PREPARATION OF SOME METHYL 3-ACETAMIDO-3,6-DIDEOXY--β-D-HEXOPYRANOSIDES*

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Azidolysis of methyl 3,4-anhydro-6-deoxy-β-D-galactopyranoside (*II*) gives a mixture of methyl 3-azido-3,6-dideoxy-β-D-gulopyranoside (*III*) and methyl 4-azido-4,6-dideoxy-β-D-glucopyranoside in a 19 : 1 ratio; the minor product of azidolysis was isolated in the form of acetate *V*. On catalytic hydrogenation of azido derivative *III* methyl 3-amino-3,6-dideoxy-β-D-gulopyranoside (*VI*) was prepared, which was converted also to corresponding acetamido derivative *I*. In a similar manner, methyl 3-amino-3,6-dideoxy-β-D-altropyranoside (*XII*), its N-acetyl derivative *IX* and peracetyl derivative *XI* were prepared from methyl 2,3-anhydro-6-deoxy-β-D-mannopyranoside (*X*). Methyl 3-acetamido-3,6-dideoxy-β-D-allopyranoside *XIII* was obtained on reaction of sodium acetate in aqueous 2-methoxyethanol with methyl 3-acetamido-2-O-acetyl-3,6-dideoxy--4-O-*p*-toluenesulfonyl-β-D-gulopyranoside (*XV*); substance *XV* was prepared from acetamidoguloside *I* by partial acetylation with acetic anhydride and tosylation. The structure of acetamido derivatives *I*, *IX* and *XIII* was confirmed by ^{1}H-NMR spectra and correlation with corresponding derivatives.

Recently we described[1] the preparation of methyl 3-acetamido-3,6-dideoxy-β-D--hexopyranosides of *gluco*, *galacto*, *manno*, *talo* and *ido* configuration. In this paper we describe the preparation of the remaining three configurational isomers which we need for the continuation of our studies of partial esterification (ref.[2] and the references therein) of acetamidoglycosides and for the study of their physico-chemical properties.

For the preparation of methyl 3-acetamido-3,6-dideoxy-β-D-gulopyranoside (*I*) we applied a procedure by which we prepared its α-anomer[3]. On reaction of methyl 3,4-anhydro-6-deoxy-β-D-galactopyranoside[4-7] (*II*) with sodium azide in 2-methoxyethanol we obtained 84·5% of methyl 3-azido-3,6-dideoxy-β-D-gulopyranoside (*III*) as the main product; from mother liquors we isolated after acetylation with acetic anhydride in pyridine and chromatographic separation also 4·5% of methyl 2,3-di--O-acetyl-4-azido-4,6-dideoxy-β-D-glucopyranoside (*V*), in addition to 3·5% of methyl 2,4-di-O-acetyl-3-azido-3,6-dideoxy-β-D-gulopyranoside (*IV*). The structure of azido derivatives *IV* (which we also prepared by acetylation of compound *III*) and *V* was

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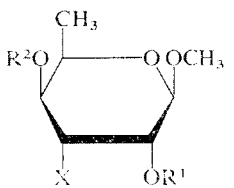
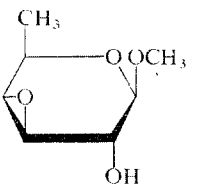
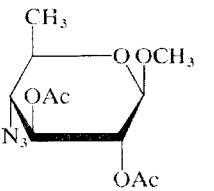
determined on the basis of their ^{1}H-NMR spectra. The magnitude of the coupling constants $J_{1,2} = 8{\cdot}0$ Hz, $J_{2,3} = 3{\cdot}5$ Hz and $J_{3,4} = 1{\cdot}5$ Hz in the ^{1}H-NMR spectrum of compound *IV* indicates that the hydrogen atoms H-1 and H-2 have a diaxial arrangement and the hydrogen atoms H-3 and H-4 a diequatorial one, which is in the case of β-D-hexopyranosides only possible if the compound *IV* possess *gulo* configuration in the $^4C_1$ conformation. The high coupling constant values in the ^{1}H-NMR spectrum of compound *V* ($J_{1,2} = 7{\cdot}5$, $J_{2,3} = J_{3,4} = 9{\cdot}5$ Hz) which correspond to an axial orientation of the hydrogen atoms are compatible only with a β-D-*gluco* configuration. The same conclusion can be reached on the basis of the comparison of the chemical shifts of protons in the positions 2, 3 and 4. While the signals of H-2 appear in both derivatives, *IV* and *V*, at almost the same field, in the case of the protons on the carbon atoms 3 or 4 carrying the acetoxy group a downfield shift of about 1 p.p.m. can be observed in comparison with the substance which has an azido group in this position. In contrast to this, for the determination of the configuration of acetylated azido derivatives the chemical shifts of the acetoxy groups[8] need not necessarily be quite decisive; in the case of substance *IV* the signals of the acetoxy groups both in the equatorial and the axial position vary within a range where the axial acetoxy groups usually occur (2·20–2·13) (ref.[8]). On catalytic hydrogenation of azido derivative *III* we obtained methyl 3-amino-3,6-dideoxy-β-D-gulopyranoside (*VI*) or its hydrochloride *VII*, respectively. The required acetamidoguloside *I* was prepared from amino-derivative *VI* on acetylation with acetic anhydride in methanol, while on acetylation with the same reagent in pyridine substance *VI* afforded methyl 3-acetamido-2,4--di-O-acetyl-3,6-dideoxy-β-D-gulopyranoside (*VIII*); its ^{1}H-NMR spectrum is in agreement with the proposed structure. Peracetyl derivative *VIII* was also prepared in 89% yield by ammonolysis of anhydro derivative *II* and acetylation of the reaction mixture with acetic anhydride in pyridine.



I, X = NHAc; $R^1 = R^2 = H$
III, X = N_3; $R^1 = R^2 = H$
IV, X = N_3; $R^1 = R^2 = Ac$
VI, X = NH_2; $R^1 = R^2 = H$
VII, X = NH_2.HCl; $R^1 = R^2 = H$
VIII, X = NHAc; $R^1 = R^2 = Ac$
XIV, X = NHAc; $R^1 = Ac$; $R^2 = H$
XV, X = NHAc; $R^1 = Ac$; $R^2 = Ts$



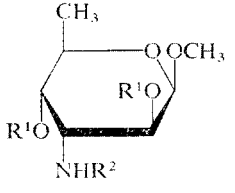
II



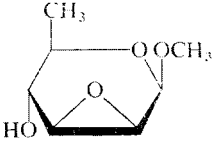
V

It is interesting that the azidolysis of anhydro derivative *II* takes place highly specifically (*gulo* : *gluco* = 19 : 1), in contrast to the same reaction in the α-series[3], where derivatives of *gluco* and *gulo* configuration are formed in a 44 : 50 ratio. Although the conformation of anhydrogalactoside *II* and of its α-anomer is flexible, it may be assumed that both anhydro derivatives will react during azidolysis in the same conformation ($^{\circ}H_1$), leading with a diaxial cleavage[9] to derivatives of D-gulose. In aqueous solution anhydro derivative *II* exists almost exclusively in $^{\circ}H_1$ conformation (ref.[6]) and it may be expected that this conformation will be still more preferred in the case of the α-anomer under the influence of the anomeric effect[10]. The lower specificity of the oxiran ring cleavage in the α-anomer is probably due to the fact that the accessibility of the azide ion in the position 3 will be impaired, in contrast to the β-anomer, by the 1,3-diaxial interaction with the methoxy group, similarly as in the case of other nucleophilic substitutions[11].

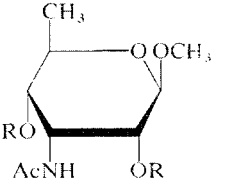
For the preparation of methyl 3-acetamido-3,6-dideoxy-β-D-altropyranoside (*IX*) we used an analogous procedure as for the preparation of substance *I*. Azidolysis of methyl 2,3-anhydro-6-deoxy-β-D-mannopyranoside[6,7] (*X*) gave a characterizable product only with difficulty, and, therefore, we worked up the reaction mixture after azidolysis by two procedures. In the first procedure, we hydrogenated the reaction mixture on PtO_2 and then submitted it to acetylation with acetic anhydride in pyridine. By crystallization and chromatography we obtained methyl 3-acetamido-2,4-di-O-acetyl-3,6-dideoxy-β-D-altropyranoside (*XI*) as the sole individual product in a 72% yield. Using the second procedure we purified first the product of azidolysis chromatographically and then we hydrogenated it catalytically; we succeeded in isolating methyl 3-amino-3,6-dideoxy-β-D-altropyranoside (*XII*), and from the mother liquors after its crystallization we isolated after acetylation again a product with *altro*-configuration only, *i.e.* compound *XI*. The ^{1}H-NMR spectrum of acetyl derivative *XI* unambigously excluded the presence of the acetamido group in the position 2, *i.e.* the structure of the alternative product of the cleavage of the oxiran ring of anhydro



IX, R^1 = H; R^2 = Ac
XI, $R^1 = R^2$ = Ac
XII, $R^1 = R^2$ = H



X



XIII, R = H
XVI, R = Ac

Ts = *p*-toluenesulfonyl
Ac = acetyl

derivative *X*. On catalytic deacetylation we obtained acetamidoaltroside *IX* from substance *XI*.

For the preparation of methyl 3-acetamido-3,6-dideoxy-β-D-allopyranoside (*XIII*) we used – similarly as in the preparation of its α-anomer[12] – acetamidoguloside *I* as starting material. On partial acetylation of substance *I* with acetic anhydride in pyridine we obtained in addition to di-O-acetyl derivative *VIII* methyl 3-acetamido-2-O-acetyl-3,6-dideoxy-β-D-gulopyranoside (*XIV*) in about 70% yield. The position of the O-acetyl group in the derivative *XIV* was determined from the values of the chemical shifts of protons H-2 and H-4 in the ^{1}H-NMR spectrum of substance *XIV*, in comparison with the shifts of the same protons in the spectrum of acetyl derivative *VIII*. Reaction of mono-O-acetyl derivative *XIV* with *p*-toluenesulfonyl chloride in pyridine led to methyl 3-acetamido-2-O-acetyl-3,6-dideoxy-4-O-*p*-toluenesulfonyl-β-D-gulopyranoside (*XV*) which we converted to acetamidoalloside *XIII* on reaction with sodium acetate in aqueous 2-methoxyethanol. Acetylation of substance *XIII* with acetic anhydride in pyridine gave the corresponding di-O-acetyl derivative *XVI*. The ^{1}H-NMR spectrum of substance *XVI*, measured in deuteriochloroform, was different from the spectra of all seven isomeric methyl 3-acetamido-2,4-di-O-acetyl-3,6-dideoxy-β-D-hexopyranosides[13], but it did not enable the assignment of single protons. In the ^{1}H-NMR spectrum measured in hexadeuterioacetone the H-4 proton signal (quartet at 4·57) and the H-5 proton signal (octet at 4·00) with the coupling constant $J_{4,5}$ = 8·9 Hz could be assigned as belonging to the diaxial arrangement of these protons; with respect to the value for $J_{3,4}$ = 3·8 the H-3 proton must be equatorial. Such an arrangement is complementary only with the isomers of the D-*altro* and D-*allo* configuration in $^4C_1$ conformation. In view of the method of preparation of compound *XVI* the configuration β-D-*allo* may be assigned to it.

EXPERIMENTAL

The melting points were determined on a Kofler block and they are not corrected. Optical rotations were measured on an Opton instrument at 20°C and 0·5–1·0 concentration. Samples for analysis were dried at 7–15 Pa and room temperature. Chromatographies were carried out on silica gel of Lachema (Brno) 100–160 μm, thin-layer chromatography on silica gel G according to Stahl (Merck, Darmstadt), 10–40 μm, using 25 – 75 mm plates and 0·2–0·3 mm layer thickness. The substances were detected by spraying with a 1% cerium(IV) sulfate solution in 10% sulfuric acid, and heating. The solvents were evaporated on a rotational evaporator *in vacuo* (water pump) at a temperature not exceeding 50°C. The light petroleum used for crystallizations had b.p. 45–60°C. The ^{1}H-NMR spectra were measured in deuteriochloroform, unless stated otherwise, using a Varian XL-100-15 instrument and tetramethylsilane as internal reference; the chemical shifts are given in δ-scale (p.p.m.) and the coupling constants *J* in Hz.

Azidolysis of Anhydrogalactoside *II*

A mixture of 500 mg (3·13 mmol) of anhydrogalactoside *II*, 500 mg of sodium azide, 300 mg of ammonium chloride, 6·5 ml of 2-methoxyethanol, and 0·5 ml of water was refluxed for 3 hours

and then evaporated to dryness. The residue was extracted with acetone and the acetone extract was evaporated. After crystallization of the residue from ethyl acetate–light petroleum 536 mg (84·5%) of azido derivative *III* were obtained, m.p. 143—146°C. For analysis the azido derivative was again crystallized from the same mixture, m.p. 145—146°C, $[\alpha]_D$ −22 ± 2° (water); IR spectrum (chloroform): 2100 cm^{-1} (N_3—). For $C_7H_{13}N_3O_4$ (203·2) calculated: 41·38% C, 6·45% H, 20·68% N; found: 41·24% C, 6·44% H, 20·65% N. The mother liquors from the crystallization of compound *III* were evaporated; attempts at the isolation of the minor azido derivative both by crystallization and thin-layer chromatography were unsuccessful. Therefore, the residue (69 mg) was dissolved in 5 ml of pyridine; after addition of 1 ml of acetic anhydride the mixture was allowed to stand at room temperature for 18 hours, then decomposed with water and evaporated twice with water (5 ml) and twice with toluene (5 ml). The residue was chromatographed on a column of silica gel (10 g). Benzene–ethyl acetate mixture (200 : 1) eluted 40 mg (4·5%) of acetylazido derivative *V* and the mixture of benzene and ethyl acetate in a 20 : 1 ratio eluted 31 mg (3·5%) of acetylazido derivative *IV*. Substance *IV* was crystallized five times from light petroleum, m.p. 78—85°C, $[\alpha]_D$ −29·7° (chloroform). For analysis substance *IV* was sublimated at 75°C and 13 Pa, the m.p. did not change. For $C_{11}H_{17}N_3O_6$ (287·3) calculated: 45·99% C, 5·97% H, 14·63% N; found: 46·10% C, 6·06% H, 14·36% N. ^{1}H-NMR spectrum: 1·19 (3 H, doublet, $J_{5,6}$ = 6·4, CH_3CH); 2·16 (3 H, singlet, CH_3COO); 2·14 (3 H, singlet, CH_3COO); 3·52 (3 H, singlet, CH_3O); 5·00 (1 H, quartet, $J_{1,2}$ = 8·0, $J_{2,3}$ = 3·5, H-2); 4·80 (1 H, quartet, $J_{3,4}$ = 3·5, $J_{4,5}$ = 1·5, H-4); 4·67 (1 H, doublet, $J_{1,2}$ = 8·0, H-1); 4·13 (1 H, triplet, $J_{3,4}$ = 3·5, $J_{2,3}$ = 3·5, H-3); 4·03 (1 H, octet, $J_{5,6}$ = 6·4, $J_{4,5}$ = 1·5, H-5). Substance *IV* with the same properties was obtained in a 90% yield by acetylation of 100 mg of azido derivative *III* (5 ml of pyridine, 1 ml of acetic anhydride).

Acetylazido derivative *V* was crystallized from light petroleum, m.p. 58—60°C, $[\alpha]_D$ 0° (chloroform), IR spectrum (chloroform): 2110 cm^{-1} (N_3—). For analysis derivative *V* was sublimated under the same conditions as derivative *IV*. For $C_{11}H_{17}N_3O_6$ (287·3) calculated: 45·99% C, 5·97% H, 14·63% N; found: 45·73% C, 6·03% H, 14·51% N. ^{1}H-NMR data: 1·41 (3 H, doublet, $J_{5,6}$ = 5·4, CH_3CH); 2·05 (3 H, singlet, CH_3COO); 2·09 (3 H, singlet, CH_3COO); 3·49 (3 H, singlet, CH_3O); 4·36 (1 H, doublet, $J_{1,2}$ = 7·5, H-1); 4·86 (1 H, quartet, $J_{1,2}$ = 7·5, $J_{2,3}$ = 9·5, H-2); 5·13 (1 H, triplet, $J_{2,3}$ = 9·5, $J_{3,4}$ = 9·5, H-3); 3·5—3·1 (2 H, multiplet, H-4, H-5).

Methyl 3-Amino-3,6-dideoxy-β-D-gulopyranoside (*VI*)

A solution of 118 mg (0·58 mmol) of azido derivative *III* in 5 ml of methanol was stirred in the presence of platinum dioxide for 30 minutes under hydrogen. The catalyst was filtered off, washed with methanol and the combined filtrates were evaporated. The residue crystallized after addition of a few drops of ethanol and light petroleum; it was then sublimated at 100°C and 30 Pa. Yield 90 mg (87%) of compound *VI*, m.p. 95—98°C. After crystallization from a mixture of ethanol and light petroleum the melting point was 97—98°C, $[\alpha]_D$ −105° (water). For $C_7H_{15}NO_4$ (177·2) calculated: 47·45% C, 8·53% H, 7·90% N; found: 47·49% C, 8·33% H, 7·60% N.

Methyl 3-Amino-3,6-dideoxy-β-D-gulopyranoside Hydrochloride (*VII*)

A solution of 890 mg (4·38 mmol) of azido derivative *III* in 50 ml of methanol was stirred in a hydrogen atmosphere and in the presence of PtO_2 for one hour. After filtration off of the catalyst the methanolic filtrate was titrated with 0·1M hydrochloric acid, using a Tashiro indicator, then filtered with charcoal and evaporated. The residue was crystallized from a mixture of ethanol and ether; yield 814 mg (87%) of hydrochloride *VII*, m.p. 163—165°C (decomp.), $[\alpha]_D$ −38 ± 2°

(water). For $C_7H_{16}ClNO_4$ (213·6) calculated: 39·36% C, 7·55% H, 6·55% N, 16·60% Cl; found: 39·58% C, 7·87% H, 6·61% N. 16·93% Cl.

Methyl 3-Acetamido-2,4-di-O-acetyl-3,6-dideoxy-β-D-gulopyranoside (*VIII*)

a) Two ml of acetic anhydride were added to a solution of 755 mg (4·26 mmol) of amino derivative *VI* in 10 ml of pyridine and the mixture was allowed to stand overnight, then decomposed with water and evaporated. The residue was evaporated again after addition of 5 ml of water, then with toluene, dried in a vacuum (oil pump) and crystallized from a mixture of ethyl acetate and light petroleum. Yield 1·043 g (81%) of acetyl derivative *VIII*, m.p. 192–194°C, which was recrystallized for analysis from the same solvent mixture; m.p. 194–196°C, $[\alpha]_D$ −6·0 ± 1° (chloroform). For $C_{13}H_{21}NO_7$ (303·3) calculated: 51·48% C, 6·98% H, 4·62% N; found: 51·87% C, 7·04% H, 4·73% N. ^{1}H-NMR spectrum: 1·23 (3 H, doublet, $J_{5,6}$ = 6·6, CH_3CH); 1·99 (3 H, singlet, CH_3CONH); 2·00 (3 H, singlet, CH_3OOO); 2·11 (3 H, singlet, CH_3COO); 3·47 (3 H, singlet, CH_3O); 5·99 (1 H, doublet, $J_{NH,3}$ = 8·0, NH); 4·61 (1 H, doublet, $J_{1,2}$ = 4·8, H-1); 5·03 (1 H, quartet, $J_{1,2}$ = 4·8, $J_{2,3}$ = 3·9, H-2); 4·65 (1 H, octet, $J_{2,3}$ = 3·9, $J_{3,4}$ = 7·4, $J_{NH,3}$ = 8·0, H-3); 5·18 (1 H, quartet, $J_{3,4}$ = 7·4, $J_{4,5}$ = 4·0, H-4); 4·15 (1 H, octet, $J_{5,6}$ = 6·6, $J_{4,5}$ = 4·0, H-5).

b) A mixture of 600 mg (3·75 mmol) of anhydro derivative *II*, 50 ml of methanol and 20 ml of liquid ammonia was heated in a stainless steel autoclave at 100–120°C for 26 hours and then evaporated. After acetylation carried out in the same manner as under *a*) acetyl derivative *VIII* was obtained in a 89% yield.

Methyl 3-Acetamido-3,6-dideoxy-β-D-gulopyranoside (*I*)

Acetic anhydride (2 ml) was added to a solution of 390 mg (2·20 mmol) of amino derivative *VI* in 10 ml of methanol and the mixture was allowed to stand overnight and then evaporated. The residue was crystallized from ethyl acetate saturated with water; yield 290 mg (56%) of hydrate of compound *I*, m.p. 78–80°C, $[\alpha]_D$ −48° (methanol). For $C_9H_{17}NO_5 \cdot H_2O$ (237·2) calculated: 45·58% C, 8·07% H, 5·90% N, found: 45·92% C, 8·16% H, 5·86% N.

Azidolysis of Anhydro Derivative *X*

A mixture of 460 mg (2·88 mmol) of anhydro derivative *X* (ref.[6,7]), 6 ml of 2-methoxyethanol, 460 mg of sodium azide, 270 mg of ammonium chloride, and 0·4 ml of water was refluxed for 1·5 hours. According to thin-layer chromatography in chloroform–ethanol 100 : 5 the starting compound *X* disappeared after this period. The reaction mixture was then evaporated and the residue extracted with acetone. The acetone extract was evaporated, and the residue dissolved in 50 ml of methanol. After addition of platinum dioxide the methanolic solution was stirred under hydrogen for 10 hours (under occasional exchange of hydrogen) at room temperature. The catalyst was filtered off, washed with methanol and the combined filtrates were evaporated. The residue (530 mg) was dissolved in 10 ml of pyridine and 1 ml of acetic anhydride was added to it. The mixture was allowed to stand at room temperature overnight, then decomposed with water, evaporated with water (2 × 10 ml) and eventually with toluene (2 × 10 ml). The residue was crystallized twice from ethyl acetate–light petroleum mixture to yield 214 mg (0·706 mmol, 24·5%) of acetyl derivative *XI*, m.p. 163–165°C, $[\alpha]_D$ −137° (chloroform). For $C_{13}H_{21}NO_7$ (303·3) calculated: 51·48% C, 6·98% H, 4·62% N; found: 51·53% C, 7·00% H, 4·64% N. ^{1}H-NMR data: 1·49 (3 H, doublet, $J_{5,6}$ = 7·0 CH_3CH); 1·95 (3 H, singlet, CH_3CONH); 2·11 (3 H, singlet, CH_3COO); 2·15 (3 H, singlet, CH_3COO); 4·06 (1 H, octet, $J_{4,5}$ = 1·6, $J_{5,6}$ = 7·0,

H-5); 5·64 (1 H, doublet, $J_{3,NH}$ = 7·6, NH); 5·19 (1 H, quartet, $J_{2,3}$ = 10·2, $J_{1,2}$ = 3·5, H-2); 3·47 (3 H, singlet, CH_3O); 4·80 (1 H, doublet, $J_{1,2}$ = 3·5, H-1); 5·0–4·7 (2 H, multiplet, H-3, H-4).

The mother liquors after crystallization were evaporated and chromatographed on a silica gel column (50 g). Benzene–ethanol mixture (100 : 2) eluted 414 mg (1·37 mmol) of compound *XI*, so that its total yield was 72%. In addition to compound *XI* 32 mg of a syrupy product were isolated which contained according to thin-layer chromatography (in benzene–ethanol 10 : 1) at least two substances with R_F values close to the R_F value of compound *XI* (about 0·3).

b) Using the same procedure as above, azidolysis was carried out with 176 mg of anhydro derivative *X*. After evaporation of the acetone extract the syrupy residue was chromatographed on a silica gel column (15 g). Elution with chloroform–ethanol 100 : 1 gave 202 mg of a chromatographically pure substance (as indicated by thin-layer chromatography in chloroform–ethanol 100 : 5) of m.p. 37–46°C. Its hydrogenation on PtO_2 in ethanol gave a basic syrup containing according to thin-layer chromatography in chloroform–ethanol 100 : 5 traces of a substance with the R_F value identical to that of the starting azido derivative, in addition to amino derivative *XII*. This syrup was dissolved in water (10 ml) and poured onto a small column of 10 ml of Dowex 50 WX 4 (H^+). The cation exchanger column was eluted first with 25 ml of water. Evaporation of the eluate gave 19 mg of a compound melting at 90–100°C. After crystallization from tetrachloromethane it had m.p. 100–108°C and the same R_F value as the starting azido derivative. In its IR spectrum (chloroform) the absorption band for the azido group (2100 cm^{-1}) was absent, while the main bands were at 3560, 3005, 2940, 1670–1740 and 1450 cm^{-1}; according to the ^{1}H-NMR spectrum (CH_3-group signal) this substance was not pure and it was not further analysed. The cation exchanger column was then eluted with 0·2% aqueous ammonia. The basic syrup obtained after the evaporation of the eluent was sublimated at 120°C and 5 Pa, yielding 130 mg of a substance with m.p. 105–112°C which was crystallized twice from ethanol–ethyl acetate. Yield, 66 mg (0·373 mmol, 34%) of aminoaltroside *XII*, m.p. 114–116°C, $[\alpha]_D$ −88·9° (water). For $C_7H_{15}NO_4$ (177·2) calculated: 47·45% C, 8·53% H, 7·90% N; found: 47·48% C, 8·51% H, 7·69% N. The mother liquors after crystallization of amino derivative *XII* were evaporated and acetylated in the same manner as described above. After crystallization from a mixture of ethyl acetate and light petroleum 76 mg (0·251 mmol, 23%) of acetyl derivative *XI* were obtained. The mother liquors (after evaporation of the solvent the residue weighed 40 mg) contained according to thin-layer chromatography in addition to the dominant acetyl derivative *XI* the same minor products as the mother liquors from procedure *a*).

Methyl 3-Acetamido-3,6-dideoxy-β-D-altropyranoside (*IX*)

To a solution of 132 mg (0·39 mmol) of acetyl derivative *XI* in 8 ml of methanol a catalytic amount of sodium was added and the mixture was allowed to stand at room temperature overnight. It was shaken with 1 ml of cation exchanger (Dowex 50 WX 4 (H^+)), filtered and the exchanger washed with methanol. The combined filtrates were evaporated. The syrupy residue (96 mg, 100%) became crystalline after addition of a few drops ethyl acetate and a droplet of water. After recrystallization from water-saturated ethyl acetate derivative *IX* was obtained (82 mg) in the form of hydrate with m.p. 72–75°C, $[\alpha]_D$ −101° (water). For $C_9H_{17}NO_5 \cdot H_2O$ (237·2) calculated: 45·58% C, 8·07% H, 5·90% N; found: 45·87% C, 8·25% H, 5·80% N.

Methyl 3-Acetamido-2-O-acetyl-3,6-dideoxy-β-D-gulopyranoside (*XIV*)

Acetic anhydride (0·24 ml; 2·5 mmol) was added to a mixture of 492 mg (2·25 mmol) of acetamidoguloside *I* and 8 ml of pyridine at −70°C and the mixture was allowed to stand at −15°C for

24 hours, and at 0°C for 48 hours. Then it was decomposed with water, evaporated, and again evaporated with 5 ml of water and toluene. The residue was dried in vacuum (oil pump) and chromatographed on a silica gel column (50 g). Chloroform–ethanol (100 : 1) mixture eluted 110 mg (0·36 mmol, 16·1%) of di-O-acetyl derivative *VIII*; a mixture of chloroform–ethanol 100 : 2 eluted 408 mg (1·56 mmol, 69·5%) of mono-O-acetyl derivative *XIV* which was crystallized from a mixture of ethyl acetate and light petroleum, m.p. 129–131°C, $[\alpha]_D$ −35 ± 2° (chloroform). For $C_{11}H_{19}NO_6$ (261·3) calculated: 50·57% C, 7·33% H, 5·36% N; found: 50·70% C, 7·32% H, 5·34% N. ^{1}H-NMR spectrum: 1·37 (3 H, doublet, $J_{5,6}$ = 6·9, CH_3CH); 2·04 (3 H, singlet, CH_3CONH); 2·11 (3 H, singlet, CH_3COO); 3·46 (3 H, singlet, CH_3O); 6·14 (1 H, doublet, $J_{NH,3}$ = 6·6, NH); 5·06 (1 H, triplet, $J_{1,2}$ = 4·1, $J_{2,3}$ = 4·1, H-2); 4·58 (1H, doublet, $J_{1,2}$ = = 4·1, H-1); 4·52 (1 H, octet, $J_{2,3}$ = 4·1, $J_{3,4}$ = 6·5, $J_{NH,3}$ = 6·6, H-3); 4·07 (1 H, octet, $J_{4,5}$ = 3·5, $J_{5,6}$ = 6·4, H-5); 3·91 (1 H, quartet, $J_{3,4}$ = 6·5, $J_{4,5}$ = 3·5, H-4).

Methyl 3-Acetamido-2-O-acetyl-3,6-dideoxy-4-O-*p*-toluenesulfonyl-β-D-gulopyranoside (*XV*)

To a solution of 132 mg (0·505 mmol) of compound *XIV* in 10 ml of pyridine 350 mg of *p*-toluenesulfonyl chloride were added at 0°C and the mixture was allowed to stand at 5°C for 100 hours (compound *XIV* reacts very reluctantly). It was decomposed with water, diluted with chloroform (20 ml) and gradually extracted with 10% sulfuric acid, water, 1% sodium hydrogen carbonate solution and water. The chloroform extract was dried over magnesium sulfate and evaporated. The residue crystallized after addition of a small amount of ethanol and light petroleum. Yield 96 mg (46%) of compound *XV*, m.p. 118–126°C, which was crystallized for analysis twice more from the same mixture of solvents. M.p. of the analytical preparation, 124–126°C, $[\alpha]_D$ 0° (chloroform). For $C_{18}H_{25}NO_8S$ (415·4) calculated: 52 05% C, 6·06% H, 7·72% S; found: 51·78% C, 6·23% H, 7·59% S. Chromatographic purification of the mother liquors (silica gel, chloroform–ethanol 100 : 2 as eluent) from various attempts at the preparation of compound *XV* gave on average another 10% of tosyl derivative *XV*, so that the total yield was about 55%.

Methyl 3-Acetamido-3,6-dideoxy-β-D-allopyranoside (*XIII*)

A mixture of 74 mg (0·178 mmol) of tosyl derivative *XV*, 200 mg of sodium acetate trihydrate, 8 ml of 2-methoxyethanol, and 0·6 ml of water was refluxed for 10 hours, then evaporated and the residue chromatographed on a silica gel column (10 g) with chloroform–ethanol (100 : 5). Chromatographically pure, syrupy substance *XIII* (36 mg; 92%) crystalized out after several weeks' standing in an unstoppered flask. After crystallization from a mixture of ethyl acetate (saturated with water) and light petroleum its hydrate was obtained, m.p. 76–80°C, $[\alpha]_D$ −35° (water). For $C_9H_{17}NO_5 . H_2O$ (237·2) calculated: 45·59% C, 8·07% H, 5·90% N; found: 45·15% C, 7·95% H, 5·82% N.

Methyl 3-Acetamido-2,4-di-O-acetyl-3,6-dideoxy-β-D-allopyranoside (*XVI*)

Acetic anhydride (0·3 ml) was added to a solution of 27 mg of acetamidoalloside *XIII* in 3 ml of pyridine and the mixture was allowed to stand at room temperature for 2 days. After decomposition with water, evaporation with water and eventually with toluene the syrupy residue was purified by column chromatography on 5 g of silica gel using benzene–ethanol 100 : 5 for elution. The main eluate contained 33 mg of a chromatographically pure syrup, $[\alpha]_D$ −22° (chloroform). ^{1}H-NMR spectrum (hexadeuterioacetone): 1·21 (3 H, doublet, $J_{5,6}$ = 6·2, CH_3CH); 1·93 (3 H, singlet, CH_3CONH); 1·98 (6 H, singlet, 2 . CH_3COO); 3·43 (3 H, singlet, CH_3O); 4·00 (1 H, octet, $J_{5,6}$ = 6·2, $J_{4,5}$ = 8·9, H-5); 4·57 (1 H, quartet, $J_{4,5}$ = 8·9, $J_{3,4}$ = 3·8, H-4); 4·68–5·00 (3 H, multiplet, H-1, H-2, H-3); 7·26 (1 H, doublet, $J_{HN,3}$ = 8, NH).

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