REACTION OF 1,6-ANHYDRO-4-O-BENZYL-2-DEOXY--2-ISOTHIOCYANATO-β-D-GLUCOPYRANOSE; PREPARATION OF 2-AMINO-1,6-ANHYDRO-2,3-DIDEOXY-β-D-*ribo*-HEXOPYRANOSE*

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1,6-Anhydro-4-O-benzyl-2-deoxy-2-isothiocyanato-β-D-glucopyranose (*IV*), prepared from 2--amino-1,6-anhydro-4-O-benzyl-2-deoxy-β-D-glucopyranose (*I*) by reaction with carbon disulfide followed by oxidation with iodine, was converted into the 3-O-*p*-toluenesulfonate *VII*. This was cyclized to give either the 2,3-epimino derivative *X* or the thiazoline *XII*. 2-Acetamido-3-S-acetyl--1,6-anhydro-4-O-benzyl-2-deoxy-3-thio-β-D-glucopyranose (*XVI*), obtained from compound *XII*, was desulfurized with Raney nickel to afford 2-acetamido-1,6-anhydro-2,3-dideoxy-β-D--*ribo*-hexopyranose (*XVII*). The isothiocyanato group was not affected upon acetylation of compound *IV* and acetolysis of the 1,6-anhydride bond with acetic anhydride and trifluoroacetic acid.

During the study of deamination reactions of aminodeoxy-1,6-anhydrohexopyranoses[1,2] we have found that treatment of the methyl dithiocarbamate *III* with nitrogen dioxide or nitrosyl chloride does not result in substitution by sulfur for nitrogen analogously as observed for the formation of acetoxy derivatives by deamination of acetylamino derivatives[3]. The reaction of *III* gave 1,6-anhydro-4-O-benzyl--2-deoxy-2-isothiocyanato-β-D-glucopyranose (*IV*) as the only isolated product.

Two types of isothiocyanato derivatives of sugars are described in the literature. The first ones are glycoside derivatives, prepared by reaction of acetylated glycosyl halides with silver thiocyanate[4-6]. In the second type of derivatives, a hydroxy group other than anomeric is replaced by the isothiocyanato group[7-9] and they are obtained either by transformation of an amino group (as in reaction of 1,3,4,6-tetra--O-acetyl-2-amino-2-deoxy-β-D-glucopyranose with thiophosgene in the presence of base[7]) or by nucleophilic substitution of an allylic methanesulfonyloxy group with thiocyanate ion which affords a mixture of thiocyanato and isothiocyanato derivatives[8,9]. The latter substitution has been utilized in the synthesis of some amino-

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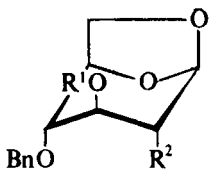
deoxy saccharides. The synthetic importance of isothiocyanates is underlined also by the possibility of their transformation into the thioureido or ureido derivatives, used recently for resolution of racemic amino acids by liquid chromatography[10].

Since isothiocyanato derivatives of 1,6-anhydrohexopyranoses have been hitherto unknown, we decided to study the reactivity of an axial isothiocyanato group in 1,6-anhydro-4-O-benzyl-2-deoxy-2-isothiocyanato-β-D-glucopyranose (*IV*) in order to prepare thio- and aminodeoxy sugar derivatives.

Compound *IV* was prepared in an 85% yield starting from 2-amino-1,6-anhydro-4-O-benzyl-2-deoxy-β-D-glucopyranose (*I*). Reaction of *I* with carbon disulfide in aqueous dioxane in the presence of sodium hydrogen carbonate afforded sodium salt of the dithiocarbamato derivative *II* which was oxidized with iodine in an alkaline medium[11]. We tried also reaction of the amine *I* with thiophosgene in the presence of triethylamine but the yield did not exceed that of the first reaction sequence. The isothiocyanato group in the product *IV* was detected by its characteristic absorption at 2 075 cm^{-1} in the IR spectrum and the structure of *IV* was proved by its ^1H NMR spectrum. According to the observed coupling constants, the compound exists in chloroform in the $^1C_4$(D) conformation with axial isothiocyanato group. The structure of the intermediate sodium salt *II* was confirmed by its transformation into the methyl thiourethane *III* with characteristic IR bands at 1 507 (ν(C=S)), 3 380 (ν(NH)) and 3 625 cm^{-1} (ν(OH)).

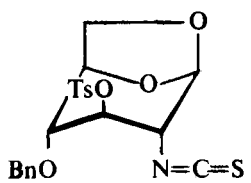
The isothiocyanate *IV* adds ammonia under formation of 1,6-anhydro-4-O-benzyl-2-deoxy-2-thioureido-β-D-glucopyranose (*V*) which is converted into 1,6-anhydro-4-O-benzyl-2-deoxy-2-ureido-β-D-glucopyranose (*VI*) by reaction with freshly precipitated moist mercuric oxide followed by hydrolysis of the formed diimide[12]. Treatment of the thioureido derivative *V* with aqueous solution of chloroacetic



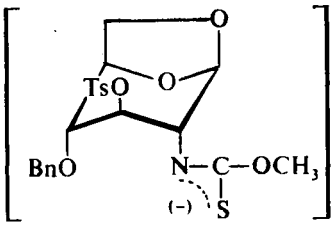
I, R^1 = H, R^2 = $-NH_2$
II, R^1 = H, R^2 = $-NHCS_2^-Na^+$
III, R^1 = H, R^2 = $-NH-CS-SCH_3$
IV, R^1 = H, R^2 = $-N=C=S$
V, R^1 = H, R^2 = $-NH-CS-NH_2$
VI, R^1 = H, R^2 = $-NH-CO-NH_2$
VII, R^1 = $CH_3C_6H_4SO_2-$, R^2 = $-N=C=S$
VIII, R^1 = CH_3CO-, R^2 = $-N=C=S$

Bn = $C_6H_5-CH_2-$

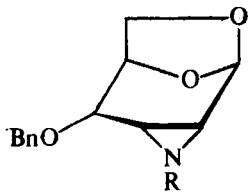
acid[13] results in degradation to the starting amino compound *I* instead of formation of the expected ureido compound *VI*.



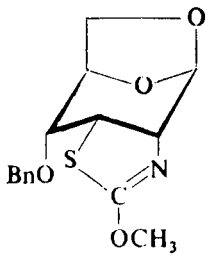
VII



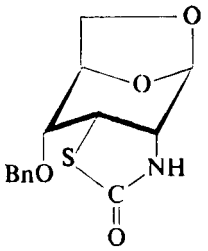
IX



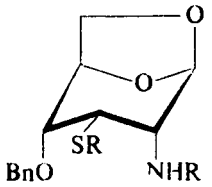
X, R=H
XI, R=*p*-$NO_2C_6H_4CO$—



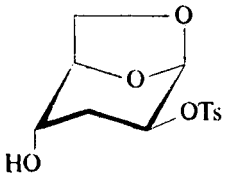
XII
XIII = *XII*. H_2SO_4



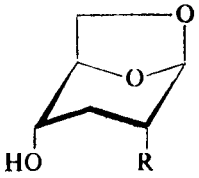
XIV



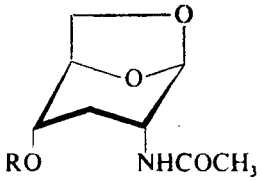
XV, R = H
XVI, R = CH_3CO—



XIX



XX, R = $-N_3$
XXI, R = $-NH_2 \cdot HCl$



XVII, R = H
XVIII, R = CH_3CO—

The isothiocyanato group is relatively resistant toward an acidic medium (no cleavage in 3 mol l^{-1} aqueous-ethanolic hydrogen chloride at room temperature) and also toward acylating reagents even under drastic conditions. This behaviour was utilized in tosylation of the relatively unreactive hydroxyl in compound *IV* with *p*-toluenesulfonyl chloride in pyridine. Whereas at room temperature the reaction is very slow, tosylation in boiling pyridine gives the desired 1,6-anhydro-4-O-benzyl--2-deoxy-2-isothiocyanato-3-O-*p*-toluenesulfonyl-β-D-glucopyranose (*VII*) in 77%

yield. Compound *VII* was used in the synthesis of 2,3-cyclic derivatives; the course of the cyclization can be influenced by choice of appropriate reaction conditions.

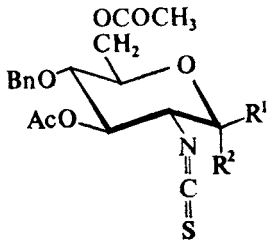
Reaction of the *p*-toluenesulfonate *VII* with sodium methoxide in 1,4-dioxane afforded 1,6-anhydro-4-O-benzyl-2,3-dideoxy-2,3-epimino-β-D-allopyranose (*X*) as the sole product. We may assume that the methoxide anion adds to the isothiocyanato group in *VII* to give an intermediate anion *IX*. The presence of the aziridine ring in compound *X* was proved by an IR band at 3 320 cm^{-1} (ref.[14]) and its structure was confirmed by transformation into the crystalline *p*-nitrobenzoyl derivative *XI* with the expected ^1H NMR parameters: the coupling constants $J_{1,2} \approx 0$ Hz, $J_{2,3} = 6{\cdot}0$ Hz, $J_{3,4} = 5{\cdot}5$ Hz and $J_{4,5} \approx 0$ Hz represent an unequivocal proof of D-allo-configuration and $^5H_0$(D) conformation.

Heating the *p*-toluenesulfonyl derivative *VII* with methanolic triethylamine in a sealed tube to 80°C afforded 1,6-anhydro-4-O-benzyl-2,3-dideoxy-β-D-allopyrano-[2,3-*d*]-2-methoxy-2-thiazoline (*XII*) in a 90% yield. Its structure was confirmed by an IR-band at 1 645 cm^{-1} due to the C=N bond and by hydrolysis with hydrochloric acid in ethanol to 1,6-anhydro-4-O-benzyl-2,3-dideoxy-β-D-allopyrano-[2,3-*d*]-2-thiazolidinone (*XIV*). In accord with the assumed structure, the IR spectrum of compound *XIV* exhibits characteristic bands[15,16] at 1 695 cm^{-1} (ν(C=O)) and at 3 335 and 3 425 cm^{-1} (ν(NH)). Also the ^1H NMR coupling constants, $J_{1,2} \leqq 1$ Hz, $J_{2,3} = 6{\cdot}0$ Hz and $J_{3,4} = 5{\cdot}5$ Hz, analogous to those of the epimine *X*, constitute a proof of the D-allo-configuration; the value $J_{4,5} = 2{\cdot}0$ Hz indicates a chair conformation of the pyranose ring. Addition of concentrated sulfuric acid to an ethanolic solution of the thiazoline *XII* precipitates the hydrogen sulfate *XIII*, stable under exclusion of moisture, whose structure was confirmed by elemental analysis and ^1H NMR spectrum. Due to the positive charge on the thiazoline ring in *XIII*, signals of all but the H-1 protons are shifted 0·4 ppm downfield relative to the corresponding signals of the thiazolidinone *XIV*, the coupling constants being unchanged.

The course of methanolysis of the *p*-toluenesulfonate *VII* may be explained by formation of the neutral thiourethane by an addition of methanol to the isothiocyanato group; the thiocarbonyl group then participates in the solvolysis of the *p*-toluenesulfonyl group closing thus the thiazoline ring. The formation of aziridine ring in the reaction with base and of thiazoline ring under conditions of solvolysis has its analogy in the reactions of vicinal *trans*-isocyanatoiodo[17] or isothiocyanatoiodo derivatives[16].

The substitution with thio group for the hydroxyl vicinal to the amino group according to above-mentioned reaction sequence was further used in the preparation of 2-acetamido-2,3-dideoxy derivative *XVII*. Hydrolysis of the thiazolidinone *XIV* with aqueous sodium hydroxide gave 2-amino-1,6-anhydro-2-deoxy-3-thio-β-D-allopyranose (*XV*). To suppress oxidation of the thiol to disulfite, the hydrolysis was performed in the presence of dipotassium disulfite and the aminothiol *XV* was isolated as the diacetate *XVI*. Desulfuration of *XVI* with Raney nickel and simultane-

ous debenzylation afforded 2-acetamido-1,6-anhydro-2,3-dideoxy-β-D-*ribo*-hexopyranose (*XVII*) which was converted into the crystalline diacetate *XVIII*, identical with the sample prepared from the *p*-toluenesulfonyl derivative *XIX via* the azide[18] *XX* and the amino derivative[19] *XXI*.



XXII, $R^1 = H$, $R^2 = CH_3COO-$
XXIII, $R^1 = CH_3COO-$, $R^2 = H$

Because of its potential alkaline hydrolysis to the starting amine, the isothiocyanato group might find application as a protecting group in the synthesis of oligosaccharides containing amino sugars. For this reason, we followed the stability of the isothiocyanato group under conditions of acetolysis of the 1,6-anhydro ring. The isothiocyanate *IV* was first converted into 3-O-acetyl-1,6-anhydro-4-O-benzyl-2-deoxy-2-isothiocyanato-β-D-glucopyranose (*VIII*) with acetic anhydride in pyridine. The acetate *VIII* was then acetolyzed in acetic anhydride at room temperature using trifluoroacetic acid as catalyst, the reaction being followed by gas–liquid chromatography. After 14 days, the starting compound had completely disappeared and the reaction mixture gave 1,3,6-tri-O-acetyl-4-O-benzyl-2-deoxy-2-isothiocyanato-α-D-glucopyranose (*XXII*) together with the corresponding β-anomer *XXIII*. The product composition was determined from the ratio of the H-1 signals in the ^1H NMR spectrum (α-anomer: δ H-1 = 7·38, $J_{1,2}$ = 3·6 Hz; β-anomer: 1 H-1 = 7·17, $J_{1,2}$ = 6·6 Hz), the ratio of the α-anomer to the β-anomer being 93 : 7. The preservation of the isothiocyanato group was confirmed by its characteristic IR band. On the other hand, acetolysis in a mixture of acetic acid and acetic anhydride with concentrated sulfuric acid as catalyst completely destroyed the isothiocyanato group.

EXPERIMENTAL

Melting points were determined on a Boetius block. Optical rotations were measured at 23 to 25°C on a Bendix-Ericsson ETL 143A automatic polarimeter. Infrared spectra were taken in chloroform (concentration 5—7%) on a UR-20 (Zeiss, Jena) spectrophotometer. ^1H NMR Spectra (250 MHz) were measured on a Cameca (Thomson-CF) instrument in the CW mode and on a Varian XL-200 spectrometer with tetramethylsilane as internal standard (δ-scale, coupling constants in Hz). Assignment of the signals and estimation of the coupling constants

was done using the double resonance and INDOR methods. Thin-layer chromatography was carried out on silica gel G (Merck, 0·2—0·3 mm layers) in solvent systems specified in the experiments; spots were detected by heating with 50% sulfuric acid. Solvents were evaporated on a rotator at 40°C. Analytical samples were dried over phosphorus pentoxide at 13 Pa. Light petroleum denotes a fraction boiling in the range 40—60°C.

1,6-Anhydro-4-O-benzyl-2-deoxy-2-methylthiocarbonylamino-β-D-glucopyranose (*III*)

A mixture of the amine *I* (ref.[20]; 100 mg; 0·4 mmol), dioxane (2 ml), saturated sodium hydrogen carbonate solution (2 ml) and carbon disulfide (0·5 ml) was shaken in the absence of air overnight. Methyl iodide (0·3 ml) was added with stirring and after shaking for 15 min the mixture was extracted with chloroform (3 × 5 ml). The combined chloroform extracts were dried over calcium chloride, the solvent was evaporated and the sirupy residue was crystallized from ether affording 110 mg (81%) of the dithiocarbamate *III*, m.p. 73—75°C, $[\alpha]_D$ +1·6° (*c* 2·6; chloroform). IR Spectrum (chloroform), cm^{-1}: 1 507 (ν(CS—NH)), 3 380 (ν(NH)), 3 625 (ν(OH)). For $C_{15}.H_{19}NO_4S_2$ (341·4) calculated: 52·76% C, 5·61% H, 4·10% N, 18·78% S; found: 52·53% C, 5·75% H, 4·17% N, 18·75% S.

1,6-Anhydro-4-O-benzyl-2-deoxy-2-isothiocyanato-β-D-glucopyranose (*IV*)

A mixture of the amine *I* (ref.[20]; 2 g; 8 mmol), dioxane (20 ml), saturated sodium hydrogen carbonate solution (20 ml) and carbon disulfide (2 ml) was shaken in the absence of air overnight. After evaporation of the reaction mixture, the obtained sodium salt *II* was dissolved in water (80 ml), the solution was made alkaline with 1M-NaOH (8 ml) and a solution of iodine (2 g) in ethanol (80 ml) was added with stirring. The mixture was acidified with hydrochloric acid to pH 4—5, filtered and concentrated to one third of the original volume. The product *IV* was filtered and dried, yield 1·97 g (85%), m.p. 85—88°C; after crystallization from chloroform–light petroleum the product melted at 89—90°C, $[\alpha]_D$ +115° (*c* 0·81; chloroform). IR Spectrum (chloroform), cm^{-1}: 2 075 (ν(N=C=S)), 3 645 (ν(OH)). ^{1}H NMR Spectrum (deuteriochloroform), 200 MHz): 3·40 m (1 H, H-4, $J_{4,3}$ = 2·7, $J_{4,5}$ = 1·7, $J_{4,2}$ = 0·9), 3·52 m (1 H, H-2, $J_{2,1}$ = 1·8, $J_{2,3}$ = 2·3, $J_{2,4}$ = 0·9, $J_{2,5}$ = 0·6), 3·73 bdd (1 H, H-6_{exo}, $J_{6,6}$ = 7·7, $J_{6,5}$ = 5·4, $J_{6,1} \approx 0{\cdot}4$), 4·00 m (1 H, H-3, unresolved), 4·02 dd (1 H, H-6_{endo}, $J_{6,6}$ = 7·7, $J_{6,5}$ = 0·9, $J_{6,1} \neq 0 \leqq 0{\cdot}2$), 4·57 m (1 H, H-5, $J_{5,6\,endo}$ = 0·9, $J_{5,6\,exo}$ = 5·4, $J_{5,4}$ = 1·7, $J_{5,1} \neq 0$, $J_{5,3} \approx 1{\cdot}5$), 4·67 d, 4·74 d (2 H, $C_6H_5CH_2O$, *J* = 12·2), 5·54 bt (1 H, H-1, $J_{1,2}$ = 1·8, $J_{1,3} \approx 1{\cdot}2$, $J_{1,4} \approx 0{\cdot}7$), 7·28 to 7·45 m (5 H, C_6H_5). For $C_{14}H_{15}NO_4S$ (293·3) calculated: 57·32% C, 5·15% H, 4·78% N, 10·93% S; found: 57·47% C, 5·28% H, 4·84% N, 11·13% S.

1,6-Anhydro-4-O-benzyl-2-deoxy-2-thioureido-β-D-glucopyranose (*V*)

Ethanol (5 ml), saturated at −15°C with ammonia, was added to the isothiocyanate *IV* (300 mg). After standing at room temperature for 1 h, the mixture was taken down and the residue crystallized from acetone–light petroleum, affording 280 mg (88%) of the thioureide *V*, m.p. 202—203°C (dec.); $[\alpha]_D$ −0·6° (*c* 3·2; acetone), R_F 0·45 (chloroform–methanol 20 : 1). For $C_{14}H_{18}N_2O_4S$ (310·3) calculated: 54·17% C, 5·85% H, 9·03% N, 10·33% S; found: 54·29% C, 5·79% H, 8·86% N, 10·36% S.

1,6-Anhydro-4-O-benzyl-2-deoxy-2-ureido-β-D-glucopyranose (*VI*)

A solution of the thioureide *V* (200 mg) in acetone (10 ml) was shaken with freshly precipitated moist HgO (prepared from 2·5 g $HgNO_3$) overnight. The mixture was evaporated and the residue

mixed with dichloromethane (20 ml). Mercuric sulfide and the excess HgO were removed by centrifugation and the supernatant was concentrated. The sirupy residue was dissolved in acetone (5 ml) and water (10 ml) with acetic acid (0·1 ml) was added. After standing for 16 h, acetone was evaporated and the mixture was made alkaline with aqueous ammonia. The separated product (R_F 0·3, chloroform–methanol 20 : 1) that crystallized in several days, was crystallized from water to afford 137 mg (72%) of the ureide *VI*, m.p. 176–177°C, $[\alpha]_D$ −12·4° (*c* 2·4; ethanol). For $C_{14}H_{18}N_2O_5$ (294·3) calculated: 57·13% C, 6·17% H, 9·52% N; found: 56·84% C, 6·10% H, 9·41% N.

1,6-Anhydro-4-O-benzyl-2-deoxy-2-isothiocyanato-3-O-*p*-toluenesulfonyl-β-D-glucopyranose (*VII*)

A solution of the isothiocyanate *IV* (950 mg) and *p*-toluenesulfonyl chloride (4 g) in pyridine (10 ml) was refluxed for 4 h. After this time, thin-layer chromatography detected a single product in the reaction mixture (R_F of *IV* 0·25, R_F of *VII* 0·7; benzene–acetone 10 : 1). The mixture was cooled and the excess *p*-toluenesulfonyl chloride was decomposed with water (0·4 ml). After addition of 4M-HCl (30 ml), the product was taken up in chloroform (3 × 15 ml), the combined chloroform extracts were dried over calcium chloride and the solvent was evaporated. The sirupy residue was dissolved in ether (30 ml), the ethereal solution was decolorized with charcoal, filtered and again stripped of the solvent to give a sirup which crystallized. The crystals were washed with cold ethanol to yield 1·12 g (77%) of the *p*-toluenesulfonyl derivative *VII*, m.p. 80–83°C; after crystallization from ethanol, m.p. 82–84°C, $[\alpha]_D$ +234° (*c* 0·83; chloroform). IR Spectrum (chloroform), cm^{-1}: 1 185–1 195 (doublet) and 1 383 ($\nu(SO_2O)$), 2 075 (ν(N=C=S)). For $C_{21}H_{21}NO_6S_2$ (447·5) calculated: 56·36% C, 4·73% H, 3·13% N, 14·33% S; found: 56·62% C, 4·67% H, 3·08% N, 14·32% S.

3-O-Acetyl-1,6-anhydro-4-O-benzyl-2-deoxy-2-isothiocyanato-β-D-glucopyranose (*VIII*)

The isothiocyanato derivative *IV* (1 g) was mixed with pyridine (10 ml) and acetic anhydride (5 ml). After standing overnight, the reaction mixture contained the acetyl derivative *VIII* as the sole product (R_F *IV*: 0·33, *VIII*: 0·75; chloroform–methanol 20 : 1) and was poured in an ice–water mixture and extracted with chloroform. The chloroform solution was washed with 5% hydrochloric acid (3 × 50 ml) and water, dried over calcium chloride and the solvent was evaporated. Crystallization of the residue from ethanol–ether–light petroleum afforded 1·1 g (96%) of the product *VIII*, m.p. 73–75°C, $[\alpha]_D$ +200° (*c* 0·44; chloroform). IR Spectrum (chloroform), cm^{-1}: 2 075 (ν(N=C=S)), 1 755 (ν(C=O)). For $C_{16}H_{17}O_5NS$ (335·4) calculated: 57·30% C, 5·11% H, 4·10% N, 9·56% S; found: 57·39% C, 5·26% H, 4·43% N, 9·72% S.

1,6-Anhydro-4-O-benzyl-2,3-dideoxy-2,3-epimino-β-D-allopyranose (*X*) and N-*p*-Nitrobenzoyl Derivative *XI*

Sodium methoxide solution (1M; 3 ml) was added to the *p*-toluenesulfonyl derivative *VII* (300 mg) in dioxane (3 ml) and the mixture was warmed to 40°C for 3 h. Thin-layer chromatography detected only one product (R_F 0·14, benzene–acetone 5 : 1). After evaporation, the residue was mixed with water and extracted with dichloromethane (3 × 5 ml). The combined extracts were dried over anhydrous calcium chloride and taken down, leaving 150 mg (96%) of sirupy 1,6-anhydro-4-O-benzyl-2,3-dideoxy-2,3-epimino-β-D-allopyranose (*X*); IR spectrum (chloroform): 3 320 cm^{-1} (ν(NH)). The product *X* was dissolved in pyridine (1 ml) and *p*-nitrobenzoyl chloride (170 mg) was added. After 15 min the mixture was decomposed with saturated solution of sodium

hydrogen carbonate (4 ml), the product was collected on a filter and crystallized from ethanol to give 197 mg (77% related to *VII*) of the *p*-nitrobenzoyl derivative *XI*, m.p. 153-154°C, $[\alpha]_D$ +58° (*c* 0·78; chloroform). ^{1}H NMR Spectrum (deuteriochloroform): 2·87 d (1 H, H-2, $J_{2,3}$ = 6·0, $J_{2,1} \cong 0$), 3·16 t (1 H, H-3, $J_{3,2} = 6{\cdot}0$, $J_{3,4} = 5{\cdot}5$, $J_{3,5} \leqq 1{\cdot}0$), 3·63 d (1 H, H-4, $J_{4,3}$ = 5·5, $J_{4,5} \cong 0$), 3·73 dd (1 H, H-6_{endo}, $J_{6endo,6exo} = 8{\cdot}0$, $J_{6endo,5} = 2{\cdot}0$), 3·99 t (1 H, H-6_{exo}, $J_{6exo,6endo} = 8{\cdot}0$, $J_{6exo,5} = 6{\cdot}5$), 4·67 dm (1 H, H-5, $J_{5,3} \leqq 1{\cdot}0$, $J_{5,6exo} = 6{\cdot}5$, $J_{5,6endo} = 2{\cdot}0$), 5·84 s (1 H, H-1, $J_{1,2} \cong 0$ Hz). IR Spectrum (chloroform): 1 705 cm^{-1} (ν(C=O)). For $C_{20}H_{18}N_2O_6$ (382·3) calculated: 62·82% C, 4·75% H, 7·33% N; found: 62·99% C, 4·72% H, 7·46% N.

1,6-Anhydro-4-O-benzyl-2,3-dideoxy-β-D-allopyrano[2,3-*d*]-2-methoxy-2-thiazoline (*XII*)

The *p*-toluenesulfonyl derivative *VII* (400 mg) and triethylamine (0·2 ml) in methanol (4 ml) were heated in a sealed tube to 80°C for 4 h. The mixture, shown by thin-layer chromatography to contain a single product (R_F 0·6, benzene–acetone 5 : 1), was taken down and the residue was treated with 1M-NaOH (8 ml). Methanol and triethylamine were distilled off and the aqueous phase was extracted with dichloromethane (3 × 5 ml). The combined extracts were dried over anhydrous magnesium sulfate and the solvent was evaporated. The remaining sirup was dissolved in ethanol (5 ml), the solution was decolorized with charcoal, filtered and evaporated to give 248 mg (90%) of sirupy product *XII*; $[\alpha]_D$ +79° (*c* 2·53; chloroform). IR Spectrum (chloroform): 1 645 cm^{-1} (ν(C=N)). For $C_{15}H_{17}NO_4S$ (307·4) calculated: 58·61% C, 5·58% H, 4·56% N, 10·43% S; found: 58·55% C, 5·60% H, 4·70% N, 10·33% S.

1,6-Anhydro-4-O-benzyl-2,3-dideoxy-β-D-allopyrano[2,3-*d*]-2-methoxy-2-thiazolinium Hydrogen Sulfate (*XIII*)

Concentrated sulfuric acid (0·1 ml) was added to a solution of the thiazoline *XII* (120 mg) in ethanol (2 ml). The separated crystals were collected on a filter, washed with ethanol and dried, yielding 130 mg (82%) of the title compound *XIII*, m.p. 122–124°C (decomposition); $[\alpha]_D$ +44° (*c* 0·84; dimethyl sulfoxide). ^{1}H NMR Spectrum (hexadeuteriodimethyl sulfoxide): 2·52 s (3 H, CH_3O–), 3·88 q (1 H, H-4, $J_{4,3}$ = 5·7, $J_{4,5}$ = 2·0), 3·99 dd (1 H, H-2, $J_{2,1}$ = 1·8, $J_{2,3}$ = 6·3), 4·05 q (1 H, H-6_{exo}, $J_{6exo,6endo}$ = 7·5, $J_{6exo,5}$ = 6·3), 4·30 dd (1 H, H-6_{endo}, $J_{6endo,6exo}$ = 7·5, $J_{6endo,5}$ = 1·5), 4·59 t (1 H, H-3, $J_{3,2}$ = 6·3, $J_{3,4}$ = 5·7), 5·17 bd (1 H, H-5, $J_{5,4}$ = 2·0, $J_{5,6endo}$ = 1·5, $J_{5,6exo}$ = 6·3), 5·44 d (1 H, H-1, $J_{2,1}$ = 1·8). For $C_{15}H_{19}NO_8S_2$ (405·4) calculated: 44·43% C, 4·72% H, 3·45% N, 15·82% S; found: 44·12% C, 4·72% H, 3·47% N, 15·93% S.

1,6-Anhydro-4-O-benzyl-2,3-dideoxy-β-D-allopyrano[2,3-*d*]-2-thiazolidine (*XIV*)

The thiazoline *XII* (248 mg), prepared from the *p*-toluenesulfonyl derivative *VII*, was dissolved in ethanol (4 ml), 6M-HCl (0·4 ml) was added and the solvent was evaporated. The residue was coevaporated with methanol (3 × 5 ml) to remove hydrogen chloride and crystallized from methanol–ether to give 130 mg (50%) of the thiazolidinone *XIV*, m.p. 157–158°C; $[\alpha]_D$ +56° (*c* 0·80; chloroform). ^{1}H NMR Spectrum (hexadeuteriodimethyl sulfoxide): 3·47 dd (1 H, H-4, $J_{4,3}$ = 5·5, $J_{4,5}$ = 2·0), 3·59 dd (1 H, H-2, $J_{2,3}$ = 6·0, $J_{2,1} \leqq 1$), 3·65 q (1 H, H-6_{exo}, $J_{6exo,6endo}$ = 8·0, $J_{6exo,5}$ = 6·0), 3·89 dd (1 H, H-6_{endo}, $J_{6endo,6exo}$ = 8·0, $J_{6endo,5} \leqq 1$), 4·19 t (1 H, H-3, $J_{3,2}$ = 6·0, $J_{3,4}$ = 5·5), 4·77 dm (1 H, H-5, $J_{5,4}$ = 2·0, $J_{5,6endo} \leqq 1$, $J_{5,6exo}$ = 6·0), 5·43 s (1 H, H-1, $J_{1,2} \leqq 1$). IR Spectrum (chloroform), cm^{-1}: 1 695 (ν(C=O)), 3 425 and 3 335 (ν(NH)). For $C_{14}H_{15}NO_4S$ (293·3) calculated: 57·32% C, 5·15% H, 4·78% N, 10·93% S; found: 56·89% C, 5·17% H, 5·09% N, 10·97% S.

2-Acetamido-3-S-acetyl-1,6-anhydro-4-O-benzyl-2-deoxy-3-thio-β-D-allopyranose (*XVI*)

Dipotassium disulfite (30 mg) was added to a suspension of the thiazolidinone *XIV* (150 mg) in 1M-NaOH (5 ml) and the mixture was refluxed. According to thin-layer chromatography (benzene–acetone 5 : 1), the starting compound (R_F 0·3) disappeared after 2 h and only the product, R_F 0·55, was present. Acetic anhydride (0·3 ml) was added to the cold mixture which was shaken and set aside for 15 min. The product was extracted with chloroform (3 × 5 ml), the combined chloroform extracts were dried over anhydrous magnesium sulfate, decolorized with charcoal, filtered and taken down. The remaining sirup was crystallized from ethanol–ether–light petroleum, affording 152 mg (84%) of the product; m.p. 88–90°C, which after recrystallization rose to 90–91°C, $[\alpha]_D$ −100° (*c* 0·86; chloroform). ^{1}H NMR Spectrum (deuteriochloroform): 1·97, 2·33 s (3 H, CH_3CO), 3·54 bs (1 H, H-3, $J_{3,2}$ = 5·0, $J_{3,4} \cong$ 3·5), 3·86 q (1 H, H-6_{exo}, $J_{6endo,6exo}$ = 8·0, $J_{6exo,5}$ = 5·0), 4·01 d (1 H, H-6_{endo}, $J_{6endo,6exo}$ = 8·0, $J_{6endo,5} \leqq$ $\leqq$ 0·5), 4·20–4·30 m (2 H, H-2, H-4, $J_{2,1}$ = 2·1, $J_{2,3}$ = 5·0, $J_{2,NH}$ = 10·0, $J_{4,3} \cong$ 3·5, $J_{4,5}$ = = 2·2), 4·67 q (1 H, H-5, $J_{5,6exo}$ = 5·0, $J_{5,4}$ = 2·2, $J_{5,6endo} \leqq$ 0·5), 5·38 d (1 H, H-1, $J_{1,2}$ = = 2·1), 6·39 d (1 H, NH, $J_{NH,2}$ = 10·0). IR Spectrum (chloroform), cm^{-1}: 1 522, 1 675 (ν(CONH)), 1 690 (ν(COS)), 3 430 (ν(NH)). For $C_{17}H_{21}NO_5S$ (351·4) calculated: 58·10% C, 6·02% H, 3·97% N, 9·12% S; found: 58·07% C, 6·18% H, 4·14% N, 9·20% S.

2-Acetamido-1,6-anhydro-2,3-dideoxy-β-D-*ribo*-hexopyranose (*XVII*) and 4-O-Acetyl Derivative *XVIII*

Raney nickel (2·5 ml) was added to a solution of the diacetyl derivative *XVI* (150 mg) in ethanol (7 ml) and water (3 ml) and the mixture was refluxed for 1·5 h. According to thin-layer chromatography (chloroform–methanol 20 : 1), the mixture contained a single product of R_F 0·17. The nickel was removed by filtration and washed several times with hot ethanol, the filtrate was taken down and the residue extracted with chloroform. Evaporation of the chloroform extract gave 66 mg (83%) of the sirupy acetamido derivative *XVII*. IR Spectrum (chloroform), cm^{-1}: 1 523, 1 676 (ν(CONH)), 3 430 (ν(NH)). The sirup was dissolved in pyridine (1·5 ml) and acetic anhydride (0·15 ml) was added. After 4 h the excess acetic anhydride was destroyed with methanol and the solvent evaporated. Several coevaporations of the sirupy residue with toluene (à 5 ml) gave crystals which after recrystallization from ethanol–ether afforded 78 mg (80%) of the deoxy derivative *XVIII*, m.p. 151–152°C (sublimes at 147°C); $[\alpha]_D$ −86° (*c* 0·87; chloroform). ^{1}H NMR Spectrum (deuteriochloroform): 2·04, 2·18 s (3 H, CH_3CO), 1·86 dd (1 H, H-3_{eq}, $J_{3eq,3ax}$ = 15·5, $J_{3eq,1} \leqq$ 1, $J_{3eq,2} \leqq$ 1, $J_{3eq,5} \leqq$ 1·5), 2·29 dt (1 H, H-3_{ax}, $J_{3ax,3eq}$ = = 15·5, $J_{3ax,2}$ = 5·9, $J_{3ax,4}$ = 4·5), 3·85 q (1 H, H-6_{exo}, $J_{6exo,6endo}$ = 8·0, $J_{6exo,5}$ = 5·2), 3·92 dd (1 H, H-6_{endo}, $J_{6endo,6exo}$ = 8·0, $J_{6endo,5} \leqq$ 1), 4·10 t (1 H, H-2, $J_{2,NH}$ = 9·0, $J_{2,3ax}$ = = 5·9, $J_{2,3eq} \leqq$ 1, $J_{2,1}$ = 1·5), 4·62 m (1 H, H-5, $J_{5,6exo}$ = 5·2, $J_{5,6endo}$ = 1, $J_{5,4}$ = 2·2), 4·79 q (1 H, H-4, $J_{4,3ax}$ = 4·5, $J_{4,5}$ = 2·2), 5·36 d (1 H, H-1, $J_{1,2}$ = 1·5, $J_{1,3eq} \leqq$ 1), 6·14 d (1 H, NH, $J_{NH,2}$ = 9·0). IR Spectrum (chloroform), cm^{-1}: 1 523, 1 676 (ν(CONH)), 1 740 (ν(CO)), 3 430 (ν(NH)). For $C_{10}H_{15}NO_5$ (229·2) calculated: 52·39% C, 6·60% H, 6·11% N; found: 52·57% C, 6·64% H, 6·21% N.

2-Acetamido-4-O-acetyl-1,6-anhydro-2,3-dideoxy-β-D-*ribo*-hexopyranose (*XVIII*)

Acetic anhydride (50 µl; 0·53 mmol) was added to a solution of the amino derivative *XXI* (25 mg 0·74 mmol) in pyridine (1 ml). After standing for 12 h, the mixture was decomposed with water (0·2 ml) and the solvent evaporated. The residue was coevaporated with toluene and dried under diminished pressure. Purification by chromatography on a column of silica gel in dichloromethane–methanol (10 : 1) yielded 30 mg (95%) of the acetyl derivative *XVIII*, m.p. 149–151°C (ether);

$[\alpha]_D$ −87° (*c* 0·33; chloroform). IR Spectrum (chloroform), cm^{-1}: 3 450, 1 519, 1 673 (ν(NH. .$COCH_3$)), 1 249, 1 742 (ν(CH_3CO)). For $C_{10}H_{15}NO_5$ (229·2) calculated: 52·39% C, 6·60% H, 6·11% N; found: 52·51% C, 6·58% H, 6·02% N.

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