.5 Hz, H-6), 5.18 (dd, 1H, $J_{2,3}$ = 10.3 Hz, H-2,), 5.20

(t, 1H, $J_{4,5}$ = 10.1 Hz, H-4,), 5.56 (t, 1H, $J_{3,4}$ = 9.7 Hz, H-3), 7.00 (d, 1H, $J_{1,2}$=3.7 Hz, H-1); ^{13}C NMR δ 214.5, 170.5, 170.1, 169.8, 169.4, 94.8, 70.2, 70.0, 69.3, 67.7, 61.2, 20.64, 20.61, 20.52, 20.47, 19.2.

Anal. Calcd for $C_{12}H_{22}O_{10}S_2$: C, 43.83; H, 5.06; S, 14.63. Found: C, 43.89; H, 5.01; S, 14.61.

(Method B). A mixture of **1** (348 mg, 1 mmol), carbon disulfide (0.6 mL, 10 mmol), iodomethane (0.62 mL, 10 mmol), tetrabutylammonium bromide (322 mg, 1 mmol) and potassium carbonate (288 mg, 2 mmol) in CH_2Cl_2 (10 mL) was vigorously stirred at room temperature. After 3 days, the mixture was filtered and concentrated *in vacuo*. Column chromatography (acetone/benzene) of the residue gave an anomeric mixture of **2** (α/β = 1.6:1); Yield 371 mg (85%).

5-*O*-Benzoyl-2,3-*O*-isopropylidene-1-*O*-(methylthio)thiocarbonyl-D-ribofuranose (4) (method A). To a mixture of a solution of 5-*O*-benzoyl-2,3-*O*-isopropylidene-D-ribofuranose (**3**) (438.2 mg, 1.5 mmol), carbon disulfide (0.2 mL, 3.3 mmol), iodomethane (0.2 mL, 3.2 mmol), tetrabutylammonium hydrogen sulphate (510 mg, 1.5 mmol) and benzene (10 mL), was added 50% aqueous sodium hydroxide (10 mL) with vigorous stirring at room temperature. After 10 min, benzene and water were added to the mixture. The organic layer was washed with water and dried with sodium sulphate and concentrated *in vacuo*. Column chromatography (ethyl acetate/hexane) of the residue gave **4α**; Yield 355 mg (67%) and **4β**; Yield 66 mg (13%). Compound **4α**: syrup; $[\alpha]_D$ -96.8° (*c* 0.84, $CHCl_3$); ^{1}H NMR δ 1.37, 1.54 (2s, 6H, isopropylidene), 2.52 (s, 3H, SMe), 4.39 (dd, 2H, H-5,5'), 4.71 (t, 1H, $J_{4,(5,5')}$ = 6.6 Hz, H-4), 4.88 (d, 1H, $J_{3,(5,5')}$ = 1.1 Hz, H-3), 4.97 (d, 1H, $J_{2,3}$ = 5.9 Hz, H-2), 6.84 (s, 1H, H-1), 7.43-7.48 (m, 2H, Bz), 7.55-7.61 (m, 1H, Bz), 8.05-8.09 (m, 2H, Bz); ^{13}C NMR δ 213.9, 165.9, 133.2, 129.7, 129.4, 128.3, 113.3, 108.7, 85.8, 85.1, 81.4, 64.3, 26.3, 24.9, 19.9.

Anal. Calcd for $C_{17}H_{20}O_6S_2$: C, 53.11; H, 5.24; S, 16.68. Found: C, 53.20; H, 5.30; S, 16.70.

Compound **4β**: syrup; $[\alpha]_D$ -55.5° (*c* 0.62, $CHCl_3$); ^{1}H NMR δ 1.38, 1.61 (2s, 6H, isopropylidene), 2.61 (s, 3H, SMe), 4.49 (dd, 1H, H-5'), 4.54 (dd, 1H, $J_{5,5'}$ = 12.1 Hz, H-5), 4.72 (q, 1H, $J_{4,5}$ = 3.7 Hz, $J_{4,5'}$ = 3.8 Hz, H-4), 4.81 (dd, 1H, $J_{3,4}$ = 2.6 Hz, H-3), 4.98 (dd, 1H, $J_{2,3}$ = 6.8 Hz, H-2), 6.95 (d, 1H, $J_{1,2}$ = 4.4 Hz, H-1), 7.44-7.51 (m, 2H, Bz), 7.57-7.64 (m, 1H, Bz), 8.01-8.09 (m, 2H, Bz); ^{13}C NMR δ 214.4, 166.0, 133.4, 129.6, 129.3, 128.5, 116.0, 102.7, 81.6, 80.6, 80.2, 64.3, 25.8, 25.5, 19.1.

Anal. Calcd for $C_{17}H_{20}O_6S_2$: C, 53.11; H, 5.24; S, 16.68. Found: C, 52.84; H, 5.35; S, 16.83.

(**Method B**). A mixture of **3** (360 mg, 1.23 mmol), carbon disulfide (0.74 mL, 12.3 mmol), iodomethane (0.76 mL, 12.3 mmol), tetrabutylammonium bromide (396 mg, 1.23 mmol) and potassium carbonate (355 mg, 2.46 mmol) in CH_2Cl_2 (12 mL) was vigorously stirred at room temperature. After 7 days, the mixture was filtered and concentrated *in vacuo*. Column chromatography (ethyl acetate/hexane) of the residue gave **4α**; Yield 407 mg (86%).

2,3,5-Tri-*O*-benzoyl-1-*S*-methylthiocarbonyl-1-thio-β-D-ribofuranose (7) (method B). A mixture of 2,3,5-tri-*O*-benzoyl-D-ribofuranose (**5**) (462 mg, 1 mmol), carbon disulfide (0.6 mL, 10 mmol), iodomethane (0.62 mL, 10 mmol), tetrabutylammonium bromide (322 mg, 1 mmol) and potassium carbonate (288 mg, 2 mmol) in CH_2Cl_2 (10 mL) was vigorously stirred at room temperature. After 7 days, the mixture was filtered and concentrated *in vacuo*. Column chromatography (acetone/benzene) of the residue gave **7**; Yield 321 mg (58%). The β-configuration of **7** was confirmed by the comparison of **7** with the compound transformed from 5-*O*-benzoyl-2,3-*O*-isopropylidene-1-*S*-(methylthio)thiocarbonyl-1-thio-β-D-ribofuranose (**24**) by deisopropylidenation and successive benzoylation. Compound **7**: syrup; $[\alpha]_D$ -24.5° (*c* 0.40, $CHCl_3$); ^1H NMR δ 2.45 (s, 3H, SMe), 4.54 (dd, 1H, H-5'), 4.68 (d, 1H, $J_{5,5'}$ = 11.9 Hz, H-5), 4.73 (dd, 1H, $J_{4,5'}$ = 3.7 Hz, H-4), 5.82 (t, 1H, $J_{3,4}$ = 5.3 Hz, H-3), 5.88 (dd, 1H, $J_{2,3}$ = 5.1 Hz, H-2), 6.24 (d, 1H, $J_{1,2}$ = 2.5 Hz, H-1), 7.36-7.58 (m, 6H, Bz), 7.88-8.12 (m, 3H, Bz); ^{13}C NMR δ 187.1, 166.0, 165.1, 164.8, 133.5, 133.1, 129.7, 129.6, 129.3, 128.6, 128.5, 128.4, 128.3, 128.2, 85.0, 80.2, 75.1, 71.7, 63.4, 13.1.

Anal. Calcd for $C_{28}H_{24}O_8S_2$: C, 60.86; H, 4.38; S, 11.60. Found: C, 60.75; H, 4.52; S, 11.31.

2,3,4,6-Tetra-*O*-acetyl-1-*O*-(methylthio)thiocarbonyl-α-D-mannopyranose (9) (method B). A mixture of 2,3,4,6-tetra-*O*-acetyl-D-mannopyranose (**8**) (348 mg, 1 mmol), carbon disulfide (0.6 mL, 10 mmol), iodomethane (0.62 mL, 10 mmol), tetrabutylammonium bromide (322 mg, 1 mmol) and potassium carbonate (288 mg, 2 mmol) in CH_2Cl_2 (10 mL) was vigorously stirred at room temperature. After 3 days, the mixture was filtered and concentrated *in vacuo*. Column chromatography (methanol/chloroform) of the residue gave **9** ; Yield 377 mg (86%). Compound **9**: mp 73-74 °C; $[\alpha]_D$ +45.5° (*c* 0.84, $CHCl_3$); ^1H NMR δ 2.02, 2.07, 2.09, 2.20 (4s, 12H, OAc), 2.62 (s, 3H, SMe), 4.05 (m, 1H, $J_{5,6}$ = 4.8 Hz, $J_{5,6'}$ = 2.4 Hz, H-5), 4.10 (dd, 1H, H-6'), 4.31 (dd, 1H, $J_{6,6'}$ = 12.3 Hz, H-6), 5.39-5.45 (m, 3H, H-2,3,4), 6.68 (d, 1H, $J_{1,2}$ = 1.3 Hz, H-1); ^{13}C NMR δ 212.9, 170.3, 169.7, 169.4, 169.3, 96.1, 71.0, 68.6, 67.8, 65.2, 61.7, 20.6, 20.52, 20.48, 20.4, 19.4.

Anal. Calcd for $C_{12}H_{22}O_{10}S_2$: C, 43.83; H, 5.06; S, 14.63. Found: C, 44.10; H, 5.02; S, 14.73.

2,3,4,6-Tetra-*O*-acetyl-1-*O*-(methylthio)thiocarbonyl-D-galactopyranose (11) (method B). A mixture of 2,3,4,6-tetra-*O*-acetyl-D-galactopyranose (**10**) (348 mg, 1 mmol), carbon disulfide (0.6 mL, 10 mmol), iodomethane (0.62 mL, 10 mmol), tetrabutylammonium bromide (322 mg, 1 mmol) and potassium carbonate (288 mg, 2 mmol) in CH_2Cl_2 (10 mL) was vigorously stirred at room temperature. After 3 days, the mixture was filtered and concentrated *in vacuo*. Column chromatography (methanol/chloroform) of the residue gave an anomeric mixture of **11** (α/β = 2.5:1); Yield 340 mg (78%). Rechromatography gave pure **11α**. Compound **11α**: syrup; $[\alpha]_D$ +117.4° (*c* 0.46, $CHCl_3$); ^{1}H NMR δ 2.02, 2.031, 2.034, 2.16 (4s, 12H, OAc), 2.62 (s, 3H, SMe), 4.08 (dd, 1H, H-6'), 4.14 (dd, 1H, $J_{6,6'}$ = 11.2 Hz, H-6), 4.34 (t, 1H, $J_{5,6}$ = 6.6 Hz, $J_{5,6'}$ = 6.8 Hz, H-5), 5.42 (m, 2H, H-2,3), 5.55 (s, 1H, H-4), 7.05 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1); ^{13}C NMR δ 214.8, 170.3, 170.1, 170.0, 95.6, 69.3, 67.6, 67.3, 66.6, 61.0, 20.62, 20.60, 20.57, 19.5.

Anal. Calcd for $C_{12}H_{22}O_{10}S_2$: C, 43.83; H, 5.06; S, 14.63. Found: C, 44.02; H, 5.30; S, 14.88.

Compound **11β**: ^{1}H NMR δ 2.01, 2.04, 2.06, 2.18 (4s, 12H, OAc), 2.58 (s, 3H, SMe), 4.10-4.18 (m, 3H , H-5,6,6'), 5.14 (dd, 1H, $J_{3,4}$ = 3.3 Hz, H-3), 5.45 (d, 1H, H-4), 5.51 (dd, 1H, $J_{2,3}$ = 10.3 Hz, H-2), 6.3 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1); ^{13}C NMR δ 214.4, 170.3, 170.0, 169.9, 169.3, 97.1, 71.7, 70.7, 67.5, 66.7, 60.9, 20.61, 20.58, 20.50, 19.2.

2,3,4-Tri-*O*-acetyl-1-*O*-(methylthio)thiocarbonyl-D-xylopyranose (13) (method B). A mixture of 2,3,4-tri-*O*-acetyl-D-xylopyranose (**12**) (276 mg, 1 mmol), carbon disulfide (0.6 mL, 10 mmol), iodomethane (0.62 mL, 10 mmol), tetrabutylammonium bromide (322 mg, 1 mmol) and potassium carbonate (288 mg, 2 mmol) in CH_2Cl_2 (10 mL) was vigorously stirred at room temperature. After 3 days, the mixture was filtered and concentrated *in vacuo*. Column chromatography (acetone/benzene) of the residue gave an anomeric mixture of **13** (α/β = 1.6:1); Yield 239 mg (66%). Crystallization of the anomeric mixture from benzene/hexane gave pure α-isomer. Compound **13α**: mp 94-95 °C (hexane-benzene); $[\alpha]_D$ +110.6° (*c* 0.62, $CHCl_3$); ^{1}H NMR δ 2.03, 2.06 (2s, 3H, 6H, OAc), 2.62 (s, 3H, SMe), 3.71 (t, 1H, H-5'), 3.98 (dd, 1H, $J_{5,5'}$ = 11.4 Hz, H-5), 5.08 (ddd, 1H, $J_{4,5}$ = 5.9 Hz, $J_{4,5'}$ = 11.2 Hz, H-4), 5.12 (dd, 1H, $J_{2,3}$ = 10.1 Hz, H-2), 5.56 (t, 1H, $J_{3,4}$ = 9.9 Hz, H-3), 6.94 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1); ^{13}C NMR δ 214.8, 170.0, 169.8, 169.7, 95.1, 69.5, 68.5, 61.0, 20.7, 20.6, 20.5, 19.4.

Anal. Calcd for $C_{13}H_{18}O_8S_2$: C, 42.61; H, 4.95; S, 17.50. Found: C, 42.90; H, 5.17; S, 17.21.

Compound **13β**: ^{1}H NMR δ 2.05, 2.08, 2.10 (3s, 9H, OAc), 2.58 (s, 3H, SMe), 3.68 (dd, 1H, H-5'), 4.21 (dd, 1H, $J_{5,5'}$ = 12.5 Hz, H-5), 4.69 (m, 1H, $J_{4,5}$ = 4.0 Hz, $J_{4,5'}$ = 5.5 Hz, H-4), 5.15 (dd, 1H, $J_{2,3}$ = 5.9 Hz, H-2), 5.20 (t, 1H, $J_{3,4}$ = 6.6 Hz, H-3), 6.47 (d, 1H, $J_{1,2}$ = 4.8 Hz, H-1); ^{13}C NMR δ 214.0, 169.6, 169.3, 169.0, 97.6, 68.8, 67.8, 67.5, 61.9, 20.6, 20.54, 20.47, 19.0.

2,3,4-Tri-*O*-acetyl-1-*O*-(methylthio)thiocarbonyl-D-arabinopyranose (15) (method B). A mixture of 2,3,4-tri-*O*-acetyl-D-arabinopyranose (**14**) (276 mg, 1 mmol), carbon disulfide (0.6 mL, 10 mmol), iodomethane (0.62 mL, 10 mmol), tetrabutylammonium bromide (322 mg, 1 mmol) and potassium carbonate (288 mg, 2 mmol) in CH_2Cl_2 (10 mL) was vigorously stirred at room temperature. After 2 days, the mixture was filtered and concentrated *in vacuo*. Column chromatography (aceton/benzene) of the residue gave an anomeric mixture of **15** (α/β = 1:2.1); Yield 225 mg (62%). Crystallization of the anomeric mixture from benzene/hexane gave pure β-isomer. Compound **15α**: ^{1}H NMR δ 2.11, 2.12 (2s, 3H, 6H, OAc), 2.60 (s, 3H, SMe), 3.80 (dd, 1H, H-5'), 4.07 (dd, 1H, $J_{5,5'}$ = 12.3 Hz, H-5), 5.21 (dd, 1H, $J_{3,4}$ = 3.3 Hz, H-3), 5.32 (1H, q, H-4, $J_{4,5}$=5.9Hz, $J_{4,5'}$=3.1Hz), 5.36 (1H, dd, H-2, $J_{2,3}$=7.3Hz), 6.38 (d, 1H, $J_{1,2}$ = 5.1 Hz, H-1); ^{13}C NMR δ 214.2, 170.1, 169.8, 169.2, 96.7, 68.6, 67.8, 66.1, 62.2, 20.8, 20.7, 20.6, 19.2.

Compound **15β**: mp 116-117 °C (hexane-benzene); $[\alpha]_D$ -114.5° (*c* 0.34, $CHCl_3$); ^{1}H NMR δ 2.04, 2.16 (2s, 3H, 6H, OAc), 2.61 (s, 3H, SMe), 3.88 (dd, 1H, H-5'), 4.07 (d, 1H, $J_{5,5'}$ = 13.0 Hz, H-5), 5.44 (m, 3H, $J_{4,5'}$ = 1.5 Hz, H-2,3,4), 7.03 (d, 1H, $J_{1,2}$ = 2.7 Hz, H-1); ^{13}C NMR δ 215.1, 170.2, 170.1, 96.2, 68.4, 67.2, 66.8, 63.3, 20.9, 20.7, 20.6, 19.4.

Anal. Calcd for $C_{13}H_{18}O_8S_2$: C, 42.61; H, 4.95; S, 17.50. Found: C, 42.35; H, 4.80; S, 17.71.

2,3,4-Tri-*O*-acetyl-1-*O*-(methylthio)thiocarbonyl-α-D-ribopyranose (17) (method B). A mixture of 2,3,4-tri-*O*-acetyl-D-ribopyranose (**16**) (379 mg, 1.37 mmol), carbon disulfide (0.82 mL, 13.7 mmol), iodomethane (0.85 mL, 13.7 mmol), tetrabutylammonium bromide (442 mg, 1.37 mmol) and potassium carbonate (395 mg, 2.74 mmol) in CH_2Cl_2 (14 mL) was vigorously stirred at room temperature. After 3 days, the mixture was filtered and concentrated *in vacuo*. Column chromatography (acetone/benzene) of the residue gave **17**; Yield 402 mg (80%). Compound **17**: syrup; $[\alpha]_D$ -14.8° (*c* 1.90, $CHCl_3$); ^{1}H NMR δ 2.08, 2.13, 2.15 (3s, 9H, OAc), 2.60 (s, 3H, SMe), 3.96 (dd, 1H, H-5'), 4.08 (dd, 1H, $J_{5,5'}$ = 12.7 Hz, H-5), 5.24 (dd, 1H, $J_{4,5}$ = 2.8 Hz, $J_{4,5'}$ =

4.0 Hz, H-4), 5.26 (t, 1H, $J_{2,3}$ = 3.5 Hz, H-2), 5.47 (t, 1H, $J_{3,4}$ = 3.5 Hz, H-3), 6.68 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1); ^{13}C NMR δ 213.9, 170.0, 169.7, 169.5, 96.8, 66.6, 66.1, 65.6, 63.4, 20.8, 20.7, 20.6, 19.5.

Anal. Calcd for $C_{13}H_{18}O_8S_2$: C, 42.61; H, 4.95; S, 17.50. Found: C, 42.84; H, 4.89; S, 17.70.

2,3;5,6-Di-*O*-isopropylidene-1-*O*-(methylthio)thiocarbonyl-α-D-mannofuranose (20) (method B). A mixture of 2,3;5,6-di-*O*-isopropylidene-α-D-mannofuranose (**18**) (260 mg, 1 mmol), carbon disulfide (0.6 mL, 10 mmol), iodomethane (0.62 mL, 10 mmol), tetrabutylammonium bromide (322 mg, 1 mmol) and potassium carbonate (288 mg, 2 mmol) in CH_2Cl_2 (10 mL) was vigorously stirred at room temperature. After 4 days, the mixture was filtered and concentrated *in vacuo*. Column chromatography (ethyl acetate/hexane) of the residue gave a mixture of **20** and 2,3;5,6-di-*O*-isopropylidene-1-*S*-methylthiocarbonyl-1-thio-α-D-mannofuranose (**21**) (**20**/**21** = 8:1); Yield 288 mg (82%). Crystallization of the mixture from ethanol gave pure **20**. Compound **20**: mp 81-82°C (ethanol) (lit.[15] 81-82 °C); $[\alpha]_D$ +62.0° (*c* 0.54, $CHCl_3$) (lit.[15] $[\alpha]_D$ +69.3° ($Cl_2CHCHCl_2$); ^{1}H NMR δ 1.36, 1.39, 1.47, 1.51 (4s, 12H, isopropylidene), 2.58 (s, 3H, SMe), 4.06 (dd, 1H, H-6'), 4.10 (dd, 1H, $J_{4,5}$ = 8.1 Hz, H-4), 4.12 (dd, 1H, $J_{6,6'}$ = 9.0 Hz, H-6), 4.43 (ddd, 1H, $J_{5,6}$ = 5.9 Hz, $J_{5,6'}$ = 4.4 Hz, H-5), 4.86 (d, 1H, $J_{2,3}$ = 5.7 Hz, H-2), 4.90 (dd, 1H, $J_{3,4}$ = 3.1 Hz, H-3), 6.69 (s, 1H, H-1); ^{13}C NMR δ 213.9, 113.4, 109.4, 107.6, 84.9, 83.0, 79.0, 72.7, 66.8, 26.9, 25.9, 25.0, 24.6, 19.2.

2,3;5,6-Di-*O*-isopropylidene-1-*S*-methylthiocarbonyl-α-D-mannofuranose (21) (rearrangement of 20). A solution of 2,3;5,6-di-*O*-isopropylidene-1-*O*-(methylthio)thiocarbonyl-α-D-mannofuranose (**20**) (107 mg, 0.3 mmol) in benzene (7.5 mL) was heated for 24h under reflux. Concentration of the solution *in vacuo* gave crude **21**. Column chromatography (ethyl acetate/benzene) of the crude **21** gave pure **21**; Yield 104 mg (97%). Compound **21**: mp 114-115 °C (ethanol); $[\alpha]_D$ +168.4° (*c* 0.50, $CHCl_3$); ^{1}H NMR δ 1.34, 1.37, 1.45, 1.50 (4s, 12H, isopropylidene), 2.44 (s, 3H, SMe), 3.86 (dd, 1H, $J_{4,5}$ = 8.1 Hz, H-4), 4.00 (dd, 1H, H-6'), 4.09 (dd, 1H, $J_{6,6'}$ = 9.0Hz, H-6), 4.42 (ddd, 1H, $J_{5,6}$ = 6.0 Hz, $J_{5,6'}$ = 4.2 Hz, H-5), 4.78-4.83 (m, 2H, $J_{3,4}$ = 2.4 Hz, H-2,3), 6.05 (s, 1H, H-1); ^{13}C NMR δ 187.4, 113.4, 109.4, 89.2, 86.2, 82.2, 79.5, 72.5, 66.9, 26.9, 25.9, 25.1, 24.7, 13.2.

Anal. Calcd for $C_{14}H_{22}O_6S_2$: C, 47.98; H, 6.33; S, 18.30. Found: C, 47.80; H, 6.91; S, 18.60.

5-*O*-Benzoyl-2,3-*O*-isopropylidene-1-*S*-methylthiocarbonyl-β-D-ribofuranose (24) (rearrangement of 4α). A solution of 5-*O*-benzoyl-2,3-*O*-iso-

propylidene-1-*O*-(methylthio)thiocarbonyl-α-D-ribofuranose (**4α**) (78 mg, 0.2 mmol) in benzene (6 mL) was heated for 25 h under reflux. Concentration of the solution *in vacuo* gave crude **24**. Column chromatography (ethyl acetate/benzene) of the crude **24** gave pure **24**; Yield 63.5 mg (81%). The β-configuration of **24** was confirmed from the observation of less than 5% but distinguishable NOE effect between H-1 and H-4. Compound **24**: mp 51-52 °C (hexane); $[\alpha]_D$ -159.6° (*c* 1.10, $CHCl_3$); ^1H NMR δ 1.36, 1.56 (2s, 6H, isopropylidene), 2.42 (s, 3H, SMe), 4.38 (dd, 1H, H-5'), 4.45 (dd, 1H, $J_{5,5'}$ = 11.9 Hz, H-5), 4.59 (dt, 1H, $J_{4,5}$ = 5.9 Hz, $J_{4,5'}$ = 5.7 Hz, H-4), 4.82 (dd, 1H, $J_{3,4}$ = 1.5 Hz, H-3), 4.90 (dd, 1H, $J_{2,3}$ = 6.1 Hz, H-2), 6.09 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 7.43-7.50 (m, 2H, Bz), 7.56-7.63 (m, 1H, Bz), 8.05-8.09 (m, 2H, Bz).; ^{13}C NMR δ 187.7, 166.2, 133.3, 129.8, 129.4, 128.5, 113.9, 89.4, 85.0, 82.1, 64.0, 26.8, 25.4, 13.1.

Anal. Calcd for $C_{17}H_{20}O_6S_2$: C, 53.11; H, 5.24; S, 16.68. Found: C, 53.36; H, 5.32; S, 16.44.

(Rearrangement of 4β). A solution of 5-*O*-benzoyl-2,3-*O*-isopropylidene-1-*O*-(methylthio)thiocarbonyl-β-D-ribofuranose (**4β**) (75 mg, 0.2 mmol) in benzene (5 mL) was heated for 24h under reflux. Concentration of the solution *in vacuo* gave crude **24**. Column chromatography (benzene) of the residue gave a mixture of **24** and **4β** (**24**/**4β** = 1:1); Yield 56.5 mg (76%).

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