PREPARATION OF PARTIALLY ACYLATED DERIVATIVES OF METHYL 3-ACETAMIDO-3,6-DIDEOXY-β-D-GLUCO- AND β-D-MANNOPYRANOSIDE*

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The authors describe the preparation of methyl 3-acetamido-3,6-dideoxy-β-D-glucopyranoside (*XIII*) and its 4-O-benzoyl-(*XII*), 2-O-acetyl-4-O-benzoyl-(*XIV*), 2-O-methanesulfonyl-4-O-benzoyl-(*XV*), 2-O-methanesulfonyl-(*XVI*), and 2-O-methanesulfonyl-4-O-acetyl derivative (*XVII*), and further the preparation of methyl 3-acetamido-3,6-dideoxy-β-D-mannopyranoside (*XX*) and its 4-O-benzoyl-(*XVIII*) and 2-O-acetyl-4-O-benzoyl derivative (*XIX*). Derivatives with D-*gluco* configuration were obtained from methyl 4,6-O-benzylidene-3-chloro-3-deoxy-β-D-allopyranoside (*I*) which was converted to methyl 4-O-benzoyl-3-chloro-3,6-dideoxy-β-D-allopyranoside (*III*) under the effect of N-bromosuccinimide and hydrogenation; after azidolysis, reduction of the azido group and N-acetylation, compound *III* afforded compound *XII* from which other derivatives were obtained. The key reaction for the preparation of derivatives with D-*manno* configuration was the solvolysis of mesyl derivative *XV*, or *XVII*, carried out with sodium acetate in aqueous 2-methoxyethanol.

In the preceding paper[1] we observed that on condensation of (2*R*,4*R*)-2-methoxy--4-methyl-3-oxapentane-1,5-dial with nitromethane a mixture of methyl 3,6-dideoxy-3-nitro-β-D-hexopyranosides is formed; from this mixture we obtained on hydrogenation under pressure and a relatively difficult separation methyl 3-amino--3,6-dideoxy-β-D-hexopyranosides of *gluco*, *galacto*, *manno*, *talo*, and *ido* configurations in pure state. From amino sugars we prepared corresponding N-acetyl derivatives which we needed as starting substances for the continuation[2] of our study of partial acylation of sugars[3–8]. In this paper we describe an alternative preparation of methyl 3-acetamido-3,6-dideoxy-β-D-gluco- (*XIII*) and -mannopyranoside (*XX*) and some of their mono-O-acylated derivatives; the comparison of the substances mentioned with the products of nitromethane condensation[1] and with those of partial acylation[2] of methyl 3-acetamido-3,6-dideoxy-β-D-glucopyranoside and methyl 3-acetamido-3,6-dideoxy-β-D-mannopyranoside enabled us to confirm the configuration of two nitro sugars formed during the nitromethane condensation on one

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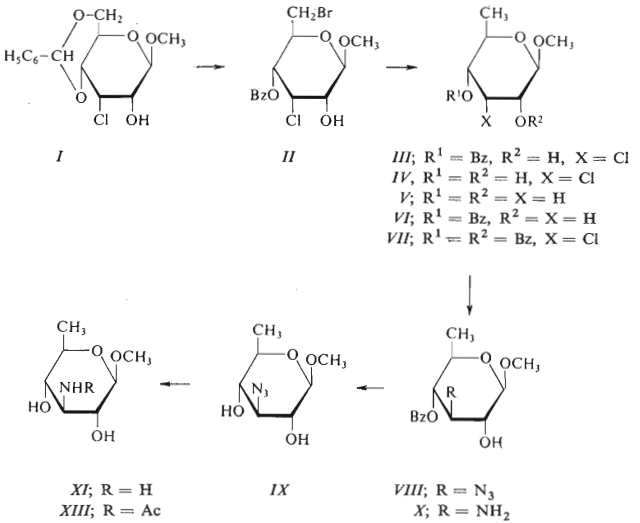
hand, and to determine the position of the O-acyl groups in the product of partial acylation on the other.



I *II* *III*; R^1 = Bz, R^2 = H, X = Cl
IV, $R^1 = R^2$ = H, X = Cl
V; $R^1 = R^2$ = X = H
VI; R^1 = Bz, R^2 = X = H
VII; $R^1 = R^2$ = Bz, X = Cl

XI; R = H
XIII; R = Ac

IX

VIII; $R = N_3$
X; $R = NH_2$

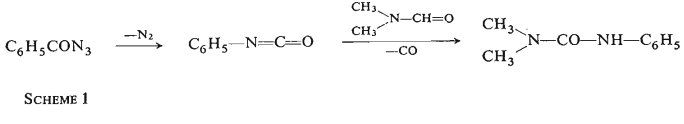
As starting material we chose methyl 4,6-O-benzylidene-3-chloro-3-deoxy-β-D-allopyranoside[9–11] (*I*) from which we prepared crystalline methyl 4-O-benzoyl-6-bromo-3-chloro-3,6-dideoxy-β-D-allopyranoside (*II*) by the method of Hanessian and Plessas[11]. In the paper[11] mentioned the syrupy compound *II* was not characterised; after its benzoylation and catalytic hydrogenation, the syrupy derivative *VII* was obtained for which $[\alpha]_D$ −43° (chloroform) is given. The syrupy derivative *VII* prepared by us has optical rotation $[\alpha]_D$ −10° (chloroform). Hydrogenation on Raney nickel of substance *II* gave methyl 4-O-benzoyl-3-chloro-3,6-dideoxy-β-D-allopyranoside (*III*) as the main product, in addition to a small amount of methyl 3-chloro-3,6-dideoxy-β-D-aliopyranoside (*IV*), methyl 3,6-dideoxy-β-D-*ribo*-hexopyranoside[12] (*V*) and methyl 4-O-benzoyl-3,6-dideoxy-β-D-*ribo*-hexopyranoside (*VI*). Catalytic debenzoylation of derivative *III* or *VI* gave compound *IV* or *V*, respectively. On benzoylation of compound *III* or *IV*, methyl 2,4-di-O-benzoyl-3-chloro-3,6-dideoxy-β-D-allopyranoside (*VII*) was prepared. Reaction of substance *III* with sodium

azide in dimethylformamide gave methyl 3-azido-4-O-benzoyl-3,6-dideoxy-β-D-glucopyranoside (*VIII*) in high yield; N,N-dimethyl-N'-phenylurea was isolated as a by-product.

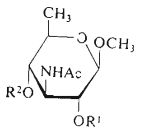
The phenyl substituent on the nitrogen atom in N,N-dimethyl-N'-phenylurea evidently originates from the benzoyl group of the starting compound *III*, because the product of azidolysis, *i.e.* compound *VIII*, does not afford N,N-dimethyl-N'-phenylurea under the same conditions. This urea derivative is not formed on heating of ethyl benzoate, sodium benzoate or benzoic acid with sodium azide in dimethylformamide, but it is formed from benzoyl chloride, sodium azide, and dimethylformamide in almost quantitative yield. Therefore it seems probable that in analogy to the azidolysis of substance *I* (references[10,13]) a partial elimination of hydrogen chloride also takes place under formation of methyl 4-O-benzoyl-3,6-dideoxy-β-D-*erythro*-hex-3-enopyranoside (Scheme 1); on reaction with sodium azide and in the presence of hydrogen chloride, the reactive enol benzoate group affords benzoic acid azide, while the sugar residue decomposes. Benzoic acid azide can be rearranged to phenyl isocyanate which on reaction with dimethylformamide would give N,N-dimethyl-N'-phenylurea (this compound cannot be detected by mineralisation with sulfuric acid and it sublimates already during the working up of the reaction mixture).

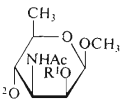
From azido derivative *VIII* we obtained on catalytic debenzoylation methyl 3-azido-3,6-dideoxy-β-D-glucopyranoside (*IX*). By hydrogenation on platinum of azido derivative *VIII* or *IX* we obtained methyl 3-amino-4-O-benzoyl-3,6-dideoxy-β-D--glucopyranoside (*X*), or methyl 3-amino-3,6-dideoxy-β-D-glucopyranoside[1] (*XI*), respectively, from which corresponding N-acetyl derivatives *XII* or *XIII* (ref.[1]) resp. were synthetized by reaction with acetic anhydride in methanol.

For the preparation of methyl 3-acetamido-4-O-benzoyl-3,6-dideoxy-β-D-glucopyranoside (*XII*) or compound *XIII* from compound *I*, also alternative syntheses could probably have been chosen in which methyl 3-azido-4,6-O-benzylidene-3-deoxy-β-D-glucopyranoside[10,11,13] would first have been prepared by reaction of *I* with sodium azide in dimethylformamide, which would then be submitted to a reaction with N-bromosuccinimide and subsequent dehalogenation either directly or after conversion to methyl 3-acetamido-3,6-dideoxy-4,6-O-benzylidene-β-D-glucopyrano-



SCHEME 1





XII; $R^1 = H$, $R^2 = Bz$
XIV; $R^1 = Ac$, $R^2 = Bz$
XV; $R^1 = Ms$, $R^2 = Bz$
XVI; $R^1 = Ms$, $R^2 = H$
XVII; $R^1 = Ms$, $R^2 = Ac$

XVIII; $R^1 = H$, $R^2 = Bz$
XIX; $R^1 = Ac$, $R^2 = Bz$
XX; $R^1 = R^2 = H$

Ac = CH_3CO, Ms = CH_3SO_2, Bz = C_6H_5CO

side[11]. However, the fact that the substitution of the chlorine atom for the azide group in substance *III* takes place in high yield makes our procedure preferable, while in the case of compound *I* the same reaction takes place with a lower yield and the isolation of the product from the reaction mixture is more tedious[10,11,13].

N-Acetyl derivative *XII* containing a benzoyl group in the position 4 was converted under the effect of acetic anhydride or methanesulfonyl chloride in pyridine to methyl 3-acetamido-2-O-acetyl-4-O-benzoyl-3,6-dideoxy-β-D-glucopyranoside (*XIV*) or methyl 3-acetamido-4-O-benzoyl-3,6-dideoxy-2-O-methanesulfonyl-β-D-glucopyranoside (*XV*), respectively. The latter was debenzoylated catalytically to methyl 3-acetamido-3,6-dideoxy-2-O-methanesulfonyl-β-D-glucopyranoside (*XVI*) which on acetylation with acetic anhydride in pyridine gave methyl 3-acetamido-4-O-acetyl-3,6-dideoxy-2-O-methanesulfonyl-β-D-glucopyranoside (*XVII*). Derivatives *XV*, *XVI* and *XVII* were used for the identification of the product of partial acylation[2] of acetamidoglucoside *XIII*.

Reaction of 2-O-mesyl derivative *XV* with sodium acetate in aqueous 2-methoxyethanol gave methyl 3-acetamido-4-O-benzoyl-3,6-dideoxy-β-D-mannopyranoside (*XVIII*), while the same reaction with 2-O-mesyl derivative *XVII* led to unsubstituted acetamidomannoside *XX*. Derivative *XX* was also obtained on debenzoylation of its 4-O-benzoyl derivative *XVIII*. Substance *XIX* which we prepared on acetylation of *XVIII* served for the identification of the products of partial acylation[2] of acetamidomannoside *XX* which by itself coincided with one of the acetamido derivatives described in our paper on nitromethane condensation[1].

EXPERIMENTAL

The melting points were determined on a Kofler block and they are not corrected. Optical rotation was measured on an Opton instrument at 20°C and 0·5—1·0 concentration. The infrared spectra were taken on a Perkin Elmer 325 apparatus, the mass spectra were measured on an LKB

9000 spectrometer. Samples for analysis were dried at 20—50°C and 0·05—0·1 Torr. Column chromatography was carried out on silica gel from Lachema (Brno), 70—200 μm particle size, while thin-layer chromatography was carried out on silica gel G according to Stahl (Merck, Darmstadt), 10—40 μm, plate size 25×75 mm, 0·2—0·3 mm thickness. Detection was carried out by spraying the plates with a 1% solution of cerium(IV) sulfate in 10% sulfuric acid and heating. The solvents were evaporated on a rotatory evaporator in a vacuum of a water pump at a temperature not exceeding 50°C. Light petroleum for crystallisation had b.p. 45—60°C. The usual method of debenzoylation or deacetylation means: the compound is dissolved in a 50-fold amount (by volume) of methanol, a drop of 1M sodium methoxide is added, and when the reaction (followed by thin layer chromatography) is over, the mixture is shaken with Amberlite IR 120 (H^+), filtered, and evaporated to dryness.

Methyl 4-O-Benzoyl-6-bromo-3-chloro-3,6-dideoxy-β-D-allopyranoside (*II*)

A mixture of 5·3 g of substance *I* (obtained according to literature[9-11], with the difference that after the elimination of the chlorosulfo group the extraction with benzene was substituted by filtration of the mixture through a layer of silica gel in benzene–acetone 9 : 1, m.p. 129—131°C, $[\alpha]_D$ —23° (chloroform), or 112—114°C, $[\alpha]_D$ —23° (chloroform) for the second, as yet undescribed modification), 7·2 g of barium carbonate, 3·6 g of N-bromosuccinimide, and 180 ml of tetrachloromethane was refluxed for 2 hours under exclusion of air humidity. The originally yellow mixture decolorized. It was filtered, the residue on the filter was washed with three 40 ml portions of tetrachloromethane and the combined filtrates were evaporated. The residue was dissolved in 100 ml chloroform, the chloroform solution extracted twice with 30 ml of water, the combined aqueous extracts were reextracted with chloroform and the organic layer with water. The combined chloroform fractions were dried and evaporated to a syrup (6·5 g, 97%) which crystallised from a mixture of ether and light petroleum. After two crystallisations from the same mixture of solvents 5·7 g (85%) of compound *II* (needles) were obtained, m.p. 102—104°C, $[\alpha]_D$ +3° (chloroform). For $C_{14}H_{16}BrClO_5$ (379·6) calculated: 44·29% C, 4·25% H; found: 44·57% C, 4·48% H.

Methyl 4-O-Benzoyl-3-chloro-3,6-dideoxy-β-D-allopyranoside (*III*)

To a solution of 7 g of substance *II* in 120 ml of methanol, 1·89 g of diethylamine and 15 ml of Raney nickel were added and the mixture was stirred under hydrogen at room temperature and normal pressure for 2 hours. The hydrogen consumption was 430 ml. After filtration and washing of the catalyst with methanol, the combined filtrates were evaporated. The residue was dissolved in chloroform and extracted with water. From the chloroform fraction 5·38 g of a syrup were obtained after drying and evaporation, which was used in some experiments without further purification for the preparation of substance *VIII*. On chromatography of this syrup on a column of 250 g of silica gel with benzene–acetone 100 : 6, substance *III* (4·0 g; 72%) was obtained first. It was crystallised from ethyl acetate–light petroleum, m.p. 116—117°C, $[\alpha]_D$ +13° (chloroform). For $C_{14}H_{17}ClO_5$ (300·7) calculated: 56·00% C, 5·72% H; found: 56·21% C, 5·82% H. In subsequent chromatographic fractions, 50 mg (1%) of a syrupy substance *VI* were eluted; its debenzoylation gave a syrupy residue which crystallized after repeated extraction with light petroleum and distillation at 0·1 Torr and 110°C (bath temperature). The substance *V* obtained was recrystallised from a mixture of ether and light petroleum, m.p. 60—65°C, mass spectrum (*m/e*): 162 (M^+), M — 31. Literature[12] gives for the compound *V* m.p. 63—65°C. The last chromatographic fractions gave 100 mg of a syrup representing a mixture of compounds *V* and *IV*. Rechromatography of this mixture on 10 g of silica gel in benzene–ethanol 100 : 1 gave pure substances *V* and *IV* in a 3 : 1 ratio.

Methyl 3-Chloro-3,6-dideoxy-β-D-allopyranoside (*IV*)

Debenzoylation of 115 mg of substance *III* in the usual manner gave syrupy derivative *IV* which crystallised out after several weeks standing. After two crystallisations from a mixture of ether and light petroleum, 70 mg (93%) of compound *IV* were obtained, m.p. 76—78°C. For analysis, the compound *IV* was crystallised twice more from the same solvent mixture and sublimated at 45°C and 0·01 Torr, m.p. 78·5—79·5°C, $[\alpha]_D$ −56° (methanol). For $C_7H_{13}ClO_4$ (196·6) calculated: 42·76% C, 6·67% H; found: 43·00% C, 6·85% H.

Methyl 2,4-di-O-Benzoyl-3-chloro-3,6-dideoxy-β-D-allopyranoside (*VII*)

A mixture of 90 mg of substance *III*, 2 ml of pyridine, and 0·05 ml of benzoyl chloride was allowed to stand at room temperature for 16 hours, then decomposed with water and processed in usual manner, *i.e.* by extraction with chloroform. After filtration of the dried chloroform extract with charcoal, 110 mg of a chromatographically pure syrupy derivative *VII*, $[\alpha]_D$ −10° (chloroform), were obtained. The same substance was also prepared by benzoylation of compound *IV*. For $C_{21}H_{21}ClO_6$ (404·9) calculated: 62·29% C, 5·22% H; found: 62·59% C, 5·51% H.

Methyl 3-Azido-4-O-benzoyl-3,6-dideoxy-β-D-glucopyranoside (*VIII*)

A mixture of 3·2 g of compound *III*, 70 ml of dimethylformamide, and 1·4 g of sodium azide was refluxed under exclusion of air humidity for 45 minutes, when the starting compound *III* (also differing from *VIII* in colour reaction on detection) could no longer be detected on a thin layer chromatogram developed in benzene–acetone 100 : 6. The mixture was evaporated, the residue dried at 60°C and 0·1 Torr and then dissolved in 100 ml of chloroform. The chloroform solution was extracted several times with water and the combined aqueous extracts again with chloroform. The chloroform extracts were combined, dried, filtered with charcoal and evaporated. The syrupy residue (3·58 g) was chromatographed on a column of silica gel (50 g) with benzene–acetone 100 : 5. First, 60 mg of a syrupy substance were eluted, which according to mass spectrum consisted of at least two compounds; this mixture was not further investigated. From subsequent chromatographic fractions, 2·876 g (88%) of azido derivative *VIII* were obtained which crystallised on addition of ether. After several crystallisations from ether–light petroleum, the m.p. of the analytical sample was 119·5—121·5°C, $[\alpha]_D$ −60° (chloroform). For $C_{14}H_{17}N_3O_5$ (307·3) calculated: 54·72% C, 5·58% H, 13·67% N; found: 55·34% C, 5·72% H, 13·86% N; IR spectrum (KBr): 1 740 cm^{-1} (benzoyl), 2 105 cm^{-1} (N_3). From the last chromatographic fractions N,N-dimethyl-N′-phenylurea was obtained in 2—5% yield. After crystallisation from ether–light petroleum its m.p. was 134—135°C (at 118—125°C and 130—132°C the change in crystal modification was observed). Literature[14] gives m.p. 134°C. Mass spectrum (*m/e*): 164 (M^+), 119, 72 (BP), 57, 55, 45, 44, 43; IR spectrum (KBr): 1 645, 1 599, 1 591, 1 525, 1 500, 1 480 cm^{-1}. Heating a mixture of 250 mg of benzoyl chloride, 300 mg of sodium azide, and 2 ml of dimethylformamide, and working up the reaction mixture in the same manner as above gave N,N-dimethyl-N′-phenylurea in an almost quantitative yield.

Methyl 3-Azido-3,6-dideoxy-β-D-glucopyranoside (*IX*)

Debenzoylation of 200 mg of derivative *VIII* in the usual manner gave 120 mg (91%) of compound *IX* which was crystallised from a mixture of ether and light petroleum, m.p. 92—93°C, $[\alpha]_D$ −26° (methanol). For $C_7H_{13}N_3O_4$ (203·2) calculated: 41·38% C, 6·45% H, 20·68% N; found: 41·92% C, 6·55% H, 21·03% N.

Methyl 3-Amino-4-O-benzoyl-3,6-dideoxy-β-D-glucopyranoside (*X*)

A solution of 700 mg of derivative *VIII* in 50 ml of ethanol containing a small amount of PtO_2, was stirred under hydrogen for 2 hours. The hydrogen was occasionally exchanged. The catalyst was filtered off, washed with ethanol and the combined filtrates were evaporated. The syrupy residue (640 mg) was washed with light petroleum (elimination of traces of ethyl benzoate) and introduced onto a small silica gel column; benzene–ethanol mixture (100 : 6) eluted 550 mg (86%) of compound *X*. Even after six crystallisations from ether the hygroscopic substance melted within the 55—70°C interval, $[\alpha]_D$ −14° (chloroform). For $C_{14}H_{19}NO_5$ (281·3) calculated: 59·78% C, 6·81% H, 4·98% N; found: 59·42% C, 7·23% H, 4·55% N.

Methyl 3-Amino-3,6-dideoxy-β-D-glucopyranoside (*XI*)

A solution of 150 mg of azido derivative *IX* in 20 ml of ethanol was stirred under hydrogen in the presence of a catalytic amount of PtO_2 for three hours. The hydrogen was occasionally exchanged. The catalyst was filtered off, washed with ethanol and the filtrate evaporated. The residue (121 mg, 92%) was crystallised from ethanol–benzene–light petroleum, m.p. 193—195°C, $[\alpha]_D$ −55° (water). IR spectrum of compound *XI* was identical with the spectrum of the same substance, described in paper[1]. N-Acetyl derivative *XIII*: it was prepared in the same manner as given in paper[1]; m.p. 247—249°C (in a sealed capillary), $[\alpha]_D$ −43° (water).

Methyl 3-Acetamido-4-O-benzoyl-3,6-dideoxy-β-D-glucopyranoside (*XII*)

A mixture of 315 mg of compound *X*, 8 ml of methanol, and 0·7 ml of acetic anhydride was allowed to stand at room temperature overnight, then evaporated, finally with 10 ml of toluene. Yield 345 mg (96%) of an amorphous, hygroscopic substance *XII*, $[\alpha]_D$ +3° (chloroform). For $C_{16}H_{21}NO_6$ (323·3) calculated: 59·43% C, 6·55% H; found: 59·71% C, 6·68% H.

Methyl 3-Acetamido-2-O-acetyl-4-O-benzoyl-3,6-dideoxy-β-D-glucopyranoside (*XIV*)

A mixture of 50 mg of compound *XII*, 0·5 ml of pyridine, and 0·1 ml of acetic anhydride was allowed to stand at room temperature for 24 hours. After decomposition with water it was mixed with 10 ml of chloroform and the solution washed several times with water. The organic layer was dried over magnesium sulfate and evaporated to give a syrupy residue which was dissolved in benzene with 6% acetone and filtered through a small column of silica gel. Yield 42 mg (75%) of compound *XIV* which was crystallised for analysis from a mixture of ether and light petroleum, m.p. 161—163°C, or 152—155°C (second modification), $[\alpha]_D$ −78° (chloroform). For $C_{18}H_{23}$·NO_7 (365·4) calculated: 59·17% C, 6·34% H, 3·83% N; found: 58·89% C, 6·59% H, 3·90% N.

Methyl 3-Acetamido-4-O-benzoyl-3,6-dideoxy-2-O-methanesulfonyl-β-D-glucopyranoside (*XV*)

To a mixture of 210 mg of compound *XII* and 7 ml of pyridine, 0·25 ml of methanesulfonyl chloride were added at −70°C. After the temperature had risen to room temperature, the mixture was allowed to stand for 2 hours, then decomposed with water and mixed with chloroform. The chloroform solution was washed several times with water, dried over magnesium sulfate and evaporated. The syrupy residue (225 mg, 86%) crystallised out after addition of ether. After three crystallisations from ethanol–ether–light petroleum mixture, needles were obtained melting under decomposition at 176—183°C, $[\alpha]_D$ −62° (chloroform). For $C_{17}H_{23}NO_8S$ (401·4) calculated: 50·87% C, 5·78% H, 3·49% N; found: 50·68% C, 6·00% H, 3·42% N.

Methyl 3-Acetamido-3,6-dideoxy-2-O-methanesulfonyl-β-D-glucopyranoside (*XVI*)

On debenzoylation of 60 mg of compound *XV* in the usual manner, 54 mg of a syrup were obtained which after crystallisation from a mixture of acetone, ether and light petroleum gave 40 mg (89%) of compound *XVI*, m.p. 184–186°C (decomp.), $[\alpha]_D$ −64° (methanol). For $C_{10}H_{19}NO_7S$ (297·3) calculated: 40·40% C, 6·44% H; found: 40·58% C, 6·62% H.

Methyl 3-Acetamido-4-O-acetyl-3,6-dideoxy-2-O-methanesulfonyl-β-D-glucopyranoside (*XVII*)

A mixture of 15 mg of compound *XVI*, 1 ml of pyridine and 0·1 ml of acetic anhydride was allowed to stand at room temperature for 24 hours, then evaporated several times with water and finally with toluene. The residue was crystallised from an acetone–ether mixture, m.p. of compound *XVII* was 179–180·5°C, $[\alpha]_D$ +3° (chloroform). For $C_{12}H_{21}NO_8S$ (339·4) calculated: 42·47% C, 6·24% H, 4·13% N; found: 42·47% C, 6·31% H, 4·28% N.

Methyl 3-Acetamido-4-O-benzoyl-3,6-dideoxy-β-D-mannopyranoside (*XVIII*)

A mixture of 100 mg of substance *XV*, 7 ml of 2-methoxyethanol, 450 mg of sodium acetate trihydrate, and 0·4 ml of water was refluxed for 15 hours, evaporated and the residue introduced onto a silica gel column (10 g). Using benzene–ethanol 10 : 1, 40 mg (50%) of compound *XVIII* were eluted which after repeated crystallisation from ethyl acetate–ether–light petroleum mixture melted in the 97–103°C interval, $[\alpha]_D$ −66° (chloroform). For $C_{16}H_{21}NO_6$ (323·3) calculated 59·43% C, 6·55% H, 4·33% N; found: 59·70% C, 6·80% H, 4·10% N. Further elution gave 5 mg of acetamido derivative *XX*.

Methyl 3-Acetamido-2-O-acetyl-4-O-benzoyl-3,6-dideoxy-β-D-mannopyranoside (*XIX*)

A mixture of substance *XVIII* (11 mg), pyridine (1 ml), and acetic anhydride (0·1 ml) was allowed to stand at room temperature for 24 hours and evaporated to dryness, finally with toluene. The residue was crystallised from acetone–ether–light petroleum to give derivative *XIX*, m.p. 106–108°C, $[\alpha]_D$ −64° (chloroform). For $C_{18}H_{23}NO_7$ (365·4) calculated: 59·17% C, 6·34% H; found: 59·11% C, 6·47% H.

Methyl 3-Acetamido-3,6-dideoxy-β-D-mannopyranoside (*XX*)

A) Debenzoylation of substance *XVIII* (26 mg) in the usual manner gave substance *XX*, which after crystallisation from ethanol–light petroleum (15 mg) had m.p. 238–240°C, $[\alpha]_D$ −117° (water).

B) A mixture of compound *XVII* (25 mg), 2-methoxyethanol (1·5 ml), water (0·1 ml), and sodium acetate trihydrate (0·1 g) was refluxed for 12 hours, evaporated and the residue introduced onto a silica gel column (8 g). Elution with benzene–ethanol 10 : 1 gave 15 mg of compound *XX* which was identical (including the IR spectrum) with the sample prepared under *A*) or in paper[1]. From compound *XX*, di-O-acetyl derivative was prepared in the usual manner, identical with the same derivative described in paper[1].

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