Carbohydrate Research, 211 (1991) 245–260
Elsevier Science Publishers B.V., Amsterdam

Branched-chain thiosugars: temperature effects in the acetolytic deacetalation of furanose sugars*

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(Received May 29th, 1990; accepted, in revised form, July 25th, 1990)

ABSTRACT

The synthesis of the branched-chain thiosugar derivatives **8** and **13** from 1,2-*O*-isopropylidene-D-xylofuranose is described. The acetolytic cleavage of the acetonide group from **8** and **13** was found to yield products arising from opening of the furanose ring when carried out at low temperatures. These include the novel thiolanes **9** and **17**. The desired 1,2-di-*O*-acetyl furanoses **6** and **14** were obtained when the reaction was performed at higher temperatures.

INTRODUCTION

Acetolysis reactions have been used extensively in carbohydrate chemistry as a means of obtaining acetylated sugars[1]. One application of the procedure is the conversion of isopropylidene derivatives to the corresponding acetylated compounds. Acetolysis is particularly useful in the case of 1,2-*O*-isopropylidene sugars where the protecting group is especially stable[2]. While the method has been widely employed, the mechanism of the conversion has not been studied in detail.

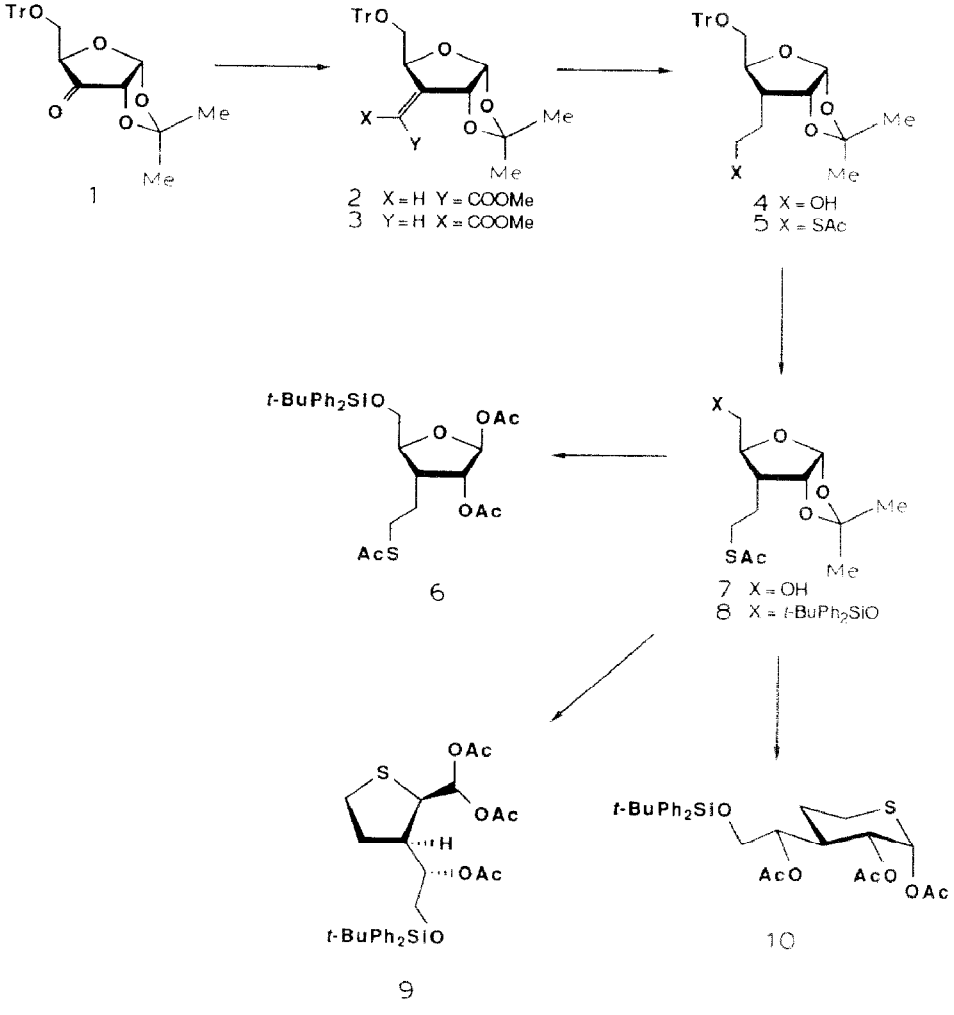
In the course of our present work involving the preparation of branched-chain nucleosides directed towards the synthesis of non-hydrolyzable oligoribonucleotide analogues, strategically protected nucleosides bearing substituted ethyl groups at the α-C-3′ position were constructed. The critical conversions in the scheme were the acetolyses of the 1,2-*O*-isopropylidene furanoses **8** and **13** to the corresponding 1,2-di-*O*-acetyl compounds **6** and **14** required for the attachment of the nitrogenous bases. Although furanose rings are generally retained under acetolytic conditions, the presence of the sulfur in our systems raises the possibility of other reactions occurring including ring-expansion to a thiopyranose[3] and intramolecular displacement of acetoxy groups by the sulfur atom[4]. In the present paper, we describe a number of unusual products arising from the acetolysis of the branched-chain thiosugars **8** and **13** and the marked dependence of their formation on the reaction temperature.

* This paper is dedicated to Prof. A. S. Perlin.

0008-6215/91/$ 03.50

RESULTS AND DISCUSSION

Preparation of isopropylidene furanoses **8** *and* **13**. — The branched-chain sugars were prepared from commercially available 1,2-*O*-isopropylidene-D-xylofuranose. The previously described[5] triphenylmethylation (tritylation) and Moffatt oxidation of the sugar was readily performed on a large scale yielding 1,2-*O*-isopropylidene-5-*O*-(triphenylmethyl)-α-D-*erythro*-pentofuranos-3-ulose (**1**) (Scheme 1). Condensation of **1** and the anion of trimethyl phosphonoacetate was initially carried out by a described[6] method, but the reaction afforded only moderate yields of **2**. The reaction employing sodium hydride in THF, however, produced excellent yields of the two isomeric α,β-unsaturated esters **2** and **3** in a 3.8:1 ratio. The olefin isomers could be easily



Scheme 1

separated by column chromatography, and the respective stereochemistries were determined through ^{1}H-n.m.r. n.O.e. experiments.

Esters **2** and **3** were found to be highly resistant to hydrogenation, and, under forcing conditions, detritylation became a problem. However, refluxing the mixture of isomers **2** and **3** in THF over lithium aluminium hydride resulted in complete stereoselective reduction of the unsaturated esters, affording the desired 3-*C*-(2′-hydroxyethyl) sugar **4**. The D-*ribo*-configuration of **4** was confirmed by ^{1}H-n.m.r. spectroscopy which showed couplings of 4.7 and 10.0 Hz for $^3J_{H2,H3}$ and $^3J_{H3,H4}$, respectively.

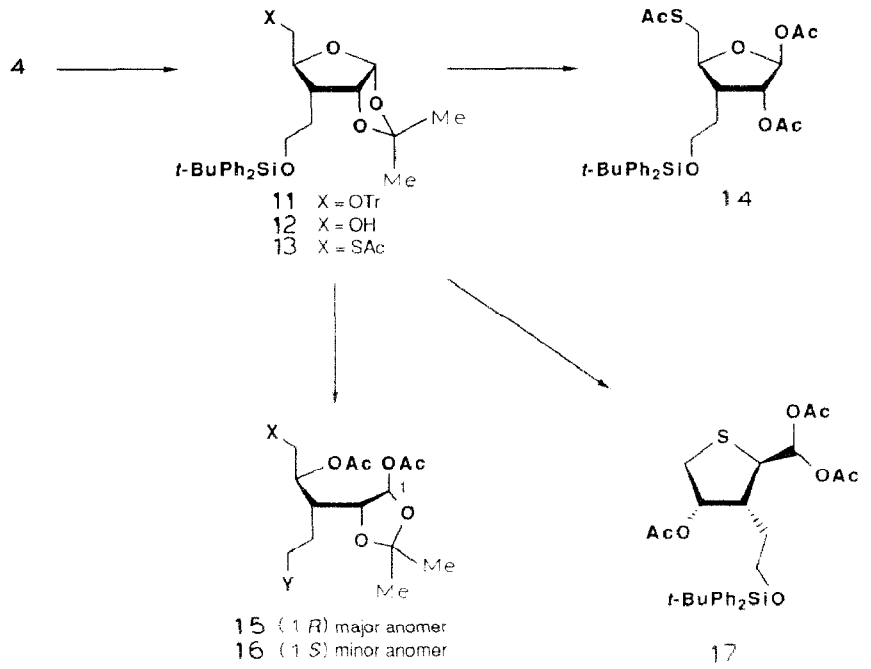
Attempts to introduce sulfur *via* the conventional route of mesylation, followed by displacement with potassium thiolacetate, proved unsatisfactory. The transformation was much more easily effected in one step using a Mitsunobu coupling of **4** and thiolacetic acid as described by Volante[7]. The presence of the acetylthio group in **5** was confirmed by ^{13}C-n.m.r. signals at δ 195.47 and 30.50.

The instability of the trityl group towards acetolytic conditions required that it be replaced with a more acid-stable functionality that would also be compatible with the planned attachment of the nitrogenous bases, as well as the eventual coupling of the nucleoside units. Treatment of **5** with anhydrous trichloroacetic acid afforded the 5-alcohol **7**, which was converted to the *tert*-butyldiphenylsilyl ether **8** by standard means[8].

A more expedient route to **8**, in which the 5-*O*-*tert*-butyldiphenylsilyl group is introduced at the beginning of the scheme, was also investigated. Selective silylation, followed by Moffatt oxidation, afforded good yields of the 5-*O*-*tert*-butyldiphenylsilyl-3-keto-sugar, but the subsequent Wittig condensation using the anion of trimethyl phosphonoacetate gave only fair yields of the unsaturated esters. It had been reported[9] that the hydrogenation of a similar unsaturated sugar bearing a 5-*O*-*tert*-butyldiphenylsilyl group showed poor stereoselectivity. Furthermore, as attempts to carry out the lithium aluminium hydride reduction on the esters afforded complex mixtures, this approach was abandoned.

The second key acetonide **13** was synthesized from **4** by changing the sequence of the conversions used in preparing **8** (Scheme 2). Alcohol **4** was first silylated to yield **11** from which the trityl group could be selectively cleaved under acidic conditions. The resulting 5-alcohol **12** was then subjected to Mitsunobu coupling with thiolacetic acid to give **13**.

Acetolysis of **8** *and* **13**. — Our initial treatment of **8** with an acetolytic mixture composed of *p*-toluenesulfonic acid (TsOH) and acetic anhydride in glacial acetic acid, when carried out at ambient temperature, afforded two products seen as two very closely spaced spots by t.l.c. The more polar product was found to be the desired 1,2-di-*O*-acetyl furanose **6** which was formed in 37% yield. The structure was confirmed by ^{1}H-n.m.r. spectroscopy which showed the anomeric proton singlet at δ 6.08, consistent with an acetyl furanose of the β-configuration, as well as three acetate peaks, including one at δ 2.31, indicative of an acetylthio function. The ^{13}C-n.m.r. spectrum of **6** included signals at δ 98.78, again consistent with an acetyl furanose[10], and characteristic acetylthio peaks at δ 194.94 and 30.46. (Note that ^{13}C-n.m.r. spectroscopy was



Scheme 2

found to be most useful in detecting the acetylthio group since the chemical shift differences between *S*- and *O*-acetates are much more pronounced than is the case for i.r. or ^{1}H-n.m.r. spectroscopy.)

The less polar component, isolated in 42% yield, was assigned the *cis*-disubstituted thiolane structure **9**. The ^{1}H-n.m.r. spectrum of this compound displayed an anomeric proton signal at δ 6.86, too far downfield for either a furanose or thiopyranose system and consistent with a diacetyl acetal[11]. The chemical shifts of δ 3.52 and 4.92 for H-2 and H-4, respectively, point to acetylation at O-4 rather than O-2. The ^{13}C-n.m.r. spectrum of **9** exhibited a C-1 signal at δ 90.63, again inconsistent with either a furanose or pyranose ring, and three carbonyl peaks in the range for O-acetyl groups. The stereochemistry at C-2 was assigned from the $^3J_{H2,H3}$ coupling of 4.7 Hz, consistent with a *cis*-geometry when compared to data obtained for other 2,3-disubstituted thiolanes[12]. Brief treatment of **9** with methanolic sodium hydroxide afforded the corresponding aldehyde which showed a characteristic ^{1}H-n.m.r. signal at δ 9.18.

The acetolysis was subsequently repeated numerous times under varying reaction conditions (summarized in Table I). Substituting the TsOH with anhydrous camphorsulfonic acid (CSA) or boron trifluoride etherate had little effect on the product distribution, which generally remained within 1.5:1 and 3:1 in favor of furanose **6**. In all cases, the β-furanose was largely favored over its α anomer. The latter could never be purified and was observed as a contaminant in early column fractions containing thiolane **9**. It was discovered, however, that the reaction temperature had a profound

influence on the course of the reaction. When cooled (0° to room temperature), the thiolane **9** was preferentially formed by a factor of 2:1, whereas heating of the reaction to 45° increased the selectivity for **6** to 6.7:1. At 70°, the desired furanose **6** was formed in 70% yield with only traces of the thiolane being formed. When the reaction temperature was further increased to 100°, the yields of **6** dropped substantially, presumably due to loss of the silyl group.

We also investigated a related method of converting isopropylidene derivatives to acetates[13,14]. When **8** was treated with boron trifluoride etherate in acetic anhydride at 0°, the 1,2-di-*O*-acetyl thiopyranose **10** was formed as the exclusive product in 70% yield. The ^{13}C-n.m.r. spectrum of the ring-expansion product shows only *O*-acetyl carbonyl signals and a C-1 peak at δ 76.58 as expected for an acetyl thiopyranose. Only the α anomer was obtained, exhibiting a $^3J_{H1,H2}$ of 2.9 Hz. This and the $^3J_{H2,H3}$ coupling of 11.4 Hz indicates that the thiosugar exists as the $^4C_1$ conformer.

The acetolysis of acetonide **13** was carried out using CSA as the acid catalyst. When performed at 75°, the treatment afforded the desired 1,2-di-*O*-acetyl furanose **14** as the sole product in 83% yield. Only the β anomer was obtained whose ^{1}H-n.m.r. spectrum displays a singlet at δ 6.02 for the anomeric proton. As expected, the reaction performed at a low temperature (15° over 24 h) produced a much lower yield (8%) of furanose **14**. The major products were the open-chain 1-*O*-acetyl-1,2-*O*-isopropylidene sugars **15** and **16** which were formed as a 5.7:1 mixture of separable anomers in a combined yield of 80%. The anomeric ^{1}H-n.m.r. doublets at δ 6.24 and 6.19, as well as the anomeric ^{13}C-n.m.r. signals at δ 96.92 and 93.77 for **15** and **16**, respectively, are consistent with the data obtained for the analogous derivatives of D-glucose[15].

Unlike the straightforward results obtained for **8**, treatment of acetonide **13** with boron trifluoride etherate in acetic anhydride afforded a complex mixture from which only the trisubstituted thiolane **17** could be isolated in a yield of 25%. This diacetyl acetal shows a C-1 ^{13}C-n.m.r. signal at δ 89.00 consistent with the value obtained for **9**.

TABLE I

Product distribution for the acetolysis of **8**

Temperature[a]	*Acid*	*Time (h)*	*% Yield*[b]		
			9	**6**	**6'**[c]
0° to RT	1.5 equiv. TsOH[d]	22	44	21	0
RT	5 equiv. TsOH	0.67	13	32	6
RT	4 equiv. TsOH	1.5	20	48	10
RT	3 equiv. TsOH	2	34	40	4
RT	0.5 equiv. BF_3OEt_2	20	9	34	9
RT	1 equiv. BF_3OEt_2	5	24	30	29
RT	4 equiv. CSA	8	34	36	9
48°	3 equiv. CSA	0.75	9	60	2
70°	3 equiv. CSA	0.25	<1	70	<1

[a] RT = room temperature. [b] Isolated yields. [c] α Anomer of **6**. [d] TsOH = *p*-toluenesulfonic acid and CSA = camphorsulfonic acid.

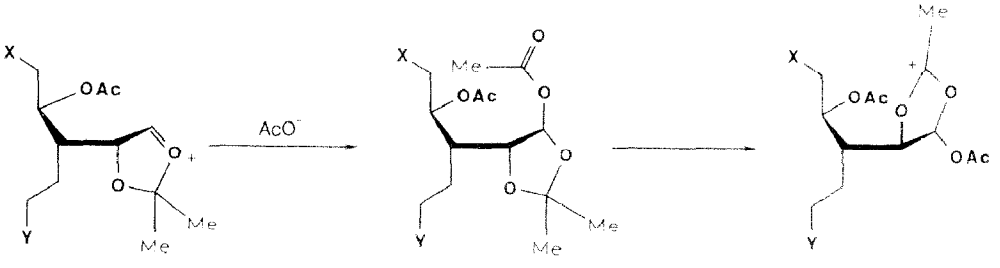
The strongly downfield-shifted acetal ^{1}H-n.m.r. peak at δ 7.26 suggested that the chemical shift of this proton is sensitive to the conformation of the acetoxy groups on C-1. At least four other compounds were obtained as an inseparable mixture which included the open-chain compounds **15** and **16**.

The formation of non-furanose products during the course of the acetolysis reactions and the marked dependence of their formation on the reaction temperature led us to speculate on the mechanisms of the processes involved. When furanoses **6** and **14** were resubjected to acetolytic conditions at room temperature, none of the low-temperature products were observed, nor were any furanose products formed from **9** upon heating to 50° in the standard solution, clearly demonstrating that the temperature-dependent product distributions do not simply represent equilibrium ratios. Studies[11,16] concerning the effect of the composition of the acetolyzing mixture on product distribution have been carried out, but we are not aware of any which have dealt with the effect of temperature.

A cyclic oxonium ion formed by scission of the exocyclic glycosylic bond is generally acknowledged to be the intermediate in the formation of 1,2-di-*O*-acetyl compounds, and this is no doubt the case for the formation of **6** and **14**. At lower temperatures, endocyclic C–O bond-cleavage is evidently favored, yielding an open-chain oxonium intermediate. The addition of an acetate would result in a 1-*O*-acetyl-1,2-*O*-isopropylidene aldehydrol such as **15** or **16**. We believe that the acetyl group at C-1 participates in the subsequent solvolysis of the isopropylidene moiety, yielding an acetoxonium ion bridging C-1 and C-2 as shown in Scheme 3. Attack at C-2 by the sulfur of an acetylthio group at either positions X or Y would give the thiolanes **17** and **9**, respectively, and account for the double inversion at this center.

Resubjecting a sample of **15** to the standard acetolytic solution at room temperature resulted only in the appearance of a small amount of its anomer **16**. Thus, these two 1-*O*-acetyl-1,2-*O*-isopropylidene compounds appear to proceed to thiolane **17** only in the presence of boron trifluoride etherate in acetic anhydride, unlike the case for the formation of **9** where the proposed 1-*O*-acetyl-1,2-*O*-isopropylidene precursor is never observed. The differing tendencies of the thiosugars to rearrange to the corresponding thiolane likely reflects the relative stabilities of the thiolane rings, **17** being less readily formed due to the additional ring substituent.

Fortunately, ring-expansion from furanose to thiopyranose was only observed in



Scheme 3

the treatment of **8** with boron trifluoride etherate in acetic anhydride, which afforded **10**. There exists ample precedent for both ring-expansion from 5-thiofuranoses to thiopyranoses[17] as well as ring-contraction from 4-thiopyranoses to thiofuranoses[18] under standard acetolytic conditions. We were concerned that rearrangement to the thermodynamically favored thiopyranoses could be a serious drawback in our strategy towards the target nucleosides.

The presence of the branch-chain at C-3 in our thiosugars no doubt destabilizes the furanose ring, facilitating the ring-opening pathway. In simple sugars, endocyclic C–O bond scission is no doubt much less favored, accounting for the generally clean formation of furanose products upon acetolytic deacetalation at the standard low temperatures. It is also possible that both pathways are operative but ultimately afford the same sugar. The formation of an open-chain oxonium ion intermidiate which eventually recloses may account for phenomena such as C-2 epimerization[19] which has been observed in the acetolysis of 1,2-*O*-isopropylidene furanoses. It was recently demonstrated[20] that this inversion at C-2 occurs during the removal of the isopropylidene group, not after its removal as previously assumed. It is hoped that our observations prove useful, both in the preparation of sugars as well as in the understanding of their chemistry.

EXPERIMENTAL

General methods. — Melting points (m.p.s) were determined using an Electrothermal m.p. apparatus and are uncorrected. Optical rotation measurements were carried out in the indicated solvent employing a Jasco DIP-140 digital polarimeter and a 1-dm cell. Low-resolution chemical ionization mass spectra (c.i.-m.s.) were obtained on a Hewlett–Packard 5980A quadrapole mass spectrometer operating in the direct-inlet mode. High-resolution c.i. and f.a.b. mass spectra (h.r.m.s.) were obtained on a VG ZAB-HS sector mass spectrometer, again operating in the direct-inlet mode. Elemental analyses were performed by Guelph Chemical Laboratories Ltd. (Guelph, Ontario). All compounds were shown to be homogeneous by t.l.c. and high-field n.m.r. spectroscopy and/or to have a purity of $>95\%$ by elemental analysis.

^{1}H-n.m.r. spectra were recorded on a Varian XL200 spectrometer, and the assignments were based on homonuclear decoupling and/or COSY experiments. Deuteriochloroform was, in all cases, used as solvent with internal tetramethylsilane as the reference. The data are listed in Tables II and III with the multiplicities of the signals recorded using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet, q^5, quintet; s^6, sextet; h, heptet; and m, multiplet. ^{13}C-n.m.r. spectra were all obtained at 75.4 MHz using a Varian XL300 spectrometer. Deuteriochloroform was used with the $^{13}CDCl_3$ signal (assigned a value of δ 77.00) used as the reference peak. The assignments, which are listed in Tables IV and V, were in some cases made with the aid of APT and/or HETCOR experiments.

Tetrahydrofuran was distilled from sodium–benzophenone ketyl. Methylene

TABLE II

^{1}H-N.m.r. chemical shift data (δ, p.p.m.)

Proton(s)	*Compound*							
	2[a]	**3**[a]	**4**	**5**	**7**	**8**	**11**	**12**
H-1	6.23 d	6.05 d	5.90 d	5.87 d	5.81 d	5.81 d	5.81 d	5.74 d
H-2	5.86 dt	5.73–5.76 m[b]	4.71 t	4.68 t	4.68 t	4.68 t	4.42 t	4.44 t
H-3	—	—	2.13–2.34 m	2.12–2.30 m	1.83–2.17 m[b]	2.19–2.36 m	2.21 tt	2.07–2.23 m
H-4	5.58 q[c]	4.95 m	3.94 dt	3.86 dt	3.82–3.95 m[b]	3.83 m	3.90 ddd	3.69–3.94 m[b]
H-5$_A$	3.39 dd	3.22 dd	3.08 dd	3.03 dd	3.55 dd	3.68 dd	3.08 dd	3.54 dd
H-5$_B$	3.51 dd	3.37 dd	3.45 dd	3.39 dd	3.82–3.95 m[b]	3.88 dd	3.35 dd	3.69–3.94 m[b]
H-1′$_A$	6.05 t	5.73–5.76 m[b]	1.38–1.53 m	1.30–1.50 m	1.46–1.66 m	1.50–1.68 m	1.35–1.57 m	1.49–1.64 m
H-1′$_B$	—	—	1.67–1.88 m	1.72–1.92 m	1.83–2.17 m[b]	1.80–2.03 m	1.62–1.80 m	1.75–1.91 m
H-2′$_A$	—	—	3.56–3.67 m[b]	2.86–2.96 m[b]	3.01 dd[b]	2.92–3.10 m[b]	3.60–3.80 m[b]	3.69–3.94 m[b]
H-2′$_B$	—	—	3.56–3.67 m[b]	2.86–2.96 m[b]	3.01 dd[b]	2.92–3.10 m[b]	3.60–3.80 m[b]	3.69–3.94 m[b]
OH	—	—	1.6	—	1.8	—	—	1.9
CMe$_2$	1.47 s	1.50 s	1.34 s	1.47 s	1.50 s	1.48 s	1.46 s	1.48 s
	1.39 s	1.46 s	1.50 s	1.33 s	1.34 s	1.33 s	1.26 s	1.26 s
Bu^t			—	—	—	1.05 s	1.00 s	1.06 s
SAc		—	—	2.25 s	2.34 s	2.31 s	—	
OAc	—	—	—	—	—	—	—	—
	—	—				—	—	—
	—	—	—	—	—	—	—	—
phenyls	7.15–7.38 m	7.20–7.46 m	7.20–7.51 m	7.20–7.48 m	—	7.32–7.76 m	7.15–7.67 m	7.33–7.72 m

Proton(s)	*Compound*							
	13	**6**	**14**	**15**	**16**	**17**[c]	**9**[c]	**10**[c]
H-1	5.69 d	6.08 s	6.02 s	6.24 d	6.19 d	7.26 d	6.86 d	6.03 d
H-2	4.37 t	5.30 d	5.15 d	4.40 dd	4.14 dd	3.56 dd	3.52 t	5.09 dd
H-3	1.60–2.04 m[b]	2.55–2.80 m[b]	2.53 h	2.33–2.45 m	2.35–2.57 m	2.58 m	2.56–2.73 m	2.35–2.52 m[b]
H-4	3.95 dq	4.00 dt	4.11 h	5.19 dt	5.30 ddd	5.35 ddd	4.92 ddd	5.18 h
$H\text{-}5_A$	3.01 dd	3.68 dd	3.04 dd	3.13 dd	3.22 dd	2.89 dd	3.73 dd	3.67 dd
$H\text{-}5_B$	3.33 dd	3.85 dd	3.32 dd	3.28 dd	3.32 dd	3.02 dd	3.81 dd	3.73 dd
$H\text{-}1'_A$	1.60–2.04 m[b]	1.48–1.90 m[b]	1.68–1.80 m[b]	1.45–1.76 m[b]	1.45–1.60 m[b]	1.50–1.84 m[b]	1.75–1.98 m	1.91 qd[d]
$H\text{-}1'_B$	1.60–2.04 m[b]	1.48–1.90 m[b]	1.68–1.80 m[b]	1.45–1.76 m[b]	1.45–1.60 m[b]	1.50–1.84 m[b]	2.15–2.30 m	2.27 dq[e]
$H\text{-}2'_A$	3.69–3.88 m[b]	2.55–2.80 m[b]	3.58–3.80 m[b]	3.72 t[f]	3.68 t[g]	3.62–3.82 m[b]	2.72–2.80 m	2.90 td[h]
$H\text{-}2'_B$	3.69–3.88 m[b]	2.86–3.02 m	3.58–3.80 m[b]	3.72 t[f]	3.68 t[g]	3.62–3.82 m[b]	2.85–2.98 m	2.35–2.52 m[b]
OH	—	—	—	—	—	—	—	—
CMe_2	1.24 s	—	—	1.46 s	1.38 s	—	—	—
	1.44 s	—	—	1.47 s	1.49 s	—	—	—
Bu^t	1.06 s	1.07 s	1.06 s	1.05 s	1.05 s	1.04 s	1.03 s	1.05 s
SAc	2.32 s	2.31 s	2.33 s	2.32 s	2.31 s	—	—	—
OAc	—	2.16 s	2.10 s	2.09 s	1.99 s	2.17 s	2.09 s	2.11 s
	—	1.91 s	2.02 s	1.97 s	1.94 s	2.07 s	2.09 s	2.06 s
—	—	—	—	—	—	2.00 s	2.06 s	1.78 s
phenyls	7.33–7.72 m	7.34–7.73 m	7.34–7.70 m	7.33–7.70 m	7.33–7.70 m	7.34–7.68 m	7.35–7.72 m	7.33–7.70 m

[a] COO*Me* signals at δ 3.57 and 3.76 for **2** and **3**, respectively. $H\text{-}1'_A$ refers to =C*H*COOMe for these compounds. [b] Overlapping signals. [c] Atom numbering based on that of the precursor furanose. [d] $J_{1,2,3} = 14$ Hz, $J_4 = 3$ Hz (indicates axial proton). [e] $J_{1,2,3} = 3$ Hz, $J_4 = 14$ Hz (indicates equatorial proton). [f] $J = 6$ Hz. [g] $J = 7$ Hz. [h] $J_{1,2} = 13$ Hz, $J_3 = 3$ Hz (indicates axial proton).

TABLE III

^{1}H-N.m.r. coupling constant data (hertz)

Spin-spin Coupling	*Compound*							
	2	**3**	**4**	**5**	**7**	**8**	**11**	**12**
$J_{H1,H2}$	4.6	4.5	3.8	3.7	3.6	3.6	3.7	3.6
$J_{H2,H3}$	—	—	4.7	4.6	4.4	4.6	4.5	4.5
$J_{H3,H4}$	—	—	10.0	10.2	[a]	[a]	10.2	[a]
$J_{H4,H5A}$	1.9	3.9	4.1	3.8	4.3	2.7	4.4	[a]
$J_{H4,H5B}$	2.4	4.1	2.8	3.1	[a]	2.9	3.0	[a]
$J_{H5A,H5B}$	−9.9	−10.0	−10.7	−10.6	−13.0	−10.8	−10.5	[a]

Spin-spin Coupling	*Compound*							
	13	**6**	**14**	**15**	**16**	**17**	**9**	**10**
$J_{H1,H2}$	3.8	0	0	3.1	3.0	9.0	5.0	2.9
$J_{H2,H3}$	4.4	4.5	4.5	4.8	9.5	7.0	4.7	11.4
$J_{H3,H4}$	9.9	9.3	9.7	4.8	3.0	3.4	8.8	2.4
$J_{H4,H5A}$	6.3	3.8	6.9	7.7	9.3	1.2	4.4	4.6
$J_{H4,H5B}$	3.1	3.5	3.4	4.6	4.6	4.7	3.0	7.8
$J_{H5A,H5B}$	−14.2	−11.4	−14.1	−14.0	−13.8	−12.4	−11.6	−10.8

[a] Unresolved.

chloride was distilled from P_2O_5. *N,N*-Dimethylformamide was dried by shaking with KOH, followed by distillation at reduced pressure from BaO. Kieselgel-60 F_{254} plates (0.2 mm thickness) were used for thin-layer chromatography and Kieselgel-60 (E. Merck 230–400 mesh) was employed for column chromatography.

Wittig reaction of **1** *to give unsaturated esters* **2** *and* **3**. — Trimethyl phosphonoacetate (2.10 mL, 12.8 mmol) was added dropwise to a cooled (0°) suspension of sodium hydride (60% oil dispersion, 510 mg, 12.8 mmol) in dry tetrahydrofuran (100 mL), and the mixture was stirred under a nitrogen atmosphere for 30 min. A solution of ketone **1** (ref. 5) (5.00 g, 11.6 mmol) in dry tetrahydrofuran (40 mL) was then added over 30 min. After 20 h of stirring at ambient temperature, the resulting clear solution was concentrated *in vacuo*, and the residue was extracted with ethyl ether (2 × 200 mL) and washed with aq. sodium hydrogencarbonate (200 mL) and water (200 mL). The combined ether extracts were then dried ($MgSO_4$), filtered and evaporated *in vacuo*, yielding esters **2** and **3** as an amorphous white solid in quantitative yield. The product was generally reduced in the next step without any further purification. The two isomeric esters were easily separated by chromatography over silica gel (5:1 v/v, hexanes–ethyl acetate), which yielded two products in a 3.8:1 ratio. The major product (R_f 0.24), obtained as colorless crystals by recrystallization from hexanes, was found to be the *Z*-ester **2**: m.p. 119–120°; $[\alpha]_D^{20}$ +110° (*c* 0.5, chloroform). For ^{1}H-n.m.r. data, see Tables II and III. For ^{13}C-n.m.r. data, see Table IV.

Anal. Calc. for $C_{30}H_{30}O_6$: C, 74.06; H, 6.21. Found: C, 73.70; H, 6.26.

The minor *E*-ester **3** (R_f 0.41) was also obtained as colorless crystals by recrystalli-

TABLE IV

^{13}C-N.m.r. chemical shift data (δ, p.p.m.)

Carbon Atom	*Compound*							
	2[a]	**3**[b]	**4**	**5**	**7**	**8**	**11**	**12**
C-1	104.56	105.27	104.92	104.88	104.77	104.79	105.05	104.92
C-2	82.34[b]	79.51[b]	81.48[b]	80.70[b]	81.81[b]	81.73[b]	81.01	82.11[b]
C-3	160.41	156.70	42.28	43.87	42.55	42.99	42.20	40.76
C-4	81.02[b]	78.51[b]	80.83[b]	80.52[b]	80.82[b]	80.70[b]	81.01	81.39[b]
C-5	65.70	65.32	63.33	62.76	61.31	62.71	62.20	62.16[d]
C-1′	116.06[c]	115.96[c]	26.40	27.19[d]	27.02[d]	27.14[d]	27.69	27.55
C-2′	165.47[e]	165.20[e]	61.14	26.69[d]	26.59[d]	26.42[d]	63.54	61.95[d]
Tr(*C*Ph$_3$)	87.16	86.88	86.56	86.38	—	—	86.50	—
Si(*C*Me$_3$)	—	—	—	—	—	19.08	19.11	19.12
Si(C*Me*$_3$)	—	—	—	—	—	26.63	26.86	26.84
*C*Me$_2$	113.30	112.73	111.36	111.42	111.60	111.35	111.21	111.48
C*Me*$_2$	27.68	27.14	26.70	24.62	24.71	24.72	26.35	26.28
	27.85	27.41	27.92	26.37	26.24	26.28	26.78	26.73
SCOMe	—	—	—	195.47	195.65	195.20	—	—
SCO*Me*	—	—	—	30.50	30.50	30.38	—	—
OCOMe	—	—			—	—	—	—
	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—
OCO*Me*	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—
Phenyls	127.01	127.01	126.98	126.90	—	127.50	126.88	127.62
	127.77	127.77	127.81	127.74	—	127.54	127.57	129.63
	128.56	128.46	128.64	128.63	—	129.48	127.59	133.68
	143.61	143.38	143.81	143.84	—	129.52	127.76	135.53
	—	—	—	—	—	132.91	128.70	135.58
	—	—	—	—	—	133.16	129.54	—
	—	—	—	—	—	135.46	129.58	—
	—	—	—	—	—	135.73	133.77	—
	—	—	—	—	—	—	133.82	—
	—	—	—	—	—	—	135.51	—
	—	—	—	—	—	—	135.57	—
	—	—	—	—	—	—	143.98	—

[a] COO*Me* signals at δ 51.36 and δ 51.56 for **2** and **3**, respectively. [b] Assignments may be exchanged. [c] *C*COOMe. [d] Assignments may be exchanged. [e] *C*OOMe. [f] Assignments may be exchanged.

zation from hexanes: m.p. 115–116°; $[\alpha]_D^{20}$ +252° (*c* 0.5, chloroform). For ^{1}H-n.m.r. data, see Tables II and III. For ^{13}C-n.m.r. data, see Table IV.

Anal. Calc. for $C_{30}H_{30}O_6$: C, 74.06; H, 6.21. Found: C, 73.81; H, 6.62.

*3-Deoxy-3-C-(2′-hydroxyethyl)-1,2-O-isopropylidene-5-O-(triphenylmethyl)-α-*D*-ribofuranose* (**4**). — A solution of the isomeric esters **2** and **3** (33.0 g, 67.8 mmol) in dry tetrahydrofuran (350 mL) was added over 20 min to a stirred suspension of lithium aluminium hydride (23.4 g, 617 mmol) in dry tetrahydrofuran (2 L) cooled to 0°. The mixture was then heated under reflux under nitrogen, resulting in the appearance of a bright red color. After 22 h the mixture was cooled in ice, and the remaining hydride was

TABLE V
^{13}C-N.m.r. chemical shift data (δ, p.p.m.)

Carbon atom	*Compound*							
	13	**6**	**14**	**15**	**16**	**17**	**9**	**10**
C-1	104.70	98.78	98.43	96.92	93.77	89.00	90.63	75.58
C-2	80.82[a]	76.72	77.19	81.29	78.88	50.84	51.99	72.85
C-3	44.59	39.79	40.57	38.64	37.35	45.67	43.85	36.59
C-4	79.83[a]	85.21	83.38	71.62	72.17	76.66	75.39	70.86
C-5	31.06	63.90	33.28	30.74[a]	31.26[a]	36.12	63.73	63.87
C-1′	27.24	27.28	27.36	29.31[a]	30.02[a]	28.58	31.59	23.66
C-2′	61.90	25.26	61.68	61.43	61.26	61.94	34.04	31.51
Tr(CPh_3)	—	—	—	—	—	—	—	—
Si(CMe_3)	19.03	19.17	19.08	19.06	19.15	19.16	19.20	18.99
Si(CMe_3)	26.77	26.69	26.73	26.71	26.82	26.86	26.66	26.51
CMe_2	111.24	—	—	111.62	111.39	—	—	—
CMe_2	26.13	—	—	25.93	25.55	—	—	—
	26.57	—	—	26.71	28.19	—	—	
SCOMe	194.91	194.94	194.86	194.28	194.57			
SCO*Me*	30.32	30.46	30.38	30.39	30.44	—	—	—
OCOMe	—	168.33	169.06	169.97	170.10	168.14	168.70	169.33
	—	169.98	169.70	170.30	170.38	168.19	168.83	169.46
	—	—	—	—	—	170.47	170.49	170.23
OCO*Me*	—	20.65	20.54	20.71	20.90	20.75	20.71	20.61
		20.99	21.06	21.19	21.16	20.91	20.71	20.92
	—	—	—		—	20.95	21.01	20.61
Phenyls	127.52	127.64	127.65	127.62	127.71	127.72	127.65	127.73
	129.51	127.69	129.64	129.59	129.68	127.76	129.71	129.77
	133.55	129.66	129.66	133.40	133.35	129.78	132.88	133.39
	133.60	129.73	133.28	133.43	133.53	129.85	132.99	133.47
	135.42	132.91	133.39	135.47	135.45	132.90	135.37	135.47
	135.47	133.01	135.34	—	—	133.05	135.43	—
	—	135.41	135.40	—		135.42	—	—
	—	135.46	—	—	—	135.52	—	—

[a] Assignments may be exchanged.

destroyed by the careful addition of water. The resulting slurry was filtered, the solids were washed with copious amounts of ethyl ether, and the solvents were evaporated *in vacuo*. Chromatography of the crude syrup over silica gel (2:1 v/v, hexanes–ethyl acetate) afforded alcohol **4** as an amorphous white solid (24.7 g, 79% yield): $[\alpha]_D^{22} + 39°$ (*c* 0.5, chloroform); h.r.m.s. (c.i.-m.s., NH_3): calc. for $C_{23}H_{27}O_5$ [MH^+ – PhH]: *m/z* 383.1858; found: *m/z* 383.1853. For n.m.r. data, see Tables II–IV.

Anal. Calc. for $C_{29}H_{32}O_5$: C, 75.63; H, 7.00. Found: C, 75.69; H, 7.25.

*3-C-[2′-(Acetylthio)ethyl]-3-deoxy-1,2-O-isopropylidene-5-O-(triphenylmethyl)-*α*-D-ribofuranose* (**5**). — Diisopropyl azodicarboxylate (1.17 mL, 5.90 mmol) was added dropwise to a stirred solution of triphenylphosphine (1.55 g, 5.90 mmol) in dry tetrahydrofuran (15 mL) cooled to 0°. After 30 min of stirring under nitrogen, a creamy white suspension formed to which was added a solution of alcohol **4** (1.35 g, 2.95 mmol) and thiolacetic acid (422 μL, 5.90 mmol) in dry tetrahydrofuran (10 mL). After an additional

30 min of stirring at 0°, the reaction was allowed to warm to room temperature. One h later, the solvent was evaporated *in vacuo*, yielding a yellow syrup which was chromatographed over silica gel (8:1 v/v, hexanes–ethyl acetate) affording thiolester **5**, contaminated with a non-sugar impurity, as a colorless solid. The subsequent hydrolysis was generally carried out on this crude material. An analytical sample was obtained by recrystallization from hexanes which afforded **5** as white crystals: m.p. 85.5–87°; $[\alpha]_D^{20}$ +54.4° (*c* 1, chloroform); h.r.m.s. (f.a.b.-m.s., glycerol): calc. for $C_{25}H_{29}O_5S$ [MH^+ – PhH] *m/z* 441.1736; found: *m/z* 441.1734. For n.m.r. data, see Tables II–IV.

Anal. Calc. for $C_{31}H_{34}O_5S$: C, 71.79; H, 6.61; S, 6.18. Found: C, 71.99; H, 6.50; S, 6.13.

3-C-[2'-(Acetylthio)ethyl]-3-deoxy-1,2-O-isopropylidene-α-D-ribofuranose (**7**). — The impure thiolester **5** prepared above was dissolved in dry methylene chloride (80 mL). A solution of trichloroacetic acid (previously dried by azeotropic distillation with benzene) in dry dichloromethane (1:4 w/v, 28.0 mL) was then added dropwise. After 3 h of stirring at ambient temperature under nitrogen, the reaction was diluted with chloroform (150 mL), washed with satd. aq. sodium hydrogencarbonate (300 mL) and water (300 mL), and re-extracted with chloroform (250 mL). For large-scale reactions, the acid was neutralized with aq. sodium hydroxide (1M) prior to the workup. The combined organic phases were then dried ($MgSO_4$), filtered, and evaporated *in vacuo*, yielding a yellow syrup which was chromatographed over silica gel (1:1 v/v, hexanes–ethyl acetate) affording alcohol **7** as a clear, colorless syrup (638 mg, 78% yield from **5** above): $[\alpha]_D^{22}$ +91.8° (*c* 1.14, chloroform); h.r.m.s. (c.i.-m.s., NH_3): calc. for $C_{12}H_{24}O_5SN$ [$M + NH_4$]: *m/z* 294.1375; found: *m/z* 294.1376. For n.m.r. data, see Tables II–V.

Anal. Calc. for $C_{12}H_{20}O_5S$: C, 52.16; H, 7.29; S, 11.60. Found: C, 51.87; H, 7.14; S, 11.82.

3-C-[2'-(Acetylthio)ethyl]-5-O-tert-butyldiphenylsilyl-3-deoxy-1,2-isopropylidene-α-D-ribofuranose (**8**). — *tert*-Butylchlorodiphenylsilane (4.27 mL, 16.7 mmol) was added dropwise to a solution of alcohol **7** (4.52 g, 16.4 mmol) and imidazole (2.34 g, 34.4 mmol) in dry *N,N*-dimethylformamide (21.5 mL), and the resulting solution was stirred at ambient temperature under nitrogen. After 2 h the solution was poured into water (800 mL), extracted with ethyl ether (2 × 750 mL), and washed with water (2 × 800 mL). The combined ether phases were dried ($MgSO_4$), filtered, and the solvent was evaporated *in vacuo*, yielding a light brown syrup. Chromatography over silica gel (12:1 v/v, hexanes–ethyl acetate) afforded **8** as a clear, colorless syrup (8.41 g, 99% yield): $[\alpha]_D^{22}$ +37.8° (*c* 1.5, chloroform); h.r.m.s. (c.i.-m.s., NH_3), calc. for $C_{24}H_{29}O_5SSi$ [MH^+ – C_4H_{10}]: *m/z* 457.1505; found: *m/z* 457.1506. For n.m.r. data, see Tables II–V.

Anal. Calc. for $C_{28}H_{38}O_5SSi$: C, 65.33; H, 7.44; S, 6.23. Found: C, 65.25; H, 7.58; S, 6.05.

3-C-[2'-O-tert-Butyldiphenylsilyloxy)ethyl]-3-deoxy-1,2-O-isopropylidene-5-O-(triphenylmethyl)-α-D-ribofuranose (**11**). — Alcohol **4** was silylated and worked up by the same procedure as described for the preparation of **8**, above. Purification of the crude product by chromatography over silica gel (9:1 v/v, hexanes–ethyl acetate) afforded **11** as an amorphous white solid (98% yield): $[\alpha]_D^{22}$ +25.6° (*c* 2, chloroform);

f.a.b.-m.s. (nitrobenzyl alcohol): *m/z* 621 [$MH^+ - PhH$]. For n.m.r. data, see Tables II–IV.

Anal. Calc. for $C_{45}H_{50}O_5Si$: C, 77.33; H, 7.21. Found: C, 77.06; H, 7.49.

3-C[2'-O-(tert-Butyldiphenylsilyloxy)ethyl]-3-deoxy-1,2-O-isopropylidene-α-D-ribofuranose (**12**). — The trityl group of **11** was selectively cleaved by the same procedure used for the preparation of **7**, described above. Purification of the crude product by chromatography over silica gel (3:1 v/v, hexanes–ethyl acetate) afforded alcohol **12** as a clear, colorless oil (92% yield): $[\alpha]_D^{20}$ +42.0° (*c* 2, chloroform); h.r.m.s. (c.i.-m.s., NH_3), calc. for $C_{22}H_{27}O_5Si$ [$MH^+ - C_4H_{10}$]: *m/z* 399.1628; found: *m/z* 399.1627. For n.m.r. data, see Tables II–IV.

Anal. Calc. for $C_{26}H_{36}O_5Si$: C, 68.39; H, 7.95. Found: C, 68.72; H, 8.13.

5-S-Acetyl-3-C-[2'-O-(tert-butyldiphenylsilyloxy)ethyl]-3,5-dideoxy-1,2-O-isopropylidene-5-thio-α-D-ribofuranose (**13**). — The Mitsunobu coupling of **12** and thiolacetic acid was carried out and worked up as described for the preparation of **5**, above. Purification of the crude product by chromatography over silica gel (6:1 v/v, hexanes–ethyl acetate) afforded **13** as a clear, colorless syrup (84% yield): $[\alpha]_D^{23}$ −38.6° (*c* 2, chloroform); h.r.m.s. (c.i.-m.s., NH_3): calc. for $C_{24}H_{30}O_5SSi$ [$MH^+ - C_4H_{10}$]: *m/z* 457.1505; found: *m/z* 457.1503. For n.m.r. data, see Tables II, III and V.

Anal. Calc. for $C_{28}H_{38}O_5SSi$: C, 65.33; H, 7.44; S, 6.25. Found: C, 65.41; H, 7.50; S, 6.25.

Acetolysis of **8**. — Acetonide **8** (150 mg, 0.291 mmol) was dissolved in glacial acetic acid (4.5 mL) containing acetic anhydride (0.690 mL, 7.28 mmol), and the solution was allowed to reach the desired reaction temperature (oil bath or ice bath). Either *p*-toluenesulfonic acid hydrate, anhydrous (±)-camphorsulfonic acid or boron trifluoride etherate was then added, and the solution was stirred under a nitrogen atmosphere. Upon completion of the reaction (t.l.c. monitoring), the solution was cooled in ice and slowly poured into a solution of sodium carbonate (8.0 g) in water (50 mL), and the resulting suspension was swirled intermittently over 30 min. The product was then extracted with ethyl ether (2 × 60 mL) and washed with satd. aq. sodium hydrogencarbonate (80 mL) and water (80 mL). The combined ether extracts were dried ($MgSO_4$), filtered, and the solvent was evaporated *in vacuo*, yielding a yellow syrup. Chromatography over silica gel (7.5:1 v/v, petroleum ether–ethyl acetate) afforded the polar component (R_f 0.16) furanose sugar **6**, as a clear, colorless syrup: $[\alpha]_D^{20}$ −18.4° (*c* 1.56, chloroform); h.r.m.s. (c.i.-m.s., NH_3): calc. for $C_{27}H_{35}O_5SSi$ [$MH^+ - AcOH$]: *m/z* 499.1974; found: *m/z* 499.1973. For n.m.r. data, see Tables II, III, and V.

Anal. Calc. for $C_{29}H_{38}O_5SSi$: C, 62.34; H, 6.85; S, 5.74. Found: C, 62.31; H, 7.05; S, 5.94.

The less polar component (R_f 0.23), thiolane **9**, was isolated as a clear, colorless syrup: $[\alpha]_D^{20}$ +35.3° (*c* 2.20, chloroform); h.r.m.s. (c.i.-m.s., NH_3): calc. for $C_{25}H_{29}O_5SSi$ [$MH^+ - C_4H_{10}$]: *m/z* 501.1403; found: *m/z* 501.1401. For n.m.r. data, see Tables II, III, and IV.

Brief exposure of thiolane **9** to methanolic sodium hydroxide (15 min, 25°)

afforded the corresponding aldehyde: ^{1}H-n.m.r. ($CDCl_3$, 200 MHz) δ 1.05 (s, 9 H, Bu^t), 1.64–1.89 (m, 1 H, H1′$_A$), 1.96 (s, 3 H, 4-OAc), 2.20–2.33 (m, 1 H, H1′$_B$), 2.79–2.97 (m, 3 H, H3 and H2′$_{A,B}$), 3.62 (dd, 1 H, H2), 3.73 (A of ABX, 1 H, H5$_A$), 3.79 (B of ABX, 1 H, H5$_B$), 4.98 (ddd, 1 H, H4), 9.18 (d, 1 H, H1), and 7.33–7.68 (m, 10 H, phenyls); coupling constants (Hz): $J_{H1\text{-}H2}$ 5.1, $J_{H2\text{-}H3}$ 8.1, $J_{H3\text{-}H4}$ 8.7, $J_{H4\text{-}H5A}$ 4.6, $J_{H4\text{-}H5B}$ 3.4, $^2J_{H5AH5B}$ −11.6.

Acetolysis of **13**. — Acetonide **13** was acetolyzed in a manner identical to that described for **8**, above. After stirring for 15 min at 75°, the reaction was worked up in the usual manner. Chromatography over silica gel (6:1 v/v, hexanes–ethyl acetate) afforded furanose **14** as a colorless syrup (80% yield): $[\alpha]_D^{22}$ −12.3° (*c* 2, chloroform); h.r.m.s. (c.i.-m.s., NH_3): calc. for $C_{27}H_{35}O_5SSi$ [MH^+ − AcOH]: *m/z* 499.1974; found: *m/z* 499.1973. For n.m.r. data, see Tables II, III and V.

Anal. Calc. for $C_{29}H_{38}O_7SSi$: C, 62.34; H, 6.85; S, 5.74. Found: C, 62.28; H, 7.01; S, 5.91.

The acetolysis reaction carried out over 24 h at 15° yielded three products after the usual workup and chromatography over silica gel (6:1 v/v, hexanes–ethyl acetate): *β*-furanose **14** (8% yield), the major (1*R*)-1-*O*-acetyl acetonide **15** as a clear, colorless syrup (68% yield): $[\alpha]_D^{22}$ +12.8° (*c* 1, chloroform); h.r.m.s. (c.i.-m.s., NH_3): calc. for $C_{30}H_{41}O_6SSi$ [MH^+ − AcOH]: *m/z* 557.2393; found: *m/z* 557.2390; and the minor (1*S*)-1-*O*-acetyl acetonide **16** as a clear, colorless syrup (12% yield): $[\alpha]_D^{22}$ −14.5° (*c* 1.30, chloroform); h.r.m.s. (c.i.-m.s., NH_3); calc. for $C_{30}H_{41}O_6SSi$]MH^+ − AcOH]: *m/z* 557.2393; found: *m/z* 557.2390. For n.m.r. data, see Tables II, III, and V.

Thiolane **17**. — Boron trifluoride etherate (0.50 mL) was added dropwise to an ice-cold solution of acetonide **13** (200 mg, 0.389 mmol) in acetic anhydride (1.0 mL), and the reaction was stirred under a nitrogen atmosphere. After 20 min the reaction was slowly added to a solution of sodium carbonate (3.7 g) in water (100 mL), and the resulting suspension was swirled intermittently over 30 min. The product was then extracted with ethyl ether (2 × 75 mL) and washed with water (100 mL). The combined ether phases were dried ($MgSO_4$), filtered and evaporated *in vacuo* yielding a yellow syrup. Chromatography over silica gel (6.5:1 v/v, hexanes–ethyl acetate) afforded thiolane **17** as a clear, colorless syrup (54 mg, 25% yield): $[\alpha]_D^{20}$ +20.0° (*c* 0.9, chloroform); h.r.m.s. (c.i.-m.s., NH_3): calc. for $C_{27}H_{35}O_5SSi$ [MH^+ − AcOH]: *m/z* 499.1974; found: *m/z* 499.1973. For n.m.r. data, see Tables II, III, and V.

*3-C[(1R)-1-Acetoxy-2-*O*-(*tert*-butyldiphenylsilyloxy)]-1,2-di-*O*-acetyl-3,4,5-trideoxy-5-thio-β-*L*-threo-pentopyranose* (**10**). — Acetonide **8** was treated with boron trifluoride etherate in acetic anhydride and worked up as described for the preparation of **17**, above. Purification of the thiosugar by chromatography over silica gel (6:1 v/v, hexanes–ethyl acetate) afforded thiopyranose **10** as a colorless glass which crystallized upon standing (70% yield): m.p. 121–122°; $[\alpha]_D^{20}$ +168° (*c* 0.6, chloroform); h.r.m.s. (c.i.-m.s., NH_3); calc. for $C_{27}H_{35}O_5SSi$ [MH^+ − AcOH]: *m/z* 499.1974; found: *m/z* 499.1973. For n.m.r. data, see Tables II, III and V.

Anal. Calc. for $C_{29}H_{38}O_7SSi$: C, 62.34; H, 6.85; S, 5.74. Found: C, 62.11; H, 6.78; S, 5.98.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada and the Ministère de l'éducation du Québec (FCAR). S. H. Kawai thanks NSERC for a postgraduate scholarship. We are grateful to Prof. O. A. Mamer and Dr. E. Osei-Twum for the measurement of mass spectra and to Prof. A. S. Perlin for the many helpful discussions. The fine work of M. Papamichelakis and T. Klysa is also acknowledged.

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