AMINO SUGARS. XXVI.*

PREPARATION OF DERIVATIVES OF 3-AMINO-3,4,6-TRIDEOXY-D-*arabino*-HEXOPYRANOSE

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On reaction of methyl-2,3-anhydro-4,6-dideoxy-α-D-*lyxo*-hexopyranoside (*I*) with ammonia methyl-3-amino-3,4,6-trideoxy-α-D-*arabino*-hexopyranoside (*V*) is formed. Hydrolysis of acetamido derivative *VI* with dilute acetic acid gave amidohexose *XII* from which 2-acetamido-2,3,5-trideoxy-D-*eryhthro*-pentofuranose (*XIV*) was formed by sodium borohydride reduction and subsequent sodium periodate oxidation. The configuration of the amino sugar *V* and its derivatives *II*— *VI* was proved by the preparation of substance *XIV* and by the NMR spectra of both anomers of 1,2-di-O-acetyl-3-acetamido-3,4,6-trideoxy-D-*arabino*-hexopyranose (*XV* and *XVI*) obtained on acetylation of compound *XII* with acetic anhydride in pyridine. The cleavage of anhydro derivative *I* with dimethylamine gave methyl-3,4,6-trideoxy-3-dimethylamino-α-D-*arabino*-hexopyranoside (*X*) which is also formed from the amino sugar *V* under the influence of formaldehyde and formic acid.

The occurrence of desosamine, *i.e.* 3,4,6-trideoxy-3-dimethylamino-D-*xylo*-hexopyranose[1,2], in some antibiotics (for example erythromycin[3], narbomycin[4], oleandomycin[5], *etc.*) stimulated our interest in the synthesis of configurational isomers of desosamine. In this paper we investigate the preparation of the isomer with the *arabino* configuration. As starting material we chose methyl-2,3-anhydro-4,6-dideoxy-α-D-*lyxo*-hexopyranoside[6] (*I*), prepared earlier, and we submitted it to the reaction with ammonia and dimethylamine.** For the separation of the reaction mixture we took procedures *A* and *B*. In the case of procedure *A* we isolated from the reaction mixture, after its neutralisation with oxalic acid, the crystalline oxalate of methyl-3-amino-3,4,6-trideoxy-α-D-*arabino*-hexopyranoside (*II*) as the main product. From the mother liquors the non basic fraction was eliminated by ion-exchange resin, and from the basic fraction, which was first N-acetylated and mesylated with methanesulfonyl chloride in pyridine, we isolated crystalline methyl-3-acetamido-3,4,6-trideoxy-2-O-methanesulfonyl-α-D-*arabino*-hexopyranoside (*III*). In

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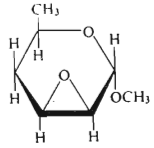
** The reaction of ethyl glycoside of racemic anhydro derivative *I* with dimethylamine was already carried out by Newman[7].

the case of procedure *B* the reaction mixture was acetylated with acetic anhydride in pyridine, giving methyl-3-acetamido-2-O-acetyl-3,4,6-trideoxy-α-D-*arabino*-hexopyranoside (*IV*) as the sole nitrogen-containing product. The opening of the epoxide ring in derivative *I* takes place stereoselectively under formation of methyl-3-amino-3,4,6-trideoxy-α-D-*arabino*-hexopyranoside (*V*); the amonolysis is accompanied by side reactions affording non-identified non-basic products.

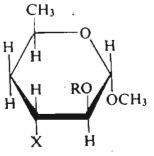
From the acetyl derivative *IV* we obtained on catalytic deacetylation the syrupy methyl-3-acetamido-3,4,6-trideoxy-α-D-*arabino*-hexopyranoside (*VI*) which under the effect of methanesulfonyl chloride in pyridine gave mesyl derivative *III* identical with the mesyl derivative *III* isolated in case *A*. The mesyl derivative *III* gave on reaction with sodium acetate in aqueous 2-methoxyethanol crystalline methyl-3-acetamido-3,4,6-trideoxy-α-D-*ribo*-hexopyranoside (*VII*). Derivative *VII* also gave on mesylation a crystalline mesyl derivative, *VIII*.

When anhydro derivative *I* was allowed to react with methanolic dimethylamine and when the reaction mixture was neutralised with hydrochloric acid, one sole product was obtained, *i.e.* the hydrochloride of methyl-3,4,6-trideoxy-3-dimethylamino-α-D-*arabino*-hexopyranoside (*IX*). The same hydrochloride *IX* was also obtained from the amino derivative *V* under the effect of aqueous formaldehyde and formic acid. As the dimethylamino derivative *X* obtained on the liberation of the base from hydrochloride *IX* under the influence of the anion exchanger was syrupy, we characterised it in the form of its crystalline methiodide *XI*.

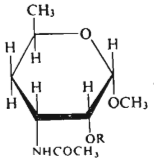
For chemical proof of the position of the amino group in derivatives *II*–*VI* (and in view of the generally valid rule on the *trans*-opening of the epoxide ring for the proof of the configurations of these derivatives) we carried out the following sequence of reactions: Hydrolysis of compound *VI* with 50% acetic acid gave the syrupy 3-acetamido-3,4,6-trideoxy-D-*arabino*-hexopyranose (*XII*) the reduction of which with sodium borohydride led to the corresponding sugar alcohol *XIII*. The latter was submitted without further purification to sodium periodate oxidation. The crystalline *XIV* obtained represented according to its NMR spectra a mixture of α- and β-anomers of 2-acetamido-2,3,5-trideoxy-D-*erythro*-pentofuranose (*XIV*) in a 9 : 1 ratio. In the NMR spectrum (in hexadeuteriodimethyl sulfoxide) of compound *XIV* the following peaks are due to the presence of the α-anomer: a doublet of three protons of the methyl group (H_5) at 1·16 p.p.m. ($J_{4,5} = 6{\cdot}8$), a singlet of the N-acetyl group protons at 1·93 p.p.m., a multiplet in the 1·6–2·0 p.p.m. due to two protons H_3, a multiplet in the 4·15–4·50 p.p.m. region corresponding to protons H_2 and H_4, a triplet of the anomeric proton H_1 at 5·25 p.p.m. ($J_{1,2} = 4{\cdot}5$ and $J_{1,OH} = 4{\cdot}5$), a doublet of the hydroxy group proton at 6·16 p.p.m. ($J = 4{\cdot}5$), and a broad doublet at 7·0 p.p.m. due to NH-proton ($J_{NH,H_2} = 7{\cdot}5$). The β-anomer gives in the NMR spectrum a doublet at 1·3 p.p.m., due to three methyl protons (H_5), a singlet at 1·9 p.p.m. of the N-acetyl group protons, a broad doublet of H_1 proton at 5·09 p.p.m. ($J_{H_1,OH} \sim 5{\cdot}0$), and a broad doublet of the hydroxyl proton, at 5·87 p.p.m. ($J \sim 5{\cdot}0$).



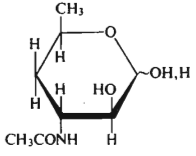
I



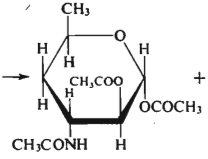
II, R—H, X = $NH_2.\frac{1}{2}(COOH)_2$
III, R = CH_3SO_2, X = $NHCOCH_3$
IV, R = CH_3CO, X = $NHCOCH_3$
V, R = H, X = NH_2
VI, R = H, X = $NHCOCH_3$
IX, R = H, X = $N(CH_3)_2.HCl$
X, R = H, X = $N(CH_3)_2$
XI, R = H, X = $\overset{(+)}{N}(CH_3)_3J^-$



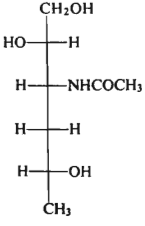
VII, R = H
VIII, R = CH_3SO_2



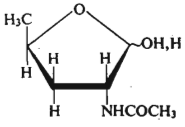
XII



XV + *XVI*



XIII



XIV

After the addition of deuteriated acetic acid signals of the OH and NH-group protons disappeared from the spectrum, while the signals of the anomeric proton H_1 changed to a doublet at 5·30 p.p.m. ($J_{1,2} = 4·5$) and a singlet at 5·15 p.p.m. ($J_{1,2} \neq 0$). The ratio of both anomers changed to approximately 1 : 1.

As substance *XIV* can arise by this reaction sequence only from 3-acetamido derivative (but not from 2-acetamido derivative), and as the starting epoxide *I* has the *lyxo* configuration, the configuration of the derivative *VI* may be considered as proved, and hence also of derivatives *II* – *V*. Hydrochloride *IX* was also obtained from derivative *V*. This proved that also in the reaction of anhydro derivative *I* with dimethylamine the epoxide ring is broken down in position 3.

The syrupy derivative *XII* which formed very easily* on hydrolysis of derivative *VI*, gave on acetylation with acetic anhydride in pyridine a mixture of both anomers of 1,2-di-O-acetyl-3-acetamido-3,4,6-trideoxy-D-*arabino*-hexopyranose from which we isolated by crystallisation the pure α-anomer *XV* and the β-anomer *XVI*. The configuration at $C_{(1)}$ follows on the basis of Hudson's rule[8] from the optical rotations of compounds *XV* or *XVI*. In the NMR spectrum. of compound *XV* (in deuteriochloroform) characteristic singlets at 2·14 p.p.m. and 2·10 p.p.m. due to the O-acetyl groups were present, further a singlet at 1·99 p.p.m. due to one N-acetyl group, a doublet at 1·24 p.p.m. ($J = 6·4$) corresponding to the secondary methyl group at $C_{(5)}$. On addition of deuterioacetic acid the proton of the NH-group was identified which formed a broad doublet at 6·28 p.p.m. ($J = 8·0$). Simultaneously the singlet due to the N-acetyl group was shifted downfield and the multiplet in the 4·20 – 4·40 p.p.m. region was simplified. A complete assignment of the protons was carried out by the double resonance method: proton H_5 gave a multiplet at 4·09 p.p.m. ($J_{5,6} = 6·4$, $J_{5,4} = 3·8$, $J_{5,4} = 10·0$) interacting with two protons H_4 which formed a complex multiplet in the 1·70 – 2·0 p.p.m. region (relative intensity 2 H). The proton H_3 gave a quartet at 4·30 p.p.m. ($J_{2,3} = 3·5$, $J_{3,4} = 4·5$) interacting with the proton H_2 which gave a quartet at 4·67 p.p.m. ($J_{1,2} = 2·0$, $J_{2,3} = 3·5$, and $J_{2,4} \neq 0$). The anomeric proton H_1 gave a broad signal at 6·06 p.p.m. ($J_{1,2} = 2·0$, and $J_{1,3} < 1·0$). The values of all vicinal interactions of protons H_1 to H_5, which were found, prove the structure of *XV* and indicate that substance *XV* probably occurs in the *C1* conformation. The chemical shifts of the acetyl groups methyl protons[9] are also in agreement with this conformation and the configuration of the pyranose ring. Substance *XVI* displayed in its NMR spectrum singlets of two O-acetyl groups (2·11 p.p.m.) and of one N-acetyl group (1·96 p.p.m.), and a doublet of the secondary methyl 1·34 p.p.m.; ($J = 6·6$). Further, multiplets of proton H_5 (4·11 p.p.m.; $J_{5,6} = 6·6$, $J_{5,4} = 2·0$, and $J_{5,4} = 10·0$), two protons H_4 in the 1·50 – 2·0 p.p.m. region, a multiplet of proton H_3 (4·44 p.p.m.; $J_{3,2} = 6·1$, $J_{3,4} = 4·6$, and $J_{3,4} = 6·0$), a quartet of proton H_2

* Hydrolysis of the epimeric derivative *VII* does not take place under the same conditions, but after a prolongation of the reaction time a complex mixture of products is formed.

(4·93 p.p.m.; $J_{1,2} = 2·5$, and $J_{2,3} = 6·1$), and a doublet of the anomeric proton H_1 (6·03 p.p.m.; $J_{1,2} = 2·5$, and $J_{1,3} < 1·0$) were also present in the spectrum. The exchangeable proton NH gave a broad signal at 6·18 p.p.m. coupled with the multiplet of proton H_3. The signal of proton H_2 is shifted downfield (for approx. 0·26 p.p.m.) with respect to the same signal in substance *XV*, which in agreement with the literature data[10] indicates that the O-acetyl group on the neighbouring centre has a changed orientation. The magnitude of the coupling constant $J_{1,2}$ (ref.[11]) is also in agreement with the *trans*-arrangement of substituents on the first two carbon atoms of the pyranose skeleton.

From the above results it is evident that the epoxide ring of the anhydro derivative *I* is cleaved both with ammonia and with dimethylamine exclusively in position 3. Such a course of the cleavage is in full agreement with present views on the stereochemistry of the epoxide ring opening in anhydro sugars. The preferred semichair conformation of anhydro derivative *I* with an equatorial methyl group and a semiaxial methoxy group (anomeric effect[12]) requires according to the Fürst–Plattner rule[13] an attack of the nucleophilic particle on the $C_{(3)}$ carbon atom; the inductive effect of the hemi-acetal group on the $C_{(1)}$ carbon atom, which is pronounced in asymmetrically substituted epoxy derivatives[14], has a similar effect.

EXPERIMENTAL

Melting points were determined on a Kofler block and they are not corrected. Mixture melting points were determined in capillaries. Optical rotations were measured with an Opton polarimeter at 21°C. The solvents were evaporated on a rotatory evaporator at 45°C and at reduced pressure (water pump). The analytical samples were dried at room temperature and 0·1 Torr for 8—10 hours. Thin-layer chromatography was carried out on silica gel G (Merck) on glass plates 75 × 25 mm. For detection chromatograms were sprayed with a 15% solution of cerium sulfate in 10% sulfuric acid and heated at approx. 100°C. For preparative chromatography silica gel of Lachema (40—100 μ) was employed. For deionisation Dowex 50 X 8 and Amberlite IRA 400 were used. Light petroleum, b.p. 45—60°C, was used for crystallisation. The NMR spectra were measured on a Varian HA-100 spectrometer, taking tetramethylsilane as the internal standard.

Amonolysis of Anhydro Derivative *I*

Procedure A: A solution of 1·014 mg (7·05 mmol) of anhydro derivative *I* in 20 ml of methanol and 25 ml of liquid ammonia was heated in stainless steel autoclave at 100°C for 30 hours. The reaction mixture was evaporated at 35°C and the remaining syrup was dried in vacuum (oil pump). The dry residue was dissolved in 15 ml of water and the aqueous solution was neutralised with 0·2M oxalic acid (Tashiro indicator). Consumption 13·7 ml. The neutral solution was filtered after decolorization with a small amount of charcoal and the filtrate was evaporated to dryness. From the crystalline residue which was crystallised twice from ethanol–ether oxalate *II* was obtained. Yield 874 mg, *i.e.* 60·2%, m.p. 197—199°C (decomp.); $[\alpha]_D$ +65·5 (*c* 1·0, water). For $C_{16}H_{32}\cdot N_2O_{10}$ (412·4) calculated: 46·60% C, 7·82% H, 6·79% N; found: 46·90% C, 7·81% H, 6·93% N. The mother liquors after the crystallisation of the oxalate were combined and evaporated to dryness. According to thin-layer chromatography (in chloroform–ethanol 5 : 1, detection as usual and with an ethanolic Tashiro solution) they contained in addition to oxalate *II* a non-basic substance of R_F approx. 0·8. Therefore the syrupy residue was dissolved in 5 ml of water and the aqueous solution was poured on a 7 ml column of Dowex. This cation exchanger column was washed first with 100 ml of water (elimination of the basic components), and then with dilute

aqueous ammonia (1 : 100). After evaporation of the ammoniacal eluent 137 mg of a basic syrup were obtained which was N-acetylated and mesylated (see the preparation of derivative *III*) to afford 128 mg (6·4%) of mesylate *III*, m.p. 167—169°C (decomp.) and 38 mg of a syrupy fraction which according to thin-layer chromatography (in benzene–ethanol 10 : 1) was a mixture of at least three substances. The latter mixture was not further investigated.

Procedure B: A solution of 1 535 mg (10·6 mmol) of anhydro derivative *I* in 20 ml of methanol and 25 ml of liquid ammonia was heated at 100°C for 30 hours and then evaporated *in vacuo* at 35°C. The dried syrupy residue was dissolved in 20 ml of pyridine and after addition of 6 ml of acetic anhydride the reaction mixture was allowed to stand for 48 hours at room temperature. It was then decomposed with water, diluted with 100 ml of chloroform and gradually extracted with 15% sulfuric acid, water, 5% sodium hydrogen carbonate solution, and again with water. The chloroform solution was dried over sodium sulfate and evaporated to dryness. The crystalline residue gave after triple crystallisation from light petroleum 1 382 mg (53·5%) of acetate *IV*, m.p. 71—73°C, $[\alpha]_D$ +14·2° (*c* 2·1, chloroform). For $C_{11}H_{19}NO_5$ (245·3) calculated: 53·86% C, 7·81% H, 5·71% N; found: 54·09% C, 7·92% H, 5·71% N. The mother liquors were combined and evaporated to dryness. The residue was chromatographed on a silica gel column (40 g). Elution with benzene gave 132 mg of a viscous liquid which according to thin-layer chromatography (in benzene–ethanol 10 : 1) was a mixture of two components of very similar R_F values; according to elemental analysis it did not contain nitrogen. Elution of the column with benzene–ethanol 100 : 1 215 mg (8·2%) of peracetyl derivative *IV* were obtained, m.p. 67—73°C. After crystallisation from light petroleum, m.p. 71—73°C.

Methyl-3-acetamido-3,4,6-trideoxy-α-D-*arabino*-hexopyranoside (*VI*)

To a solution of 1·25 g of derivative *IV* in 25 ml of methanol a catalytic amount of sodium was added and the reaction mixture was allowed to stand overnight at room temperature. It was then shaken with a small amount of cation exchanger, filtered, and evaporated to dryness. The syrupy derivative *VI* was dried to constant weight at 40°C and 0·1 Torr pressure; its optical rotation was $[\alpha]_D = +48{\cdot}4 \pm 1{\cdot}5°$ (*c* 1·2, water). The yield was quantitative. For $C_9H_{17}NO_4$ (203·2) calculated: 53·20% C, 8·43% H, 6·89% N; found: 52·95% C, 8·73% H, 6·74% N. Upon storage for several months compound *VI* crystallized, m. p. 89—91°C (ethyl acetate–light petroleum).

Methyl-3-acetamido-3,4,6-trideoxy-2-O-methanesulfonyl-α-D-*arabino*-hexopyranoside (*III*)

Methanesulfonyl chloride (0·4 ml) was added at −70°C to a mixture of 194 mg (0·95 mmol) of derivative *VI* and 5 ml of pyridine and the reaction mixture was allowed to stand at −15°C overnight. It was then decomposed with ice, diluted with 25 ml of chloroform, an the chloroform solution was extracted gradually with 15% sulfuric acid, water, 5% sodium bicarbonate solution, and again with water. The chloroform extract was dried over sodium sulfate, filtered and evaporated to dryness. From 234 mg of the residue 180 mg of derivative *III* were obtained on crystallisation from ethanol–light petroleum; m.p. 168—170°C, $[\alpha]_D$ +27·5 (*c* 1·1, chloroform). The mother liquors were purified chromatographically on a silica gel column (10 g, eluent benzene–ethanol (150 : 1), yielding additional 31 mg of derivative *III* (total yield 79%). For $C_{10}H_{19}NO_6S$ (281·3) calculated: 42·70% C, 6·81% H, 4·98% N, 11·40% S; found: 42·88% C, 6·86% H, 4·77% N, 11·47% S.

Methyl-3-acetamido-3,4,6-trideoxy-α-D-*ribo*-hexopyranoside (*VII*)

To a solution of 993 mg (3·53 mmol) of mesyl derivative *III* in 20 ml of 2-methoxyethanol and 2 ml of water 3 g of sodium acetate trihydrate were added and the mixture was refluxed for 6 hours.

After evaporation to dryness the solid residue was chromatographed on a silica gel column (15 g) using benzene–ethanol (from 1 to 5% of ethanol) as eluent; 688 mg (96%) of chromatographically pure derivative *VII* were obtained. The purity was checked in chloroform–ethanol 5 : 1. After recrystallisation from a mixture of ethyl acetate and light petroleum the m.p. was 122—123·5°C, $[\alpha]_D$ +41·0 (*c* 1·0, chloroform). For $C_9H_{17}NO_4$ (203·2) calculated: 53·20% C, 8·43% H, 6·89% N; found: 53·15% C, 8·42% H, 6·79% N.

Methyl-3-acetamido-3,4,6-trideoxy-2-O-methanesulfonyl-α-D-*ribo*-hexopyranoside (*VIII*)

To a mixture of 120 mg (0·59 mmol) of derivative *VII* and 4 ml of pyridine 0·3 ml of methanesulfonyl chloride were added at —70°C. This reaction mixture was allowed to stand at —15°C for 24 hours and then worked up in the same manner as described for derivative *III*. Crystallisation from a mixture of ethyl acetate and light petroleum gave 123 mg (75%) of derivative *VIII*, m.p. 126—128°C, $[\alpha]_D$ +44·4 (*c* 1·0, chloroform). For $C_{10}H_{19}NO_6S$ (281·3) calculated: 42·70% C, 6·81% H, 4·98% N, 11·40% S; found: 42·46% C, 6·90% H, 5·28% N, 11·42% S.

Methyl-3,4,6-trideoxy-3-dimethylamino-α-D-*arabino*-hexopyranoside hydrochloride (*IX*)

From anhydro derivative I: A solution of anhydro derivative *I* (1·08 g; 7·5 mmol) in methanol (10 ml) and anhydrous dimethylamine (20 ml) was heated at 100°C for 30 hours. The reaction mixture was evaporated to dryness and the basic syrupy residue was dried *in vacuo*. The dried residue was dissolved in 15 ml of water and the aqueous solution was titrated with 0·97M-HCl (Tashiro as indicator). The consumption of the acid corresponded to a 78% conversion. The neutral solution was filtered with charcoal and evaporated to dryness. The crystalline residue was recrystallised from a mixture of ethanol and ether giving 1·234 g (73·5%) of derivative *IX*, m.p. 169—170°C (decomp.), $[\alpha]_D$ +42·0 (*c* 0·8, water). From another experiment the same derivative *IX*, m.p. 161—163°C, was obtained, having the same optical rotation. Its melting point increased after three months standing to 169—170°C. For $C_9H_{20}ClNO_3$ (225·7) calculated: 47·90% C, 8·94% H, 6·21% N; found: 47·98% C, 8·80% H, 6·08% N.

From amino derivative V: A solution of oxalate *II* (446 mg) (corresponding to 2·17 mmol of derivative *V*) in 5 ml of water was poured onto a 5 ml column of anion exchange resin and the column was eluted with water. After evaporation of the eluent a basic syrup (349 mg) was obtained (derivative *V*). To this material 3 ml of 38% aqueous formaldehyde and 3 ml of 96% formic acid were added. The reaction mixture was heated at 120°C for 3 hours, then evaporated to dryness, and, eventually, evaporated twice more with toluene. The syrupy residue was dissolved after two-hours drying *in vacuo* in 9 ml of 1M-NaOH and this solution was extracted with fifteen 15 ml portions of chloroform. The combined chloroform extracts were dried over magnesium sulfate and evaporated to dryness. The residue was dissolved in 10 ml of water and titrated with 0·97M-HCl (Tashiro as indicator). The consumption was 1·3 ml. The neutral solution was filtered with charcoal and evaporated to dryness. A syrup was obtained, weighing 319 mg, which after seeding with derivative *IX* of m.p. 161—163°C crystallised. After recrystallisation from ethanol–ether the yield was 254 mg (52%) of derivative *IX*, m.p. 161—163°C, $[\alpha]_D$ +41·3 (*c* 1·0, water). The IR spectra (in Nujol) of the products obtained by both procedures (derivative *IX*) were identical. Recrystallisation of derivative *IX* (m.p. 161—163°C) from ethanol–ether and seeding with the derivative melting at 169—170°C gave the higher melting modification.

Methyl-3,4,6-trideoxy-3-dimethylamino-α-D-*arabino*-hexopyranoside methiodide (*XI*)

A solution of 225 mg (1 mmol) of hydrochloride *IX* in 5 ml of water was poured onto a column (4 ml) of the anion exchanger which was then eluted with water. The eluate was evaporated and

the residue, a syrupy base *X*, weighed 185 mg. A solution of 171 mg of this base *X* in 4 ml of ethanol was mixed with 2 ml of methyl iodide and the reaction mixture was allowed to stand at room temperature overnight. It was then evaporated to dryness and the residue was crystallised from a mixture of ethanol and ether. Derivative *XI* was obtained in 78·5% yield (235 mg), m.p. 142 to 143°C, $[\alpha]_D$ +27·9 (*c* 1·0, water). For $C_{10}H_{22}INO_3$ (331·2) calculated: 36·27% C, 6·70% H, 38·32% I, 4·23% N; found: 36·59% C, 6·89% H, 38·71% I, 4·36% N.

1,2-Di-O-acetyl-3-acetamido-3,4,6-trideoxy-α-D-(*XV*) and β-D-hexopyranose (*XVI*)

A solution of 760 mg (3·75 mmol) of acetamido derivative *VI* in a mixture of 10 ml water and 10 ml of acetic acid was refluxed and the hydrolysis course was followed by thin-layer chromatography with chloroform–ethanol 5 : 1. After 30 minutes reaction time the mixture contained an appreciable amount of derivative *XII*, while after 2·5 hours the reaction mixture contained only traces of the starting material *VI*. The reaction mixture was evaporated to dryness and the syrupy residue was purified chromatographically on a 10 g column of silica gel. Chloroform–ethanol mixture (100 : 3) eluted 44 mg (5·8%) of the unreacted starting material and 45 mg of a mixture of compounds *VI*, *XII*, and two additional non-identified products. Elution with chloroform–ethanol (20 : 1) gave 557 mg (80%) of chromatographically pure derivative *XII*.

To a solution of derivative *XII* (302 mg) in 10 ml of pyridine 2 ml of acetic anhydride were added and the reaction mixture was allowed to stand at room temperature overnight. It was then decomposed with a small amount of water, evaporated to half its volume, and diluted with 30 ml of chloroform. The chloroform solution was extracted with 15% sulfuric acid, water, 5% sodium hydrogen carbonate solution, and again with water. It was then dried over magnesium sulfate and evaporated to dryness. The residual syrup (331 mg) was dried after which it partly crystallised. After repeated crystallisation of this residue from ethanol–ether–light petroleum mixture 108 mg of derivative *XV* were obtained, m.p. 141·5–143·5°C, $[\alpha]_D$ +42·5° (*c* 0·8, chloroform). The mother liquors after the crystallisation of derivative *XV*, melting at 141·5–143·5°C, gave after slow evaporation in air crystals, m.p. 131–132°C, $[\alpha]_D$ +42·5° (*c* 0·8, chloroform); this melting point did not increase on further crystallisation from the ethanol–ether–light petroleum mixture. The IR spectra of the compound of m.p. 131–132°C and 141·4–143·5°C (in chloroform) were identical, that means the compound *XV* crystallises in two modifications. In one experiment we isolated the lower melting modification only. For $C_{12}H_{19}NO_6$ (273·3) calculated: 52·74% C, 7·00% H, 5·13% N; found: 52·94% C, 7·20% H, 5·31% N.

The mother liquors after the crystallisation and filtration off of the compound melting at 141·5–143·5°C were crystallised systematically first from ethanol–ether–light petroleum mixture, then from ethyl acetate–light petroleum mixture. In addition to derivative *XV* (in the form of the lower melting modification, the total yield of substance *XV* in both modifications was 143 mg) 60 mg of derivative *XVI* were obtained, m.p. 153–154·5°C, $[\alpha]_D$ −34·3° (*c* 0·8, chloroform). All mother liquors (which contained according to thin-layer chromatography on silica gel in benzene–ethanol 10 : 1 a single substance (were combined, evaporated, and dried *in vacuo*. According to the optical rotation value ($[\alpha]_D = +6·5$, chloroform) these mother liquors contained both anomers, *XV* and *XVI*, in a 1 : 1 ratio.

2-Acetamido-2,3,5-trideoxy-D-*erythro*-pentofuranose (*XIV*)

Glycoside *VI* (1·1 g, 5·42 mmol) was hydrolysed to acetamidohexose *XII* by the same procedure as shown above, but derivative *XII* was not purified chromatographically but only by filtration of its aqueous solution after the addition of charcoal. The derivative *XII* thus obtained was dissolved in 10 ml of water and to this solution 300 mg of sodium borohydride was added

in several portions and the reaction mixture was allowed to stand at room temperature for 5 hours. After this, cation exchange resin was added carefully to the stirred mixture and this was then filtered and the exchanger washed with water. The combined filtrates were evaporated to dryness and the residue was evaporated to dryness with three 50 ml portions of methanol. The residual syrupy derivative *XIII* (729 mg, 70%) was dissolved in 15 ml of water and sodium periodate (900 mg) was added to it at 10°C under stirring. The reaction mixture was allowed to stand at 10°C for one hour and at room temperature for another hour. After freeze-drying the residue was transferred onto a silica gel column (15 g). Elution with chloroform–methanol 100 : 1 and 100 : 3 gave 313 mg (1·97 mmol, 52%) of chromatographically pure derivative *XIV*. For analysis the substance *XIV* was crystallised from a mixture of ethanol, ether, and light petroleum, m. p. 109–112°C; $[\alpha]_D$ +41·4 (*c* 0·9, water). For $C_7H_{13}NO_3$ (159·2) calculated: 52·81% C, 8·23% H, 8·80% N; found: 53·05% C, 8·40% H, 8·74% N.

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