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REACTIONS OF D-GLUCOSE, D-XYLOSE, AND D-ERYTHROSE WITH 2-METHYL-2-PROPANETHIOL

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ABSTRACT

The reaction of D-glucose and D-xylose with 2-methyl-2-propanethiol in conc. hydrochloric acid yielded *tert*-butyl 1-thioglycopyranosides (products of kinetic and thermodynamic control). Di-*tert*-butyl dithioacetals (**12–14**) were obtained from the acetylated *aldehydo*-derivatives of D-glucose, D-xylose, and D-erythrose. On brief treatment with conc. hydrochloric acid, **12** and **13** gave *tert*-butyl 1-thio-α- and -β-glycopyranosides and **14** gave the corresponding furanosides.

INTRODUCTION

Numerous thiols have been used in the preparation of sugar dithioacetals, especially ethanethiol, α-toluenethiol, 1,2-ethanedithiol, and benzenethiol. The effects of the functional groups present are reflected in variations in the rate and/or course of the mercaptalation. Optimal yields of dithioacetals (products of kinetic control) from D-glucose[1], D-mannose[2], D-galactose[3,4], and D-xylose[5,6] are obtained after short reaction times. Prolonged treatment of sugars with alkanethiols in concentrated aqueous acid gives 1-thioglycopyranosides[7,8] (products of thermodynamic control).

The reaction of some 1,5-dialdehydes and 2-methyl-2-propanethiol in conc. hydrochloric acid affords various types of heterocyclic derivatives[9–12]. We now report on the reaction of some D-aldoses with 2-methyl-2-propanethiol in conc. hydrochloric acid.

RESULTS AND DISCUSSION

When the reactions of 2-methyl-2-propanethiol with D-glucose and D-xylose at room temperature in conc. hydrochloric acid were monitored by t.l.c., the di-*tert*-

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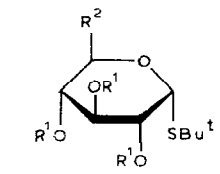
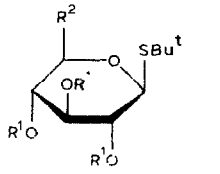
butyl dithioacetals were not detected. *tert*-Butyl 1-thio-α,β-D-glucopyranosides and -D-xylopyranosides had been formed in small proportions after 10 min and the proportions increased up to ~12 h.

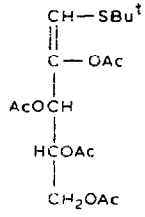
Thus, D-glucose gave *tert*-butyl 1-thio-α- (**1**, 24.2%) and -β-D-glucopyranoside (**2**, 27.3%) isolated as the tetra-acetates. An equimolar mixture of D-glucose and ethanethiol gave 15% of ethyl 1-thio-α-D-glucopyranoside and, probably, some β anomer; no diethyl dithioacetal was detected[13]. D-Xylose yielded *tert*-butyl 1-thio-α- (**3**, 25.6%) and -β-D-xylopyranoside (**4**, 11.1%), isolated as the triacetates, and (*E*)- or (*Z*)-2,3,4,5-tetra-*O*-acetyl-1-*S*-*tert*-butyl-1-thio-D-*threo*-pent-1-enitol (**5**, 3.7%), which had ν_{max} 3051 (C=C–H) and 1640 cm^{-1} (C=C), a ^{1}H-n.m.r. signal at δ 6.30 (H–C=), and ^{13}C-n.m.r. signals at δ 139.39 (C-2) and 118.46 (C-1).



1 R^1 = Ac, R^2 = CH_2OAc
3 R^1 = Ac, R^2 = H
20 R^1 = H, R^2 = CH_2OH
22 R^1 = R^2 = H



2 R^1 = Ac, R^2 = CH_2OAc
4 R^1 = Ac, R^2 = H
21 R^1 = H, R^2 = CH_2OH
23 R^1 = R^2 = H



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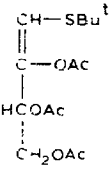

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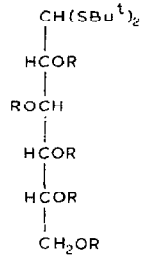
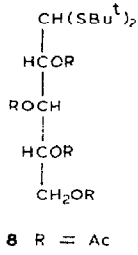
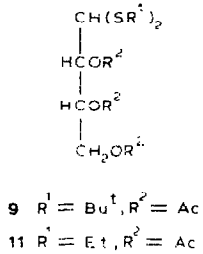


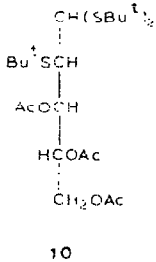
7 R = Ac
12 R = H



8 R = Ac
13 R = H



9 R^1 = Bu^t, R^2 = Ac
11 R^1 = Et, R^2 = Ac
14 R^1 = Bu^t, R^2 = H
15 R^1 = Et, R^2 = H



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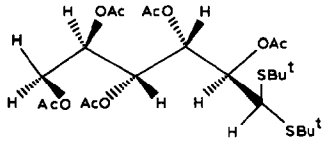
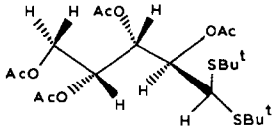
Reaction of 2,4-*O*-ethylidene-D-erythrose (precursor of D-erythrose) with 2-methyl-2-propanethiol under the above conditions gave a complex mixture of products. However, reaction for 15 min and acetylation of the crude product gave a mixture of (*E*)- and (*Z*)-2,3,4-tri-*O*-acetyl-1-*S*-*tert*-butyl-1-thio-D-*glycero*-tetr-1-enitol (**6**, 11.1%), which was identified tentatively on the basis of spectroscopic data (see Experimental). Thioglycosides were not detected.

Anomeric configurations were assigned to the 1-thio-D-glycopyranosides **1–4** on the basis of Hudson's rules[7,8,14] and the $J_{1,2}$ values. The α-anomers **1** and **3** were more dextrorotatory than the β-anomers **2** and **4**, and the $J_{1,2}$ values were ~5.5 Hz. The signals of H-1 of **1** and **3** were at lower field than those of **2** and **4**, respectively, reflecting an equatorial position in the preferred $^4C_1$(D) conformation. The 1-thio-pyranosides **1** and **2** had physical constants in good agreement with literature values[15].

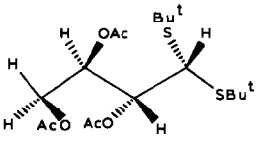
The acetylated di-*tert*-butyl dithioacetals **7–9** have been synthesised by reaction of 2,3,4,5,6-penta-*O*-acetyl-*aldehydo*-D-glucose[16], 2,3,4,5-tetra-*O*-acetyl-*aldehydo*-D-xylose[17], and 2,3,4-tri-*O*-acetyl-*aldehydo*-D-erythrose, respectively, with 2-methyl-2-propanethiol and a catalytic amount of boron trifluoride–ether complex[18]. The reaction of 2,3,4,5-tetra-*O*-acetyl-*aldehydo*-D-xylose yielded a minor product, tentatively identified as 3,4,5-tri-*O*-acetyl-2-*S*-*tert*-butyl-2-thio-D-lyxose di-*tert*-butyl dithioacetal (**10**) on the basis of a displacement at position 2 with inversion of configuration[19,20] and $J_{1,2}$, $J_{2,3}$, $J_{3,4}$, $J_{4,5}$, and $J_{4,5'}$ values which accorded[20] with a **P** conformation[21] in chloroform solution and with a segment (C-1,2,3) having the *manno* configuration[20].



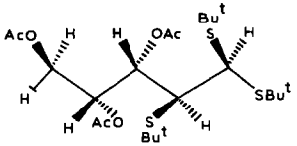
D-*gluco* **7**-$_2G^-$, $_5G^+$



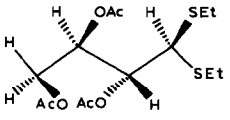
D-*xylo* **8**-$_2G^-$



D-*erythro* **9**-P $_1G^-$



D-*lyxo* **10**-P



D-*erythro* **11**-P

The J values for 2,3,4,5,6-penta-*O*-acetyl-D-glucose di-*tert*-butyl dithioacetal (**7**) (see Table I) indicate a preponderant $_2G^-$ conformation of the backbone chain similar to that reported[22] for the diethyl dithioacetal analogue.

The J values for 2,3,4,5-tetra-*O*-acetyl-D-xylose di-*tert*-butyl dithioacetal (**8**) (see Table I) are in agreement with the $_2G^-$ sickle conformation, similar to that reported[6] for 2,3,4,5-tetra-*O*-acetyl-D-xylose diphenyl dithioacetal.

For 2,3,4-tri-*O*-acetyl-D-erythrose di-*tert*-butyl (**9**) and diethyl dithioacetal (**11**), the $J_{2,3}$ values indicate *trans*-periplanar protons. The $J_{1,2}$ value for **11** is somewhat low for exclusive population of the rotamer having H-1,2 *trans*-periplanar and indicate a substantial population of a rotamer ($_1G^+$) having these protons *gauche*.

TABLE I

^{1}H-N.M.R. DATA ($CDCl_3$, 200 MHz) FOR PERACETYLATED ALDOSE DI-*tert*-BUTYL DITHIOACETALS AND THEIR DIETHYL AND DIPHENYL ANALOGUES

	D-gluco		D-xylo			D-erythro	
	Diethyl[a]	*Di*-tert-*butyl*	*Diethyl*[b]	*Diphenyl*[c]	*Di*-tert-*butyl*	*Diethyl*[d]	*Di*-tert-*butyl*
First-order coupling constants (Hz)							
$J_{1,2}$	4.4	3.1	5.2	3.0	3.5	5.4	2.1
$J_{2,3}$	7.5	7.8	5.9	7.0	6.4	~9	8.1
$J_{3,4}$	2.9	2.0	4.2	3.1	3.7	3.0	2.5
$J_{3,4'}$	—	—	—	—	—	5.0	4.6
$J_{4,4'}$	—	—	—	—	—	12.5	12.6
$J_{4,5}$	8.0	8.6	4.3	5.1	4.7		
$J_{4,5'}$	—	—	6.6	7.2	6.8		
$J_{5,5'}$	—	—	11.8	11.9	11.7		
$J_{5,6}$	3.0	[e]					
$J_{5,6'}$	4.6	[e]					
$J_{6,6'}$	12.6	—					
Chemical shifts (δ scale)							
H-1	4.08(d)	4.34(d)	3.98	4.41	4.21(d)	3.93(d)	4.19(d)
H-2	5.29(dd)	5.36(dd)	5.35	5.42	5.38(dd)	5.45(dd)	5.55(dd)
H-3	5.77(dd)	5.87(dd)	5.74	5.78	5.83(dd)	5.50(m)	5.42(ddd)
H-4	5.44(dd)	5.58(dd)	5.38	5.38	5.45(m)	4.35(dd)	4.37(dd)
H-4′	—	—	—	—	—	4.22(dd)	4.16(dd)
H-5	5.07(m)	5.1–4.9(d pseudo t)	4.33	4.23	4.33(dd)		
H-5′	—	—	4.01	3.87	3.92(dd)		
H-6	4.25(q)	4.19(m)					
H-6′	4.14(q)	4.19(m)					
Other signals		2.16, 2.09, and 2.04 (3 s, 15 H, 5 Ac), 1.51 and 1.33 (2 s, 18 H, 2 Me_3C)			2.13, 2.12, 2.09, and 2.04 (4 s, 12 H, 4 Ac), 1.46 and 1.33 (2 s, 18 H, 2 Me_3C)	2.7 (m, 4 H, 2 CH_3CH_2S), 2.12, 2.08, and 2.07 (3 s, 9 H, 3 Ac), 1.28 and 1.26 (2 t, 6 H, *J* 7 Hz, 2 CH_3CH_2S)	2.12, 2.11, and 2.05 (3 s, 9 H, 3 Ac), 1.40 and 1.39 (2 s, 18 H, 2 Me_3C)

[a]Data from ref. 22. [b]Data from ref. 23. [c]Data from ref. 6. [d]At 80 MHz. [e]$J_{5,6} + J_{5,6'}$ ~6.7 Hz.

However, the $J_{1,2}$ value for **9** indicates preferential *gauche*-disposed protons in order to remove the parallel interaction between AcO-3 and one *tert*-butyl group.

The $J_{3,4}$ value (8 Hz) for **5** suggests *trans*-periplanar protons, and the sequence of asymmetric centres C-3,4 corresponds to the sequence of asymmetric centres C-2,3 in the *threo* arrangement with a ${}_3G^+$ conformation.

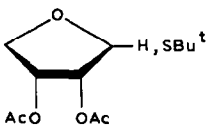
The small values of $J_{5,6} + J_{5,6'}$ for **7**, $J_{3,4} + J_{3,4'}$ for **9** and **11**, and $J_{4,5} + J_{4,5'}$ for **5** showed that there is substantial population of the ${}_5G^+$, ${}_3G^+$, and ${}_4G^+$ rotamers, respectively, similar to those reported[22] for 2,3,4,5,6-penta-*O*-acetyl-D-glucose diethyl dithioacetal.

Comparison of the *J* values in Table I for the acetylated di-*tert*-butyl dithioacetals **7–9** with those of the diethyl dithioacetal analogues reveals that there is little difference in the magnitude of the corresponding couplings, except for $J_{1,2}$. On the other hand, this difference for the $J_{1,2}$ values has not been observed with the diphenyl dithioacetal analogue of D-xylose.

For the di-*tert*-butyl derivatives **7–9**, the H-1 signal appeared ~0.25 p.p.m. to lower field than its position for the diethyl analogues (see Table I).

The di-*tert*-butyl dithioacetals **12–14** were obtained by saponification of the corresponding acetates **7–9**. Treatment of **12** and **13** with 2-methyl-2-propanethiol and conc. hydrochloric acid for 5 min at room temperature followed by acetylation yielded the 1-thioglucopyranosides **1** and **2**, and the 1-thioxylopyranosides **3** and **4**, respectively. Similar treatment of **14** gave **16** (α,β-mixture) and **6**. These results suggest that, when 2-methyl-2-propanethiol is used, the 1-thioglycosides are formed by kinetically and thermodynamically controlled reactions which do not resemble those reported[7,8], where sugar dithioacetals are the products of kinetic control and 1-thioglycosides those of thermodynamic control.

The fact that **6** was obtained both from **14**, with simultaneous formation of **16** in similar yield, and from D-erythrose, without the formation of **16**, suggests more than one way of formation from the intermediate **14**. The formation of **5** was not studied due to this result and since it was a minor product.



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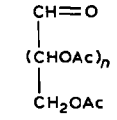

17 $n = 4$
18 $n = 3$
19 $n = 2$

EXPERIMENTAL

The general methods have been described[24]. N.m.r. spectra (^{1}H, 80 MHz, ^{13}C, 20 MHz) were recorded with a Bruker WP-80-SY spectrometer, and for com-

pounds **7–10** with a 200-MHz spectrometer of the Central University of Barcelona (Spain).

Reaction of D-*glucose and* D-*xylose with 2-methyl-2-propanethiol. — General method.* A mixture of the aldose (5 g), conc. hydrochloric acid (7 mL), and 2-methyl-2-propanethiol (10 mL) was shaken vigorously at ~15° for 12 h, then diluted with water (60 mL), basified with K_2CO_3, and extracted with hexane (2 × 50 mL) followed by ethyl acetate (6 × 50 mL). The combined ethyl acetate extracts were dried, filtered, and concentrated. The syrupy residue was treated conventionally with pyridine–acetic anhydride.

(*a*) The crude product obtained from D-glucose was purified by column chromatography (3:1 hexane-ether), to give, first, *tert*-butyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**2**; 3.19 g, 27.3%), m.p. 144–146° (from hexane), $[\alpha]_D^{18}$ −6° (*c* 0.9, chloroform); lit.[15] m.p. 145–146° (from ethanol–pentane), $[\alpha]_D^{20}$ −5.9° (chloroform); ν_{max}^{KBr} 1745, 1252, 1228, 1086, 1060, 1040, and 910 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.3–4.8 (m, 3 H, H-2,3,4), 4.65 (d, 1 H, *J* 10 Hz, H-1), 4.1 (m, 2 H, H-6,6′), 3.8–3.6 (m, 1 H, H-5), 2.05, 2.03, and 2.00 (3 s, 12 H, 4 Ac), and 1.37 (s, 9 H, Me_3C) (Found: C, 51.17; H, 6.54. $C_{18}H_{28}O_9S$ calc.: C, 51.42; H, 6.71%).

Eluted second was *tert*-butyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-glucopyranoside (**1**; 2.82 g, 24.2%), m.p. 59° (from hexane), $[\alpha]_D^{20}$ +183° (*c* 0.5, chloroform); lit.[15] m.p. 62–64°, $[\alpha]_D^{20}$ +185° (chloroform); ν_{max}^{KBr} 1740, 1230, 1085, 1030, and 900 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.85 (d, 1 H, *J* ~5.5 Hz, H-1), 5.4–4.8 (m, 3 H, H-2,3,4), 4.6–3.9 (m, 3 H, H-5,6,6′), 2.08, 2.07, 2.03, and 2.02 (4 s, 12 H, 4 Ac), and 1.36 (s, 9 H, Me_3C) (Found: C, 51.71; H, 6.81. $C_{18}H_{28}O_9S$ calc.: C, 51.42; H, 6.71%).

(*b*) The crude product obtained from D-xylose was purified by column chromatography (2:1 hexane–ether), to give, first, *tert*-butyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranoside (**4**; 1.29 g, 11.1%), m.p. 84–86° (from hexane–ether), $[\alpha]_D^{16}$ −42° (*c* 1, chloroform); ν_{max}^{KBr} 1760, 1246, 1225, 1066, 1040, 960, 940, 908, and 876 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.3–4.7 (m, 4 H, H-1,2,3,4), 4.24 (dd, 1 H, *J* 11.5 and 5.0 Hz, H-5*e*), 3.40 (dd, 1 H, *J* 11.5 and 8.5 Hz, H-5*a*), 2.06 and 2.04 (2 s, 9 H, 3 Ac), and 1.38 (s, 9 H, Me_3C) (Found: C, 51.89; H, 7.09. $C_{15}H_{24}O_7S$ calc.: C, 51.71; H, 6.94%).

Eluted second was *tert*-butyl 2,3,4-tri-*O*-acetyl-1-thio-α-D-xylopyranoside (**3**; 2.97 g, 25.6%), m.p. 127–129° (from hexane), $[\alpha]_D^{18}$ +155° (*c* 1.3, chloroform); ν_{max}^{KBr} 1750, 1230, 1068, 1040, 939, 908, 904, and 880 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.67 (d, 1 H, *J* 5.5 Hz, H-1), 5.24 (pseudo t, 1 H, $J_{2,3} + J_{3,4}$ ~18 Hz, H-3), 5.03–4.85 (m, 2 H, H-2,4), 4.03 (pseudo t, 1 H, $J_{4,5} + J_{5,5'}$ ~21 Hz, H-5*a*), 3.75 (dd, 1 H, *J* 11.0 and 6.0 Hz, H-5*e*), 2.02 and 2.00 (2 s, 9 H, 3 Ac), and 1.30 (s, 9 H, Me_3C) (Found: C, 51.70; H, 7.07. $C_{15}H_{24}O_7S$ calc.: C, 51.71; H, 6.94%).

Eluted third was (*E*)- or (*Z*)-2,3,4,5-tetra-*O*-acetyl-1-*S*-*tert*-butyl-1-thio-D-*threo*-pent-1-enitol (**5**; 0.48 g, 3.7%), m.p. 64° (from hexane), $[\alpha]_D^{25}$ −78° (*c* 1, chloroform); ν_{max}^{KBr} 3051, 1766, 1745, 1735, 1640, 1370, 1249, 1225, 1194, 1052, 969, and 862 cm^{-1}. N.m.r. data ($CDCl_3$): ^{1}H, δ 6.30 (s, 1 H, H-1), 5.62 (d, 1 H, *J* 8 Hz, H-3), 5.35 (m, 1 H, H-4), 4.42 (dd, 1 H, *J* 12.2 and 3.2 Hz, H-5), 4.05 (dd, 1 H, *J*

12.2 and 5.1 Hz, H-5'), 2.18, 2.06, and 2.02 (3 s, 12 H, 4 Ac), and 1.36 (s, 9 H, Me_3C); ^{13}C*, δ 170.19, 169.78, 169.50, and 167.06 (4 COO), 139.39 (C-2), 118.46 (C-1), 71.76 (C-4), 69.62 (C-3), 62.08 (C-5), 44.40 (*C*Me_3), 30.85 (C*Me*$_3$), 20.63 and 20.31 (4 *Me*CO) (Found: C, 52.11; H, 6.95. $C_{17}H_{26}O_8S$ calc.: C, 52.29; H, 6.71%).

*Reactions of 2,4-O-ethylidene-*aldehydo-D-*erythrose*[26] *with thiols. — General method.* A solution of 4,6-*O*-ethylidene-α,β-D-glucopyranose (5 g) in water (120 mL) was treated with $NaIO_4$ (12.5 g), the resulting crude product was shaken at room temperature with the appropriate thiol (10 mL) and conc. hydrochloric acid (8 mL), and the mixture was then diluted with water (60 mL), basified with K_2CO_3, and extracted with ethyl acetate (4 × 50 mL). The combined ethyl acetate extracts were dried, filtered, and concentrated.

(*a*) *With ethanethiol.* A reaction time of 4 min, followed by column chromatography (1:1 hexane–ethyl acetate) of the crude product, gave D-erythrose diethyl dithioacetal** (**15**; 3.3 g, 60%), isolated as a syrup, $[\alpha]_D^{23}$ +10° (*c* 1, chloroform); ν_{max}^{film} 3400, 1376, 1264, 1071, 1032, and 972 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 4.13 (d, 1 H, *J* 4 Hz, H-1), 3.85 (m, 4 H, H-2,3,4,4'), 3.48 (s, 3 H, exchangeable with D_2O, 3 OH), 2.73 and 2.69 (2 q, 4 H, *J* 7.5 Hz, 2 CH_3CH_2S), and 1.29 (t, 6 H, *J* 7.5 Hz, 2 CH_3CH_2S); ^{13}C, δ 74.05 (C-3), 72.09 (C-2), 63.57 (C-4), 54.87 (C-1), 25.54 and 25.43 (2 CH_3CH_2S), 14.63 and 14.48 (2 CH_3CH_2S) (Found: C, 42.60; H, 8.27. $C_8H_{18}O_3S_2$ calc.: C, 42.45; H, 8.02%).

Conventional acetylation of **15** (2.6 g) and column chromatography (5:1 hexane–ethyl acetate) of the product afforded 2,3,4-tri-*O*-acetyl-D-erythrose diethyl dithioacetal (**11**; 3.8 g, 94%), isolated as a syrup, $[\alpha]_D^{23}$ +13° (*c* 1, chloroform); ν_{max}^{film} 1747, 1370, 1216, 1049, and 955 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H (see Table I); ^{13}C, δ 170.45, 169.58, and 169.50 (3 COO), 72.03 (C-3), 70.86 (C-2), 61.53 (C-4), 51.54 (C-1), 24.99 (2 CH_3CH_2S), 20.76 and 20.58 (3 *Me*CO), 14.19 and 14.07 (2 CH_3CH_2S).

(*b*) *With 2-methyl-2-propanethiol.* A reaction time of 15 min, followed by conventional treatment with pyridine–acetic anhydride and column chromatography (3:1 hexane–ether) of the crude product, gave a mixture of (*E*)- and (*Z*)-2,3,4-tri-*O*-acetyl-1-*S*-*tert*-butyl-1-thio-D-*glycero*-tetr-1-enitol (**6**; 0.85 g, 11%), isolated as a syrup, $[\alpha]_D^{23}$ +53° (*c* 1, chloroform); ν_{max}^{film} 1746, 1635, 1457, 1369, 1219, 1047, and 952 cm^{-1}. ^1H-N.m.r. data ($CDCl_3$): δ 6.26 (s, ~0.75 H, H-1), 6.19 (s, ~0.25 H, H-1), 5.62 (m, 1 H, H-3), 4.25 (m, 2 H, H-4,4'), 2.21, 2.10, and 2.09 (3 s, 9 H, 3 Ac), 1.41 and 1.35 (2 s, 9 H, Me_3C) (Found: C, 52.80; H, 6.78. $C_{14}H_{22}O_6S$ calc.: C, 52.52; H, 7.00%).

*Peracetylated aldose di-*tert*-butyl dithioacetals* **7–9**. *— General method.* Boron trifluoride–ether complex was added to a solution of the corresponding per-

*Signal assignments confirmed by DEPT subprogramme and chemical shift values reported[25] for C-3,4 in acyclic sugars.

C. E. Ballou *et al.*[27] reported the synthesis of **15 without describing any physical properties.

acetylated *aldehydo*-D-aldose in a mixture of chloroform and 2-methyl-2-propanethiol. Each mixture was stored at room temperature for the reported time and then basified with saturated, aqueous sodium hydrogencarbonate (75 mL). The chloroform phase was dried, filtered, and concentrated. The following amounts and conditions were used.

Starting material (g)[a]	*Thiol (mL)*	*Chloroform (mL)*	*BF_3 (mL)*	*Time (min)*	*Products (g, %)*
17 (5)	25	55	1	40	**7** (6.44, 91)
18 (5.5)	25	50	1	300	**10** (1.80, 20)
					8 (3.52, 42)
19 (1.68)	10	25	0.5	50	**9** (1.68, 60)

[a] **17**, 2,3,4,5,6-penta-*O*-acetyl-*aldehydo*-D-glucose[16]; **18**, 2,3,4,5-tetra-*O*-acetyl-*aldehydo*-D-xylose[17]; **19**, 2,3,4-tri-*O*-acetyl-*aldehydo*-D-erythrose, which has been obtained from **15** (3.63 g) by conventional demercaptalation[16].

(*a*) *From* **17**. Crystallisation of the crude product from methanol gave **7**, m.p. 91–92°, $[\alpha]_D^{16}$ −17° (*c* 1.1, chloroform); ν_{max}^{KBr} 1765, 1740, 1230, 1210, 1050, and 1015 cm^{-1}. For the ^{1}H-n.m.r. data ($CDCl_3$), see Table I (Found: C, 52.29; H, 7.39. $C_{24}H_{40}O_{10}S_2$ calc.: C, 52.16; H, 7.29%).

(*b*) *From* **18**. Column chromatography (15:1 hexane–ether) of the crude product gave, first, **10**, m.p. 96–97° (from hexane), $[\alpha]_D^{16}$ +12° (*c* 1.1, chloroform); ν_{max}^{KBr} 1760, 1755, 1248, and 1215 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.54 (ddd, 1 H, *J* 6.9, 5.2, and 3.1 Hz, H-4), 5.14 (dd, 1 H, *J* 9.9 and 3.1 Hz, H-3), 4.37 (d, 1 H, *J* 1.8 Hz, H-1), 4.34 (dd, 1 H, *J* 11.6 and 5.2 Hz, H-5), 4.20 (dd, 1 H, *J* 11.6 and 6.9 Hz, H-5'), 3.58 (dd, 1 H, *J* 9.9 and 1.8 Hz, H-2), 2.15, 2.07, and 2.05 (3 s, 9 H, 3 Ac), 1.44, 1.43, and 1.38 (3 s, 27 H, 3 Me_3C) (Found: C, 54.37; H, 8.22. $C_{23}H_{42}O_6S_3$ calc.: C, 54.08; H, 8.29%).

Eluted second was **8**, m.p. 82–83° (from hexane), $[\alpha]_D^{16}$ ~0° (*c* 1, chloroform); ν_{max}^{KBr} 1752, 1234, 1208, 1050, 1022, and 953 cm^{-1}. For the ^{1}H-n.m.r. data, see Table I (Found: C, 52.65; H, 7.57. $C_{21}H_{36}O_8S_2$ calc.: C, 52.47; H, 7.55%).

(*c*) *From* **19**. Column chromatography (3:1 hexane–ether) of the crude product gave **9**, isolated as a syrup, $[\alpha]_D^{23}$ +7° (*c* 1, chloroform); ν_{max}^{film} 1750, 1368, 1221, 1163, 1053, and 964 cm^{-1}. For the ^{1}H-n.m.r. data, see Table I (Found: C, 52.70; H, 8.00. $C_{18}H_{32}O_6S_2$ calc.: C, 52.91; H, 7.89%).

Deacetylation of **1–4** *and* **7–9**. — *General method.* A mixture of acetylated derivative, methanol, and sodium methoxide (~25 mg) was left at room temperature for 6 h, acetic acid (0.25 mL) was added, and the mixture was concentrated. The following amounts and conditions were used.

(*a*) *From* **1**. Column chromatography (ether) of the crude product gave **20**, m.p. 143–144° (from ethyl acetate), $[\alpha]_D^{30}$ +231° (*c* 0.5, water); lit.[15] m.p. 142–143° (from ethyl acetate–pentane), $[\alpha]_D^{20}$ +233° (water); ν_{max}^{KBr} 3550–3100, 1120, 1086, 1053, 1028, 1007, 965, 910, 860, and 838 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.51 (d, 1 H, *J* 4.5 Hz, H-1), 4.1–3.4 (m, 6 H, H-2,3,4,5,6,6'), 2.53 (bs, 4 H, exchangeable

Starting material (g)	*Methanol (mL)*	*Product (g, %)*
1 (1.00)	24	**20** (0.48, 80)
2 (0.50)	12	**21** (0.22, 73)
3 (0.50)	10	**22** (0.31, 86)
4 (0.50)	10	**23** (0.31, 86)
7 (2.76)	50	**12** (1.71, 90)
8 (1.21)	20	**13** (0.70, 89)
9 (1.30)	16	**14** (0.83, 92)

with D_2O, 4 OH), and 1.42 (s, 9 H, Me_3C) (Found: C, 47.47; H, 7.86. $C_{10}H_{20}O_5S$ calc.: C, 47.60; H, 7.99%).

(*b*) *From* **2**. Column chromatography (ether) of the crude product gave **21**, m.p. 100–101° (from ethyl acetate), $[\alpha]_D^{26}$ −35° (*c* 1, methanol); lit.[15] m.p. 115–116° (from acetone–pentane), $[\alpha]_D^{20}$ −52.8° (water); ν_{max}^{KBr} 3390, 1365, 1271, 1165, 1028, 886, 822, and 755 cm^{-1} ^{1}H-N.m.r. data ($CDCl_3$): δ 4.5 (d, 1 H, *J* 9 Hz, H-1), 3.98–3.25 (m, 6 H, H-2,3,4,5,6,6′), 2.7 (m, 4 H, exchangeable with D_2O, 4 OH), and 1.44 (s, 9 H, Me_3C) (Found: C, 47.62; H, 8.07. $C_{10}H_{20}O_5S$ calc.: C, 47.60; H, 7.99%).

(*c*) *From* **3**. Column chromatography (ether) of the crude product gave **22**, m.p. 101–102° (from ether), $[\alpha]_D^{26}$ +185° (*c* 1, methanol); ν_{max}^{KBr} 3426, 1364, 1261, 1196, 1119, 1091, 1037, 922, and 766 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.4 (d, 1 H, *J* 4 Hz, H-1), 3.93–3.25 (m, 5 H, H-2,3,4,5,5′), 2.5 (bs, 3 H, exchangeable with D_2O, 3 OH), and 1.42 (s, 9 H, Me_3C) (Found: C, 48.78; H, 7.86. $C_9H_{18}O_4S$ calc.: C, 48.62; H, 8.16%).

(*d*) *From* **4**. Column chromatography (ether) of the crude product gave **23**, m.p. 102–103° (from ether), $[\alpha]_D^{26}$ −54° (*c* 1, methanol); ν_{max}^{KBr} 3378, 3244, 1367, 1241, 1101, 1055, 995, 958, 904, and 822 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 4.4 (d, 1 H, *J* 9 Hz, H-1), 4.2–3.1 (m, 5 H, H-2,3,4,5,5′), 2.8 (bs, 3 H, exchangeable with D_2O, 3 OH), 1.42 (s, 9 H, Me_3C) (Found: C, 48.82; H, 8.04. $C_9H_{18}O_4S$ calc.: C, 48.62; H, 8.16%).

(*e*) *From* **7**. Column chromatography (20:1 ether–methanol) of the crude product gave **12**, m.p. 119–120° (from ether), $[\alpha]_D^{16}$ −20° (*c* 1, methanol); ν_{max}^{KBr} 3550, 3450–3100, 1365, 1160, 1090, 1073, 1042, 1020, and 1015 cm^{-1}. ^{1}H-N.m.r. data ($CDCl_3$): δ 4.25 (m, 2 H, H-1,3), 3.80 (m, 5 H, H-2,4,5,6,6′), 3.40 (bs, 5 H, exchangeable with D_2O, 5 OH), and 1.45 (s, 18 H, 2 Me_3C) (Found: C, 49.33; H, 8.79. $C_{14}H_{30}O_5S_2$ calc.: C, 49.09; H, 8.82%).

(*f*) *From* **8**. Column chromatography (ether) of the crude product gave **13**, m.p. 100° (from ether), $[\alpha]_D^{16}$ −24° (*c* 0.8, methanol); ν_{max}^{KBr} 3500–3150, 1358, 1155, 1105, 1064, 996, and 926 cm^{-1} ^{1}H-N.m.r. data ($CDCl_3$): δ 4.20 (m, 2 H, H-1,3), 3.80 (m, 4 H, H-2,4,5,5′), 2.95–2.70 (m, 4 H, exchangeable with D_2O, 4 OH), and 1.45 (s, 18 H, 2 Me_3C) (Found: C, 50.23; H, 9.25. $C_{13}H_{28}O_4S_2$ calc.: C, 49.96; H, 9.03%).

(*g*) *From* **9**. Column chromatography (1:2 hexane–ether) of the crude product gave **14**, m.p. 81° (from hexane), $[\alpha]_D^{25}$ −13.5° (*c* 1, chloroform); ν_{max}^{KBr} 3418, 1365, 1282, 1164, 1069, 1031, 881, and 757 cm^{-1}. N.m.r. data ($CDCl_3$): ^1H, δ 4.42 (d, 1 H, *J* 2 Hz, H-1), 3.98–3.75 (m, 4 H, H-2,3,4,4'), 2.41 (s, 3 H, exchangeable with D_2O, 3 OH), and 1.43 (s, 18 H, 2 Me_3C); ^{13}C, δ 75.12 (C-3), 71.97 (C-2), 64.24 (C-4), 50.34 (C-1), 45.82 and 44.42 (2 Me_3C), 31.86 and 31.48 (2 Me_3C) (Found: C, 51.13; H, 9.54. $C_{12}H_{26}O_3S_2$ calc.: C, 51.02; H, 9.28%).

Reactions of **12–14** *and 2-methyl-2-propanethiol in conc. hydrochloric acid.* — Conditions similar to those reported above, with a reaction time of 5 min followed by acetylation of the crude product, gave the following results.

Starting material (g)	*Thiol (mL)*	*Acid (mL)*	*Product (g, %)*
12 (1.40)	10	5	**2** (0.68, 39.5)
			1 (0.25, 14.5)
13 (0.67)	7	4	**4** (0.11, 14.7)
			3 (0.26, 34.8)
14 (0.70)	6	5	**16** (0.16, 23.3)
			6 (0.17, 21.5)

Column chromatography (4:1 hexane–ether) of the crude product from **14** gave, first, a mixture of *tert*-butyl 2,3-di-*O*-acetyl-1-thio-α- and -β-D-erythrofuranoside (**16**), isolated as a syrup, $[\alpha]_D^{23}$ −16° (*c* 1, chloroform); ν_{max}^{film} 1748, 1368, 1221, 1164, 1053, and 963 cm^{-1}. ^1H-N.m.r. data ($CDCl_3$): δ 5.6–5.2 (m, 2 H, H-2,3), 4.35–4.05 (m, 3 H, H-1,4,4'), 2.19, 2.10, 2.09, and 2.05 (4 s, 6 H, 2 Ac), and 1.42 (s, 9 H, Me_3C) (Found: C, 51.80; H, 7.45. $C_{12}H_{20}O_5S$ calc.: C, 52.16; H, 7.30%).

Eluted second was **6**.

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