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THE ACTION OF THIOLS ON DERIVATIVES OF D-XYLOSE

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ABSTRACT

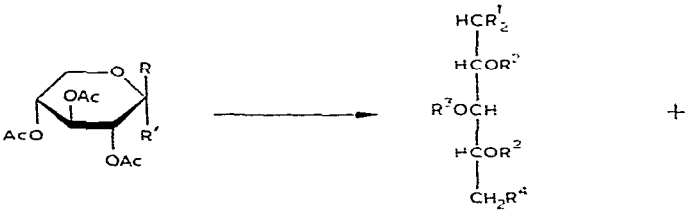
The action of thiols on 1,2,3,4-tetra-*O*-acetyl-β-D-xylopyranose gave 2- and 5-alkylthiopentose dithioacetals and alkyl 1-thio-D-xylopyranosides. On treatment with thiols and trifluoroacetic acid, 3-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose derivatives rapidly formed 4-*O*-acetyl-2,3-dialkylthio-D-ribose dithioacetal derivatives, which were in turn converted into 4-*O*-acetyl-3-*S*-benzyl-2,5-epithio-3-thio-D-ribose (or D-arabinose) dithioacetal.

INTRODUCTION

The reaction of thiols with carbohydrates has been reviewed previously[1]. The products are usually dithioacetals, but, depending on the substituents present in the carbohydrate residue, additional thioalkyl groups may be introduced at positions other than C-1 with eventual inversion of configuration. Treatment of monosaccharide peresters with thiols under acidic conditions gave a variety of products. Thus, ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-D-glucopyranoside and 3,4,5,6-tetra-*O*-acetyl-2-*S*-ethyl-2-thio-D-mannose diethyl dithioacetal were obtained from 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose[2], 2,3,4-tri-*O*-acetyl-5-*S*-ethyl-5-thio-L-arabinose diethyl dithioacetal from 1,2,3,4-tetra-*O*-acetyl-α-L-arabinopyranose[3], 2,3,5-tri-*O*-acetyl-4-*S*-methyl-4-thio-L-lyxose dimethyl dithioacetal and methyl 2,3,4-tri-*O*-acetyl-1,5-dithio-β-D-ribopyranoside from 1,2,3,4-tetra-*O*-acetyl-β-D-ribopyranose[4], and 4,5,6-tri-*O*-benzoyl-2,3-di-*S*-ethyl-2,3-dithio-D-allose diethyl dithioacetal from 3,5,6-tri-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose[5]. With the view to preparing sugars containing sulfur or selenium in the pyranose or furanose ring by intramolecular cyclization of dibenzyl dithio-(diseleno-)acetals containing a tosyl group in the appropriate position[6], we studied the effect of thiols on substituted monosaccharides.

DISCUSSION

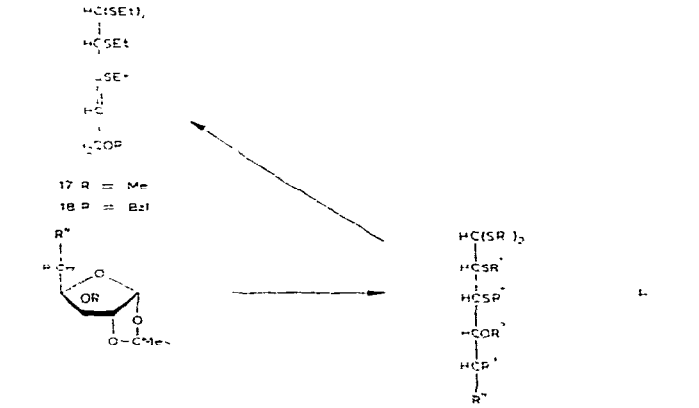
Treatment of 1,2,3,4-tetra-*O*-acetyl-β-D-xylopyranose (**1**) with ethanethiol and anhydrous zinc chloride for 2 days at room temperature gave 2,3,4-tri-*O*-acetyl-5-*S*-ethyl-5-thio-D-xylose diethyl dithioacetal (**4**) and the known[7,8] 3,4,5-tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-lyxose diethyl dithioacetal (**12**) as the major products. In addition,



1 R = OAc, R′ = H
2 R = SBzl, R′ = H
3 R = H, R′ = Br

4 R^1 = R^4 = SEt, R^2 = R^3 = Ac
5 R^1 = SEt, R^2 = R^3 = Me, R^4 = OH
6 R^1 = SEt, R^2 = H, R^3 = Me, R^4 = OMe
7 R^1 = SEt, R^2 = R^3 = H, R^4 = OH
8 R^1 = SEt, R^2 = R^3 = H, R^4 = SBzl
9 R^1 = SEt, R^2 = H, R^3 = Ts, R^4 = OTs
10 R^1 = SEt, R^2 = Ac, R^3 = Ts, R^4 = OTs
11 R^1 = SBzl, R^2 = H, R^3 = Ts, R^4 = OTs

12 R = R′ = SEt, R″ = Ac
13 R = R′ = SBzl, R″ = Ac
14 R = R′ = SBzl, R″ = H
15 R = R′ = H, R″ = Ac
16 R = R′ = R″ = H



17 R = Me
18 R = Bzl

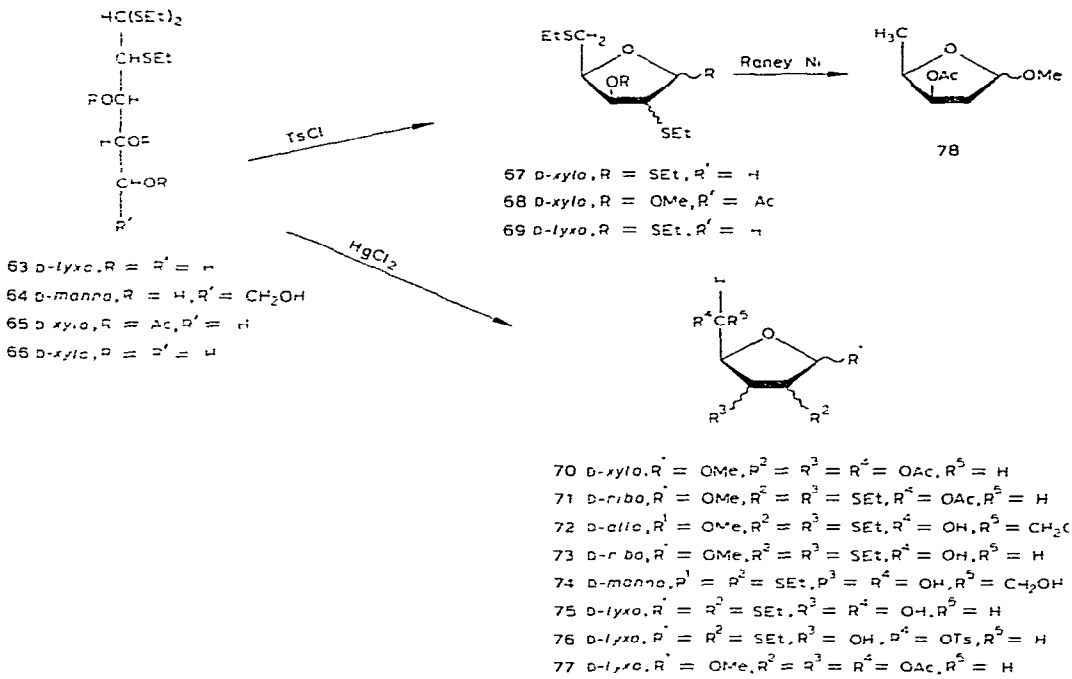
19 R = S
20 R = Se

21 R = H, R′ = SEt, R″ = H
22 R = Ac, R′ = OAc, R″ = CH_2OAc
23 R = Bz, R′ = OBz, R″ = CH_2OBz
24 R = Ac, R′ = OAc, R″ = H
25 R = Ac, R′ = OTs, R″ = H
26 R = Ac, R′ = SBzl, R″ = H
27 R = Ac, R′ = SEt, R″ = H
28 R = Ac, R′ = SeBzl, R″ = H
29 R = Ac R′ = OMe, R″ = H
30 R = Ac, R′ = OBzl, R″ = H
31 R = Me, R′ = OMe, R″ = H
32 R = R″ = H, R′ = OH
33 R = R″ = H, R′ = SBzl
34 R = Ts, R′ = OTs, R″ = H

35 R^1 = Et, R^2 = Ac, R^3 = OAc, R^4 = CH_2OAc
36 R^1 = Et, R^2 = Bz, R^3 = OBz, R^4 = CH_2OBz
37 R^1 = Et, R^2 = Ac, R^3 = OAc, R^4 = H
38 R^1 = Et, R^2 = H, R^3 = OH, R^4 = CH_2OH
39 R^1 = Et, R^2 = R^4 = H, R^3 = OH
40 R^1 = Et, R^2 = R^4 = H, R^3 = OTs
41 R^1 = Et, R^2 = Ac, R^3 = SBzl, R^4 = H
42 R^1 = Et, R^2 = Ac, R^3 = SeBzl, R^4 = H
43 R^1 = Bzl, R^2 = Ac, R^3 = OAc, R^4 = H
44 R^1 = Bzl, R^2 = R^4 = H, R^3 = OH
45 R^1 = Bzl, R^2 = R^4 = H, R^3 = OTs
46 R^1 = Bzl, R^2 = Ac, R^3 = SBzl, R^4 = H
47 R^1 = Et, R^2 = Ac, R^3 = OMe, R^4 = H
48 R^1 = Et, R^2 = Ac, R^3 = OBzl, R^4 = H
49 R^1 = Bzl, R^2 = Ac, R^3 = OMe, R^4 = H

50 D-*ribo*, R^1 = R^2 = SEt, R^3 = Ac, R^4 = S
51 D-*ribo*, R^1 = R^3 = SBzl, R^2 = Ac, R^4 = S
52 D-*arabino*, R^1 = R^2 = SEt, R^3 = Ac, R^4 = S
53 D-*arabino*, R^1 = R^2 = SEt, R^3 = Ac, R^4 = Se
54 D-*lyxo*, R^1 = SBzl, R^2 = OH, R^3 = H, R^4 = S
55 D-*lyxo*, R^1 = SBzl, R^2 = OAc, R^3 = Ac, R^4 = S
56 D-*lyxo*, R^1 = OMe, R^2 = OAc, R^3 = Ac, R^4 = S
57 D-*arabino*, R^1 = R^3 = SBzl, R^2 = Ac, R^4 = S
58 D-*lyxo*, R^1 = SEt, R^2 = OH, R^3 = H, R^4 = S
59 Unknown cont. R^1 = SEt, R^2 = OH, R^3 = H, R^4
60 D-*xylo*, R^1 = SEt, R^2 = OTs, R^3 = H, R^4 = O
61 D-*xylo*, R^1 = OMe, R^2 = OTs, R^3 = H, R^4 = O
62 D-*xylo*, R^1 = SBzl, R^2 = OTs, R^3 = H, R^4 = O

compound(s) that contained four ethylthio groups were isolated but were not identified. Compound **4** was also prepared from 5-*S*-ethyl-1,2-*O*-isopropylidene-5-thio-α-D-xylofuranose (**21**) by treatment with ethanethiol, followed by acetylation of the resultant dithioacetal, and **12** was obtained in excellent yield by treatment of methyl 2,3,5-tri-*O*-acetyl-D-xylofuranosides (**70**) with ethanethiol and trifluoroacetic acid.



Treatment of 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**22**) with ethanethiol and trifluoroacetic acid gave 4,5,6-tri-*O*-acetyl-2,3-di-*S*-ethyl-2,3-dithio-D-allose diethyl dithioacetal (**35**). The structure of **35** was confirmed by *O*-deacylation followed by *O*-benzoylation to give the known compound[5] **36**. Because the nature of the ester group did not influence the outcome of this reaction, we next investigated whether a change in the structure of the carbohydrate would give similar results. Ethanethiol and 3,5-di-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**24**) gave 4,5-di-*O*-acetyl-2,3-di-*S*-ethyl-2,3-dithio-D-ribose diethyl dithioacetal (**37**), and varying proportions (depending on the reaction time) of 4-*O*-acetyl-3-*S*-ethyl-2,5-epithio-3-thio-D-ribose diethyl dithioacetal (**50**) and 4-*O*-acetyl-3-*S*-ethyl-2,5-epithio-3-thio-D-arabinose diethyl dithioacetal (**52**). Compound **37** was converted into methyl 5-*O*-acetyl-2,3-di-*S*-ethyl-2,3-dithio-β-D-ribofuranoside (**71**) by the procedure reported[5] for the conversion of 2,3-di-*S*-ethyl-2,3-dithio-D-allose diethyl dithioacetal (**38**) into methyl 2,3-di-*S*-ethyl-2,3-dithio-β-D-allofuranoside (**72**). Compound **71** was also prepared by oxidation of **72** with sodium periodate, and reduction of the resultant 5-aldehyde with sodium borohydride gave methyl 2,3-di-*S*-ethyl-2,3-dithio-β-D-ribofuranoside (**73**), which was acetylated to give **71**. On treatment with *p*-toluenesulfonyl chloride in pyridine, 2,3-di-*S*-ethyl-2,3-dithio-D-ribose diethyl dithioacetal (**39**), prepared by *O*-deacylation of **37**, gave **50**. Compound **50** is believed to be formed by the attack of the sulfur atom of SEt-2 on C-5 in the reactive intermediate 2,3-di-*S*-ethyl-5-*O*-tosyl-2,3-dithio-D-ribose diethyl dithioacetal (**40**). This reaction resembles the formation of 2,5-anhydro compounds by treatment of pentose dithio-

acetals with *p*-toluenesulfonyl chloride[9]. The presence of the 2,5-epithio ring in **50** and **52** was shown by treatment of these compounds with mercuric chloride in buffered aqueous acetone to give 2-thiophenecarbaldehyde (**19**). Compound **19** arose by removal of the dithioacetal group, followed by the loss of ethanethiol by *β*-elimination and loss of acetic acid. Compounds **50** and **52** were also obtained when 3-*O*-acetyl-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-xylofuranose (**25**) was treated with ethanethiol and trifluoroacetic acid.

It was of interest to investigate the reaction of ethanethiol with derivatives of **24** that had substituents other than OAc-5. Treatment of 3-*O*-acetyl-5-*S*-benzyl-1,2-*O*-isopropylidene-5-thio-α-D-xylofuranose (**26**) with ethanethiol gave as a major product **52** and as a minor product **50**. Compound **52** was presumably formed by the attack on C-2 of the sulfur atom of SBzl-5 of 4-*O*-acetyl-5-*S*-benzyl-2,3-di-*S*-ethyl-2,3,5-trithio-D-ribose diethyl dithioacetal (**41**). Compound **50** was presumably formed by the attack of the sulfur atom of SEt-2 of **41** on C-5. The other product of these reactions, benzyl ethyl sulfide, was identified by g.l.c. The formation of **50** and **52** from **26** was very rapid, the acyclic dithioacetal **41** being isolated in poor yield after a reaction time of 4 min. After a reaction time of 15 min, **41** could not be detected. Also, treatment of 3-*O*-acetyl-5-*S*-ethyl-1,2-*O*-isopropylidene-5-thio-α-D-xylofuranose (**27**) with ethanethiol and trifluoroacetic acid gave **52** as the main product. 3-*O*-Acetyl-5-*Se*-benzyl-1,2-*O*-isopropylidene-5-seleno-α-D-xylofuranose (**28**) rapidly formed with ethanethiol 4-*O*-acetyl-5-*Se*-benzyl-2,3-di-*S*-ethyl-5-seleno-2,3-dithio-D-ribose diethyl dithioacetal (**42**). The cyclization of this compound to the 2,5-episeleno derivative was much slower than that found for **41**, because, after a reaction time of 2 h, **42** was still the major product. However, a small proportion of impure 4-*O*-acetyl-2,5-episeleno-3-*S*-ethyl-3-thio-D-arabinose diethyl dithioacetal (**53**) was isolated. The structure of **53** was inferred from the observation that on *β*-elimination with mercuric chloride, **53** gave 2-selenophenecarbaldehyde (**20**). A smaller proportion of 2-thiophenecarbaldehyde (**19**) was also detected. The presence of **19** implies the presence of **50**, which was presumably formed by the attack of the sulfur atom of SEt-2 on C-5 of **42**. Compound **53** must have been formed by rearside attack of the selenium atom of SeBzl-5 on C-2 of **42**.

It was of interest to investigate the influence of the chemical structure of the thiol on this unusual reaction. Reactions similar to those discussed previously but using phenylmethanethiol instead of ethanethiol were investigated. When **1** was treated with phenylmethanethiol and anhydrous zinc chloride for 2 days at room temperature, the main products were 3,4,5-tri-*O*-acetyl-2-*S*-benzyl-2-thio-D-lyxose dibenzyl dithioacetal (**13**) and benzyl 2,3,4-tri-*O*-acetyl-1-thio-*β*-D-xylopyranoside (**2**). Compound **2** was synthesized from 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide (**3**) and phenylmethanethiol. Upon reductive desulfurization with Raney nickel, **13** gave **15**, the 3,4,5-tri-*O*-acetyl derivative of the known[7] 1,2-dideoxy-D-*threo*-pentitol (**16**). Compound **13** was the major product when **70** was briefly treated with phenylmethanethiol and trifluoroacetic acid. The D-*lyxo* configuration of **13** was assumed on the basis that the D-*lyxo* compound **12** was obtained under similar conditions from

1 and **70**. It was hoped that the configuration at C-2 in **13** could be conclusively proven. 2-*S*-Benzyl-2-thio-D-lyxose dibenzyl dithioacetal (**14**) was treated with *p*-toluenesulfonyl chloride to yield 2,5-epithio-D-lyxose dibenzyl dithioacetal (**54**). Compound **54** was presumably formed by the attack of S-2 on OTs-5. The acetate **55** showed the expected n.m.r. data and elemental analysis. Compound **55** was treated with mercuric chloride in methanol to give 3,4-di-*O*-acetyl-2,5-epithio-D-lyxose dimethylacetal (**56**). The same compound was to be prepared from 2-*S*-ethyl-2-thio-D-lyxose diethyl dithioacetal (**63**). However, when **63** (prepared by deacylation of **12**) was treated with *p*-toluenesulfonyl chloride, the expected 2,5-epithio-D-lyxose diethyl dithioacetal (**58**) was not formed; instead, ethyl 2,5-di-*S*-ethyl-1,2,5-trithio-D-xylo(lyxo)furanoside (**67**) was isolated. The acetate of **67** was converted into methyl 3-*O*-acetyl-2,5-di-*S*-ethyl-2,5-dithio-D-xylo(lyxo)furanoside (**68**) with mercuric chloride and cadmium carbonate in methanol. Treatment of **68** with Raney nickel gave methyl 3-*O*-acetyl-2,5-dideoxy-D-*threo*-pentofuranoside (**78**). A similar type of rearrangement has been observed[8] in the tosylation of 2,3,4-tri-*O*-methyl-D-xylose diethyl dithioacetal (**5**), which would indicate the D-*xylo* configuration for **67**. However, because of this rearrangement, the actual configuration of the benzyl compound **13** could not be determined.

In order to prove the structure of **67**, the following synthesis was developed. Treatment of 2-*S*-ethyl-2-thio-D-mannose diethyl dithioacetal (**64**) with one mol of mercuric chloride has been reported[10] to yield ethyl 2-*S*-ethyl-1,2-dithio-D-manno-furanoside (**74**). The same reaction was applied to 2-*S*-ethyl-2-thio-D-lyxose diethyl dithioacetal (**63**), to yield ethyl 2-*S*-ethyl-1,2-dithio-D-lyxofuranoside (**75**). The primary hydroxyl group on C-5 was converted into the tosyl ester by treating **75** with one mol of *p*-toluenesulfonyl chloride. This tosyl compound (**76**) with ethanethiolate ions gave ethyl 2,5-di-*S*-ethyl-1,2,5-trithio-D-lyxofuranoside (**69**), a compound similar, but not identical, to **67**. Because both **67** and **69** were converted into methyl 3-*O*-acetyl-2,5-dideoxy-D-*threo*-pentofuranoside (**78**), the D-*xylo* structure of **67** was confirmed. Furthermore, when treated with ethanethiol and trifluoroacetic acid, methyl 2,3,5-tri-*O*-acetyl-D-lyxofuranosides (**77**) gave 3,4,5-tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-xylose diethyl dithioacetal (**65**) in poor yield. This reaction is analogous to the formation of 2-*S*-ethyl-2-thio-D-lyxose derivative (**12**) from methyl 2,3,5-tri-*O*-acetyl-D-xylofuranosides (**70**). Treatment of **4** or **65** with Raney nickel gave **15**, the acetate of the known[6] compound **16**. As **4** and **65** were not identical, and yet both gave **15** on reduction, **65** should have the D-*xylo* configuration. Hydrolysis of the acetate groups of **65** and treatment of the resulting 2-*S*-ethyl-2-thio-D-xylose diethyl dithioacetal (**66**) with one mol of *p*-toluenesulfonyl chloride gave **69**.

Prolonged treatment of methyl 2,3,5-tri-*O*-acetyl-D-xylofuranosides (**70**) with phenylmethanethiol and trifluoroacetic acid gave 4-*O*-acetyl-3-*S*-benzyl-2,5-epithio-3-thio-D-ribose dibenzyl dithioacetal (**51**). The presence of a 2,5-epithio ring in **51** was shown by the formation of 2-thiophenecarbaldehyde (**19**) on *β*-elimination of **51** with mercuric chloride.

When **24** was treated with phenylmethanethiol, **51** and 4,5-di-*O*-acetyl-2,3-

di-*S*-benzyl-2,3-dithio-D-ribose dibenzyl dithioacetal (**43**) were obtained. It was also shown that, on treatment with trifluoroacetic acid, the acyclic compound **43** gave **51**. This reaction resembles the formation, reported recently[11], of 2,5-anhydro compounds from pentose dibenzyl dithioacetals on treatment with acid. The acyclic dithioacetal **43** was deacylated to 2,3-di-*S*-benzyl-2,3-dithio-D-ribose dibenzyl dithioacetal (**44**), which, when treated with *p*-toluenesulfonyl chloride followed by acetylation, gave **51**. The suspected intermediate 2,3-di-*S*-benzyl-2,3-dithio-5-*O*-tosyl-D-ribose dibenzyl dithioacetal (**45**) could not be isolated, presumably because it is unstable and cyclizes to **51**. It is suggested that **51** is formed by the attack of the sulfur atom of 2-SBzl on C-5. Further evidence for this reaction mechanism was afforded by the following observations: Treatment of 3-*O*-acetyl-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-xylofuranose (**25**) with phenylmethanethiol and trifluoroacetic acid gave mainly **51** and, after acetylation, a small proportion of **55**.

Treatment of **26** with phenylmethanethiol again led to the rapid formation of three 2,5-epithio derivatives. After a reaction time of 4 min, a small proportion of the acyclic compound 4-*O*-acetyl-2,3,5-tri-*S*-benzyl-2,3,5-trithio-D-ribose dibenzyl dithioacetal (**46**) was isolated. A longer reaction time gave **51**, its suspected C-2 isomer (4-*O*-acetyl-3-*S*-benzyl-2,5-epithio-3-thio-D-arabinose dibenzyl dithioacetal) (**57**), and a third isomer, all as crystalline compounds. Compound **57** and the third isomer were both 2,5-epithio derivatives, because both gave 2-thiophenecarbaldehyde (**19**) by β-elimination with mercuric chloride. The third isomer showed the presence of one acetate and three thiobenzyl groups, and may have arisen from the participation of the 5-benzylthio group.

The cyclization between C-2 and C-5 of the 2,3-di-*S*-alkyl-2,3-dithio-D-ribose dialkyl dithioacetal derivatives requires, in the 3-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose derivatives, the presence of a suitable group at C-5, such as acetate (**24**), *p*-tolylsulfonyl (**25**), or benzylthio (**26**). The presence of the *O*-alkyl group at C-5 gave different results. When 3-*O*-acetyl-1,2-*O*-isopropylidene-5-*O*-methyl-α-D-xylofuranose (**29**) was treated with ethanethiol, the expected 4-*O*-acetyl-2,3-di-*S*-ethyl-5-*O*-methyl-2,3-dithio-D-ribose diethyl dithioacetal (**47**) was rapidly formed. This product was slowly transformed into the corresponding 3-ene (**17**). N.m.r. spectral analysis of **17** showed the presence of one methyl and four ethylthio groups, and one olefinic proton, but the acetate group was absent. Similarly, 3-*O*-acetyl-5-*O*-benzyl-1,2-*O*-isopropylidene-D-xylofuranose (**30**) and ethanethiol gave mainly, after 2 h, 4-*O*-acetyl-5-*O*-benzyl-2,3-di-*S*-ethyl-2,3-dithio-D-ribose diethyl dithioacetal (**48**). After a reaction time of 24 h, the product was the 3-ene (**18**). Both **17** and **18** were formed by acid-catalyzed elimination of acetic acid from C-3 and C-4. However, when **29** was treated with phenylmethanethiol, the initial product, namely, 4-*O*-acetyl-2,3-di-*S*-benzyl-5-*O*-methyl-2,3-dithio-D-ribose dibenzyl dithioacetal (**49**) was transformed into two compounds, namely, **51** and a compound that contained one methyl and five benzylthio groups, but no olefinic proton. The structure of this compound was not investigated further, but it is, presumably, 2,3,4-tri-*S*-benzyl-5-*O*-methyl-2,3,4-trithiopentose dibenzyl dithioacetal. Compound **51**, in this case, was

formed by the attack of SBzl-2 on C-5 resulting in the expulsion of the methoxyl group.

The presence of an ester group at C-3 of the 1,2-*O*-isopropylidene-D-xylose derivatives is essential for the rapid, sequential introduction of alkylthio groups. On prolonged reaction with ethanethiol, 1,2-*O*-isopropylidene-3,5-di-*O*-methyl-α-D-xylofuranose (**31**) gave as the main product 3,5-di-*O*-methyl-D-xylose diethyl dithioacetal (**6**). Similarly, by treatment with ethanethiol for as long as three weeks at room temperature, 1,2-*O*-isopropylidene-α-D-xylofuranose (**32**) gave D-xylose diethyl dithioacetal (**7**) as the major product. 5-*S*-Benzyl-1,2-*O*-isopropylidene-5-thio-α-D-xylofuranose (**33**) treated with ethanethiol gave initially 5-*S*-benzyl-5-thio-D-xylose diethyl dithioacetal (**8**); however, after a reaction period of three weeks, in addition to **8**, a second product, **59**, was isolated. Compound **59** was a 2,5-epithiopentose of unknown configuration, because the acetate of **59** showed the presence of two acetate and two ethylthio group. Treatment of **59** with mercuric chloride in aqueous acetone gave 2-thiophenecarbaldehyde (**19**).

1,2-*O*-Isopropylidene-3,5-di-*O*-tosyl-α-D-xylofuranose (**34**) and ethanethiol in trifluoroacetic acid gave 3,5-di-*O*-tosyl-D-xylose diethyl dithioacetal (**9**), which, on treatment with pyridine at room temperature, yielded 2,3-anhydro-3-*O*-tosyl-D-xylose diethyl dithioacetal (**60**). Further reaction with mercuric chloride in buffered methanol gave the known[12] 2,5-anhydro-3-*O*-tosyl-D-xylose dimethylacetal (**61**). Similar results were obtained when phenylmethanethiol was used instead of ethanethiol. Compound **34** gave 3,4-di-*O*-tosyl-D-xylose dibenzyl dithioacetal (**11**). When treated with pyridine, **11** gave 2,5-anhydro-3-*O*-tosyl-D-xylose dibenzyl dithioacetal (**62**), and further reaction with mercuric chloride in buffered methanol again gave **61**.

EXPERIMENTAL

General methods. — I.r. spectra were recorded with a Perkin–Elmer Model 700 spectrophotometer, mass spectra with a Hitachi–Perkin–Elmer RMU-7 mass spectrometer, and ^{1}H-n.m.r. spectra with a Varian T-60 spectrometer. Chemical shifts are given in p.p.m., with tetramethylsilane as the internal standard. Melting points were obtained on a Fisher–Johns apparatus and are uncorrected. G.l.c. analyses were performed in a Bendix 2600 Gas Chromatograph equipped with a column (1.8 m × 2 mm) containing 10% EGSS-X Gas Chrom-P (Applied Science Labs., Inc., State College, PA 16801), with nitrogen as the carrier gas. Column chromatography was performed on silica gel (60–200 mesh, Baker). Liquid chromatography (l.c.) was performed on a column (3.2 × 250 mm) of Lichrosorb (5 μm, Merck) at 160 atm, with detection at 211 nm with a Schoeffel detector. All reactions were monitored by t.l.c. and l.c. methods. In all cases, n.m.r. spectra, used for characterization purposes, were in agreement with the proposed structures. When compounds were formed that had been reported in the literature, these were shown to be identical with the reported compounds by appropriate physical methods, such as t.l.c., l.c., mixed m.p., and n.m.r. and i.r. spectra.

Reaction with thiols. — *Method a.* The compound (1.0 g), thiol (6 mol equiv),

and anhydrous zinc chloride (0.2 g) were stirred for different periods of time at room temperature. The mixture was diluted with chloroform and washed successively with water and sodium hydrogencarbonate solution, dried, and evaporated to a syrup. Chromatography with 1:99 (v/v) methanol–benzene (unless otherwise indicated) gave the products described.

Method b. As described for *Method a*, but instead of zinc chloride, trifluoroacetic acid (2 mL) was used.

β-Elimination. — The compound (1.0 g) was dissolved in acetone (15 mL) containing water (0.5 mL). Mercuric oxide (1.5 g) was added, and the suspension was stirred while a saturated, aqueous solution of mercuric chloride (1.25 g) was added within 15 min. The suspension was stirred for an additional hour at 40°. The solids were removed, and chloroform (50 mL) was added. The solution was successively washed with water, potassium cyanide solution, and water, dried, and evaporated. The residue was examined by g.l.c. at 120°, and the peaks were identified by retention time and co-injection with 2-thiophenecarbaldehyde (Aldrich) or 2-selenophenecarbaldehyde[13].

p-*Toluenesulfonylation.* — The compound (1.0 g) was dissolved in pyridine (10 mL) and the solution was cooled to 0–5°. *p*-Toluenesulfonyl chloride (2 mol. equiv.) was added in small amounts, while the solution was stirred. The solution was kept overnight at room temperature; acetic anhydride (5 mL) was added, and the solution was kept for a further 6 h, poured into saturated sodium hydrogencarbonate solution, and extracted with chloroform. The extract was successively washed with ice-cold, dilute hydrochloric acid, sodium hydrogencarbonate solution, and water, dried, and evaporated to a syrup.

O-*Acetylation.* — The compound (1.0 g) was dissolved in pyridine (5 mL) and acetic anhydride (5 mL) slowly added. The solution was kept overnight at room temperature, and the product isolated as described for *p*-toluenesulfonylation.

O-*Deacetylation.* The compound (1.0 g) was dissolved in methanol (20 mL), a solution of sodium (0.05 g) in methanol (10 mL) was added, and the solution was kept overnight. The base was neutralized with an ion-exchange resin (H^+). The resin was removed, and the solution evaporated.

Conversion of dithioacetals into dimethyl acetals, and of thioglycosides into methyl glycosides. — A suspension of the compound (1.0 g), mercuric chloride (2.0 g), cadmium carbonate (5.0 g), and methanol (20 mL) was boiled overnight under reflux, cooled, filtered, and the filtrate partitioned between chloroform and water. The chloroform layer was successively washed with a concentrated solution of potassium cyanide and water, dried, and evaporated.

2,3,4-Tri-O-*acetyl-5*-S-*ethyl-5-thio*-D-*xylose diethyl dithioacetal* (**4**). — (*i*). Treatment of 1,2,3,4-tetra-*O*-acetyl-β-D-xylopyranose[14] (**1**) with ethanethiol for 4 days by method (*a*) gave, after chromatography with 1:19 (v/v) methanol–benzene, **4** (syrup, 0.50 g) and 3,4,5-tri-*O*-acetyl-2-*S*-ethyl-2-thio-D-lyxose diethyl dithioacetal (**12**) (0.36 g), m.p. 60–61° (from ethanol); lit.[6,7] m.p. 61–62°.

(*ii*). 5-*S*-Ethyl-1,2-*O*-isopropylidene-5-thio-α-D-xylofuranose[15] (**21**) was treated

with ethanethiol by method (*b*), and the resultant product converted into the acetate **4** (0.95 g, after chromatography), $[\alpha]_D^{20}$ +8° (*c* 2.3, chloroform).

Anal. Calc. for $C_{17}H_{30}O_6S_3$: C, 47.9; H, 7.0; S, 22.5. Found: C, 48.0; H, 6.8; S, 22.0.

*3,4,5-Tri-O-acetyl-2-S-ethyl-2-thio-*D*-lyxose diethyl dithioacetal* (**12**). — Methyl 2,3,5-tri-*O*-acetyl-D-xylofuranosides[16] (**70**) gave, with ethanethiol by procedure (*b*) for 1 day, **12**, 0.60 g (from ethanol), m.p. 60–61°.

*4,5,6-Tri-O-benzoyl-2,3-di-S-ethyl-2,3-dithio-*D*-allose diethyl dithioacetal* (**36**). — 3,5,6-Tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose[5] (**22**) gave with ethanethiol, for 3 h by procedure (*b*), **35** (1.18 g) as a syrup. Compound **35** was deacetylated and the resultant syrup was dissolved in pyridine (10 mL), and the solution treated with benzoyl chloride (4 mol. equiv.). The benzoate was isolated as described under the *p*-toluenesulfonylation procedure. Crystallization gave **36**, m.p. 92° (from ethanol); lit.[5] m.p. 91.5–92.5°.

*4,5-Di-O-acetyl-2,3-di-S-ethyl-2,3-dithio-*D*-ribose diethyl dithioacetal* (**37**). — 3,5-Di-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose[17] (**24**) gave by procedure (*b*) for 1 h **37** (0.9 g), and a mixture of 4-*O*-acetyl-2,5-epithio-3-*S*-ethyl-3-thio-D-ribose diethyl dithioacetal (**50**) and 4-*O*-acetyl-2,5-epithio-3-*S*-ethyl-3-thio-D-arabinose diethyl dithioacetal (**52**) (total yield 0.1 g) was isolated after chromatography with 1:49 (v/v) methanol–benzene. Compound **24** by procedure (*b*) for 24 h gave 0.5 g of **50** and **52**, and only 0.2 g of **37**; compound **37**: $[\alpha]_D^{20}$ +26° (*c* 1.9, chloroform).

Anal. Calc. for $C_{17}H_{32}O_4S_4$: C, 47.6; H, 7.5; S, 29.9. Found: C, 47.5; H, 7.7; S, 30.0.

The mixture of **50** and **52** could not be separated, except by l.c., and gave, by β-elimination, 2-thiophenecarbaldehyde (**19**). Compound **37** was *O*-deacetylated into 2,3-di-*S*-ethyl-2,3-dithio-D-ribose diethyl dithioacetal (**39**), which was treated with *p*-toluenesulfonyl chloride (1.1 mol) to give **50** (syrup, 0.72 g), $[\alpha]_{D\,[i]}^{20}$ −95° (*c* 1.2, chloroform).

Anal. Calc. for $C_{13}H_{24}O_2S_4$: C, 45.9; H, 7.1; S, 37.6. Found: C, 46.0; H, 7.0; S, 37.9.

*Methyl 5-O-acetyl-2,3-di-S-ethyl-2,3-dithio-β-*D*-ribofuranoside* (**71**). (*i*). Compound **39** was dissolved in dry methanol (20 mL), and yellow mercuric oxide (1.20 g) was added, followed by a saturated solution of mercuric chloride (1.50 g) in dry methanol. The mixture was stirred for 3 h, the solids were removed, and dry pyridine (10 mL) was added to the filtrate. Methanol was removed under diminished pressure, and acetic anhydride (5 mL) was added at 0–5°. The solution was kept for 12 h at ambient temperature. The product was isolated as described under *O*-acetylation, to give **71** as a syrup (0.6 g).

(*ii*). Methyl 2,3-di-*S*-ethyl-2,3-dithio-β-D-allofuranoside[5] (**72**) (1.41 g) was dissolved in methanol (100 mL), and a solution of sodium periodate (1.18 g) in water (50 mL) was added slowly with stirring. After 2 h, sodium borohydride (1.5 g) was added in small portions. Glacial acetic acid was added dropwise to the mixture after 1 h to decompose the excess of sodium borohydride. The solution was evaporated

to a syrup which was treated by several additions and evaporations of methanol. The syrup was acetylated to give **71**, $[\alpha]_D^{20}$ +32° (*c* 2.5, chloroform).

Anal. Calc. for $C_{12}H_{22}O_4S_2$: C, 49.0; H, 7.5; S, 21.8. Found: C, 48.7; H, 7.5; S, 22.1.

*4-O-Acetyl-2,5-epithio-3-S-ethyl-3-thio-*D*-ribose (and -*D*-arabinose) diethyl dithioacetal* (**50** *and* **52**). — (*i*). 3-*O*-Acetyl-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-xylofuranose[18] (**25**) gave with ethanethiol, by procedure (*b*) for 3 h, a mixture of **50** and **52** (0.7 g); l.c. analysis indicated that **50** was the major product.

(*ii*). 3-*O*-Acetyl-5-*S*-benzyl-1,2-*O*-isopropylidene-5-thio-α-D-xylofuranose[19] (**26**) gave with ethanethiol, by procedure (*b*) for 3 h, a mixture of **50** and **52** (0.50 g); l.c. analysis showed that **52** was the major product. When the reaction was performed for only 4 min, chromatography gave 4-*O*-acetyl-5-*S*-benzyl-2,3-di-*S*-ethyl-2,3,5-trithio-D-ribose diethyl dithioacetal (**41**) (0.12 g, impure syrup).

(*iii*). 3-*O*-Acetyl-5-*S*-ethyl-1,2-*O*-isopropylidene-5-thio-α-D-xylofuranose[15] (**27**) gave with ethanethiol, by procedure (*b*) for 3 h, a mixture of **50** and **52** (0.40 g), with **52** as the major component.

*4-O-Acetyl-5-Se-benzyl-2,3-di-S-ethyl-5-seleno-2,3-dithio-*D*-ribose diethyl dithioacetal* (**42**). — 3-*O*-Acetyl-5-*Se*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose[13] (**28**) gave with ethanethiol, by procedure (*b*) for 2 h, the acyclic compound **42** (0.60 g) and **53** (0.11 g), impure syrup: compound **42**: $[\alpha]_D^{21}$ −70° (*c* 0.2, chloroform).

Anal. Calc. for $C_{22}H_{36}O_2S_4Se$: C, 48.9; H, 6.7; S, 23.7. Found: C, 49.1; H, 6.5; S, 24.0.

The impure compound **53** gave mainly by the β-elimination procedure 2-selenophenecarbaldehyde (**20**) and a minor proportion of 2-thiophenecarbaldehyde (**19**).

*3,4,5-Tri-O-acetyl-2-S-benzyl-2-thio-*D*-lyxose dibenzyl dithioacetal* (**13**). — (*i*). 1,2,3,4-Tetra-*O*-acetyl-β-D-xylopyranose (**1**) gave with phenylmethanethiol, by procedure (*b*) for 4 days, **13** (syrup, 0.60 g) and the known **2** (0.20 g), m.p. 88° (ethyl acetate–hexane); lit.[20] m.p. 88°). Compound **13**: $[\alpha]_D^{20}$ +77° (*c* 0.70, chloroform).

Anal. Calc. for $C_{32}H_{36}O_6S_3$: C, 62.7; H, 5.9; S, 15.7. Found: C, 62.3; H, 6.0; S, 15.9.

(*ii*). Methyl 2,3,5-tri-*O*-acetyl-D-xylofuranosides (**70**) gave with phenylmethanethiol, by procedure (*b*) for 5 h, **13** (0.60 g) after chromatography in 1:49 (v/v) methanol–benzene.

*3,4,5-Tri-O-acetyl-1,2-dideoxy-*D*-threo-pentitol* (**15**). — (*i*). A suspension of **13** (3.0 g) and Raney nickel (approximately 10 g) in absolute ethanol (24 mL) was boiled under reflux overnight. The solids were removed and washed repeatedly with hot ethanol. The combined filtrates were evaporated to a syrup, and chromatography in 1:99 (v/v) methanol–benzene gave **15** (0.63 g), syrup, g.l.c. (165°); R_T 6.50 min, identical to that of **15** obtained by acetylation of the known[7] 1,2-dideoxy-D-*threo*-pentitol (**16**).

(*ii*). Treatment of **65** (1.0 g) with Raney nickel by the same procedure gave **15** (0.19 g).

3,4-Di-O-acetyl-2,5-epithio-D-lyxose dimethyl acetal (**56**). — Compound **13** (2.0 g) was *O*-deacetylated to give **14** (1.8 g). This product was treated with *p*-toluenesulfonyl chloride (2.1 mol) by the *p*-toluenesulfonylation procedure, and chromatography of the product with 1:24 (v/v) methanol–benzene gave 2,5-epithio-D-lyxose-dibenzyl dithioacetal (**54**; 0.9 g), $[\alpha]_D^{20}$ +26° (*c* 0.8, chloroform).

Anal. Calc. for $C_{23}H_{26}O_4S_3$: C, 59.7; H, 5.6; S, 20.8. Found: C, 59.6; H, 5.4; S, 21.2.

O-Acetylation of **54** gave **55**, and conversion of **55** (1.0 g) the dimethyl acetal **56** (0.6 g).

Anal. Calc. for $C_{11}H_{18}O_6S$: C, 47.5; H, 6.5. Found: C, 47.7: H, 6.4.

Ethyl 2,5-di-S-ethyl-1,2,5-trithio-D-xylofuranoside (**67**). — Compound **12** (1.5 g) was *O*-deacetylated to **63** (1.2 g), which was treated with *p*-toluenesulfonyl chloride (1.1 mol) by the *p*-toluenesulfonylation procedure, to give **67** (0.8 g), after chromatography with 1:19 (v/v) methanol–benzene.

Anal. Calc. for $C_{11}H_{22}O_2S_3$: C, 49.6; H, 8.3. Found: C, 49.4; H, 8.1.

Methyl 3-O-acetyl-2,5-di-S-ethyl-2,5-dithio-D-xylofuranoside (**68**). — The acetate of **67** (1.0 g) was converted to the methyl glycoside by the general procedure. Chromatography of the crude product in 1:49 (v/v) methanol–benzene gave **68** (0.65 g), syrup.

Anal. Calc. for $C_{12}H_{22}O_4S_2$: C, 49.0; H, 7.5. Found: C, 48.8; H, 7.6.

Methyl 3-O-acetyl-2,5-dideoxy-D-threo-pentofuranoside (**78**). — (*i*). Compound **68** (0.5 g) was treated with Raney nickel as described for **16** to yield, after chromatography with 1:99 (v/v) methanol–benzene, **78** (0.2 g).

Anal. Calc. for $C_8H_{14}O_4$: C, 55.2; H, 8.1. Found: C, 55.0; H, 8.2.

(*ii*). Compound **69** was converted to the methyl glycoside with mercuric chloride in buffered methanol by the general procedure, and the resultant syrup, without purification, was treated with Raney nickel as described in (*i*). The resultant deoxy compound was converted to the acetate **78**.

Ethyl 2,5-di-S-ethyl-1,2,5-trithio-D-lyxofuranoside (**69**). — (*i*). Compound **63** (5.7 g), barium carbonate (10 g), acetone (30 mL), and water (30 mL) were stirred while a solution of mercuric chloride (5.7 g) in water (30 mL) was added. After stirring for 2 h at room temperature, the mixture was filtered and the solid was repeatedly washed with methanol. The combined filtrates were evaporated and ethyl 2-*S*-ethyl-1,2-dithio-D-lyxofuranoside (**75**) was crystallized from ethyl acetate–hexane (1.3 g), m.p. 46–48°.

Anal. Calc. for $C_9H_{18}O_3S_2$: C, 45.4; H, 7.6. Found: C, 45.5, H, 7.6.

Compound **75** (0.3 g) was treated with *p*-toluenesulfonyl chloride (1.1 mol) by the *p*-toluenesulfonylation procedure to give **76** (0.4 g), which was directly treated with ethanethiol (1.0 mL) and sodium (0.1 g) in methanol (10 mL) under reflux for 4 h. The solution was diluted with chloroform, washed with water, and evaporated. Chromatography of the residue in 1:19 (v/v) methanol–benzene gave **69** (0.2 g).

Anal. Calc. for $C_{11}H_{22}O_2S_3$: C, 49.6; H, 8.3. Found: C, 49.1; H, 8.0.

(*ii*). Compound **69** (0.22 g) was also obtained from **66** (0.40 g, prepared by

O-acetylation of **65**) by the method described for the preparation of **67** from **12**. Compound **65** (0.50 g) was prepared from methyl 2,3,5-tri-*O*-acetyl-D-lyxofuranosides[16] (5.0 g) and ethanethiol by procedure (*b*) for 1 day, m.p. 56° (ethanol).

Anal. Calc. for $C_{17}H_{30}O_6S_3$: C, 47.9; H, 7.0. Found: C, 48.0; H, 6.8.

4-O-Acetyl-2,5-epithio-3-S-benzyl-3-thio-D-ribose dibenzyl dithioacetal (**51**). — (*i*). Methyl 2,3,5-tri-*O*-acetyl-D-xylofuranosides[16] (**70**) gave with phenylmethanethiol, by procedure (*b*) for 5 days at 50°, **51** (0.50 g), m.p. 89–90° (methanol), $[\alpha]_D^{20}$ −160° (*c* 0.6, chloroform).

Anal. Calc. for $C_{28}H_{30}O_2S_4$: C, 63.9; H, 5.7; S, 24.3. Found: C, 64.2; H, 5.7; S, 23.8.

(*ii*). 3,5-Di-*O*-acetyl-1,2-*O*-isopropylidene-α-D-xylofuranose gave **24** with phenylmethanethiol, by procedure (*b*) for 0.5 h, syrupy **43** (1.0 g) and **54** (0.10 g), m.p. 89–90° (from methanol), $[\alpha]_D^{20}$ +18° (*c* 4.5, chloroform).

Anal. Calc. for $C_{37}H_{40}O_4S_4$: C, 65.7; H, 5.9; S, 18.9. Found: C, 65.8; H, 6.0; S, 19.0.

When the reaction time was increased to 40 h, **51** (1.0 g) crystallized from the crude product by the addition of methanol.

(*iii*). Compound **43** was *O*-deacetylated to give **44** which, without purification, was treated with *p*-toluenesulfonyl chloride as described under *p*-toluenesulfonylation, and the product from this reaction was *O*-acetylated to give **51** (0.52 g).

(*iv*). 3-*O*-Acetyl-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-xylofuranose (**25**) gave with phenylmethanethiol, by procedure (*b*) for 4 h, **51** (0.82 g) by addition of methanol to the crude syrup. The mother liquor was evaporated and the residue *O*-acetylated. Chromatography with 1:19 (v/v) methanol–benzene gave **55** (syrup 0.20 g).

(*v*). 3-*O*-Acetyl-5-*S*-benzyl-1,2-*O*-isopropylidene-5-thio-α-D-xylofuranose (**26**) gave with phenylmethanethiol, by procedure (*b*) for 1 h, a mixture of **51** (0.36 g) and a compound (0.15 g), m.p. 108° (ethyl acetate-hexane). $[\alpha]_D^{20}$ −7° (*c* 1.5, chloroform). Structure **57** or that of an isomer was assigned to the compound.

Anal. Calc. for $C_{28}H_{30}O_2S_4$: C, 63.9; H, 5.7; S, 24.3. Found: C, 64.4; H, 5.7; S, 24.7.

A third compound (0.24 g), m.p. 86–87° (ethyl acetate–hexane) was separated from the mixture. $[\alpha]_D^{20}$ −32° (*c* 0.5, chloroform); this compound was an isomer of the compound having m.p. 108°.

Anal. Calc. for $C_{28}H_{30}O_2S_4$: C, 63.9; H, 5.7; S, 24.3. Found: C, 64.2; H, 5.9; S, 24.0.

All three isomers gave by β-elimination 2-thiophenecarbaldehyde (**19**).

4-O-Acetyl-2,3-di-S-ethyl-5-O-methyl-2,3-dithio-D-ribose diethyl dithioacetal (**47**). — 3-*O*-Acetyl-1,2-*O*-isopropylidene-5-*O*-methyl-α-D-xylofuranose[21] (**29**) gave, with ethanethiol by procedure (*b*) for 1 h, (*i*) compound **47** (0.76 g): syrup, $[\alpha]_D^{20}$ +2° (*c* 3.1, chloroform).

Anal. Calc. for $C_{16}H_{32}O_3S_4$: C, 48.0; H, 8.0; S, 32.0. Found: C, 48.2; H, 7.9; S, 31.8.

and (*ii*) the 3-ene **17** (0.40 g), syrup, $[\alpha]_D^{20}$ +6° (*c* 2.1, chloroform).

Anal. Calc. for $C_{14}H_{28}OS_4$: C, 49.4; H, 8.2; S, 37.7. Found: C, 49.3; H, 8.3; S, 38.0.

Compound **29** gave with phenylmethanethiol, by procedure (*b*) for 22 h, **51** (0.30 g) and a syrup (0.18 g) of undetermined structure, presumably a 2,3,4-tri-*S*-benzyl-5-*O*-methyl-2,3,4-trithiopentose dibenzyl dithioacetal.

4-O-Acetyl-5-O-benzyl-2,3-di-S-ethyl-2,3-dithio-D-ribose diethyl dithioacetal (**48**). — 3-*O*-Acetyl-5-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose[22] (**30**) gave with ethanethiol by procedure (*b*) for 2 h mainly **48** (0.80 g), syrup, $[\alpha]_D^{20}$ −23° (*c* 0.9, chloroform).

Anal. Calc. for $C_{22}H_{36}O_3S_4$: C, 55.5; H, 7.6; S, 26.9. Found: C, 55.1; H, 7.8; S, 27.0.

After 24 h of reaction, however, the main product was the 3-ene **18** (0.42 g), syrup, $[\alpha]_D^{20}$ −9° (*c* 2.4, chloroform).

Anal. Calc. for $C_{20}H_{32}OS_4$: C, 57.7; H, 7.7; S, 30.8. Found: C, 57.6; H, 7.7; S, 30.6.

3,5-Di-O-methyl-D-xylose diethyl dithioacetal (**6**). — 1,2-*O*-Isopropylidene-3,5-di-*O*-methyl-α-D-xylofuranose (**31**) gave with ethanethiol by procedure (*b*), after chromatography with 1:9 (v/v) methanol-benzene, **6** (0.43 g), syrup, $[\alpha]_D^{20}$ +20° (*c* 2.9, chloroform).

Anal. Calc. for $C_{11}H_{24}O_4S_2$: C, 46.5; H, 8.5; S, 22.5. Found: C, 46.6; H, 8.3; S, 22.8.

5-S-Benzyl-5-thio-D-xylose diethyl dithioacetal (**8**). — (*i*) 5-*S*-Benzyl-1,2-*O*-isopropylidene-5-thio-α-D-xylofuranose[19] (**33**) gave with ethanethiol, by procedure (*b*) for 2 h, **8** (0.92 g), m.p. 61–62° (ethyl acetate–hexane), $[\alpha]_D^{20}$ +57° (*c* 2.8, chloroform).

Anal. Calc. for $C_{16}H_{26}O_3S_3$: C, 53.0; H, 7.2; S, 26.5. Found: C, 52.9; H, 7.3; S, 27.0.

(*ii*) When the same reaction was performed for 3 weeks, chromatography with 1:9 (v/v) methanol–benzene gave **8** (0.45 g) and **59** (0.40 g), syrup, $[\alpha]_D^{20}$ +3° (*c* 0.2, chloroform).

Anal. Calc. for $C_9H_{18}O_2S_3$: C, 42.5; H, 7.1; S, 37.8. Found: C, 42.3; H, 7.3; S, 37.5.

Compound **59** gave by β-elimination in the absence of mercuric oxide 2-thiophenecarbaldehyde (**19**).

2,5-Anhydro-3-O-tosyl-D-xylose diethyl dithioacetal (**60**). — 1,2-*O*-Isopropylidene-3,5-di-*O*-tosyl-α-D-xylofuranose[23] (**34**) gave with ethanethiol, by procedure (*b*) for 3 h, 3,5-di-*O*-tosyl-D-xylose diethyl dithioacetal (**9**) (1.1 g) after chromatography with 1:19 (v/v) methanol–benzene. Compound **9** (1.0 g) was treated with pyridine (10 mL) for 1 h at 60°, and the product isolated as described under the *p*-toluenesulfonylation procedure. Chromatography with 1:9 (v/v) methanol–benzene gave **60** (0.9 g), syrup.

Anal. Calc. for $C_{16}H_{24}O_6S_3$: C, 49.0; H, 6.1. Found: C, 48.8; H, 6.0.

2,5-Anhydro-3-O-tosyl-D-xylose dibenzyl dithioacetal (**62**). — Compound **34**

was treated with phenylmethanethiol by procedure (*b*) for 3 h. The crude product (**11**) was heated with pyridine at 60° for 1 h, and the product isolated as described for **60**. Chromatography with 1:19 (v/v) methanol–benzene gave **62** (0.9 g), syrup. Compound **62** was *O*-acetylated to give a solid acetate, which was crystallized from ethyl acetate–hexane, m.p. 92–93°.

Anal. Calc. for $C_{28}H_{30}O_6S_3$: C, 60.2: H, 5.4: S, 17.2. Found: C, 60.0; H, 5.5; S, 17.5.

2,5-Anhydro-3-O-tosyl-D-xylose dimethyl acetal (**61**). — (*i*). Compound **60** (1.0 g) was converted into the dimethyl acetal with mercuric chloride and methanol to give **61** (0.78 g), m.p. 71–72° (ethyl acetate–hexane); lit.[12] m.p. 76–78°.

Anal. Calc. for $C_{14}H_{20}O_7S$: C, 50.6; H, 6.0; S, 9.6. Found: C, 50.5; H, 6.1; S, 9.6.

(*ii*). Compound **62** (1.0 g) was converted to **61** (0.5 g) by the same procedure described under (*i*).

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REFERENCES

1 J. D. WANDER AND D. HORTON, *Adv. Carbohydr. Chem. Biochem.*, 32 (1976) 15–123.
2 R. U. LEMIEUX, *Can. J. Chem.*, 29 (1951) 1079–1091; R. U. LEMIEUX AND C. BRICE, *ibid.*, 33 (1955) 109–119.
3 M. W. WOLFROM AND T. E. WHITELEY, *J. Org. Chem.*, 27 (1962) 2109–2110.
4 N. W. HUGHES, R. ROBSON, AND S. A. SAEED, *Chem. Commun.*, (1968) 1381–1383.
5 G. S. BETHELL AND R. J. FERRIER, *J. Chem. Soc., Perkin Trans. 1*, (1972) 1033–1037; 2873–2878; (1973) 1400–1405.
6 K. BLUMBERG, A. FUCCELLO, AND T. VAN ES, *Carbohydr. Res.*, 70 (1979) 217–232.
7 M. L. WOLFROM AND W. VON BEBENBURG, *J. Am. Chem. Soc.*, 82 (1960) 2817–2819.
8 T. VAN ES, *Carbohydr. Res.*, 37 (1974) 373–380.
9 J. DEFAYE, *Adv. Carbohydr. Chem. Biochem.*, 25 (1970) 181–228.
10 B. BERRANG AND D. HORTON, *Chem. Commun.*, (1970) 1038–1039.
11 T. VAN ES, *Carbohydr. Res.*, 58 (1977) 488–493.
12 J. DEFAYE AND J. HILDESHEIM, *Tetrahedron Lett.*, (1968) 313–317.
13 T. VAN ES AND R. L. WHISTLER, *Tetrahedron*, 23 (1967) 2849–2853.
14 C. S. HUDSON AND J. M. JOHNSON, *J. Am. Chem. Soc.*, 37 (1915) 2748–2753.
15 A. L. RAYMOND, *J. Biol. Chem.*, 107 (1934) 85–96.
16 B. GREEN AND H. REMBOLD, *Chem. Ber.*, 99 (1966) 2162–2171.
17 P. A. LEVENE AND A. L. RAYMOND, *J. Biol. Chem.*, 102 (1933) 317–330.
18 R. S. TIPSON, *Methods Carbohydr. Chem.*, 2 (1963) 249.
19 D. L. INGLES AND R. L. WHISTLER, *J. Org. Chem.*, 27 (1962) 3896–3898.
20 H. ZINNER, A. KOINE, AND H. NIMZ, *Chem. Ber.*, 93 (1960) 2705–2712.
21 P. A. LEVENE AND A. L. RAYMOND, *J. Biol. Chem.*, 102 (1933) 331–346.
22 H. KUZUHARA AND S. EMOTA, *Agric. Biol. Chem.*, 28 (1964) 900–907.
23 P. KARRER AND A. BOETTCHER, *Helv. Chim. Acta*, 36 (1953) 837–838.