Carbohydrate Research, 54 (1977) 199–208

ASPECTS OF THE TAUTOMERISM OF 2-(D-*galacto*-1,2,3,4,5-PENTAHYDROXYPENTYL)BENZOTHIAZOLINE

REGINA BLATTNER, ROBERT J. FERRIER, AND PETER C. TYLER
Department of Chemistry, Victoria University of Wellington, Wellington (New Zealand)
(Received June 17th, 1976, accepted for publication, June 24th, 1976)

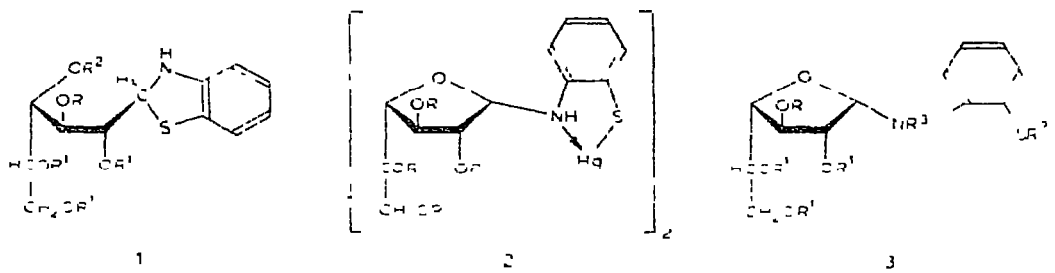
ABSTRACT

The benzothiazoline (**1**, $R^1 = R^2 = H$) formed by the reaction of D-galactose with *o*-aminobenzenethiol gives bis[*o*-(α-D-galactofuranosylamino)benzenethiol]-mercury(II) (**2**, R = H) on treatment with mercury(II) acetate in refluxing acetic acid. *O*-Acetylation of the chelate occurs smoothly, and demercuration of the product with hydrogen sulphide gives the thiol (**3**, $R^1 = Ac$, $R^2 = R^3 = H$) which, with catalytic acid or when kept in chloroform solution, isomerises to the thiazoline compound (**1**, $R^1 = Ac$, $R^2 = H$). Under mild acetylating conditions, this product (and the starting material) gives diastereoisomeric 2,3,4,5,6-penta-acetates (**1**, $R^1 = R^2 = Ac$), but appreciable reversion to thiol occurs with acyl chlorides, with the consequence that thioesters (**3**, $R^1 = R^2 = Ac$, $R^3 = H$, $R^1 = Ac$, $R^2 = Bz$, $R^3 = H$) were major products. The value of the tetraester (**1**, $R^1 = Ac$, $R^2 = H$) as a means of obtaining galactose derivatives specifically modified at C-4 is therefore limited.

INTRODUCTION

The reaction undergone by free sugars and *o*-aminobenzenethiol is potentially complex, since the amino and thio groups may condense with the sugar carbonyl group to give two diastereoisomeric benzothiazolines, or the amino group or the thiol function may pair with a sugar hydroxyl group to condense to give glycosylamines or 1-thioglycosides, respectively. With the additional possibilities of furanoid or pyranoid structures, α- or β-anomeric configurations, and the formation of an imine, there are eleven tautomeric forms for a condensation product. In an earlier report[1], we confirmed that, in keeping with several related reagents[2], *o*-aminobenzenethiol gives the heterocyclic products with acyclic carbohydrate moieties, and that the benzothiazolines formed from D-glucose react with mercury(II) ions to give a discrete glycosylamine chelate from which various acetylated compounds were obtained. The present work examines related compounds in the D-*galacto* series, with a view to assessing their possible value as intermediates through which galactose derivatives modified at C-4 could be obtained.

From D-galactose and *o*-aminobenzenethiol, the known condensation product[3] was obtained in high yield, and by mild acetylation with acetic anhydride in pyridine followed by hydrolysis, 2,3.4.5,6-penta-*O*-acetyl-D-galactose was produced therefrom From this evidence, it is concluded that the initial product was a mixture of diastereoisomeric benzothiazolines (**1**, $R^1 = R^2 = H$), and that no tautomeric change occurred prior to esterification (Evidence is given below to support this assumption.) Treatment of these initial products with mercury(II) acetate gave a discrete chelate (**2**, R = H) in quantitative yield, and this was acetylated smoothly to afford a readily handled octa-acetate (**2**, R = Ac) from which, by use of hydrogen sulphide, the thiol (**3**, R^1 = Ac, $R^2 = R^3 = H$) was obtained. This compound was identified by its weak S-H stretching absorption at 2700 cm^{-1}, and by an exchangeable SH singlet at τ 7.15 in its n m r spectrum. Mild acetylation gave the thioacetate (**3**, $R^1 = R^2$ = Ac, R^3 = H) in high yield, which showed C=O stretching[4] at 1690 cm^{-1}, gave an *S*-acetyl 3-proton resonance at τ 7 60, and gave a strong mass-spectral nolecular ion (*m/e* 497). Intense fragments with *m/e* 331 $(M-NHC_6H_4SAc)^+$ and 251 $(M-CH_2OAc$ $CHOAc-OAc-CH_2CO)^+$ were observed. The latter ion established the furanoid character of all compounds **2** and **3**, in confirmation of this conclusion, less-intense ions at *m/e* 352 $(M-CH_2OAc.CHOAc)^+$ and 293 $(M-CH_2OAc$ $CHOAc-OAc)^+$ were also found[5] No fragments for corresponding degradations of the pyranosyl isomer were found in the mass spectrum Benzoylation of the thiol (**3**, R^1 = Ac, $R^2 = R^3 = H$) gave the thiobenzoate, which was characterised by n m r. methods and by the presence of an appropriate C=O stretching frequency[4] in the infrared (1690 cm^{-1}) Further acetylation of the thioacetate (**3**, $R^1 = R^2$ = Ac, R^3 = H) with sodium acetate in hot acetic anhydride gave a hexa-acetyl derivative (**3**, $R^1 = R^2 = R^3$ = Ac) with a typical *N*-acetyl resonance (τ 8 36) and carbonyl-stretching frequency[4] (1670 cm^{-1}) The unexpected mutarotation of this compound was not examined further.



1 2 3

The acyclic nature of the penta-acetate (**1**, $R^1 = R^2$ = Ac) was readily determinable by n.m r methods (Table I) Thus, the C-6 protons showed typical characteristics of the AB part of an ABX spectrum, and all the other chain protons resonated as overlapping multiplets between τ 4 5 and 5.1, while the aryl resonances appeared as one complex multiplet between τ 3.1 and 3 6. These chemical shifts for carbohydrate protons are in good agreement with expectations based on the spectrum

of galactitol hexa-acetate[6] and *aldehydo*-D-galactose penta-acetate (see Table 1), and the observed coupling constants ($J_{5,6}$ 7 5, $J_{5,6'}$ 4; $J_{6,6'}$ 11 3 Hz) are also in agreement with values observed for these model compounds. On the other hand, the furanoid compounds **2** (R = Ac, **3** (R^1 = Ac, R^2 = R^3 = H), **3** (R^1 = R^2 = Ac, R^3 = H), and **3** (R^1 = Ac, R^2 = Bz, R^3 = H) all showed quite different and common spectral features The H-6 resonances were merged and the resultant broad singlets also incorporated the H-4 signals (τ 5 9) the H-1 resonances were clearly visible near τ 5 3 as broadened triplets ($J_{1,2}$ 8, $J_{NH,1}$ 8 Hz) which reduced to doublets on deuterium exchange of the nitrogen-bonded protons, the H-2, H-3, and H-5 resonances were unresolved between τ 4.5 and 4 9, and the phenyl signals were resolved into two multiplets centred at τ 2 8 and 3 3 [In the case of the peracetyl derivative (**3**, R^1 = R^2 = R^3 = Ac), however, H-1 and the phenyl protons were deshielded, and resonated anomalously at τ 4 05 ($J_{1,2}$ 8 Hz) and τ 2 52 (s), respectively] These features are consistent with expectations based on the characteristics of the spectrum of 2,3,5,6-tetra-*O*-acetyl-β-D-galactofuranosyl fluoride[7] (H-6, 5 65, H-6', 5 80, H-4, 5.51, H-2,3,5, 4.58–4 92) On the above bases, therefore, it was readily possible to characterise compounds of this series as having acyclic or furanoid carbohydrate components

Although its relative insolubility might have accounted for the isolation of the initial compound in the benzothiazoline form (**1**, R^1 = R^2 = H), it was considered probable that this was the thermodynamically favoured product, and therefore that the thiol (**3**, R^1 = Ac, R^2 = R^3 = H) would isomerise into the tetra-*O*-acetylthiazoline (**1**, R^1 = Ac, R^2 = H) under equilibrating conditions A chloroform solution of compound **3** (R^1 = Ac, R^2 = R^3 = H) was thus allowed to stand in the presence of a catalytic amount of toluene-*p*-sulphonic acid N m r examination showed that the thiol resonance (τ 7 10) slowly disappeared and that the spectrum altered concurrently from the "furanoid type" (two aromatic proton multiplets, discrete H-1 triplet at τ 5 3, combined H-4,6,6' resonances at τ 5 9) to the "benzothiazoline type" (one aromatic multiplet, unresolved H-2,3,5 resonances, resolved quartets for H-6,6') Relative to the spectrum of compound **1** (R^1 = R^2 = Ac), there was a one-proton signal near τ 6 (H-4) in place of that near τ 4 8, which was expected on the grounds that the deshielding ester function was absent from C-4 In addition, however, a doublet (J 9 Hz) at a new low-field position (τ 4 3) was observed and is assigned to H-3 because of the large coupling constant[6] The nature of the cause of this deshielding is not known, but is presumably a consequence of the proton's existence in a deshielding zone of one of the neighbouring acetyl-carbonyl groups Whatever the cause, it is not general: in a geometrically comparable case, the H-1 and H-3 resonances of 1,3,4,6-tetra-*O*-acetyl-α-D-glucose (τ 3 82, 4.75) are not deshielded with respect to those of 1,2,3,4,6-penta-*O*-acetyl-α-D-glucose[8] (τ 3.7, 4 5) As with the acyclic penta-acetate (**1**, R^1 = R^2 = Ac), the N–H resonance of the hydroxy compound (**1**, R^1 = Ac, R^2 = H) occurred at high field relative to those for the furanoid compounds (Table 1)

In later experiments, the thiol was isomerised simply by keeping it in chloroform solution or by warming it in this solvent, and the resulting benzothiazoline gave

TABLE I

CHEMICAL SHIFTS[a] OF COMPOUNDS 1–3 AND RELATED COMPOUNDS

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*NH*	*Ph*
1, $R^1 = R^2 = Ac$	←			4.5–4.9	→	5.80	6.29	5.9	3.0–3.6
1, $R^1 = Ac$, $R^2 = H$	← 4.8–5.0 →		4.3	6.0 ± 0.2	4.9 ± 0.1	5.9	6.15	6.0 ± 0.2	2.9–3.5
2,3,4,5,6-Penta-*O*-acetyl-D-galactose	0.65	←		4.45–4.85	→	5.75	6.16	—	—
Galactitol hexa-acetate[c]	—	4.71	4.65	4.65	4.71	5.73	6.16	—	—
2, R = Ac	5.23	← 4.5–4.9 →		5.9	4.7 ± 0.2	5.9	5.9	4.11	2.5–3.1, 3.2–3.5
3, $R^1 = Ac$, $R^2 = R^3 = H$	5.30	← 4.4–4.9 →		5.9	4.7 ± 0.2	5.9	5.9	4.45	2.5–3.0, 3.2–3.5
3, $R^1 = R^2 = Ac$, $R^3 = H$	5.32	← 4.5–4.9 →		5.95	4.6 ± 0.2	5.95	5.95	4.42	2.7–3.0, 3.1–3.5
3 $R^1 = R^2 = R^3 = Ac$	3.95	← 4.6–5.0 →		5.9 ± 0.2	4.8 ± 0.2	6.05	6.05	—	2.52
4, $R^1 = Ac$, $R^2 = Bz$, $R^3 = H$	5.26	4.8	4.55	5.90	4.8	5.9	5.9	4.22	2.4–2.7, 3.05–3.3

[a] τ, 60 MHz in chloroform.

the penta-acetate (**1**, $R^1 = R^2 = Ac$) on treatment with acetic anhydride in pyridine. However, benzoylation with benzoyl chloride did not give the analogous 4-benzoate (**1**, $R^1 = Ac$, $R^2 = Bz$), but a mixture of products in which the major component was the thiobenzoate (**3**, $R^1 = Ac$, $R^2 = Bz$, $R^3 = H$) identical to the product of direct esterification of the thiol (**3**, $R^1 = Ac$, $R^2 = R^3 = H$). The isomerisation of the thiol was thus reversed prior to benzoylation. Differences in the detailed action of acylating agents have been recognised before[9], and preferential esterifications are dependent on such factors as solvent[10]. Therefore, in order to further examine esterifications in this series, the hydroxy tautomer (**1**, $R^1 = Ac$, $R^2 = H$) was acetylated by using acetyl chloride, a mixture was obtained, containing ~60% of the thioacetate which was readily recognised by its characteristic *S*-acetyl resonance at τ 7.60. For compound **1** ($R^1 = Ac$, $R^2 = H$) to be of value in the preparation of 4-*O*-modified galactoses, therefore, mild reagents which do not affect the delicate tautomeric state of the molecule must be applied. A re-examination of the acetic anhydride acetylation showed that 5% of thioacetate was formed together with the acetate, and thus this reagent substantially esterifies without causing rearrangement.

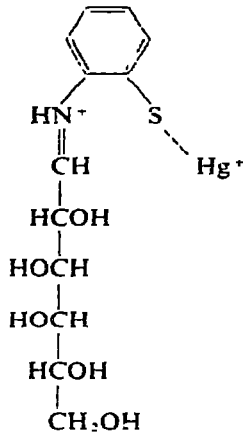
Attempts to obtain the 4-ulose from the thiol (**3**, $R^1 = Ac$, $R^2 = R^3 = H$) and the alcohol (**1**, $R^1 = Ac$, $R^2 = H$) with methyl sulphoxide and acetic anhydride were unsuccessful. From the former, the thioacetate (**3**, $R^1 = R^2 = Ac$, $R^3 = H$) was isolated in high yield, and the latter also gave appreciable proportions of this product. No evidence for ketone formation was obtained.

Triplets for the H-1 resonances of the furanoid compounds **2** (R = Ac) and **3** ($R^1 = Ac$, $R^2 = R^3 = H$, $R^1 = R^2 = Ac$, $R^3 = H$, $R^1 = Ac$, $R^2 = Bz$, $R^3 = H$) all integrated for one proton and indicated that each was enantiomerically pure, which shows that the furanoid ring-closure step (**1**, $R^1 = R^2 = H \rightarrow$ **2**, R = H) was stereospecific. This behaviour can be accounted for by invoking the intermediacy of the imino-species **4**, which would be expected to ring close under kinetic control to give an α-anomeric product[11]. Consistent with this are the high, positive, optical rotations for all the furanosyl compounds (except the thiol, see below), and the $J_{1,2}$ values of 7 Hz, but it is recognised that none of this evidence established the point definitively. Although it is not clear why the thiol ($[\alpha]_D$ −18°) should show anomalous optical rotation, it can be noted that the D-*gluco*-thiol was similarly exceptional[1], and it is suggested that, in chloroform, an intramolecular hydrogen-bonding pattern is established between sulphur and nitrogen, which confers chirality on the nitrogen and leads to the unexpected property. Although the thiol (**3**, $R^1 = Ac$, $R^2 = R^3 = H$) decomposed when kept in hydroxylic solvents, it clearly was dextrorotatory initially, which supports the hypothesis.

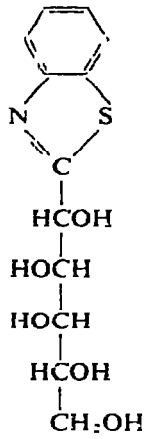
The benzothiazoline (**1**, $R = R^1 = H$) was expected to comprise a mixture of diastereoisomers; in keeping with this, the derived penta-acetate was readily fractionated by preparative t.l.c. into two isomeric components which gave the same mass spectra (except for ion intensities), containing strong molecular $(M)^+$ and $(M-2)^+$ ions, the latter presumably deriving from the thiazole analogue (see below). The isomers had opposite signs for their optical rotation and also showed circular

dichroism maxima of opposite sign at 290 nm; the isomer having the positive maximum is assigned the *R*-configuration at C-1[12].

After collection of the benzothiazoline (**1**, $R^1 = R^2 = H$) in the initial reaction, a second product was obtained and characterised as the benzothiazole (**5**) which has previously been made by condensation of acetylated D-galactonyl chloride and



4



5

o-aminobenzenethiol followed by deacetylation of the product[13]. Although benzothiazolines readily undergo this oxidation[14], previous attempts with carbohydrate derivatives have failed[15]. Acetylation of the oxidation product gave the known penta-acetate, from which the only fully-resolved, 60-MHz n.m.r. spectrum in the study was obtained.

EXPERIMENTAL

2-(D-galacto-1,2,3,4,5-Pentahydroxypentyl)benzothiazoline (**1**, $R^1 = R^2 = H$) — D-Galactose (30 g) and *o*-aminobenzenethiol (30 ml) were heated in refluxing acetic acid (300 ml) for 20 min. On cooling the clear solution, the product (42 g, 88%) crystallised, and recrystallisation from ethanol (×5) gave the benzothiazoline derivative, m.p. 189–190°, $[\alpha]_D$ −46° (*c* 0.9, pyridine). lit.[3] m.p. 191°, $[\alpha]_D$ −51° (pyridine).

Anal. Calc. for $C_{12}H_{17}NO_5S$: C, 50.2; H, 5.9; N, 4.9; S, 11.2. Found: C, 50.3; H, 5.9; N, 4.6; S, 11.3.

2-(D-galacto-1,2,3,4,5-Penta-acetoxypentyl)benzothiazoline (**1**, $R^1 = R^2 = Ac$). — (*a*) *By acetylation of the thiazoline* Acetic anhydride (3.5 ml) was added to a suspension of the benzothiazoline (0.5 g) in pyridine (5 ml), the mixture was shaken for 2 h at room temperature, and the solution was then poured onto ice to give a solid product (0.75 g, 87%). Recrystallised from ethanol (×4), it had m.p. 145–147°, $[\alpha]_D$ +49° (*c* 1, chloroform); lit.[3] m.p. 143–144°, $[\alpha]_D$ −5° (pyridine). N.m.r. data are given in Table I.

Anal. Calc for $C_{22}H_{27}NO_{10}S$ C, 53.1 H, 5.4 N, 2.8, S, 6.4 Found: C, 53.3, H, 5.5, N, 2.8, S, 6.7

This crystalline product contained two components (t.l.c., silica gel, 1% of methanol in chloroform, R_F 0.6, 0.4), a sample (0.5 g) fractionated by preparative t.l.c. gave two isomeric solids; the *S*-isomer (0.17 g), R_F 0.6, m.p. 140–146°, $[\alpha]_D$ −16° (*c* 1, chloroform), and the *R*-isomer (0.18 g), R_F 0.4, m.p. 112–120°, $[\alpha]_D$ +88° (*c* 1, chloroform) (Calc. for $C_{22}H_{27}NO_{10}S$ M^+, 497.1355 Found M^+, 497.1355

(*b*) *By acetylation of the rearranged thiol* (**1**, $R^1 = Ac$, $R^2 = H$) The 2,3,5,6-tetra-acetate (0.2 g) was acetylated with acetic anhydride (4 ml) and pyridine (10 ml) for 16 h at room temperature. The solid product (0.13 g, 60%, $[\alpha]_D$ +69°), which could not be recrystallised, had an n.m.r. spectrum identical to that of the product of direct acetylation of the initial benzothiazoline (**1**, $R^1 = R^2 = H$).

2,3,4,5,6-Penta-O-acetyl-D-galactose — A solution of the acetylated benzothiazoline (0.20 g) in methanol–chloroform (4 ml, 9:1) was added to a solution of mercury(II) chloride (0.2 g) in aqueous methanol (4 ml, 1:1). A yellow-green solid formed immediately, and after stirring for 5 min, the solids were removed and the filtrate was shaken with chloroform–water (30 ml, 1:1). After drying of the organic phase and evaporation of the solvent, a colourless syrup was obtained which crystallised spontaneously (0.13 g, 82%) Recrystallised from toluene, the aldehyde had m.p. 124–126°, $[\alpha]_D$ −18° (*c* 1, ethanol-free chloroform), addition of a drop of ethanol caused a change[16] to +22°, lit. m.p. 121°[17], $[\alpha]_D$ −25° (chloroform)[16] N.m.r. data are given in Table I

Bis[o-(α-D-galactofuranosylamino)benzenethiol]mercury(II) (**2**, $R = H$) — The benzothiazoline (7 g) was dissolved in refluxing ethanol (1.7 l), and mercury(II) acetate (3.7 g, 0.47 mol equiv.) and acetic acid (5 ml) in hot ethanol (500 ml) were added. On cooling, the chelate (8.9 g, 95%) precipitated as a fine, white solid. Recrystallised (×4) from *N*,*N*-dimethylformamide–chloroform, it had m.p. 182–184° (dec.), $[\alpha]_D$ +120° (*c* 0.9, pyridine).

Anal. Calc. for $C_{24}H_{32}HgN_2O_{16}S_2$. C, 37.3, H, 4.2 N, 3.6, S, 8.3. Found. C, 37.3, H, 4.5, N, 3.6; S, 7.5

Bis[o-(2,3,5,6-tetra-O-acetyl-α-D-galactofuranosylamino)benzenethiol]mercury-(II) (**2**, $R = Ac$). — Acetic anhydride (160 ml) was added to a solution of the mercury compound (8 g) in pyridine (160 ml), and after 2 h at room temperature, the mixture was poured onto ice to give a pink solid, which was dissolved in boiling ethanol (300 ml) and heated with decolourising charcoal. Removal of the charcoal and concentration of the solution to 100 ml caused the precipitation of the product (9.2 g, 81%) as pale-yellow needles Recrystallised from ethanol (×4), it had m.p. 121–124°, $[\alpha]_D$ +306° (*c* 1, chloroform). N.m.r. data are given in Table I

Anal. Calc. for $C_{40}H_{48}HgN_2O_{18}S_2$. C, 43.3, H, 4.3, N, 2.5, S, 5.9 Found C, 43.4, H, 4.5; N, 2.4, S, 5.1.

o-(2,3,5,6-Tetra-O-acetyl-α-D-galactofuranosylamino)benzenethiol (**3**, $R^1 = Ac$, $R^2 = R^3 = H$). — Passage of hydrogen sulphide into a solution of the acetylated chelate (5.0 g) in chloroform (50 ml) for 10 min caused precipitation of mercury(II)

sulphide (1.05 g, 100%) Removal of the solid and the solvent gave an almost colourless syrup which crystallised on trituration with ethanol The product (3.95 g, 96%), which could not be recrystallised, had m.p. 69–73°, $[\alpha]_D$ −18° (*c* 1, chloroform), +22° (methanol), +63° (aqueous methanol, 30%), and decomposed when kept in hydroxylic solvents It was characterised as its *S*-acetyl derivative N.m r data are given in Table I

S-*Acetyl*-O-(*2,3,5,6-tetra*-O-*acetyl*-α-D-*galactofuranosylamino*)*benzenethiol* (**3**, $R^1 = R^2 = Ac$, $R^3 = H$) — Freshly prepared thiol (3 9 g) was dissolved in pyridine (40 ml) and treated with acetic anhydride (16 ml) for 20 h at room temperature. The solution was poured onto ice, the mixture was stirred well before extraction with chloroform, and the chloroform extract gave a crystalline product (4 2 g, 97%) after drying and removal of the solvent. Recrystallised (×4) from ethanol, it had m.p 170–171°, $[\alpha]_D$ +116° (*c* 1, chloroform). N m.r. data are given in Table I.

Anal Calc for $C_{22}H_{27}NO_{10}S$· C, 53 1, H, 5 4 N, 2 8, S, 6.5. Found· C, 53.0: H, 5 5, N, 2.8, S, 6.3

N-*Acetyl*-S-*acetyl*-O-(*2,3,5,6-tetra*-O-*acetyl*-α-D-*galactofuranosylamino*)*benzenethiol* (**3**, $R^1 = R^2 = R^3 = Ac$) — The thioacetate (0.5 g) was heated with sodium acetate (0 2 g) in refluxing acetic anhydride (3 ml) for 1 h. Isolation of the product in the usual manner, with recrystallisation from ethanol, gave the title compound (0 4 g, 74%), m p. 146–147°, $[\alpha]_D$ −70° (*c* 0.9, chloroform) The specific rotation changed to −1° when the chloroform solution was allowed to stand for 1 h Unchanged product was then recovered. N.m r. data are given in Table I.

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 2, H, 5 3; N, 2.7 S, 5 9

2-(D-galacto-*1,2,4,5-Tetra-acetoxy-3-hydroxypentyl*)*benzothiazoline* (**1**, $R^1 = Ac$, $R^2 = H$) — A solution of freshly prepared thiol (0.7 g) in chloroform (20 ml, Analar) was kept at room temperature until the thiol resonance (τ 7 1) was no longer visible This took 10 days, but the reaction could be accelerated by elevation of temperature (5 h at 70°) or by addition of catalytic acid. (Control experiments showed that *o*-aminobenzenethiol was unaltered under these conditions) Removal of the solvent left a glassy residue, $[\alpha]_D$ +28° (*c* 0 3, chloroform), the n.m.r. spectrum of which (Table I) was consistent with the assigned structure.

S-*Benzoyl*-O-(*2,3,5,6-tetra*-O-*acetyl*-α-D-*galactofuranosylamino*)*benzenethiol* (**3**, $R^1 = Ac$, $R^2 = Bz$, $R^3 = H$). — (*a*) *By benzoylation of the thiol* The thiol (0.15 g) was treated with benzoyl chloride (0 75 g, 1.5 mol equiv.) in pyridine (4 ml) for 16 h at room temperature. The solution was poured onto ice, and the product was extracted into chloroform and, after the usual treatment, was obtained as an oil (0 17 g, 100%), $[\alpha]_D$ +70° (*c* 1, chloroform) The n m r spectrum was consistent with expectation (see Table I)

(*b*) *By benzoylation of the rearranged thiol.* The rearranged compound (0.7 g) was treated, as described above, with benzoyl chloride (0 33 g, 1.5 mol equiv) in pyridine (10 ml). The product was isolated, and a fraction (0 2 g) was purified by preparative t l c. to give a chromatographically pure, syrupy product, $[\alpha]_D$ +80°

(*c* 1, chloroform) (Calc. for $C_{27}H_{29}NO_{10}S$: M^+, 559.1505 Found M^+, 559.1512).

Oxidation of the thiol (**3**, $R^1 = Ac$, $R^2 = R^3 = H$) *and alcohol* (**1**, $R^1 = Ac$, $R^2 = H$) *with methyl sulphoxide–acetic anhydride* — The compounds (0.2 g) were separately treated with methyl sulphoxide (3 ml) and acetic anhydride (2 ml) for 2 h at room temperature. Extraction with ether and washing and drying of the extracts, followed by removal of the solvent, gave, in the first case, a crystalline residue (0.21 g), which was recrystallised from ethanol to give the thioacetate (**3**, $R^1 = R^2 = Ac$, $R^3 = H$), m.p. 170–171°, the n.m.r spectrum was identical with that of an authentic sample. In the second case, n.m.r. spectroscopy indicated that the thioacetate was again a substantial product.

2-(D-galacto-1,2,3,4,5-Pentahydroxypentyl)benzothiazole. — From the mother liquors of the preparation and purification of the benzothiazoline, the thiazole was obtained directly. Recrystallised from ethanol, it had m.p. 210–214°, $[\alpha]_D$ +40° (*c* 0.8, pyridine), +53° (*c* 0.6, aqueous ethanol 1:1, constant), lit.[13] m.p. 212–213°, $[\alpha]_D$ +41° (pyridine).

2-(D-galacto-1,2,3,4,5-Penta-acetoxypentyl)benzothiazole — The thiazole (4.0 g) was acetylated with acetic anhydride (25 ml) in pyridine (40 ml) for 16 h at room temperature. The mixture was poured onto ice to give a solid (5.7 g, 82%). Recrystallised from ethanol (×4), it had m.p. 134–135°, $[\alpha]_D$ +46 (*c* 1, chloroform), lit.[13] m.p. 132–133°, $[\alpha]_D$ +46° (chloroform). The n.m.r spectrum was identical to that published[18] (Table I).

ACKNOWLEDGMENTS

Dr. M. H. G. Munro, University of Canterbury, is thanked for assistance in obtaining the mass-spectral data, and Mr. J. E. Reeve for measuring the c.d. spectra.

REFERENCES

1 D. S. Bolieris, R. J. Ferrier, and L. A. Branda, *Carbohydr. Res.*, 35 (1974) 131–139
2 L. Szilágyi and R. Bognar, *Carbohydr. Res.*, 15 (1970) 371–377
3 R. Bognar, Z. Kodolynska, L. Somogyi, Z. Gyorgydeak, L. Szilagyi, and E. N. Nemes, *Acta. Chim. (Budapest)*, 62 (1969) 65–74
4 L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen, London, 1954
5 S. Hanessian, *Methods Biochem. Anal.*, 19 (1971) 105–228, N. K. Kochetkov and O. S. Chizhov *Adv. Carbohydr. Chem.*, 21 (1966) 39–93
6 S. J. Angyal, R. Le Fur, and D. Gagnaire, *Carbohydr. Res.* 23 (1972) 121–134
7 K. Bock, C. Pedersen and L. Wiebe *Acta Chem. Scand.*, 27 (1973) 3586–3590
8 R. U. Lemieux and J. D. Stevens, *Can. J. Chem.*, 43 (1965) 2059–2070
9 K. W. Buck, J. M. Duxbury, A. B. Foster, A. R. Perry, and J. M. Webber, *Carbohydr. Res.*, 2 (1966) 122–131.
10 J. Staněk and J. Jary, *Justus Liebigs Ann. Chem.*, (1976) 163–173
11 J. W. Green *Adv. Carbohydr. Chem.* 21 (1966) 95–142 R. J. Ferrier, *Fortschr. Chem. Forsch.* 14 (1970) 389–429
12 G. Snatzke, F. Werner-Zamojska, L. Szilagyi, R. Bognár, and I. Farkas, *Tetrahedron*, 28 (1972) 4197–4208
13 R. Bognár, I. Farkas, L. Szikágyi, M. Menyhart, E. N. Nemes, and I. F. Szábo, *Acta Chim. (Budapest)*, 62 (1969) 179–189

14 J M SPRAGUE AND A H LAND, in R C ELDERFIELD (Ed), *Heterocyclic Compounds*, Vol 5 Wiley, New York, 1957, p 677
15 L SATTLER, F W ZERBAN, G L CLARK, AND C -C CHU, *J Am Chem Soc* 73 (1951) 5908–5910
16 M L WOLFROM *J Am Chem Soc*, 52 (1930) 2464–2473
17 M L WOLFROM, *J Am Chem Soc*, 53 (1931) 2275–2279
18 L SZILAGYI R BOGNAR, AND I FARKAS *Carbohydr Res* 26 (1973) 305–313