The Path of the Conversion of 3,5,6-Tri-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucose into 4,5,6-Tri-*O*-benzoyl-2,3-di-*S*-ethyl-2,3-dithio-D-allose Diethyl Dithioacetal

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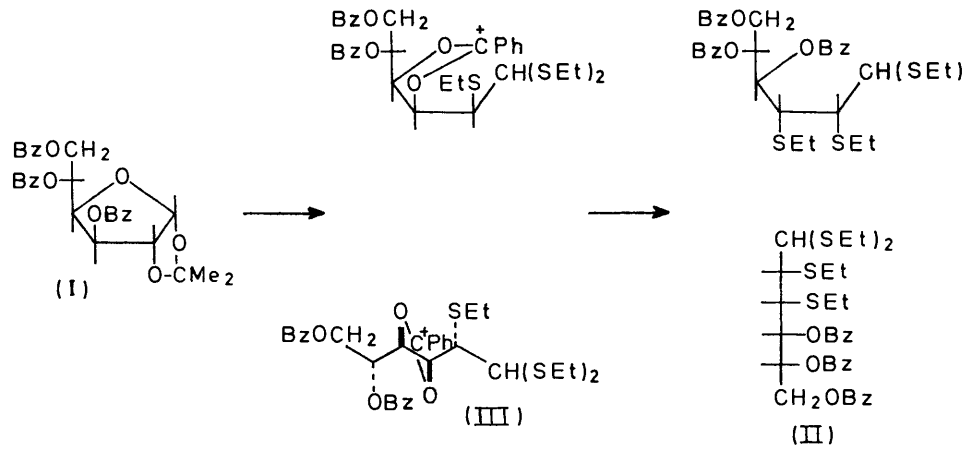
The reaction whereby 4,5,6-tri-*O*-benzoyl-2,3-di-*S*-ethyl-2,3-dithio-D-allose diethyl dithioacetal can be obtained efficiently by direct ethanethiolysis of 3,5,6-tri-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucose is shown to take place by way of 2-*S*-ethyl-2-thio-D-mannose intermediates. Migration of the 2-ethylthio-group to C-3 and of the 3-benzoyl substituent to C-4 follow, and an additional ethylthio-group is introduced at C-2.

In a recent report [1] we have shown that the reaction undergone by 3,5,6-tri-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose (I) with ethanethiol in the presence of hydrogen chloride gives 4,5,6-tri-*O*-benzoyl-2,3-di-*S*-ethyl-2,3-dithio-D-allose diethyl dithioacetal (II) with good efficiency, and we speculated that the ion (III) was the key intermediate (Scheme 1).



Scheme 1

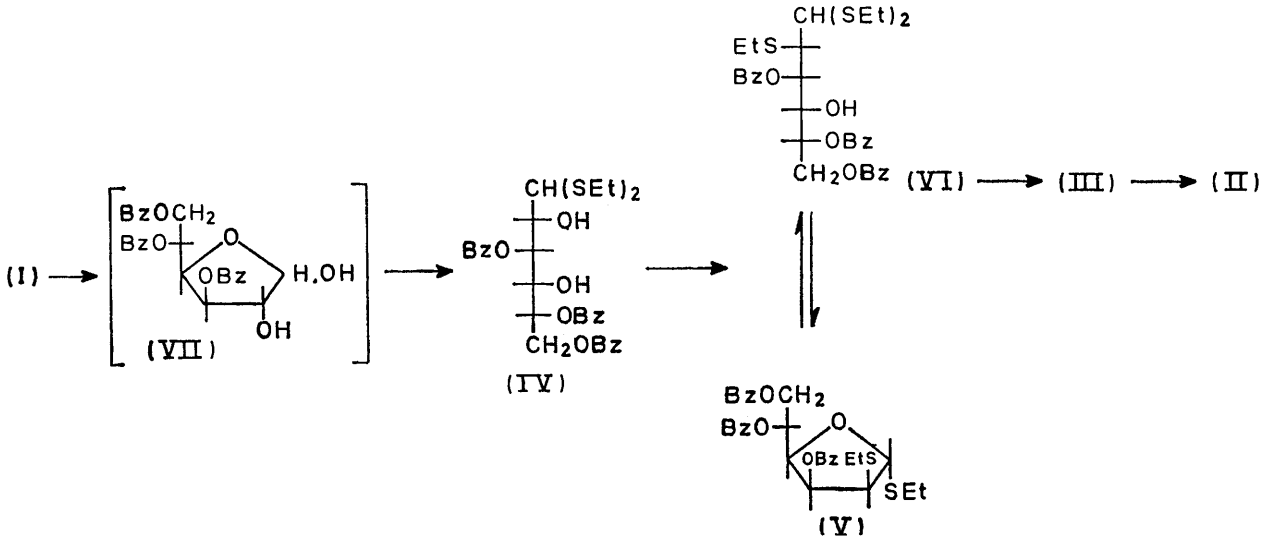
Evidence is now supplied in support of the suggested reaction path; in particular, it is shown that the reaction proceeds by way of 2-*S*-ethyl-2-thio-D-mannose intermediates which are then converted into the *allo*-product by (i) solvent attack at C-1, (ii) migration of an ethylthio-group from C-1 to C-2, (iii) migration of the 2-ethylthio-group to C-3 and, finally, (iv) migration of the 3-ester function to C-4. Since synthesis of the *manno*-intermediate involves configurational inversion at C-2, and the later steps involve inversions at C-2 and C-3, the net stereochemical consequence of the reaction is inversion at C-3 *i.e.* a transposition from the D-*gluco*- to the D-*allo*-series.

Examination by t.l.c. of the reaction mixture prior to completion of the reaction revealed the presence of five detectable intermediates, the most abundant three of which were isolated as syrups by preparative t.l.c. and characterised as compounds (IV)—(VI). The first of these on debenzoylation gave D-glucose diethyl dithioacetal, and the esterification pattern was assumed to be that of the tribenzoate (VI) which on benzoylation gave the known crystalline 3,4,5,6-tetra-*O*-benzoyl-2-*S*-ethyl-2-thio-D-mannose diethyl dithioacetal. Since the 4-H resonance in the n.m.r. spectrum of the tribenzoate (VI) was specifically moved to lower field on benzoylation, it is concluded that in compound (VI) [and in the precursor (IV)] the ester groups occupied positions 3, 5, and 6, *i.e.* that no benzoyl migration had occurred at this stage. The furanoside (V) was readily characterised by debenzoylation to the known crystalline ethyl 2-*S*-ethyl-1,2-dithio-α-D-mannofuranoside and by comparison of its optical rotation and n.m.r. spectrum with those of an authentic sample prepared from this mannofuranoside derivative. The two unisolated intermediates were believed to be 3,5,6-tri-*O*-benzoyl-D-glucose (VII) and ethyl 3,5,6-tri-*O*-benzoyl-2-*S*-ethyl-1,2-dithio-β-D-mannofuranoside on account of their chromatographic characteristics and their positions in the sequence of the overall reaction.

At very early stages in the reaction, t.l.c. showed that small amounts of a product with the mobility of the free sugar (VII) were formed which apparently gave way to the thioacetal (IV). It is not known whether the dihydroxy-derivative (VII) arose by solvolytic removal of the acetal ring of the starting material following attack at the acetal carbon atom rather than at C-1 (as happens in the methanolysis of 1,2-*O*-isopropylidene-D-glucofuranose [2]) or whether it is the product of slight amounts of hydrolysis, or indeed whether it is an

[1] G. S. Bethell and R. J. Ferrier, *J.C.S. Perkin I*, 1972, 1033.
[2] P. M. Collins, *Tetrahedron*, 1965, **21**, 1809.

intermediate at all. The acyclic product (IV) could have arisen by a two-stage attack of solvent at C-1 of the starting material. The finding of the acetal (IV) rather than furanosides as the next intermediate may suggest that this last possibility represents the true reaction path since the free sugar might have been expected under kinetic control to be converted to glycosides.[3]* Compound (IV) was then converted into the 2-thio-D-mannose derivatives (V) and (VI) [and into smaller amounts of the second uncharacterised intermediate



SCHEME 2

which was presumed to be the β-anomer of the furanoside (V)] but it was not possible to ascertain which of these was formed first. Clearly the acetal (VI) could have been derived from diol (IV) in the same way as 3,4,5,6-tetra-*O*-benzoyl-2-*S*-ethyl-2-thio-D-mannose diethyl dithioacetal is produced by thiolysis of 3,4,5,6-tetra-*O*-benzoyl-D-glucose diethyl dithioacetal,[4] but a synchronous process involving attack by O-4 at C-1 and migration of an ethylthio-group to C-2 (*cf.* refs. 5 and 6) would afford the furanoside (V).† Thiolysis of both compounds (V) and (VI) independently indicated that they interconvert very rapidly, and therefore it is difficult if not impossible to determine which is formed first and from which the ion (III) and hence the final product (II) are derived. The overall reaction, it is suggested, is as outlined in Scheme 2.

As an independent test for the intermediacy of 2-thio-D-mannose compounds in the reaction, 3,5,6-tri-*O*-benzoyl-2-*S*-ethyl-2-thio-D-mannofuranose and its 1-thio-*S*-ethyl α-glycoside were separately converted in 69 and 71% yield, respectively, into the tetrathio-product (II).

At this stage it became necessary to identify the sources of the 3-thio-group and the 4-benzoyl group in the final product (II), because the former could have been introduced directly from the solvent or by migration from C-2, while the latter could have arisen from one of the ester functions other than that at C-3 in the starting material. To identify the source of the 3-ethylthio-group in the product (II), therefore, 3,5,6-tri-*O*-benzoyl-2-*S*-ethyl-2-thio-D-mannose (VIII), prepared by specific hydrolysis of the thiofuranoside (V) and characterised by its conversion into the known 1,3,4,5,6-penta-*O*-acetyl-2-*S*-ethyl-2-thio-D-mannitol, was thiolysed using methanethiol and converted into the analogue (IX) of the tetraethyl derivative (II) (Scheme 3). For reasons of practical convenience trifluoroacetic acid was used as catalyst for this reaction after it had been established that the original conversion [(I) ⟶ (II)] and the reaction of the free sugar (VIII) to give the product (II) were readily effected under these modified conditions. Comparison of the n.m.r. spectra of the *allo*-dithioacetals (IX) and (II) revealed their close structural and stereochemical relationship (maximum discrepancies for chemical shifts and coupling constants 0·18 p.p.m. and 1·2 Hz, respectively), but did not establish for the trimethyl compound (IX) the crucial point *i.e.* the specific substituents on S-2 and S-3.

Earlier [1] it has been shown that the tetraethylthio-compound (II) on treatment with mercury(II) oxide–mercury(II) chloride in wet acetone underwent hydrolysis at C-1 and subsequent β-elimination to give an enal. On similar treatment the trimethyl analogue (IX) gave a second enal (X), shown by n.m.r. spectroscopy to

* However, ethanethiolysis under the same conditions of the free sugar (VII), prepared directly by hydrolysis of the acetal (I), gave an identical pattern of products which suggests that it may have been a genuine intermediate.

† It is considered probable that C-2—C-3 benzoxonium ions participate in the incorporation of the ethylthio-groups at C-2, and that resonance stabilised C-1 thiocarbonium ions (N. A. Hughes, R. Robson, and S. A. Saeed, *Chem. Comm.*, 1968, 1381) may also be involved in these processes.

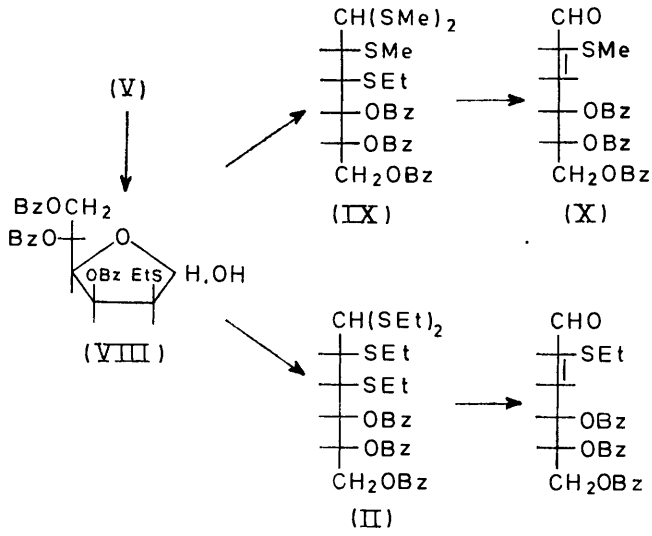
[3] R. J. Ferrier, L. R. Hatton, and W. G. Overend, *Carbohydrate Res.*, 1968, **6**, 87.

[4] B. Berrang and D. Horton, *Chem. Comm.*, 1970, 1038; D. Horton and D. H. Hutson, *Adv. Carbohydrate Chem.*, 1963, **18**, 123.

[5] J. Defaye, T. Nakamura, D. Horton, and K. D. Philips, *Carbohydrate Res.*, 1971, **16**, 133.

[6] K. J. Ryan, E. M. Acton, and L. Goodman, *J. Org. Chem.*, 1971, **36**, 2646.

contain one methylthio-group, three benzoyl groups, a formyl group (singlet) and five other carbon chain

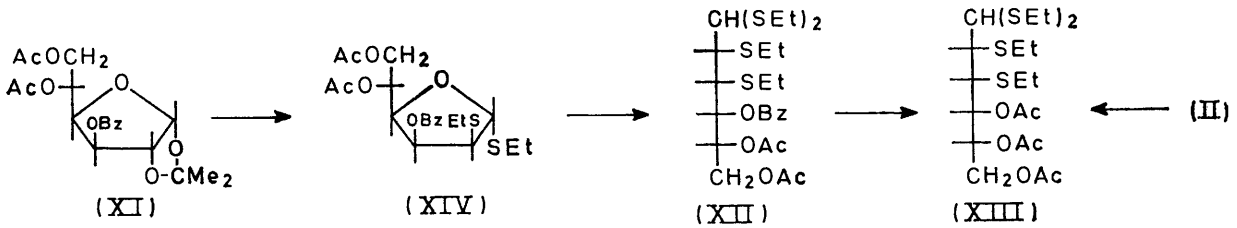


SCHEME 3

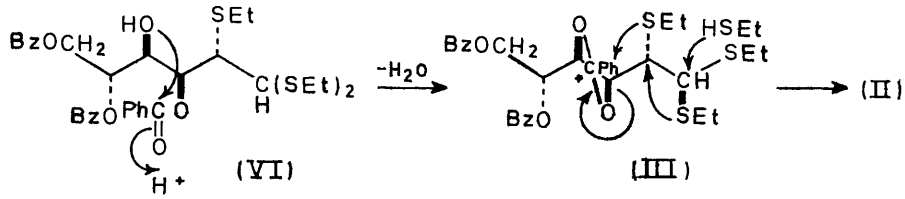
protons.* Since none of these resonated at high field, it was concluded that the methylthio-group was vinylic, and since the one vinylic proton coupled with 4-H (quartet) and not with 1-H, the enal system was ascribed

benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose (XI) for 8 h gave a chromatographically homogeneous product (XII) (Scheme 4) which on de-esterification followed by acetylation gave the tetrathio-D-*allo*-triacetate (XIII) which was also obtained by debenzoylation and acetylation of compound (II). Comparison of the chemical shifts of 4-, 5-, 6-, and 6'-H for compounds (XII), (XIII), and (II) establishes that the benzoyl group in the mixed ester (XII) is located at C-4, *i.e.* that the ester function at this position has migrated from C-3. Chemical shift values of 5-, 6-, and 6'-H of the diacetate-benzoate (XII) correlate with those of the triacetate (XIII) (maximum discrepancy 0·20 p.p.m.), whereas the 4-H values do not (0·42 p.p.m. discrepancy). Furthermore, the 4-H value for compound (XII) correlates with that of the tribenzoate (II) (0·19 p.p.m. discrepancy) while the 5-, 6-, and 6'-H values do not correlate (minimum discrepancy 0·35 p.p.m.).

Migration of the benzoate group as now established is in keeping with expectations, and should be particularly ready in the intermediate thioacetal (VI), which because of its *manno*-configuration will adopt the regular zig-zag conformation.[7] The hydroxy-group at C-4 and the ester function at C-3 are *cis*-related and thus ideally disposed for orthoacid formation and hence ester migration.[8] Under the acidic conditions of the reaction acyloxonium ions can then be produced, and these are



SCHEME 4



SCHEME 5

the illustrated structure. In keeping with this the compound showed u.v. absorption at *ca.* 300 nm in addition to aromatic absorption. It follows, therefore, that the ethylthio-group was located at C-3 in compound (IX), and that it was introduced by migration from C-2. The same conclusion is drawn regarding compound (II).

Finally it was established that the benzoyl group at C-4 in compound (II) was introduced by direct migration from C-3. Ethanethiolysis of 5,6-di-*O*-acetyl-3-*O*-

* Comparison of the n.m.r. spectra of compound (X) and 3-deoxy-2,4,5,6-tetra-*O*-methyl-D-*erythro*-hex-2-enose (E. F. L. J. Anet, *Carbohydrate Res.*, 1968, **7**, 453) indicates their close relationship.

well known to ring-open following intramolecular nucleophilic attack.[9] The participation of the ethylthio-groups in this ring opening and their sequential migration from C-1 to -2 to -3 are entirely in keeping with the known properties of such groups.[10]

The reaction of compound (VI) to give the final product can therefore be represented as shown in Scheme 5

[7] D. Horton and J. D. Wander, *Carbohydrate Res.*, 1969. **10**, 279.

[8] R. U. Lemieux in 'Molecular Rearrangements,' Part 2, ed. P. De Mayo, Interscience, New York, 1964, p. 709.

[9] H. Paulsen, H. Behre, and C.-P. Herold, *Fortschr. Chem. Forsch.*, 1970, **14**, 472.

[10] B. Capon, *Quart. Rev.*, 1964, **18**, 45.

[although it remains possible that ion (III) could have arisen directly from the thiofuranoside (V) by solvent attack at C-1 and synchronous migration of the O(4)–C(1) bond to the C-3 ester carbonyl group].

During the ethanethiolysis of compound (XI) it was observed that an intermediate [isolated and characterised as ethyl 5,6-di-*O*-acetyl-3-*O*-benzoyl-2-*S*-ethyl-1,2-dithio-α-D-mannofuranoside (XIV)] was present in large proportions after short reaction times.

EXPERIMENTAL

N.m.r. spectra were measured on a Perkin-Elmer–Hitachi R-20 instrument using tetramethylsilane as internal reference. All reactions were followed by t.l.c. and preparative t.l.c. was carried out on 1 m plates using silica gel (0·75 mm) layers and loadings of 0·5—1 g per plate. No elemental analyses were performed on syrupy products; in all cases appropriate n.m.r. spectra were used for characterisation purposes.

Isolation of Intermediates (IV)—(VI).—The isopropylidene compound (I) (1·0 g) was dissolved in chloroform–ethanethiol–trifluoroacetic acid (12 ml; 1 : 1 : 1) and left at room temperature for 0·5 h. after which the solution was diluted with chloroform and extracted with aqueous sodium hydrogen carbonate. The solution was dried and the solvents were removed to leave a syrup which was shown by t.l.c. [solvent light petroleum (b.p. 40—60°)–ether (2 : 1)] to contain seven components [R_F 0·67 [compound (II)], 0·63, 0·53 (I), 0·41, 0·29, 0·18, and 0·05]. The most mobile intermediate (R_F 0·63) was found to be *ethyl* 3,5,6-*tri*-O-*benzoyl*-2-S-*ethyl*-1,2-*dithio*-α-D-*mannofuranoside* (V) (0·046 g), $[\alpha]_D$ −4° (*c* 1·2 in $CHCl_3$); n.m.r. spectrum identical with that of an authentic sample (see below). On debenzoylation (0·1 g, obtained in a subsequent preparation) with sodium methoxide in methanol it gave ethyl 2-*S*-ethyl-1,2-dithio-α-D-mannofuranoside (0·026 g, 56%), m.p. and mixed m.p. 93—94° (lit.,[5] m.p. 92—93°).

The component with R_F value 0·29 (0·40 g) had $[\alpha]_D$ −80° (*c* 1·2 in $CHCl_3$) and gave an n.m.r. spectrum (see Table) consistent with its being 3,5,6-*tri*-O-*benzoyl*-2-S-*ethyl*-2-*thio*-D-*mannose diethyl dithioacetal* (VI). On benzoylation with benzoyl chloride in pyridine it gave 3,4,5,6-tetra-*O*-benzoyl-2-*S*-ethyl-2-thio-D-mannose diethyl dithioacetal in 65% yield, m.p. and mixed m.p. 82—84° (from ethanol), $[\alpha]_D$ +56° (*c* 1·0 in Me_2CO) {lit.,[11] m.p. 84—85°, $[\alpha]_D$ +58° (Me_2CO)}.

The compound with R_F value 0·18 (0·10 g) had $[\alpha]_D$ −17° (*c* 1·7 in $CHCl_3$) and was shown by n.m.r. spectroscopy to contain three benzoyl groups, two ethyl groups, and two hydroxy-groups. On debenzoylation it gave D-glucose diethyl dithioacetal in 35% yield, m.p. and mixed m.p. 119—120°; resolidified and then 127°, $[\alpha]_D$ −35° (*c* 0·6 in H_2O) {lit.,[12] m.p. 127—128°, $[\alpha]_D$ −30° (H_2O)}. Hydrolysis in dilute acid of the debenzoylated product gave glucose (chromatographic identification) and the triester is concluded to be 3,5,6-*tri*-O-*benzoyl*-D-*glucose diethyl dithioacetal* (IV).

The minor components with R_F values 0·41 and 0·05 were not isolated (see Discussion section).

Ethyl 3,5,6-*Tri*-O-*benzoyl*-2-S-*ethyl*-1,2-*dithio*-α-D-*mannofuranoside* (V).—Ethyl 2-*S*-ethyl-1,2-dithio-α-D-mannofuranoside (1·0 g) was dissolved in dry pyridine (5 ml) and freshly purified benzoyl chloride (1·4 ml, 3·3 mol) was added slowly at 0° with shaking. After 0·5 h at 0° and 18 h at room temperature crushed ice (20 g) was added and the mixture was extracted with chloroform (50 ml). After extraction with dilute sulphuric acid followed by aqueous sodium hydrogen carbonate and washing with water the organic phase was dried and taken to dryness to give a syrup (2·06 g, 95%), $[\alpha]_D$ −3° (*c* 1·1 in $CHCl_3$). For n.m.r. spectrum see Table.

4,5,6-*Tri*-O-*benzoyl*-2,3-*di*-S-*ethyl*-2,3-*dithio*-D-*allose* *Di-*

N.m.r. parameters (first order; measured in deuteriochloroform at 60 MHz unless otherwise stated)

Compound	Chemical shifts (τ) 1-H	2-H	3-H	4-H	5-H	6-H	6'-H	Other protons	Coupling constants (Hz) $J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
(V)	4·66(d)	6·60(q)	4·10(q)	5·24(q)	4·32(sx)*	5·13(q)	5·42(q)	15 Bz, 10 Et	7·0	5·2	3·4	6·0	2·3	5·8	13·5
(XIV)	4·69(d)	6·65(q)	4·16(q)	5·52(q)	4·78(o)†	5·50(q)	5·82(q)	6 Ac, 5 Bz, 10 Et	8·0	5·0	3·0	8·5	3·0	5·0	12·5
Triacetyl analogue [a]	4·83(d)	6·80(q)	4·44(q)	*ca.* 5·7	4·78(m)	5·42—5·95		9 Ac, 10 Et	8	4·5	3·5				
Free sugar [b]	4·4	6·5	4·0	5·2	4·4	5·2	5·2	15 Bz, 5 Et, OH							
(XIII)	5·43(d)	6·96(q)	6·54(q)	4·20(t)	4·50(o)	5·53(q)	5·89(q)	9 Ac, 20 Et	4·7	8·0	5·0	5·0	2·8	6·0	12·0
(XII)	5·36(d)	6·89(q)	6·39(q)	3·78(t)	4·32(o)	5·33(q)	5·82(q)	6 Ac, 5 Bz, 20 Et	4·5	8·5	5·0	5·0	3·0	5·5	12·0
(II) (data from ref. 1)	5·42(d)	6·85(q)	6·31(q)	3·59(t)	3·88(o)	4·98(q)	5·46(q)	15 Bz, 20 Et	4·5	8·5	4·8	4·8	3·0	6·0	12·5
(IX)	5·52(d)	6·79(q)	6·17(q)	3·54(t)	3·77(o)	4·87(q)	5·28(q)	15 Bz, 5 Et, 9 Me	5·7	7·4	5·3	5·3	3·0	6·4	12
(X)	0·48(s)		3·08(d)	3·31(q)	4·00(o)	5·15(q)	5·37(q)	15 Bz, 3 Me			8·3	4·3	4·0	6·0	12
Ethyl analogue [c]	0·70(s)		3·21(d)	3·50(q)	4·20(o)	5·20(q)	5·53(q)	15 Bz, 5 Et			8·4	4·8	4·5	6·0	12·0
(VI)	5·92(d)	6·28(q)	4·23(d)	5·12(d)	4·70(h)	5·22(d)	5·22(d)	15 Bz, 15 Et, OH	3·3	9·5	<0·5	9·5	3·8	3·8	
Tetrabenzoate [d]	5·83(d)	6·50(q)	4·08(q)	3·61(q)	4·20(o)	5·11(q)	5·46(q)	20 Bz, 15 Et	3·5	9·5	2·0	7·2	3·8	5·7	12·0

[a] Ethyl 3,5,6-tri-*O*-acetyl-2-*S*-ethyl-1,2-dithio-α-D-mannofuranoside (100 MHz).[5] [b] 3,5,6-Tri-*O*-benzoyl-2-*S*-ethyl-D-mannose; poorly resolved spectrum, anomer mixture. [c] 4,5,6-Tri-*O*-benzoyl-3-deoxy-2-*S*-ethyl-2-thio-D-*erythro*-hex-2-enose.[1] [d] 3,4,5,6-Tetra-*O*-benzoyl-2-*S*-ethyl-2-thio-D-mannose diethyl dithioacetal.

* sx = sextet. † o = octet.

[11] P. Brigl, H. Mühlschlegel, and R. Schinle, *Ber.*, 1931, **64**, 2921.

[12] E. Fischer, *Ber.*, 1894, **27**, 673.

ethyl Dithioacetal (II).—(a) *From the thiofuranoside derivative* (V). The thiofuranoside (0·25 g) was dissolved in dry chloroform (4 ml) containing ethanethiol (3 ml) and dry hydrogen chloride was passed in for 2 h. The solution was diluted with chloroform (10 ml) and extracted with saturated aqueous sodium hydrogen carbonate, washed, and dried. Removal of the solvents and recrystallisation from ethanol gave the tetrathio-product (II) (0·21 g, 71%), m.p. and mixed m.p. 91—92°, $[\alpha]_D$ −1° (*c* 1·0 in Me_2CO) {lit.,[1] m.p. 92°, $[\alpha]_D$ −1·2° (Me_2CO)}. The n.m.r. spectrum was identical with that already described.

(b) *From* 3,5,6-*tri*-O-*benzoyl*-2-S-*ethyl*-2-*thio*-D-*mannose* (VIII). The free sugar (0·25 g, see below) was treated as in (a) to give the allose acetal (II) in 69% yield. Recrystallised from ethanol it had m.p. and mixed m.p. 91—92°, $[\alpha]_D$ −2° (c 1·0 in Me_2CO).

(c) *From* 3,5,6-*tri*-O-*benzoyl*-1,2-O-*isopropylidene*-α-D-*glucofuranose* (I) *with trifluoroacetic acid as catalyst.* The tribenzoyl compound (0·5 g) was dissolved in chloroform (2 ml)–ethanethiol (1·5 ml) and trifluoroacetic acid (1·5 ml) was added. After 8 h at 22° the tetrathio-product (0·37 g, 57%) was isolated in the usual way; m.p. and mixed m.p., after recrystallisation from ethanol, 92°; $[\alpha]_D$ −1° (*c* 1 in Me_2CO).

3,5,6-*Tri*-O-*benzoyl*-2-S-*ethyl*-2-*thio*-D-*mannofuranose* (VIII).—The tribenzoylthiofuranoside (V) (0·57 g) was dissolved in acetone containing a little water (4 ml), cadmium carbonate (0·42 g) and mercury(II) chloride (1·28 g) in wet acetone (3 ml) were added slowly, and the mixture was stirred for 17 h. The solids and solvent were removed and the residue was extracted with chloroform (50 ml) which was then washed with water and dried. Evaporation to dryness gave a light brown syrup (0·50 g, 94%), which was purified by preparative t.l.c., $[\alpha]_D$ −51° (*c* 1·0 in $CHCl_3$). The n.m.r. and i.r. spectra were consistent with expectations and the compound was characterised by conversion into the known 1,3,4,5,6-penta-*O*-acetyl-2-*S*-ethyl-2-thio-D-mannitol. The free sugar (0·88 g) in dry tetrahydrofuran (4 ml) was added slowly to a stirred suspension of lithium aluminium hydride (0·25 g) in tetrahydrofuran (6 ml) at 0°. The mixture was stirred at 25° for 17 h, when wet ethyl acetate was added until all unchanged hydride had decomposed. After addition of water (100 ml) inorganic material was removed by filtration and treatment with Dowex 50W-X8 resin (H^+) (5 g) and removal of the solvents gave a syrup which was acetylated with acetic anhydride–pyridine (10 ml; 1 : 1). After 24 h at 25° the solution was processed as usual to give a pale yellow syrup which was resolved on a column of silica gel to give the penta-acetate (0·22 g, 31%), m.p. and mixed m.p. 117—118° (from methanol), $[\alpha]_D$ +20° (*c* 0·4 in $CHCl_3$) (lit.,[5] m.p. 120—121°, $[\alpha]_D$ +21°). The n.m.r. spectrum was identical with that of an authentic sample. (We thank Dr. J. Defaye for providing a sample of this compound and its n.m.r. spectrum.)

4,5,6-*Tri*-O-*benzoyl*-3-S-*ethyl*-2-S-*methyl*-2,3-*dithio*-D-*allose Dimethyl Dithioacetal* (IX).—3,5,6-Tri-*O*-benzoyl-2-*S*-ethyl-2-thio-D-mannose, (VIII) (0·35 g) was dissolved in dry chloroform–trifluoroacetic acid (4 ml; 1 : 1) and cooled in liquid air. Methanethiol (2 ml) was added and the solution was sealed in an ampoule and left at room temperature for 24 h. The product was isolated in the usual manner and purified by preparative t.l.c. to give a syrup (0·22 g, 52%), $[\alpha]_D$ +15° (*c* 2·0 in Me_2CO). The n.m.r. spectrum (Table) showed the presence of three methyl groups, three benzoyl groups, one ethyl group, and appropriate carbon chain hydrogen atoms.

4,5,6-*Tri*-O-*benzoyl*-3-*deoxy*-2-S-*methyl*-2-*thio*-D-erythro-*hex*-2-*enose* (X).—The dimethyl dithioacetal (IX) (0·20 g) was dissolved in acetone (3 ml) containing water (0·1 ml). Mercury(II) oxide (0·3 g) was added and the suspension was stirred while an aqueous solution of mercury(II) chloride (0·25 g) was added over 15 min and stirring was continued for a further 30 min. The solids were then removed, chloroform (25 ml) was added, the chloroform solution was washed with water and dried, and the solvent was removed to leave a syrupy residue which was purified by preparative t.l.c. to give the *enal* as a colourless syrup (0·09 g, 58%), $[\alpha]_D$ −30° (*c* 0·9 in Me_2CO), $\lambda_{max.}$ (EtOH) 298 nm. The n.m.r. spectrum (see Table) indicated the presence of three benzoyl groups, one methyl group, one formyl group, and appropriate carbon chain hydrogen atoms one of which was vinylic.

5,6-*Di*-O-*acetyl*-4-O-*benzoyl*-2,3-*di*-S-*ethyl*-2,3-*dithio*-D-*allose Diethyl Dithioacetal* (XII).—5,6-Di-*O*-acetyl-3-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose (XI) (0·4 g), prepared according to the method of Brigl and Grüner,[13] was dissolved in chloroform (8 ml)–ethanethiol (6 ml) and dry hydrogen chloride was passed into the solution for 8 h. The *tetrathio-product* (0·36 g, 66%) was isolated in the usual manner, final purification being effected by preparative t.l.c., $[\alpha]_D$ −6° (*c* 1·0 in Me_2CO). The n.m.r. spectrum (see Table) indicated the presence of two acetyl groups, one benzoyl group, four ethyl groups, and appropriate carbon chain hydrogen atoms.

4,5,6-*Tri*-O-*acetyl*-2,3-*di*-S-*ethyl*-2,3-*dithio*-D-*allose Diethyl Dithioacetal* (XIII).—(a) *From the diacetate-benzoate* (XII). The mixed ester (0·26 g) was de-esterified under standard catalytic conditions with sodium methoxide in methanol and the product was treated with dry pyridine (3 ml) and acetic anhydride (1 ml) at 0°. After 18 h at room temperature the solution was mixed with crushed ice to give a crystalline product. After recrystallisation from ethanol the *triacetate* (0·16 g, 69%) had m.p. 64—65°, $[\alpha]_D$ +18° (*c* 1·1 in Me_2CO) (Found: C, 48·1; H, 7·3; S, 26·1. $C_{20}H_{36}O_6S_4$ requires C, 48·0; H, 7·2; S, 25·6%).

(b) *From the tribenzoate* (II). De-esterification and acetylation were effected with 79% efficiency and gave a crystalline product identical to that prepared in (a), m.p. and mixed m.p. 63—65°, $[\alpha]_D$ +21° (*c* 0·9 in Me_2CO).

Ethyl 5,6-*Di*-O-*acetyl*-3-O-*benzoyl*-2-S-*ethyl*-1,2-*dithio*-α-D-*mannofuranoside* (XIV).—5,6-Di-*O*-acetyl-3-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose (XI) (0·2 g) was dissolved in dry chloroform (4 ml)–ethanethiol (3 ml) and dry hydrogen chloride was passed in for 2 h. At this time t.l.c. indicated that the starting material had almost all undergone reaction and had been converted largely into a product other than the diethyl dithioacetal (XII). This intermediate was isolated in the usual manner, preparative t.l.c. giving the *thiofuranoside derivative* (XIV) as a syrup (0·08 g, 36%), $[\alpha]_D$ +40° (*c* 1·6 in $CHCl_3$). The n.m.r. spectrum (see Table) showed the presence of two acetyl and two ethyl groups, one benzoyl group, and appropriate carbon ring hydrogen atoms. De-esterification carried out in the usual manner with catalytic amounts of sodium methoxide in methanol gave ethyl 2-*S*-ethyl-1,2-dithio-α-D-mannofuranoside (0·03 g, 65%), m.p. and mixed m.p.

[13] P. Brigl and H. Grüner, *Ber.*, 1933, **66**, 1977.

90—92°, $[\alpha]_D$ +104° (*c* 0·9 in $CHCl_3$) after its recrystallisation from chloroform {lit.,[5] m.p. 92—93°, $[\alpha]_D$ +108° (*c* 1·6 in $CHCl_3$)}.

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