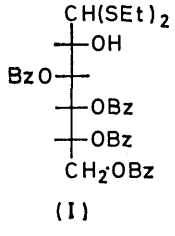
The Relayed Introduction of Alkylthio-groups into Carbohydrate Derivatives: a Novel Synthesis of Amicetose

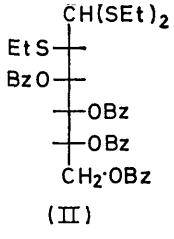
By **Geoffery S. Bethell** and **Robert J. Ferrier,*** Department of Chemistry, Victoria University of Wellington, New Zealand

The ethanethiolysis of 3-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose gives ethyl 4-*O*-benzoyl-2,3,6-tri-*S*-ethyl-1,2,3,6-tetrathio-α-D-mannopyranoside as main product. The thio-groups are shown to be introduced first at C-1 and are then relayed as follows: C-1 → C-2 → C-3 → C-6. The tetrathio-compound affords a new route to the antibiotic sugar amicetose (2,3,6-trideoxy-D-*erythro*-hexose).

ETHANETHIOLYSIS of 3,4,5,6-tetra-*O*-benzoyl-D-glucose diethyl dithioacetal (I) gives the 2-thio-D-mannose derivative (II), the C-2 thio-group being introduced by transfer from C-1.[1] Participation by the ester group

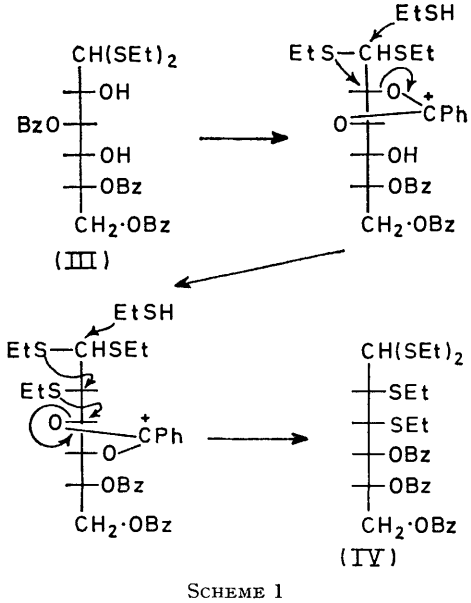


(I)



(II)

at C-3 could conceivably be implicated in the displacement of the hydroxy-group since further reaction occurs in the case of the 3,5,6-tribenzoyl analogue (III), the benzoyl group at C-3 migrating to C-4 and a further sulphur-containing group entering at C-3.[2] In a previous report[3] we have shown that these changes were effected as illustrated in Scheme 1, *i.e.* each chain sulphur atom is introduced at C-1 and is transmitted down the chain by way of episulphonium ion intermediates. At each stage sulphur enters the asymmetric centre with configurational inversion, and the product is thus the 2,3-dithio-D-allose derivative (IV).

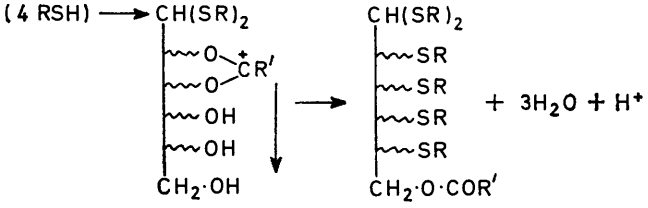


SCHEME 1

On the grounds of these findings, it was thought possible that alkylthio-groups could be introduced

[1] B. Berrang and D. Horton, *Chem. Comm.*, 1970, 1038.
[2] G. S. Bethell and R. J. Ferrier, *J.C.S. Perkin I*, 1972, 1033.
[3] G. S. Bethell and R. J. Ferrier, *J.C.S. Perkin I*, 1972, 2873.

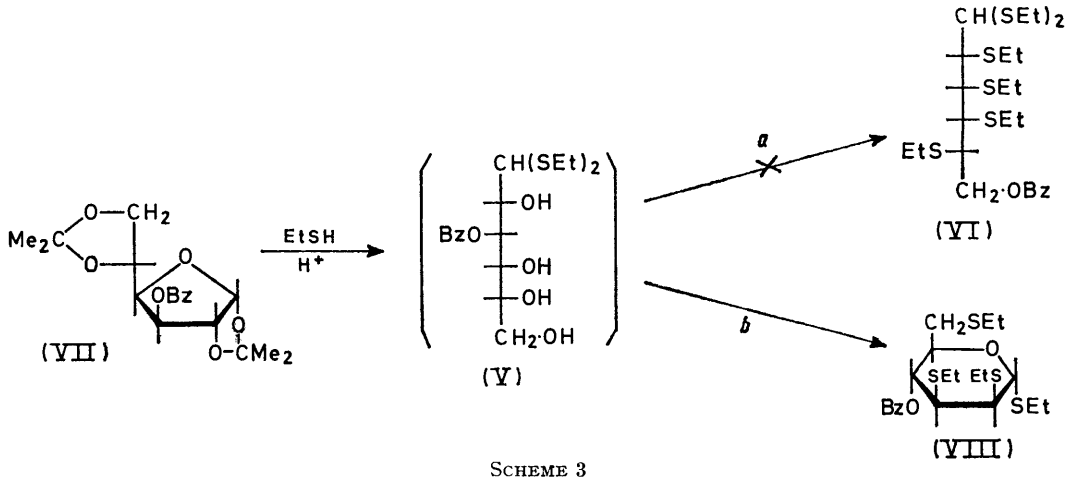
successively into C-1 of a sugar dialkyl dithioacetal bearing a suitable ester function, and that this group could be forced to migrate by a series of steps to the terminal position. At each step an oxygen function attached to the carbon chain would be replaced by an



SCHEME 2

alkylthio-group (Scheme 2). In terms of this hypothetical scheme 3-*O*-benzoyl-D-glucose diethyl dithioacetal (V) would be expected to yield 6-*O*-benzoyl-2,3,4,5-tetra-*S*-ethyl-2,3,4,5-tetrathio-L-talose diethyl dithioacetal (VI) on acid-catalysed ethanethiolysis (Scheme 3a). To test this possibility 3-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (VII), which under acidic conditions would be expected to be readily deacetalised, was treated with ethanethiol in the presence of trifluoroacetic acid, and eventually gave mainly one product which was isolated in 40% yield by column chromatography. By n.m.r. spectroscopy it was shown to contain four ethylthio-groups and one benzoate ester and to be devoid of hydroxy-groups. It therefore was not a diethyl dithioacetal but a glycoside, and a triplet with 9·3 Hz splitting in the spectrum indicated that the ring was pyranoid. The H-5 resonance was readily recognised from its multiplicity (sextet), and since it contained a 9·3 Hz splitting the proton was considered to be axially oriented and adjacent to an axial H-4. Furthermore, since the H-4 resonance was the broad triplet already referred to, H-3 was axial, and a $J_{2,3}$ value of 4·0 Hz revealed that H-2 was equatorial. The overall configuration therefore was *manno*; from the chemical shifts of H-2, H-3, H-6, and H-6′ it was evident that they were attached to sulphur-bonded carbon atoms, and the low-field position of the H-4 signal showed the ester group was attached to C-4. Since α-mannopyranosides are appreciably favoured thermodynamically over their β-isomers,[4] and since the tetrathio-product was produced under equilibration conditions, the α-anomeric configuration can be assigned. A $J_{1,2}$ value of 1·7 Hz is consistent with this assignment,[5] as is the optical rotation ($[\alpha]_D$ +30°) relative to that of the β-anomer mentioned later ($[\alpha]_D$ −11°), since the compound belongs to the D-series, as was shown by its conversion into the known methyl 2,3,6-trideoxy-α-D-*erythro*-hexopyranoside (XII) (Scheme 4). The tetrathio-compound is therefore ethyl 4-*O*-benzoyl-2,3,6-tri-*S*-ethyl-1,2,3,6-tetrathio-α-D-manno-pyranoside (VIII) (Scheme 3b).

Debenzoylation afforded the alcohol (IX), which was



SCHEME 3

methanolysed to give the corresponding methyl glycoside (X), assumed (and proved by the reactions illustrated in Scheme 4) to have the pyranose ring form on the grounds that in the mannose series furanosides are thermodynamically unfavoured.[4] This product readily gave the crystalline 3,5-dinitrobenzoate (XI), and by Raney nickel desulphurisation was converted into the trideoxy-D-hexoside (XII), methyl amicetoside [characterised as the ester (XIII)], which has previously been synthesised,[6] and also obtained by methanolysis of the antibiotic amicetin.[7] Albano and Horton [6] record +142° as the optical rotation of the glycoside, and since their synthetic method afforded it in anomerically pure state this can be taken as a reliable figure. In the present synthesis the methanolysis step (IX) ⟶ (X) would be expected to give an anomeric mixture of

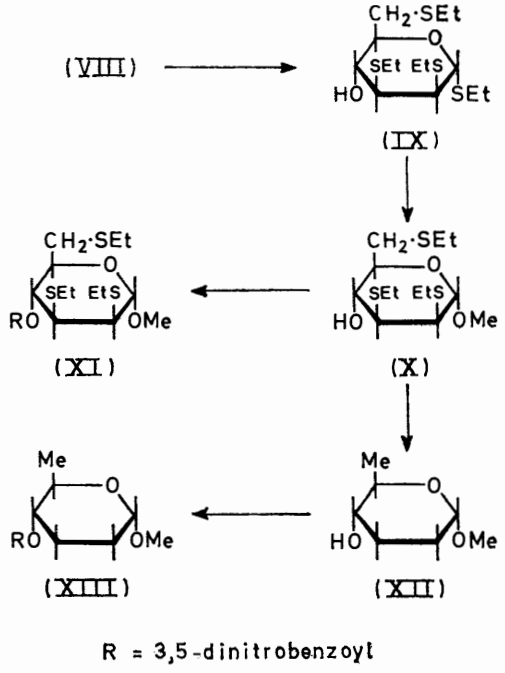
[4] V. Smirnyagin and C. T. Bishop, *Canad. J. Chem.*, 1968, **46**, 3085.

[5] B. Coxon, *Tetrahedron*, 1965, **21**, 3481.

[6] (*a*) E. L. Albano and D. Horton, *J. Org. Chem.*, 1969, **34**, 3519; (*b*) J. S. Brimacombe, L. W. Doner, and A. J. Rollins, *J.C.S. Perkin I*, 1972, 2977.

[7] C. L. Stevens, K. Nagarajan, and T. H. Haskell, *J. Org. Chem.*, 1962, **27**, 2991.

pyranosides in which the α-compound would be largely favoured by both the anomeric effect and the absence of steric interaction between the groups at C-1 and C-2;



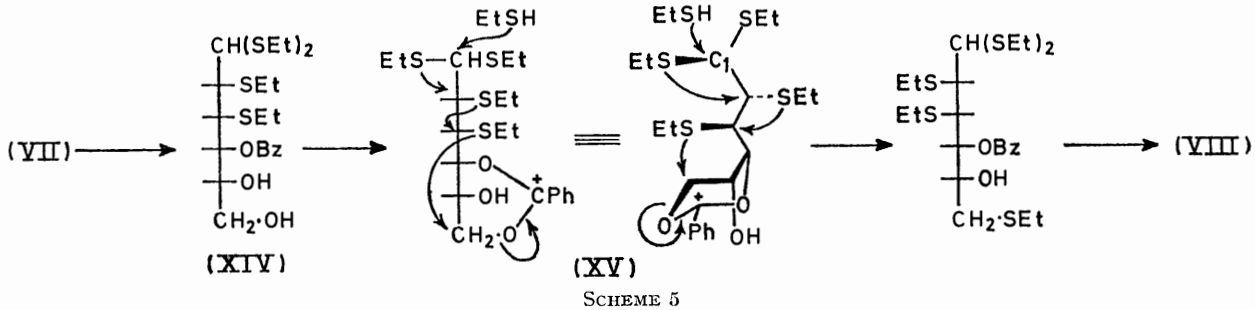
SCHEME 4

therefore small amounts of the β-anomers of compounds (X) and (XII) would have been present. It is thus to be expected that the measured optical rotation (+130°) for our sample of compound (XII) would be less than +142°. In the case of the glycoside sample prepared from the antibiotic,[7] equilibration between anomers occurred at the glycoside stage, and since the β-form of this compound has no destabilising C-1,C-2 interaction it would be expected to be formed in large proportions by this procedure, and hence give rise to a lower value (+75° found) for the optical rotation of the mixed anomers.

Although there are disadvantages in this synthetic approach to amicetose {most notably the need to purify the key tetrathio-compound (VIII) by chromatography [or conceivably by conversion into the dinitrobenzoate (XI), which has not been tried]} it appears to offer a more convenient route to the sugar than has been described to date.[6-8] In view of the continuing interest in the chemical synthesis of antibiotics containing amicetose,[9] this new approach could represent a useful advance.

3-*O*-Benzoyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose was not in fact thiolysed exactly according to Scheme 2 to give a 2,3,4,5-tetrathio 6-benzoate; instead, after sulphur groups were introduced at C-2 and C-3 the next such group was introduced at C-6. If it is assumed (a) that benzoxonium ion formation precedes sulphur incorporation, and (b) that all sulphur atoms are introduced (at positions other than C-1) by intramolecular procedures, the formation of the product (VIII) can be rationalised as indicated in Scheme 5. That is, the starting material gives a 2,3-dithio-D-*allo*-intermediate (XIV) [analogous to (IV)] from which a 4,6-benzoxonium ion (XV) is then formed. The reaction continues by further solvent attack at C-2 and relay of ethylthio-groups to C-2, then to C-3, and finally to C-6, the last step occurring, as illustrated, with the ethylthio-group at C-3 migrating, in a known kind of reaction, by way of a five-membered cyclic sulphonium ion,[10] to C-6 instead of to C-4.

Evidence which enhances the likelihood that a 2,3-dithio-D-allose intermediate was involved was obtained by finding that 1,4-di-*O*-benzoyl-2,3-di-*S*-ethyl-6-*O*-triphenylmethyl-2,3-dithio-D-allopyranose (prepared by selective tritylation of the free sugar [2] at C-6,[11] followed by complete benzoylation) also gave the tetrathio-mannoside (VIII) as main product on ethanethiolysis.



SCHEME 5

Since it has earlier been shown that a 2,3-dithio-D-allose intermediate would be produced by way of a 2-thio-D-mannose by successive introduction of thiol groups at C-1 and migration to C-2 and thence to C-3,[3] it remained to establish, before a complete relay mechanism for the formation of product (VIII) was proved, that the ethylthio-group at C-6 had migrated from C-3 (Scheme 5). To do this, 3-*O*-benzoyl-2-*S*-ethyl-5,6-*O*-

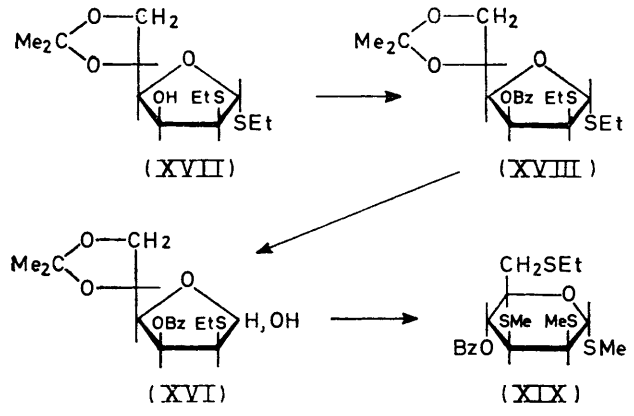
[8] C. L. Stevens, P. Blumbergs, and D. L. Wood, *J. Amer. Chem. Soc.*, 1964, **86**, 3592; A. H. Haines, *Carbohydrate Res.*, 1972, **21**, 99.

[9] C. L. Stevens, J. Němec, and G. H. Ransford, *J. Amer. Chem. Soc.*, 1972, **94**, 3280.

[10] N. A. Hughes, R. Robson, and S. A. Saeed, *Chem. Comm.*, 1968, 1381.

[11] B. Helferich, *Adv. Carbohydrate Chem.*, 1948, **3**, 79; D. D. Reynolds and W. L. Evans, *J. Amer. Chem. Soc.*, 1938, **60**, 2559.

isopropylidene-2-thio-D-mannofuranose (XVI), prepared from the known thioglycoside (XVII) [12] by way of the ester (XVIII), was methanethiolysed, and it gave as major product the crystalline tri-*S*-methyl mono-*S*-ethyl derivative (XIX) (Scheme 6). Since it has been



SCHEME 6

established that in such a compound as the benzoate (XVI) the thio-group migrates to C-3,[3] the finding of product (VIII). The two were interconvertible by treatment with ethanethiol–trifluoroacetic acid and did not give any detectable diethyl dithioacetal, which further establishes that this acyclic compound is unfavoured relative to the pyranosides. Normally thiolysis of sugars gives the acetals in high yield,[13] and these have been shown to be favoured relative to thioglycosides and not just readily isolated products,[14] but with the 2,3-dithio-compounds this is not the case. It is not clear to us why this should be so, since mannopyranosides having an axial group at C-2 are not particularly favoured energetically, and the acyclic forms of this sugar can assume the least energetic zig-zag conformation devoid of destabilising 1,3-interactions.[15] Of related interest is the observation that benzenethiolysis of 2,3-di-*S*-ethyl-2,3-dithio-β-D-allopyranose was found to give an anomeric mixture of pyranosides rather than the diphenyl dithioacetal.

EXPERIMENTAL

N.m.r. spectra were measured on a Perkin-Elmer–Hitachi R-20 instrument (tetramethylsilane as internal reference); data are given in the Table. Mass spectra were measured at Massey University on an A.E.I. MS 902 instrument.

N.m.r. parameters (first-order, measured in deuteriochloroform at 60 MHz)

Compound	Chemical shifts (τ) 1-H	2-H	3-H	4-H	5-H	6-H	6'-H	Other protons	Coupling constants (Hz) $J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$
(VIII)	4·52 (d)	6·73 (q)	6·49 (q)	4·67 (t)	5·61 (sx) †	← *ca.* 7·2 →		5 Bz, 20 Et	1·7	4·0	9·3	9·3	6·0	6·0
(XX)	5·08 (s)	6·66 (s)	6·73 (d)	4·73 (t)	6·32 (o)	← *ca.* 7·2 →		5 Bz, 20 Et	<0·5	<0·5	9·7	9·7	5·0	6·0
(XIX)	4·63 (d)	6·77 (q)	6·54 (q)	4·63 (t)	5·67 (sx) †	← *ca.* 7·2 →		5 Bz, 5 Et, 9 Me, (τ 7·70, 7·77, 7·88)	1·5	4·0	9·5	9·5	6·0	6·0
(XII)	5·36 (s)	← 8·0—8·36 →		← 6·24—6·53 →		← 8·75 (d) →		3 OMe (τ 6·67), H-6'', OH					5·5	
(XII) [6a]	5·38 (s)	← 8·0—8·35 →		← 6·27—6·58 →		← 8·62 (d) →		3 OMe (τ 6·65), H-6'', OH					6·0	
(XIII)	5·25	← 7·66—8·18 →		5·08	5·95	← 8·76 (d) →		3 OMe (τ 6·60), H-6'', 4 Aryl				9	6	
(XIII) [6a]	5·29	← 7·80—8·20 →		5·06	5·95	← 8·77 (d) →		3 OMe (τ 6·60), H-6'', 4 Aryl				9	6	
(XVIII)	4·76 (d)	6·63 (q)	4·16 (q)	← 5·6—6·1 →				5 Bz, 10 Et, 6 Me	8	5·5	2·5			
(XVI)	4·46 (d)	6·52 (m)	4·06 (m)	← 5·4—6·1 →				5 Bz, 5 Et, 6 Me		5				
(XVII) [13]	4·89 (d)	6·74 (q)							8	4·5				
(XVII)	4·96 (d)	6·77 (q)							8	4				

† Sextet

the ethylthio-group at C-6 in the final product (XIX) confirms the final migration from C-3 to C-6. The position of the ethylthio-group in compound (XIX) was established by mass spectrometry. The molecular ion (*m/e* 418) lost benzoic acid and, almost concurrently, $C_3H_7S^{\bullet}$, (which could be either $CH_2{\cdot}SEt^{\bullet}$ or $SCH_3^{\bullet} + C_2H_4$), to give an ion *m/e* 221·0120 (calc. for $C_8H_{13}OS_3$: 221·0128). The fact that the former radical was indeed involved (and therefore that the $CH_2{\cdot}SEt$ group was present) was shown by the finding that the tetraethyl analogue (VIII) (*m/e* 460), which does not contain a methylthio-group, suffered analogous almost concurrent loss of benzoic acid and $C_3H_7S^{\bullet}$ to give an ion *m/e* 263·0603 (calc. for $C_{11}H_{19}OS_3$: 263·0597).

A second, minor product was obtained crystalline from the original ethanethiolysis of 3-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (VII) and was shown by analysis, n.m.r. spectroscopy, and mass spectrometry to be the β-anomer (XX) of the main

All reactions were followed by t.l.c. methods and preparative t.l.c. was carried out on 1 m plates with silica gel as adsorbent.

Ethyl 4-O-*Benzoyl*-2,3,6-*tri*-S-*ethyl*-1,2,3,6-*tetrathio*-α-D-*mannopyranoside* (VIII).—(a) *From* 3-O-*benzoyl*-1,2:5,6-*di*-O-*isopropylidene*-α-D-*glucofuranose* (VII). The isopropylidene benzoate (5·65 g) [16] was dissolved in chloroform–ethanethiol (35 ml; 3 : 4) and trifluoroacetic acid (15 ml) was added with shaking during 5 min. T.l.c. showed that many compounds were formed, but indicated that after 3 days at room temperature one dominant product was present. The solution was then poured into aqueous sodium hydrogen carbonate and the products were extracted with chloroform. Drying of the extract and removal of the solvent gave a syrup which was separated on a column of silica gel. The chromatographically homogeneous *tetrathio-derivative* (2·83 g, 40%) had $[\alpha]_D$ +30° (*c* 1·3 in $CHCl_3$) (Found: C, 55·0; H, 7·2; S, 26·8. $C_{21}H_{32}O_3S_4$ requires C, 54·8; H, 7·0; S, 27·8%).

(b) *From* 1,4-*di*-O-*benzoyl*-2,3-*di*-S-*ethyl*-6-O-*triphenylmethyl*-2,3-*dithio*-D-*allopyranose*. The trityl ether (0·15 g)

[12] J. Defaye, T. Nakamura, D. Horton, and K. D. Philips, *Carbohydrate Res.*, 1971, **16**, 133.
[13] D. Horton and D. H. Hutson, *Adv. Carbohydrate Chem.*, 1963, **18**, 123.
[14] R. J. Ferrier, L. R. Hatton, and W. G. Overend, *Carbohydrate Res.*, 1968, **6**, 87.
[15] P. L. Durette and D. Horton, *Adv. Carbohydrate Chem. and Biochem.*, 1971, **26**, 49.
[16] E. Fischer and H. Noth, *Ber.*, 1918, **51**, 321.

(see later) was dissolved in chloroform–ethanethiol–trifluoroacetic acid (1·5 ml; 1 : 1 : 1), and after 3 days at room temperature the products were isolated as before, the main component of the mixture being purified by preparative t.l.c. The syrupy product (0·035 g, 38%) had $[\alpha]_D$ +27° (*c* 0·35 in $CHCl_3$) and gave an n.m.r. spectrum identical with that of the sample prepared by route (a).

Ethyl 4-O-*Benzoyl*-2,3,6-*tri*-S-*ethyl*-1,2,3,6-*tetrathio*-β-D-*mannopyranoside* (XX).—The material eluted after the main product from the column used in method (a) above was subjected to preparative t.l.c. and a component having mobility slightly less than that of the α-pyranoside was isolated (0·18 g, 2·5%). Recrystallised from methanol it had m.p. 92·5—93·5°, $[\alpha]_D$ −11° (*c* 1 in $CHCl_3$) (Found: C, 54·8; H, 6·8; S, 27·8%).

Interconversion of the Anomeric Thiomannopyranosides.—The syrupy and the crystalline thioglycosides (0·01 g) were separately dissolved in chloroform–ethanethiol–trifluoroacetic acid (0·3 ml; 1 : 1 : 1), and after 0·5 h t.l.c. showed that partial interconversion had occurred, the same equilibrated mixture (which contained mainly the α-anomer) being obtained from each isomer. No other product was detected after this reaction time, but after several days several products (indicative of degradation) were observed.

Ethyl 2,3,6-*Tri*-S-*ethyl*-1,2,3,6-*tetrathio*-α-D-*mannopyranoside* (IX).—The α-benzoate (VIII) (2·83 g) was debenzoylated under standard conditions (sodium methoxide in methanol) and the product was purified on a column of silica gel to give the syrupy tetrathioglycoside (1·16 g, 53%), $[\alpha]_D$ +79° (*c* 0·9 in $CHCl_3$).

Methyl 2,3,6-*Tri*-S-*ethyl*-2,3,6-*trithio*-α-D-*mannopyranoside* (X).—The tetrathioglycoside (0·61 g) was heated under reflux in methanol (5 ml) containing 3% hydrogen chloride for 6 h, after which the acid was neutralised with sodium hydrogen carbonate. The solvent was then removed and the syrupy residue was partitioned between chloroform and water. The organic phase was dried and taken to dryness to leave the methyl glycoside (0·39 g, 70%), which after purification on a column of silica gel had $[\alpha]_D$ +24° (*c* 1 in $CHCl_3$). Treatment of this product (0·16 g) with 3,5-dinitrobenzoyl chloride (1·1 mol. equiv.) in pyridine (3 ml) for 0·5 h at room temperature gave the crystalline *dinitrobenzoyl ester* (XI). Recrystallisation from ethanol gave material (0·18 g, 69%), $[\alpha]_D$ +13° (*c* 1·2 in $CHCl_3$) (Found: C, 46·0; H, 5·3; N, 5·7; S, 18·8. $C_{20}H_{28}N_2O_8S_3$ requires C, 46·2; H, 5·4; N, 5·4; S, 18·5%).

Methyl 2,3,6-*Trideoxy*-α-D-erythro-*hexopyranoside* (XII).—The trithioglycoside (X) (0·51 g) was dissolved in ethanol (20 ml) and was added to a slurry of active Raney nickel (13 g) in ethanol (10 ml). The mixture was then heated under reflux for 1 h; the catalyst was removed by filtration through asbestos, and the solvent by distillation to leave the syrupy trideoxyglycoside (0·20 g 88%), $[\alpha]_D$ +130° (*c* 1·9 in H_2O) {lit.,[6a] $[\alpha]_D$ +142° (*c* 1·2 in H_2O)}. The n.m.r. spectrum of the trideoxyglycoside was consistent with that already described [6] (see Table). 3,5-Dinitrobenzoylation gave the known ester (78%), m.p. 96—97°, mixed m.p. 97—98°, $[\alpha]_D$ +128° (*c* 0·7 in $CHCl_3$) {lit.,[6] m.p. 100—101°, $[\alpha]_D$ +134° (*c* 0·4 in $CHCl_3$)}. The n.m.r. spectrum was in agreement with the published data for the compound (see Table),[6a] and the *X*-ray diffraction pattern and i.r. spectrum were identical with those of an authentic sample. We thank Professor D. Horton for making the comparisons between the samples.

1,4-*Di*-O-*benzoyl*-2,3-*di*-S-*ethyl*-6-O-*triphenylmethyl*-2,3-*dithio*-D-*allopyranose*.—2,3-Di-*S*-ethyl-2,3-dithio-D-allose (0·1 g) [2] was dissolved in dry pyridine (1 ml) and a solution of triphenylmethyl chloride (0·11 g, 1·1 mol. equiv.) in pyridine (1 ml) was added. After 1 h at room temperature benzoyl chloride (0·1 ml, 2·1 mol. equiv.) was added and the mixture was kept for a further 0·5 h at room temperature before the addition of ice–water (10 ml). The product did not crystallise and was purified by preparative t.l.c. to give a syrup (0·15 g, 55%), which was shown by n.m.r. spectroscopy to contain one triphenylmethyl group, two benzoyl groups, and two ethylthio-groups. Two anomeric resonances integrating for one proton were observed, which indicates that the product was a mixture of anomers.

Ethyl 3-O-*Benzoyl*-2-S-*ethyl*-5,6-O-*isopropylidene*-1,2-*dithio*-α-D-*mannofuranoside* (XVIII).—Ethyl 2-*S*-ethyl-5,6-*O*-isopropylidene-1,2-dithio-α-D-mannofuranoside (XVII) (1·6 g) [12] was dissolved in pyridine (10 ml) and benzoyl chloride (0·64 ml, 1·1 mol. equiv.) was added at 0°. After 0·5 h at room temperature ice–water (40 ml) was added and the mixture was extracted with chloroform. The product was isolated from the organic phase and purified on a column of silica gel to give a syrup (1·92, 90%), $[\alpha]_D$ +54° (*c* 1·0 in $CHCl_3$). The n.m.r. spectrum was consistent with the assigned structure.

3-O-*Benzoyl*-2-S-*ethyl*-5,6-O-*isopropylidene*-2-*thio*-D-*mannose* (XVI).—The benzoylated thiofuranoside (XVIII) (1·7 g) was dissolved in acetone (15 ml) and was slowly added to a stirred suspension of mercury(II) chloride (5·5 g) and cadmium carbonate (1·88 g) in acetone (15 ml) containing water (1 ml). After being stirred at room temperature for 18 h the mixture was filtered; the filtrate was taken to dryness and the residue dissolved in chloroform. After being washed successively with aqueous potassium iodide and water the solution was dried and evaporated to leave the chromatographically homogeneous free sugar (1·43 g, 94%), $[\alpha]_D$ +18° (*c* 1·9 in $CHCl_3$). The n.m.r. spectrum indicated the presence of one ethylthio-group per molecule, and the complex nature of the signal for H-2 revealed that the compound was a mixture of anomers.

Methyl 4-O-*Benzoyl*-6-S-*ethyl*-2,3-*di*-S-*methyl*-1,2,3,6-*tetrathio*-α-D-*mannopyranoside* (XIX).—The 2-thiomannofuranose derivative (XVI) (1·0 g) was dissolved in chloroform–trifluoroacetic acid (7 ml; 4 : 3) and cooled in liquid air in an ampoule. Methanethiol (4 ml) was added and the ampoule was sealed and allowed to attain room temperature. After 3 days the product was isolated as usual and purified on a column of silica gel to give the *methyl thiopyranoside* (0·26 g, 23%), which crystallised on trituration with methanol. Recrystallised twice from methanol it had m.p. 94—95°, $[\alpha]_D$ +32° (*c* 1·4 in $CHCl_3$) (Found: C, 51·6; H, 6·2; S, 30·4. $C_{18}H_{26}O_3S_4$ requires C, 51·7; H, 6·2; S, 30·6%). The n.m.r. spectrum (see Table) and the mass spectrum (see Discussion) were consistent with the assigned structure.

Benzenethiolysis of 2,3-*Di*-S-*ethyl*-2,3-*dithio*-β-D-*allopyranose*.—The free sugar (0 5 g) [2] was dissolved in benzenethiol–concentrated hydrochloric acid (2 ml; 1 : 1) at 0°, and after 1 h the acid was neutralised and the crude products were isolated in the usual fashion. Two major components were revealed by t.l.c. and these were resolved on preparative plates to give two chromatographically homogeneous syrups. Each of these was shown by n.m.r. to contain phenyl and ethyl groups in the ratio 1 : 2 and

therefore to be glycosidic in nature rather than an acyclic dithioacetal. The most deshielded proton in each spectrum resonated at τ 4·62 and 5·21 (J 4·5 and 10·5 Hz, respectively), consistent with their assignment to the anomeric protons of the α- and β-pyranosides, respectively.

We thank Professors J. F. Duncan and W. G. Overend for their assistance. One of us (G. S. B.) acknowledges with thanks the award of an S.R.C. studentship in England and its continuance in New Zealand, and also of grants from the British Council and Victoria University of Wellington. We are indebted to Professor D. Horton for assistance in the comparison of amicetose derivatives, and to Professor R. Hodges for measuring the mass spectra and for comment on them.

[2/2804 *Received*, 13*th December*, 1972]