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A METAL-ASSISTED SYNTHESIS OF GLYCOFURANOSYLAMINE DERIVATIVES*

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ABSTRACT

The known benzothiazoline formed by condensation between D-glucose and *o*-aminobenzenethiol gives the chelate bis[*o*-(D-glucofuranosylamino)benzenethiol]-mercury(II) (**3**, R = H) on treatment with mercury(II) acetate in methanol. The tetra-*O*-acetyl derivative (**3**, R = Ac) of the chelate is readily obtained, and on demercuration with hydrogen sulphide it gives the disulphide (**5**) or the corresponding thiol (**12**) according to whether or not oxidising conditions are used. From the thiol **12**, the tetra-*O*-acetyl-*S*-acetyl derivative (**13**, R = H) and the fully acetylated compound (**13**, R = Ac) are readily obtainable. These model experiments indicate a possible route to *N*-D-glucosylcysteine and also provide compounds with structural resemblances to nucleosides. Anomeric configurations could be assigned only tentatively.

INTRODUCTION

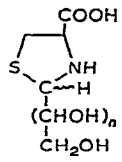
Although glycosylamines are a well-known class of compound[1] and various glycosylated amino acids have received considerable attention, mainly because of their significance as joining points in glycoproteins and related substances[2], little is apparently known about α-*N*-glycosylated amino acids. This can be attributed, in part, to the well-known Amadori rearrangement[3], which occurs when free sugars are caused to react with amino acids, and also to the fact that such compounds do not appear to play a well-established role in biochemical processes.

It was the particular objective of this work to investigate *N*-glycosylated derivatives of L-cysteine in connection with planned studies on specifically substituted peptide hormones. Although *S*-glycosylcysteines have been identified in peptides from natural sources[4], little seems to be known about other sugar–cysteine derivatives, save the general nature of the compounds (**1**) obtainable directly on condensation of

*Dedicated to Dr. Horace S. Isbell, in honour of his 75th birthday.

aldoses with the amino acid[5]. Our initial investigations of the reactions undergone between various sugar derivatives and cysteine and some of its derivatives indicated that they were somewhat complex, and so our attention was turned to D-glucose derivatives of the model compound *o*-aminobenzenethiol.

Several investigations have been made of the crystalline products obtainable by condensation between this and closely related bases and free sugars[6–8]; most notably, Bognár and co-workers[7] established that, in common with other aldehydic compounds, aldoses give benzothiazolines, *e.g.*, compound **2** (R = H), and they have utilised spectroscopic and circular dichroism[8] methods to assign configurations at the new chiral centres at C-2 of the heterocyclic ring in the *N*-methyl derivatives, *e.g.*, **2** (R = Me).



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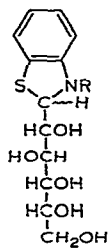

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We now report on the utilisation of compound **2** (R = H) in the preparation of glycosylamine derivatives.

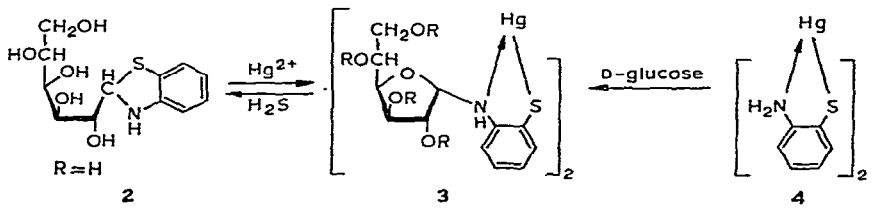
DISCUSSION

Since mercury(II) salts can be used to effect $O \rightarrow N$ and $S \rightarrow N$ glycosyl rearrangements in related systems[9], it was initially proposed that the required glycosylamines be prepared from *o*-aminophenyl 1-thio-β-D-glucopyranoside, but attempted rearrangement using mercury(II) chloride in refluxing acetonitrile gave a product which did not contain an aromatic ring.

Attention was then turned to the benzothiazoline **2** (R = H). The compound was obtained in high yield as an ethanolate with physical constants appreciably different from those of the product isolated by Bognár and co-workers[7], but similar to those of the 2-propanolate described by Sattler *et al.*[6]. Since Bognár's sample and that reported here both have the structure **2** (R = H), it is presumed that they differ with regard to stereochemistry at the new asymmetric centre. Whereas the former compound was structurally characterised by acetylation and comparison with the thiazoline formed from penta-*O*-acetyl-*aldehydo*-D-glucose, our compound was characterised by acetylation and hydrolysis in the presence of a mercury(II) salt to give the *aldehydo*-sugar derivative in good yield. In view of the almost quantitative yield of the thiazoline obtained in the present work, and of our inability to detect circular dichroism down to 280 nm, we suspect that our sample is a mixture of the

two possible diastereoisomers. Previous work[8b] has indicated that a pure diastereoisomer would give a c.d. maximum near 290 nm.

Treatment of the benzothiazoline **2** (R = H) with mercury(II) acetate (0.5 mol. equiv.) in methanol gave, in excellent yield, a compound to which structure **3** (R = H) is assigned (Scheme 1). It is assumed that the soft-acid affinity which mercury has for the soft base sulphur[10] initiates the reaction and renders position 1 of the carbohydrate susceptible to the intramolecular nucleophile O-4. The furanoid nature of the product was established by mass spectrometry (see below), and was expected since it is well established that five-membered rings are preferentially formed when oxygen is involved as the nucleophile in such ring-closure processes[11,12]. Since the main, kinetically controlled products also have[12] the *cis*-relationship between groups at C-1 and C-2, compound **3** (R = H) is assigned the α-D-configuration. The only direct evidence for the α-D-configuration of **3** is the high, positive specific rotation (+164°) and the positive c.d. maximum centred at 327 nm. Although a pyranosylamine would be expected to be the thermodynamically most-stable product of this reaction, it is not inconsistent to find a furanosylamine as main product since it crystallised at room temperature from the reaction medium and was thus unable to isomerise. Furthermore, it is not inconsistent to ascribe to it a specific anomeric configuration, since diastereoisomeric benzothiazolines (**2**, R = H) could give one product by way of a C-1 carbonium ion. Compound **3**, (R = H) was also obtained on treatment of bis(*o*-aminobenzenethiol)mercury(II) (**4**) with D-glucose in ethanolic solution in the presence of small amounts of acetic acid (Scheme 1), and so an effort to obtain the more

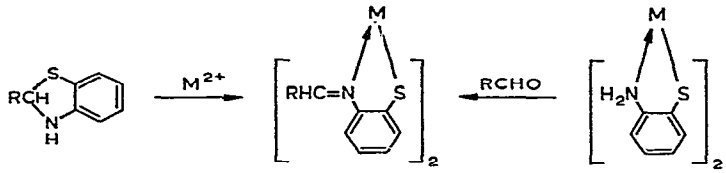


2 3 4

Scheme 1

usual pyranosylamine was unsuccessful. However, the product again crystallised from the reaction solution and isolation of a kinetic product is therefore not unexpected. These results are consistent with those obtained for related, non-carbohydrate, aldehyde benzothiazolines, which are converted into chelated Schiff-base derivatives by treatment with metal(II) salts and, as in the present work, the same products are obtainable by condensation of the appropriate *o*-aminobenzenethiol chelates with aldehydes (Scheme 2)[13].

Attempts to *O*-methylate and *O*-benzylate the chelate **3** (R = H) did not yield simple products, but the tetra-*O*-acetyl derivative (**3**, R = Ac) was obtained in excellent yield by use of acetic anhydride in pyridine; *N*-acetylation was not expected to occur under these conditions[1a]. Again, the α-D configuration is tentatively assigned on the basis of a strongly positive, specific rotation and a positive c.d. maximum near



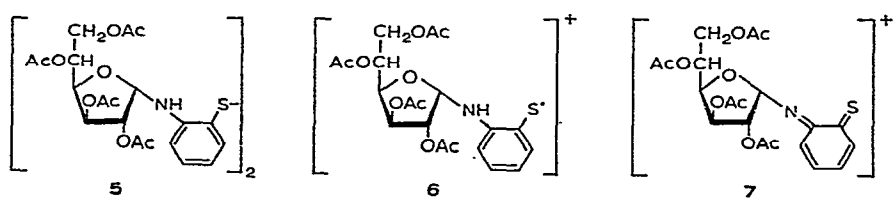
Scheme 2

330 nm. The anomeric configuration could not be determined by n.m.r. methods since the resonance of the anomeric proton was superimposed on those of H-2 and H-3.

Demercuration of the tetra-acetate **3** (R = Ac) with hydrogen sulphide, followed by air oxidation, gave the disulphide **5** in almost quantitative yield. Again the n.m.r. data did not assist with the assignment of the anomeric configuration, but the similarities between the spectra of compounds **3** (R = Ac) and **5** indicated close structural similarity. The only significant difference was in the position of resonance of the amino proton, which was τ 7.1 for the disulphide **5** and 4.3 for the ester **3** (R = Ac). This is consistent with expectations based on increasing acidity following co-ordination, and with the chemical shifts of the amine protons of bis(*o*-aminophenyl)disulphide (τ 5.0) and compound **4** (τ 4.2).

A molecular ion was not observed in the mass spectrum of the disulphide **5**, but an ion with *m/e* 876 $(M—32)^+$ was observed and was formed by loss of a sulphur atom—a fragmentation which is characteristic of aromatic disulphides[14]. Cleavage of the disulphide bond also occurred to give an ion *m/e* 454 (**6**) which by loss of hydrogen can give the *o*-quinonoid species **7**, and this is observed to fragment by loss of the C-5,C-6 unit to give the ion **8** (*m/e* 308), thus indicating the furanosyl nature of the compound[15]. Ions with *m/e* 248 (**9**), 206 (**10**), and 145 $[CH_2(OAc)–CHOAc]^+$ were also observed in confirmation of this feature. No ions indicative of C-5–C-6 bond rupture of a pyranosyl structure were observed.

When demercuration of the chelate **3** (R = Ac) was repeated in the absence of air, a product, readily distinguishable from the disulphide **5**, was obtained. By



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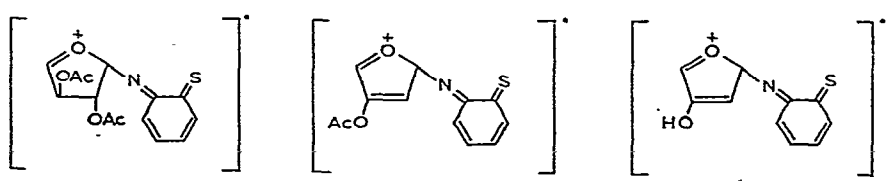
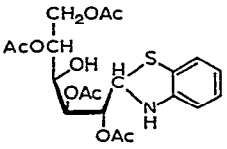


8 9 10

analogy with the demercuration of the original chelate **3** (R = H), which gave back the benzothiazoline **2** (R = H), it was anticipated that the product would have been the corresponding tetra-*O*-acetyl compound (**11**) having an acyclic carbohydrate moiety with HO-4 unsubstituted. However, no O-H stretching absorption was observed in the infrared spectrum, and the alternative glycosylamine structure (**12**) is assigned, despite



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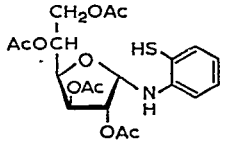

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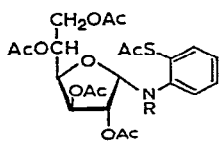
the fact that the thiol group was also undetected by infrared spectroscopy. However, the S-H stretching absorption is often of weak intensity[16] and, furthermore, the n.m.r. spectrum of the compound was closely similar to that of the disulphide **5**. The mass spectra of compounds **12** and **5** differed only in details which are explicable in terms of the former having one hydrogen atom added to the monomeric component of the disulphide.

The apparent difference in the reaction of the chelate **3** (R = H) and its acetate **3** (R = Ac) on treatment with hydrogen sulphide is attributed to the conditions used. Whereas the former demercuration was carried out in pyridine in which the products could equilibrate (as evidenced by the mutarotation of the pure product), the latter reaction was accomplished in chloroform and the product was isolated before isomerisation occurred. Deacetylation of the thiol **12** gave the starting benzothiazoline **2** (R = H), so presumably the direct product also isomerised in the methanol used. Chemical evidence was furthermore consistent with the assigned structure **12**. Air oxidation of **12** gave the disulphide **5**; in contrast, the benzothiazoline **2** (R = H) was recovered unchanged after similar treatment. With acetic anhydride in pyridine [the reagents used to *O*-acetylate compound **2** (R = H)], **12** afforded a penta-acetate which showed a 3-proton resonance at τ 7.6, indicative of an *S*-acetyl group, and a twelve-proton resonance near τ 7.9 (*O*-acetyl)[17]. The presence of the thioester group was further indicated by an i.r. carbonyl-stretching frequency near 1720 cm^{-1}, beside the ester-carbonyl absorption at 1750 cm^{-1}, and the compound is thus assigned structure **13** (R = H). Mercuration of the thiol **12** regenerated the chelate **3** (R = Ac), and similar treatment of the penta-acetate **13**, (R = H) with mercury(II) chloride in the presence of water gave the same product.



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Further acetylation of compound **13** (R = H) with hot acetic anhydride–sodium acetate gave the amide **13** (R = Ac) in excellent yield. Infrared spectroscopy indicated conversion of the NH group into an amido function (C=O, ν_{max} 1685 cm^{-1}). An *N*-acetyl group was also detected by n.m.r. spectroscopy (τ 8.35)[18], and the H-1 resonance was visible as a broadened doublet ($J_{1,2}$ ~8 Hz). Unfortunately, the anomeric configuration cannot be assigned on this evidence[19].

EXPERIMENTAL

2-(D-gluco-*1,2,3,4,5-Pentahydroxypentyl)benzothiazoline* (**2**, R = H). — (*a*) *By condensation of* D-*glucose with* o-*aminobenzenethiol.* To a suspension of D-glucose (10 g) in ethanol (100 ml), *o*-aminobenzenethiol (19 ml) was added, and the mixture was heated under reflux for 2 h, by which time dissolution had occurred. On cooling, the product crystallised, and recrystallisation from ethanol (×5) gave the benzothiazoline monoethanolate (16 g, 86%), m.p. 108–110°, $[\alpha]_D$ −20° (constant; *c* 1, water), $[\alpha]_D$ −74 → −54° (25 min, constant; *c* 1, pyridine). Lit. m.p. 118–119°, (mono-2-propanolate from 2-propanol), $[\alpha]_D$ −15.6° (water)[6]; m.p. 166–167° (unsolvated from 2-propanol), $[\alpha]_D$ −66.3° (constant, pyridine)[7].

Anal. Calc. for $C_{12}H_{17}NO_5S \cdot C_2H_5OH$: C, 50.4; H, 6.9; N, 4.2; S, 9.6. Found: C, 50.4; H, 7.0; N, 4.2; S, 9.4.

(*b*) *By demercuration of the chelate* **3** (R = H). The glycosylated mercury chelate (0.5 g) was dissolved in pyridine (20 ml), and hydrogen sulphide was bubbled through the solution. Excess of hydrogen sulphide was removed with nitrogen, and mercury(II) sulphide by filtration, and evaporation of the solvent gave a syrup which, on crystallisation and recrystallisation from ethanol, gave the benzothiazoline **2** (R = H). The product was identical (m.p., $[\alpha]_D$, t.l.c., and i.r. spectrum) with the sample prepared in (*a*).

(*c*) *By deacetylation of the acetylated furanosylamine* **12**. The thiol was deacetylated under standard conditions using sodium methoxide in methanol. Sodium ions were removed by use of cation-exchange resin and the solvent by evaporation to leave a red-brown syrup which afforded the benzothiazoline **2** (R = H) on trituration with ethanol. Again, the product was identical with the sample prepared in (*a*).

*Penta-*O*-acetyl-*aldehydo-D-*glucose.* — Acetic anhydride (6 ml) was added to a chilled solution of the benzothiazoline **2** (R = H) (1 g) in pyridine (10 ml). The solution was shaken at 0° for 1 h, left at room temperature for 16 h, and then poured on to ice to give a solid (1.5 g) which could not be recrystallised. A portion (1 g) in methanol–chloroform (10 ml, 9:1) was added to a solution of mercury(II) chloride (0.8 g) in aqueous methanol (20 ml, 1:1) and gave a yellow-green precipitate. The suspension was stirred for 2 h, the solids (1.3 g) were removed, and the filtrate was shaken with water–chloroform (1:1). From the dried, organic phase, the *aldehydo*-penta-acetate (0.56 g, 66%) was obtained. Recrystallised from acetone–ether–light petroleum (b.p. 60–80°) (2:3:4), it had m.p. 115–118°; lit.,[20] m.p. 119–120°. Appropriate resonances were observable in the n.m.r. spectrum, including a formyl

proton resonance at τ 0.50. The infrared spectrum of the yellow-green precipitate showed it to be bis(*o*-aminobenzenethiol)mercury(II).

Bis[o-(D-*glucofuranosylamino)benzenethiol*]*mercury(II)* (3, R = H). — (*a*) *From the benzothiazoline* **2**, (R = H). A methanolic solution (50 ml) of mercury(II) acetate (3.8 g) was added to a similar solution (100 ml) of the benzothiazoline ethanolate (8 g, 2.0 mol. equiv.), and the resulting yellow solution was allowed to stand for 2 h, by which time a pale yellow-green solid had formed. Removal of the solid and two recrystallisations from *N*,*N*-dimethylformamide–chloroform gave the glycosylated mercury chelate **3** (R = H) (9.0 g, 95%), m.p. 186–188° (dec.), $[\alpha]_D$ +164° (*c* 1, pyridine).

Anal. Calc. for $C_{24}H_{32}HgN_2O_{10}S_2$: C, 37.3; H, 4.1; Hg, 26.0; N, 3.7. Found: C, 36.7; H, 4.1; Hg, 26.3; N, 3.7.

The same compound was obtained by mixing the reactants in *N*,*N*-dimethylformamide, allowing the solution to stand for 1 h, and then precipitating with chloroform. After recrystallisation from these solvents, the product was obtained in 85% yield.

(*b*) *By reaction between* D-*glucose and bis*(o-*aminobenzenethiol*)*mercury(II)*. A suspension of bis(*o*-aminobenzenethiol)mercury(II) (1 g) and D-glucose (0.8 g, 2.0 mol. equiv.) in ethanol containing acetic acid (0.1 ml) was heated under reflux for 3 h. Dissolution initially occurred, and then a pale yellow-green product crystallised. After cooling, the product was removed, washed with ethanol, and recrytallised from *N*,*N*-dimethylformamide–chloroform to give the glycosylated mercury chelate **3** (R = H) (0.96 g, 56%), m.p. and mixture m.p. 186–188°, $[\alpha]_D$ +161° (*c* 1, pyridine). The infrared spectrum and paper-chromatographic mobility of the samples prepared by methods (*a*) and (*b*) were identical.

Bis[o-(*2,3,5,6-tetra*-O-*acetyl*-D-*glucofuranosylamino)benzenethiol*]*mercury(II)* (3, R = Ac). — (*a*) *By acetylation of the tetraol* **3** (R = H). The glycosylated mercury chelate (2.0 g) was acetylated with acetic anhydride (30 ml) and pyridine (40 ml) at room temperature for 16 h. On pouring the mixture on to ice–water, a yellow, crystalline solid was produced, which was washed with water and recrystallised from aqueous acetone to give the title tetra-acetate (2.6 g, 91%), m.p. 143–145°, $[\alpha]_D$ +240° (*c* 1, chloroform).

Anal. Calc. for $C_{40}H_{48}HgN_2O_{18}S_2$: C, 43.3; H, 4.3; N, 2.3; S, 5.8; mol. wt., 1108. Found: C, 43.2; H, 4.4; N, 2.3; S, 5.7; mol. wt. (Rast), 1020.

(*b*) *By mercuration of the acetylated furanosylamine* **12**. The thiol **12** (0.5 g) was dissolved in chloroform (4 ml), and a solution of mercury(II) chloride (0.4 g) in methanol–water (9:1, 10 ml) was added. After 1 h at room temperature, when t.l.c. showed that the starting material had been converted completely into a less-mobile product, the components were partitioned between chloroform and water, the chloroform solution was dried, and the solvent was removed to leave a solid (0.32 g, 53%). Recrystallisation from aqueous acetone gave the acetylated mercury chelate **3** (R = Ac), m.p. 140–143°, mixture m.p. 139–145°, $[\alpha]_D$ +249° (*c* 1, chloroform).

(*c*) *By dethioacylation–mercuration of the thioester* **13** (R = H). To a solution of the thioester (0.5 g) in wet acetone (10 ml), mercury(II) chloride (1 g) in wet acetone

(10 ml) was added. A yellow precipitate was formed after stirring for 0.5 h, and after 2 h it was removed and recrystallised from ethanol to give the chelate **3** (R = Ac), m.p. 145–146°, $[\alpha]_D$ +233° (*c* 1, chloroform). It had the same infrared spectrum and t.l.c. mobility as the samples prepared in (*a*) and (*b*).

Bis[o-(*2,3,5,6-tetra*-O-*acetyl*-D-*glucofuranosylamino*)*phenyl*] *disulphide* (**5**). — (*a*) *By removal of mercury from the chelate* **3** (R = Ac). The acetylated chelate (1 g) was dissolved in chloroform (10 ml), and hydrogen sulphide was passed through the solution for 15 min. Air was then blown through the solution for 25 min, mercury(II) sulphide was removed, the filtrate was dried, and the solvent was evaporated to give a syrup which crystallised on trituration with ethanol; yield, 0.8 g (98%). Three recrystallisations from ethanol gave the pale-yellow disulphide, m.p. 160–162°; $[\alpha]_D$ +600° (*c* 1, chloroform), +515° (*c* 1, pyridine).

Anal. Calc. for $C_{40}H_{48}N_2O_{18}S_2$: C, 52.8; H, 5.3; N, 3.1; S, 7.0. Found: C. 52.8; H, 5.5; N, 3.0; S, 6.8.

(*b*) *By oxidation of the thiol* **12**. Air was passed through a solution of the thiol in chloroform for 0.5 h. After drying, the solvent was removed to leave a syrup from which the disulphide was obtained by crystallisation from ethanol. It had m.p. 157–159°, $[\alpha]_D$ +598° (*c* 1, chloroform), and the infrared spectrum was identical to that of the sample prepared by method (*a*).

o-(*2,3,5,6-Tetra*-O-*acetyl*-D-*glucofuranosylamino*)*benzenethiol* (**12**). — The acetylated glycosyl mercury chelate **3** (R = Ac) (1.5 g) was dissolved in chloroform (20 ml), and hydrogen sulphide was passed through the solution for 15 min. Removal of the mercury(II) sulphide and solvent gave a syrup which solidified to give the thiol (1.16 g, 95%) on trituration with ethanol. Two recrystallisations from ethanol gave the colourless thiol **12**, m.p. 120–122°, $[\alpha]_D$ −62° (*c* 1, chloroform).

Anal. Calc. for $C_{20}H_{25}NO_9S$: C, 52.8; H, 5.5; N, 3.1; S, 7.0. Found: C, 52.5; H, 5.5; N, 3.1; S, 7.1.

S-*Acetyl*-o-(*2,3,5,6-tetra*-O-*acetyl*-D-*glucofuranosylamino*)*benzenethiol* (**13**, R = H). — The acetylated glucosylamine **12** (0.70 g) was treated with acetic anhydride (2 ml) and pyridine (5 ml) at room temperature for 16 h, and the mixture was then poured or to ice. After the ice had melted, the organic components were extracted into chloroform, and the extract was dried and concentrated to a syrup which, on trituration with ethanol, gave a white solid. Recrystallisation from ethanol gave the title thioacetate (0.53 g, 69%), m.p. 122–124°, $[\alpha]_D$ +104° (*c* 1, chloroform).

Anal. Calc. for $C_{22}H_{27}NO_{10}S$: C, 53.1; H, 5.4; N, 2.8; S, 6.5. Found: C, 53.1; H, 5.6; N, 2.8; S, 6.7.

Di-N,S-*acetyl*-o-(*2,3,5,6-tetra*-O-*acetyl*-D-*glucofuranosylamino*)*benzenethiol* (**13**, R = Ac). — The thioacetate **13** (R = H) (0.50 g) was heated with sodium acetate (0.2 g) in acetic anhydride (3 ml) under reflux for 1 h. The mixture was poured on to ice and, after melting of the ice, the organic components were extracted into chloroform. The extract was washed, dried, and concentrated to a syrup which, on trituration with ethanol, gave a white, crystalline solid. Recrystallisation from ethanol gave **13** (R = Ac) (0.50 g, 92%), m.p. 134–136°, $[\alpha]_D$ +3.5° (*c* 1, chloroform).

Anal. Calc. for $C_{24}H_{29}NO_{11}S$: C, 53.4; H, 5.4; N, 2.6; S, 5.9. Found: C, 53.6; H, 5.5; N, 2.4; S, 5.9.

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REFERENCES

1 (*a*) G. P. Ellis and J. Honeyman, *Advan. Carbohyd. Chem.*, 10 (1955) 95; (*b*) H. Paulsen and H. Pflughaupt, in W. Pigman and D. Horton (Eds.), *The Carbohydrates*, Vol. 1B, Academic Press, New York, 1974.
2 P. W. Kent, *Essays Biochem.*, 3 (1967) 105.
3 J. E. Hodge, *Advan. Carbohyd. Chem.*, 10 (1955) 169.
4 C. J. Lote and J. B. Weiss, *Biochem. J.*, 123 (1971) 25p; J. B. Weiss, C. J. Lote, and H. Bobinski, *Nature, New Biol.*, 234 (1971) 25.
5 G. Agren, *Enzymologia*, 9 (1939) 321; M. P. Schubert, *J. Biol. Chem.*, 130 (1939) 601; Y. Hosaka, *Jap. Pat.*, 68, 23, 457 [*Chem. Abstr.*, 70 (1969) 115562 x]; R. Bognár, L. Szilágyi, and Z. Györgydeak, *Ann.*, 738 (1970) 68.
6 L. Sattler, F. W. Zerban, G. L. Clark, and C.-C. Chu, *J. Amer. Chem. Soc.*, 73 (1951) 5908.
7 R. Bognár, Z. Kolodynska, L. Somogyi, Z. Györgydeak, L. Szilágyi, and E. Nemes-Nanasi, *Acta Chim. (Budapest)*, 62 (1969) 65.
8 (*a*) L. Szilágyi and R. Bognár, *Carbohyd. Res.*, 15 (1971) 371; (*b*) G. Snatzke, F. Werner-Zamojska, L. Szilágyi, R. Bognár, and I. Farkas, *Tetrahedron*, 28 (1972) 4197.
9 G. T. Rogers and T. L. V. Ulbricht, *J. Chem. Soc.*, (1965) 6130; *J. Chem. Soc., C*, (1971) 2995.
10 R. G. Pearson, *J. Chem. Educ.*, 45 (1968) 581.
11 B. Capon, *Quart. Rev. Chem. Soc.*, 18 (1964) 45.
12 J. W. Green, *Advan. Carbohyd. Chem.*, 21 (1966) 95.
13 H. Jadamus, Q. Fernando, and H. Freiser, *J. Amer. Chem. Soc.*, 86 (1964) 3056; L. F. Lindoy, *Quart. Rev. Chem. Soc.*, 25 (1971) 379.
14 J. H. Bowie, S.-O. Lawesson, J. O. Madsen, C. Nolde, G. Schroll, and D. H. Williams, *J. Chem. Soc., B*, (1966) 946.
15 N. K. Kochetkov and O. S. Chizhov, *Advan. Carbohyd. Chem.*, 21 (1966) 39; S. Hanessian, *Methods Biochem. Anal.*, 19 (1971) 105.
16 R. T. Conley, *Infrared Spectroscopy*, Allyn and Baker, Boston, 1966, p. 178.
17 C. V. Holland, D. Horton, and M. J. Miller, *J. Org. Chem.*, 32 (1967) 3077.
18 F. W. Lichtenthaler and P. Emig, *Carbohyd. Res.*, 7 (1968) 121.
19 R. U. Lemieux and D. R. Lineback, *Ann. Rev. Biochem.*, 32 (1963) 155.
20 M. L. Wolfrom, L. W. Georges, and S. Soltzberg, *J. Amer. Chem. Soc.*, 56 (1934) 1794.