PARTIAL ACYLATION OF METHYL 3-ACETAMIDO-3,6-DIDEOXY-β-D-GLUCOPYRANOSIDE AND METHYL 3-ACETAMIDO-3,6-DIDEOXY-β-D-MANNOPYRANOSIDE*

K. ČAPEK, J. STANĚK JR and J. JARÝ

Laboratory of Monosaccharides,
Prague Institute of Chemical Technology, 166 28 Prague 6

Received November 23rd, 1973

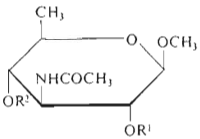
On partial acetylation of methyl 3-acetamido-3,6-dideoxy-β-D-glucopyranoside (*I*) with acetyl chloride or acetic anhydride in pyridine, a mixture of 2,4-di-O-acetyl derivative *III*, 2-O-acetyl derivative *XIII*, and 4-O-acetyl derivative *XV* is formed in which *XIII* prevails over *XV*; acetyl chloride reacts more specifically than acetic anhydride. Partial acetylation of methyl 3-acetamido-3,6-dideoxy-β-D-mannopyranoside (*II*) takes place in a similar manner. Partial mesylation of acetamidoglucoside *I* gives in addition to 2,4-di-O-mesyl derivative *XXI* also, highly specifically, 4-O-mesyl derivative *XI*, while partial mesylation of acetamidomannoside *II* affords predominantly 2-O-mesyl derivative *V* in addition to 2,4-di-O-mesyl derivative *XXII*. On partial deacetylation of di-O-acetyl derivative *III* or *IV* on alkaline alumina, 4-O-acetyl derivative *XV* or *VIII* is formed predominantly. The position of the O-acyl groups in single mono-O-acyl derivatives was determined by PMR spectra and chemical reactions. When approximately one half of an equivalent of the acylating reagent was used for reaction with a mixture of the corresponding 2-O-acyl derivative and 4-O-acyl derivative, the ratios of the rate constants k'_2/k'_4 for the acylation of the two mono-O-acyl derivatives to the common 2,4-di-O-acyl derivative were determined. From the values of k'_2/k'_4 and from the composition of the reaction mixture after partial acylation of compound *I* or *II*, the ratios of the rate constants k_2/k_4, expressing the ratio of the reactivity of the hydroxyl groups in the position 2 and 4 in the acylated diols *I* or *II*, were calculated. An attempt is presented at the comparison of partial acylations of substances *I* and *II* and of their α-anomers.

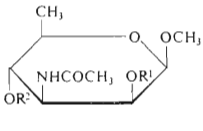
In preceding papers[1-5] we investigated partial acetylation of methyl 3-acetamido-3,6-dideoxy-α-D(L)-hexopyranosides with acetyl chloride and acetic anhydride in pyridine and partial deacetylation of the corresponding 2,4-di-O-acetyl derivatives on alkaline alumina. We found that on acetylation with acetyl chloride 2-O-acetyl derivative was always formed predominantly, while the results of partial acetylation with acetic anhydride depended on the configuration of the acetylated acetamidoglycoside. With some configurational isomers we also carried out partial mesylation with methanesulfonyl chloride in pyridine[1,4,5]. We found that the mesylation takes place similarly as acetylation with acetyl chloride, *i.e.* that 2-O-mesyl derivative is

* Part XXXI in the series Amino Sugars; Part XXX: This Journal *39*, 1479 (1974).

formed predominantly. Partial deacetylation of methyl 3-acetamido-2,4-di-O-acetyl--3,6-dideoxy-α-D(L)-hexopyranosides always gave the 4-O-acetyl derivative as the dominant mono-O-acetyl derivative.

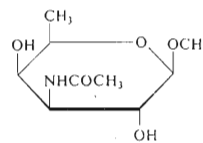
In order to judge to what extent the configuration on the anomeric centre would affect the result of partial acylation or deacetylation we now investigated the partial acylation of methyl 3-acetamido-3,6-dideoxy-β-D-glucopyranoside[6,7] (*I*) and methyl 3-acetamido-3,6-dideoxy-β-D-mannopyranoside[6,7] (*II*) and partial deacetylation of methyl 3-acetamido-2,4-di-O-acetyl-3,6-dideoxy-β-D-glucopyranoside[6] (*III*) or methyl 3-acetamido-2,4-di-O-acetyl-3,6-dideoxy-β-D-mannopyranoside[6] (*IV*). During partial acylation of substance *I* or *II*, a mixture of the corresponding 2,4-di-O-acyl derivative, 2-O-acyl derivative, 4-O-acyl derivative and the starting compounds was always formed. Only in the case of the mesylation of acetamidomannoside *II* we were unable to separate methyl 3-acetamido-3,6-dideoxy-2-O-methanesulfonyl-β-D-manno-pyranoside (*V*) from methyl 3-acetamido-3,6-dideoxy-4-O-methanesulfonyl-β-D-man-nopyranoside (*VI*) chromatographically on silica gel, and, therefore, we determined their relative amounts in the mixture indirectly from the integration curve of the singlets of the acetamido groups in the PMR spectrum, or from the value of optical



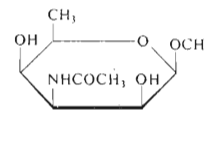


I; $R^1 = R^2 = H$
III; $R^1 = R^2 = CH_3CO$
XI; $R^1 = H$, $R^2 = CH_3SO_2$
XII; $R^1 = CH_3SO_2$, $R^2 = H$
XIII; $R^1 = CH_3CO$, $R^2 = H$
XIV; $R^1 = CH_3CO$, $R^2 = CH_3SO_2$
XV; $R^1 = H$, $R^2 = CH_3CO$
XVI; $R^1 = CH_3SO_2$, $R^2 = CH_3CO$
XXI; $R^1 = R^2 = CH_3SO_2$

II; $R^1 = R^2 = H$
IV; $R^1 = R^2 = CH_3CO$
V; $R^1 = CH_3SO_2$, $R^2 = H$
VI; $R^1 = H$, $R^2 = CH_3SO_2$
VII; $R^1 = CH_3CO$, $R^2 = H$
VIII; $R^1 = H$, $R^2 = CH_3CO$
IX; $R^1 = CH_3CO$, $R^2 = CH_3SO_2$
X; $R^1 = CH_3SO_2$, $R^2 = CH_3CO$
XVII; $R^1 = CH_3CO$, $R^2 = C_6H_5CO$
XVIII; $R^1 = C_6H_5CO$, $R^2 = CH_3CO$
XXII; $R^1 = R^2 = CH_3SO_2$



XIX



XX

rotation of their mixture. The authentic samples necessary for this work were obtained by mesylation of methyl 3-acetamido-2-O-acetyl-3,6-dideoxy-β-D-mannopyranoside (*VII*) or methyl 3-acetamido-4-O-acetyl-3,6-dideoxy-β-D-mannopyranoside (*VIII*) and by alkaline deacetylation of the methyl 3-acetamido-2-O-acetyl-3,6-dideoxy-4-O-methanesulfonyl-β-D-mannopyranoside (*IX*) or methyl 3-acetamido-4-O--acetyl-3,6-dideoxy-2-O-methanesulfonyl-β-D-mannopyranoside (*X*) formed. From Table I it is evident that on acetylation of substances *I* and *II* with both acetylating reagents more of the corresponding 2-O-acetyl derivative was always formed than of the 4-O-acetyl derivative; acetyl chloride was more specific than acetic anhydride. On mesylation of compound *II*, 2-O-mesyl derivative *V* was also formed predominantly, while after the mesylation of compound *I* methyl 3-acetamido-3,6-dideoxy-4-O-methanesulfonyl-β-D-glucopyranoside (*XI*) surprisingly prevailed in the reaction mixture over methyl 3-acetamido-3,6-dideoxy-2-O-methanesulfonyl-β-D-glucopyranoside (*XII*).

The position of the O-acyl group in single mono-O-acyl derivatives was demonstrated both by chemical reactions and by PMR spectroscopy. Thus, on reaction of methanesulfonyl chloride in pyridine with methyl 3-acetamido-2-O-acetyl-3,6-dideoxy-β-D--glucopyranoside (*XIII*), methyl 3-acetamido-2-O-acetyl-3,6-dideoxy-4-O-methanesulfonyl-β-D-glucopyranoside (*XIV*) was prepared which we also obtained by acetylation of compound *XI*. Mesylation of methyl 3-acetamido-4-O-acetyl-3,6-dideoxy--β-D-glucopyranoside (*XV*) gave methyl 3-acetamido-4-O-acetyl-3,6-dideoxy-2-O-methanesulfonyl-β-D-glucopyranoside (*XVI*) which we prepared earlier[7]. By this we proved the position of the O-acyl groups in derivatives *XI*–*XIII* and *XV*. On reaction with benzoyl chloride in pyridine, methyl 3-acetamido-2-O-acetyl-3,6-dideoxy-β-D-mannopyranoside (*VII*) or 4-O-acetyl derivative *VIII* gave methyl 3-acetamido-2-O-acetyl-4-O-benzoyl-3,6-dideoxy-β-D-mannopyranoside (*XVII*) or methyl 3-acetamido-4-O-acetyl-2-O-benzoyl-3,6-dideoxy-β-D-mannopyranoside (*XVIII*), respectively; derivative *XVII* was identical with the same derivative obtained earlier[7] which proves the position of the O-acyl groups in compounds *VII* and *VIII*.

In the PMR spectra of mesylacetyl derivatives *XIV* and *XVI*, or *IX* and *X*, the coupling constants $J_{4,5}$ and $J_{3,4}$ were always higher than 9 Hz, so that the conformation $^4C_1$ may be assigned to the compounds mentioned. In comparison with the PMR spectra[7] of di-O-acetyl derivatives *III* and *IV*, the N-acetyl group signals are shifted by about 0·1 p.p.m. downfield in consequence of the presence of the adjacent methanesulfonyloxy group. Hence, the signal of the N-acetyl group in equatorial position appears in a region assigned to the axial N-acetyl group[8]. A similar effect of the methanesulfonyloxy group on the shift of the vicinal acetoxy group was observed in cyclitols[9]. The shift of the O-acetyl group in the β-position practically does not change when the acetoxy group is substituted for the methanesulfonyloxy group. However, the upfield shift of the α-hydrogen by 0·3–0·5 p.p.m. caused by this exchange is substantial; equally as the downfield shift (by 0·15 p.p.m.) of the doublet

of the $C_{(5)}$-methyl group caused by the substitution of the 4-O-Ac for 4-O-Ms, the above mentioned exchange is decisive for the determination of the position of the methanesulfonyloxy group on the sugar skeleton by PMR spectroscopy.

Similarly as in our preceding work we submitted mono-O-mesyl derivatives containing the methanesulfonyloxy group in *trans*-position to the acetamino group to reaction with sodium acetate in aqueous 2-methoxyethanol. Thus, we obtained from 4-O-methanesulfonylglucoside *XI* methyl 3-acetamido-3,6-dideoxy-β-D-galactopyranoside (*XIX*) which we described recently[6]. Instead of the poorly accessible 4-O-methanesulfonylmannoside (*VI*) we used for solvolysis directly a mixture of compounds *VI* and *V*; 2-O-mesyl derivative *V* did not react under the conditions used, and from 4-O-mesyl derivative *VI* we obtained methyl 3-acetamido-3,6-dideoxy-β-D--talopyranoside (*XX*) which we separated easily from the unreacted compound *V*.

Partial deacetylation of di-O-acetyl derivative *III* on alkaline alumina in benzene gave 4-O-acetyl derivative *XV* in a relatively high yield in addition to a small amount of 2-O-acetyl derivative *XIII* (ratio *XV* : *XIII* was 88 : 12). The same reaction with di-O-acetyl derivative *IV* took place selectively under formation of 4-O-acetyl derivative *VIII*. Simultaneously we also observed that this, preparatively very advantageous, reaction (giving usually that mono-O-acetyl derivative which is less accessible by partial acetylation) does not take place in the presence of a protic solvent (for example benzene with 5% ethanol), and that it is at least partly analogous to alkaline hydrolysis because we also achieved the selective hydrolysis of the 4-O-acetyl group in the reaction with 0·05M sodium hydroxide.

TABLE I
Composition of the Reaction Mixture after Partial Acylation

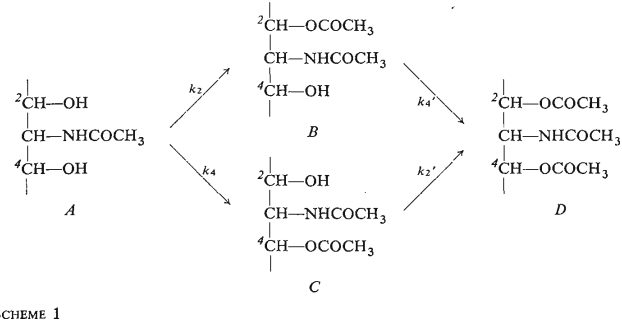
Reagent	Regenerated %	2-O-Acyl %	4-O-Acyl %	2,4-Di-O--acyl, %	2-O-Acyl: 4-O-Acyl
Methyl 3-acetamido-3,6-dideoxy-β-D-glucopyranoside (*I*)					
$(CH_3CO)_2O$	15·0	28·1	14·8	41·6	65 : 35
CH_3COCl	18·8	23·7	7·1	50·3	77 : 23
CH_3SO_2Cl	9·0	8·1	51·5	30·8	13 : 87
Methyl 3-acetamido-3,6-dideoxy-β-D-mannopyranoside (*II*)					
$(CH_3CO)_2O$	30·0	22·6	16·9	29·5	57 : 43
CH_3COCl	18·3	39·1	3·9	38·5	91 : 9
CH_3SO_2Cl	6·4	38·4	25·6	29·0	60 : 40

From Table I it is evident that during partial acylation an appreciable amount of 2,4-di-O-acyl derivative is also formed in addition to mono-O-acyl derivatives. As the 2,4-di-O-acyl derivative is formed quite undoubtedly by subsequent acylation of mono-O-acyl derivatives (Scheme 1), the final result of acylation may be determined not only by the different reactivity of the hydroxyl groups of the starting substance, but also by the different reactivity of the hydroxyl groups in mono-O-acyl derivatives. For a more detailed interpretation of the results of partial acylation it is necessary to know the extent to which both mentioned effects are operative. Such information may be obtained *via* the determination of the ratio of rate constants k_2/k_4 and k'_2/k'_4. In our preceding paper[10] we demonstrated that the set of kinetic equations describing the partial acylation of a substance with two hydroxyl groups may be transformed to equations (*1*) and (*2*):

$$c_B = \frac{d}{b-1}\left(c_A - c_{Ao}^{1-b} \cdot c_A^b\right), \qquad (1)$$

$$c_C = \frac{1-d}{Kb-1}\left(c_A - c_{Ao}^{1-Kb} \cdot c_A^{Kb}\right), \qquad (2)$$

where c_{Ao} is the starting concentration of the acylated compound A, c_A is the concentration of the unreacted starting substance A, c_B or c_C is the concentration of the mono-O-acyl derivative B or C. On solving equations (*1*) and (*2*), the values of the constants d and b may be calculated when the value of $K = k'_2/k'_4$ is known, and from equation $d = k_2/(k_2 + k_4)$ and $b = k'_4/(k_2 + k_4)$ the ratios of rate constants k_2/k_4, k'_4/k_2, k'_4/k_4, k'_2/k_4 and k'_2/k_2 may be computed. The ratio $K = k'_2/k'_4$ can be obtained from the results of acylation to the second stage, *i.e.* from the acylation of the



SCHEME 1

mixture of mono-O-acyl derivatives B and C to di-O-acyl derivative D, for which it applies that

$$k'_2/k'_4 = \frac{\log c_{Co} - \log c_C}{\log c_{Bo} - \log c_B}, \qquad (3)$$

where c_{Co} or c_{Bo} are the starting concentrations of substance C or B, and c_C or c_B are the concentrations of substances C and B in time t.

Therefore, we acted on the mixture of 2-O-acyl derivative and 4-O-acyl derivative with approximately one half of an equivalent of the acylating reagent under the same conditions as in the case of partial acylation. The reaction mixture was analysed by preparative chromatography on a silica gel column, and in the case of acetylation of the mixture of mono-O-acetyl derivatives *XIII* and *XV* with acetic anhydride by means of PMR spectroscopy and gas chromatography. The determined values k'_2/k'_4, and the values of k_2/k_4, k'_4/k_2, k'_4/k_4, k'_2/k_4 and k'_2/k_2 calculated, are listed in Table II.

From Table II it is evident that during the acetylation of acetamidoglucoside *I* with acetyl chloride in pyridine both hydroxyl groups of compound *I* are acetylated at approximately the same rate ($k_2/k_4 = 1{\cdot}2$). The hydroxyl groups in mono-O-acetyl derivatives *XIII* and *XV* are acetylated more rapidly than the corresponding hydroxyl groups in compound *I* ($k'_4/k_4 = 1{\cdot}4$, $k'_2/k_2 = 3{\cdot}5$); the increase in acetylation rate caused evidently by acetylation of the β-position is in the case of 4-O-acetyl derivative *XV* approximately 3 times higher than in the case of 2-O-acetyl derivative *XIII* ($k'_2/k'_4 = 3{\cdot}0$). This means that the specific result of acetylation (Table I) is the consequence of the different reactivity of mono-O-acetyl derivatives *XIII* and *XV* and not a consequence of the different reactivity of the hydroxyl groups in the starting substance *I*. In the acetylation of compound *I* with acetic anhydride in pyridine the hydroxyl group in the position 2 is more easily acetylated ($k_2/k_4 = 2{\cdot}4$). The hydroxyl group in 2-O-acetyl derivative *XIII* is again acetylated faster than the hydroxyl group

TABLE II

The Ratios of Rate Constants of Acylations of Acetamido Derivatives *I* and *II*

Reaction	k'_2/k'_4	k_2/k_4	k'_4/k_2	k'_4/k_4	k'_2/k_4	k'_2/k_2
$I + (CH_3CO)_2O$	0·7	2·4	0·9	2·2	1·5	0·6
$I + CH_3COCl$	3·0	1·2	1·2	1·4	4·3	3·5
$I + CH_3SO_2Cl$	0·6	0·2	2·4	0·5	0·3	1·4
$II + (CH_3CO)_2O$	1·1	1·2	1·4	1·8	2·0	1·6
$II + CH_3COCl$	1·9	6·2	0·7	4·2	7·9	1·3

in the position 4 of the starting diol *I* ($k'_4/k_4 = 2{\cdot}2$), but the hydroxyl group in 4-O--acetyl derivative *XV* when compared with the hydroxyl group in the position 2 of the starting diol *I* is acetylated slower ($k'_2/k_2 = 0{\cdot}6$). Hence in the last mentioned case the acetylation in the β-position causes further acetylation to be retarded. In contrast to acetylation of compound *I* with acetyl chloride its acetylation with acetic anhydride to the first step takes place specifically, while the acetylation to the second step takes place with a lower, and with respect to its direction, opposite specificity. In mesylation of compound *I* with methanesulfonyl chloride in pyridine the hydroxyl group in the position 4 of the starting compound *I* is about five times more reactive that the hydroxyl group in the position 2 ($k_2/k_4 = 0{\cdot}2$). The hydroxyl group in the 2-O-mesyl derivative *XII* is mesylated more slowly and the hydroxyl group in 4-O-mesyl derivative *XI* faster than the same hydroxyl group in the starting compound *I*. The high mesylation specificity of compound *I* is therefore determined both by the differing reactivity of the hydroxyl groups in compound *I*, and by the higher reactivity of the minor 2-O-mesyl derivative *XII*.

In the acetylation of acetamidomannoside *II* with acetyl chloride in pyridine the hydroxyl group in the position 2 is approximately six times more reactive that that in the position 4 ($k_2/k_4 = 6{\cdot}2$). Acetylation in the position β increases the reactivity of the hydroxyl group on the carbon atom 4 approximately four times ($k'_4/k_4 = 4{\cdot}2$), the reactivity of the hydroxyl group on the carbon atom 2 scarcely changes ($k'_2/k_2 = 1{\cdot}3$). The minor 4-O-acetyl derivative *VIII* is acetylated to di-O-acetyl derivative *III* approximately twice as fast as 2-O-acetyl derivative *VII*. The high specificity of the

TABLE III

Partial Acylation of Methyl 3-Acetamido-3,6-dideoxy-hexopyranosides

Acylated compound	Reagent[a]	Regenerated %	2-O-Acyl %	4-O-Acyl %	2,4-Di-O--acyl, %	2-O-Acyl: 4-O-Acyl	Degree of acylation
α-L-*gluco*[b]	Ac_2O	43·3	21·2	14·8	21·4	59 : 41	0·79
β-D-*gluco*	Ac_2O	43·3	29·6	13·6	14·5	69 : 31	0·72
α-L-*gluco*[b]	AcCl	41·8	38·0	3·8	3·2	91 : 9	0·48
β-D-*gluco*	AcCl	41·8	23·6	11·2	23·4	68 : 32	0·82
α-L-*gluco*[b]	MsCl	32·9	35—45	—	19—26	100 : 0	0·83—0·87
β-D-*gluco*	MsCl	32·9	8·8	47·7	10·6	16 : 84	0·78
α-D-*manno*[c]	Ac_2O	23·8	24·6	13·3	34·9	65 : 35	1·08
β-D-*manno*	Ac_2O	23·8	21·8	16·4	38·0	57 : 43	1·14
α-D-*manno*[c]	AcCl	6·1	60·3	3·2	24·4	95 : 5	1·12
β-D-*manno*	AcCl	6·1	28·0	2·0	63·9	94 : 6	1·58

[a] Ac_2O acetic anhydride, AcCl acetyl chloride, MsCl methanesulfonyl chloride; [b] ref.[1]; [c] ref.[4].

acetylation of compound *II* with acetyl chloride is thus a consequence of the different reactivity of the hydroxyl groups in compound *II* and also the different reactivity of the hydroxyl groups in mono-O-acetyl derivatives *VII* and *VIII*. In contrast to this, when the same compound *II* is acetylated with acetic anhydride in pyridine, both hydroxyl groups react approximately equally ($k_2/k_4 = 1{\cdot}1$) and after acetylation to the first step the reactivity of the hydroxyl groups in compound *VII* and *VIII* is also increased approximately to the same extent.

From the above it follows that in some cases further acylation of mono-O-acyl derivatives to 2,4-di-O-acyl derivatives affects the total result of acylation to such an extent that the ratio of mono-O-acyl derivatives in the reaction mixture is not in agreement with the ratio of reactivities of hydroxyl groups in the acylated starting substance. In order to be able to compare partial acylation of compounds *I* and *II* with that of their α-anomers more thoroughly we also need to know for the α-series at least the values k_2/k_4 and k'_2/k'_4. As these values are not yet at our disposal, we tried to compare the compositions of the reaction mixtures after partial acylations of compounds *I* and *II* when their reaction took place with the same degree of the conversion of the starting compound as was in the α-series. The results of this calculation, carried out according to the procedure described in the preceding paper[10], are given in Table III. From this table it is evident that on acetylation with acetyl chloride of compounds *I* and *II*, acetylation to the second stage is much more pronounced than in the case of their α-anomers. When methyl 3-acetamido-3,6-dideoxy-α-L-glucopyranoside is acetylated with acetyl chloride only 3·2% of 2,4-di-O-acetyl derivative are formed; hence, it is evident that in contrast to compound *I*, the different reactivity of the hydroxyl groups of the starting compound has a decisive effect on the specific result of acetylation. A similar situation was found also in the case of the α-anomer of compound *II*. In the case of the acetylation of compounds *I* a *II* with acetic anhydride the situation is more complex; in comparison with the α-series, acetamidoglucoside *I* is acetylated to the second stage less, while the acetamidomannoside *II* more. However, it cannot be decided to what extent the α-anomer differs from the β-anomer in acetylations to the first stage. A quite different behaviour of acetamidoglucoside *I* and of its α-anomer during mesylation is evident even from the composition of the reaction mixture. In contrast to this, partial deacetylation of di-O-acetyl derivatives *III* and *IV* on alkaline alumina affords the same results as in the α-series.

EXPERIMENTAL

The melting points were measured on a Kofler block and they are not corrected. Optical rotations were determined on an Opton apparatus at 20°C and 0·5 to 1·0 g/100 ml concentration. The infrared spectra were taken with a Perkin-Elmer 325 spectrophotometer. The PMR spectra were measured in deuteriochloroform on a Varian EMS-30 and Varian XL-100 instrument with tetramethylsilane as internal reference; chemical shifts are given in δ-values (p.p.m.), coupling

constants in Hz. Samples for analysis were dried at 20—50°C and 0·05—0·1 Torr. Chromatographies were carried out on silica gel of Lachema (Brno), 70—200 μm, thin-layer chromatography on silica gel according to Stahl (Merck, Darmstadt), 10—40 μm, plate dimensions 25 × × 75 mm, layer thickness 0·2—0·3 mm. Substances were detected by spraying with 1% cerium (IV) sulfate solution in 10% sulfuric acid and heating. The solvents were evaporated on a rotatory evaporator *in vacuo* (water pump), at maximum 50°C. Light petroleum used for crystallisation had b.p. 45—60°C. If certain substances described here were prepared by several procedures, their melting points and optical rotations were always in agreement, within experimental errors, with the values given for analytical preparations and their identity was checked by IR spectra.

Acetylation of Acetamidoglucoside *I*

a) *With acetic anhydride*: Acetic anhydride (0·33 ml; 3·49 mmol) was added at −70°C to a mixture of 600 mg (2·74 mmol) of acetamidoglucoside *I* and 15 ml of pyridine and the mixture was allowed to stand at −17°C for 48 hours, at 0°C for 24 hours, and at room temperature for another 24 hours. After decomposition with water it was evaporated several times with water and eventually with toluene to dryness. The residue was dried in a vacuum (oil pump) and introduced onto a column of 50 g of silica gel. After elution with 250 ml of benzene a mixture of benzene and ethanol (100 : 2·5) eluted 346 mg (1·14 mmol, 41·6%) of di-O-acetyl derivative[6] *III*. Benzene–ethanol mixture (100 : 5) eluted 201 mg (0·77 mmol; 28·1%) of 2-O-acetyl derivative *XIII* and 106 mg (0·41 mmol; 14·8%) of 4-O-acetyl derivative *XV*. With benzene–ethanol (10:1) 90 mg (0·41 mmol; 15%) of the starting compound *I* were eluted. The total yield was 99·5%. 2-O-Acetyl derivative *XIII* was crystallised from an acetone–ether-light petroleum mixture, m.p. 193—195°C (at 140—160°C change of crystal modification), $[\alpha]_D$ −28° (chloroform). For analysis derivative *XIII* was sublimated at 60°C and 0·01 Torr. For $C_{11}H_{19}NO_6$ (261·3) calculated: 50·57% C, 7·33% H, 5·36% N; found: 50·75% C, 7·51% H, 5·33% N. 4-O-Acetyl derivative *XV* was crystallised from a mixture of ethyl acetate and light petroleum, m.p. 194—195·5°C, $[\alpha]_D$ +10° (chloroform). Substance *XV* sublimated under the same conditions as substance *XIII*. For $C_{11}H_{19}NO_6$ (261·3) calculated: 50·57% C, 7·33% H, 5·36% N; found: 50·87% C, 7·49% H, 5·36% N.

b) *With acetyl chloride*: Acetyl chloride (0·175 ml; 2·48 mmol) was added to a mixture of 414 mg (1·89 mmol) of compound *I* and 12 ml of pyridine at −70°C and the mixture allowed to stand at −17°C for 24 hours. After another 24 hours standing at 0°C it was decomposed with water, evaporated several times with water and eventually with toluene. The residue was transferred onto a column of silica gel (40 g) and it was chromatographed in the same manner as above. Yield: 288 mg (0·95 mmol; 50·3%) of compound *III*, 117 mg (0·45 mmol; 23·7%) of 2-O-acetyl derivative *XIII*, 35 mg (0·13 mmol; 7·1%) of 4-O-acetyl derivative *XV*, and 78 mg (0·36 mmol; 18·8%) of the starting compound *I*. The total yield was 99·9%.

Acetylation of a Mixture of 2-O-Acetyl Derivative *XIII* and 4-O-Acetyl Derivative *XV*

a) *With acetic anhydride*: A mixture of 49·61 mg (0·190 mmol) of compound *XIII* and 50·93 mg (0·195 mmol) of compound *XV* was dissolved in 3 ml of pyridine and to 1·4 ml of this solution acetic anhydride (8·5 μl; 0·09 mmol) was added at −70°C. The mixture was allowed to stand at −17°C for 48 hours, then at 0°C for 24 hours, and eventually at room temperature for another 24 hours. After decomposition with water it was evaporated first with water and then with toluene. The residue was dried *in vacuo* (oil pump) and analysed by PMR and gas chromatography. Integration of doublets of the NH-protons in the PMR spectrum gave for the areas of compounds *XIII* : *XV* : *III* the ratio 1·42 : 1·61 : 1·00, corresponding to 34% of *XIII*, 38%

of *XV* and 28% of *III*. By integration of the peaks of the protons of the acetyl groups and a comparison with the areas of the peaks of the protons on the methyl groups on carbon 5 the ratio of the areas was determined, $G = 2{\cdot}21$, from which it was computed that the mixture contained 24% of di-O-acetyl derivative *III*. Using gas chromatography (Chrom III, 4% SE – 52 on Chromosorb G-HMDS-AW 40–60 mesh, 183°C, temperature of the injection 210°C, nitrogen flow 46 cm^3/min, overpressure 0·33 kp/cm^2) substance *XIII* was separated (retention time 4·9 min) from a mixture of compounds *XV* and *III* (retention time about 7 min); ratio of areas *XIII* : (*XV* + *III*) = 0·62; responses *XIII* : *XV* : *III* = 1·3 : 1·0 : 1·4. From this it follows that the reaction mixture contains 35% of 2-O-acetyl derivative *XIII* and 41% of 4-O-acetyl derivative *XV*.

b) *With acetyl chloride*: A mixture of 46·0 mg of 2-O-acetyl derivative *XIII* and 41·3 mg of 4-O-acetyl derivative *XV* (*i.e.* 87·3 mg or 0·334 mmol of a mixture of *XIII* and *XV*) was dissolved in 3 ml of pyridine, cooled to −70°C, and additioned with 17·5 μl (0·248 mmol) of acetyl chloride. The reaction mixture was allowed to stand at −17°C for 24 hours and at 0°C for another 24 hours and then worked up as in the case of the acetylation of compound *I* with acetyl chloride. After chromatographic separation on a silica gel column (10 g) 48·8 mg of di-O-acetyl derivative *III*, 31·5 mg of 2-O-acetyl derivative *XIII*, and 13·5 mg of 4-O-acetyl derivative *XV* were obtained; 68·5% of compound *XIII* and 32·7% of compound *XV* remained unreacted.

Mesylation of Acetamidoglucoside *I*

Methanesulfonyl chloride (0·22 ml; 2·90 mmol) was added to a mixture of 500 mg (2·28 mmol) of acetamidoglucoside *I* and 15 ml of pyridine at −70°C and the mixture was allowed to stand at −17°C for 48 hours. After decomposition with water and repeated evaporation with water it was also evaporated with toluene and the residue chromatographed on a column of silica gel (50 g). After elution with 200 ml of benzene the column was further eluted with benzene–ethanol 100 : 3, yielding 264 mg (0·70 mmol; 30·8%) of di-O-mesyl derivative[6] *XXI*. Benzene–ethanol mixture 100 : 4 eluted 55 mg (0·185 mmol; 8·1%) of 2-O-mesyl derivative[7] *XII* and 349 mg (1·174 mmol; 51·5%) of 4-O-mesyl derivative *XI*, and benzene–ethanol 10 : 1 eluted 45 mg (0·206 mmol; 9·0%) of the starting compound *I*. Derivative *XI* was dissolved in acetone, filtered with charcoal, and crystallised from acetone–light petroleum. M.p. 160·5–162·5°C, $[\alpha]_D$ +12° (methanol). For $C_{10}H_{19}NO_7S$ (297·3) calculated: 40·40% C, 6·44% H, 4·71% N; 40·23% C, 6·67% H, 4·56% N.

Mesylation of a Mixture of 2-O-Mesyl Derivative *XII* and 4-O-Mesyl Derivative *XI*

Methanesulfonyl chloride (14 μl; 0·18 mmol) was added at −70°C to a mixture of 53 mg of 2-O--mesyl derivative *XII* and 52 mg of 4-O-mesyl derivative *XI* in 4 ml of pyridine and the mixture allowed to stand at −17°C for 24 hours. The mixture was worked up as in the case of mesylation of *I*. After chromatographic separation on a column with 20 g of silica gel, 26 mg (0·069 mmol) of di-O-mesyl derivative *XXI*, 32 mg (0·11 mmol) of 2-O-mesyl derivative *XII*, and 39 mg (0·13 mmol) of 4-O-mesyl derivative *XI* were obtained; 60% of compound *XII* and 75% of *XI* remained unreacted.

Acetylation of Acetamidomannoside *II*

a) *With acetic anhydride*: Acetic anhydride (0·20 ml; 2·12 mmol) was added to a mixture of 401 mg (1·83 mmol) of acetamidomannoside *II* and 10 ml of pyridine at −70°C and allowed to stand at −17°C for 48 hours, at 0°C for 24 hours, and at room temperature for another 24

hours. After decomposition with water and evaporation with water and eventually with toluene the residue was chromatographed on a column of silica gel (45 g). Elution was first carried out with benzene, followed by benzene–ethanol 100 : 3 which eluted 164 mg (0·54 mmol; 29·5%) of di-O-acetyl derivative[6] *IV*; benzene–ethanol 100 : 5 eluted 81 mg (0·31 mmol; 16·9%) of 4-O--acetyl derivative *VIII*, benzene–ethanol 10 : 1 eluted first 108 mg (0·41 mmol; 22·6%) of 2-O--acetyl derivative *VII* followed by 121 mg (0·55 mmol; 30·0%) of the unreacted compound *II*. The total yield was 99·0%. 2-O-Acetyl derivative *VII* in acetone solution was filtered with charcoal and crystallised from ethyl acetate–light petroleum, m.p. 166—168°C (at 155—157°C change of crystal modification), $[\alpha]_D$ −36° (chloroform). For $C_{11}H_{19}NO_6$ (261·3) calculated: 50·57% C, 7·33% H, 5·36% N; found: 50·53% C, 7·43% H, 5·42% N. 4-O-Acetyl derivative *VIII* was sublimated at 140°C and 0·05 Torr and crystallised from ethyl acetate–light petroleum, m.p. 173—175°C (crystal modification change at 145—160°C), $[\alpha]_D$ −21° (chloroform). For $C_{11}H_{19}NO_6$ (261·3) calculated: 50·57% C, 7·33% H, 5·36% N; found: 50·22% C, 7·04% H, 5·12% N.

b) *With acetyl chloride*: Acetyl chloride (0·12 ml; 1·70 mmol) was added to a mixture of 300 mg (1·37 mmol) of acetamidomannoside *II* in 15 ml of pyridine at −70°C and the mixture allowed to stand at −17°C for 48 hours and at −5°C for 24 hours. After decomposition with water and evaporation with water and eventually with toluene the residue was chromatographed on a silica gel column (40 g) in the same manner as described above. Yield 160 mg (0·53 mmol; 38·5%) of compound *IV*, 14 mg (0·054 mmol; 3·9%) of compound *VIII*, 140 mg (0·54 mmol; 39·1%) of compound *VII*, and 55 mg (0·25 mmol; 18·3%) of the starting compound *II*; total yield 99·8%.

Acetylation of a Mixture of 2-O-Acetylmannoside *VII* and 4-O-Acetylmannoside *VIII*

a) *With acetic anhydride*: Acetic anhydride (15·3 μl; 0·162 mmol) was added to a mixture of 30·52 mg of compound *VII* and 30·12 mg of compound *VIII* in 2 ml of pyridine at −70°C. The mixture was allowed to stand at −17°C for 48 hours and at 0°C for another 24 hours, and worked up in the same manner as in the case of acetylation of *II*. After chromatographic separation on a column of 15 g of silica gel, 26·1 mg of di-O-acetyl derivative *IV*, 18·1 mg of 4-O-acetyl derivative *VIII*, and 19·3 mg of 2-O-acetyl derivative *VII* were obtained; 60·1% of substance *VIII* and 63·2% of substance *VII* remained unreacted.

b) *With acetyl chloride*: Acetyl chloride (13·6 μl; 0·193 mmol) was added to a mixture of 35·1 mg of compound *VII* and 28·5 mg of compound *VIII* in 2 ml of pyridine at −70°C. The mixture was allowed to stand at −17°C for 24 hours and at −5°C for another 24 hours and then worked up as above. Yield 37·1 mg of di-O-acetyl derivative *IV*, 11·0 mg of 4-O-acetyl derivative *VIII*, and 21·0 mg of 3-O-acetyl derivative *VII*; 38·6% of compound *VIII* and 59·8% of compound *VII* remained unreacted.

Mesylation of Acetamidomannoside *II*

69 μl (0·91 mmol) of methanesulfonyl chloride were added at −70°C to 157 mg (0·72 mmol) of compound *II* in 10 ml of pyridine and the mixture allowed to stand at −15°C for 48 hours and at 0°C for 24 hours. After decomposition with water and evaporation, toluene was added and evaporated again. The residue was chromatographed on a column of 25 g of silica gel. Benzene–ethanol mixture 100 : 5 eluted first 78 mg (0·21 mmol; 29·0%) of di-O-mesyl derivative *XXII* and then 137 mg (0·46 mmol; 64·0%) of a mixture of mono-O-mesyl derivative *V* and *VI*; benzene–ethanol mixture 10 : 1 eluted 10 mg (0·05 mmol; 6·4%) of compound *II*. Derivative *XXII* was dissolved in acetone and filtered with charcoal and crystallised from a mixture of acetone and light petroleum; m.p. 171·5—173·5°C (decomp.), $[\alpha]_D$ −69° (chloroform). For $C_{11}H_{21}NO_9S_2$

(375·4) calculated: 35·20% C, 5·14% H, 3·40% N; found: 35·42% C, 5·38% H, 3·37% N. In the PMR spectrum of the mixture of compound *V* and *VI* the bands at 1·41 (3 H, doublet, $J_{5,6} = 6{\cdot}5$, CH_3—CH), 2·06 (3 H, singlet, CH_3CONH—), 3·14 (3 H, singlet, CH_3SO_2O—), 3·55 (3 H, singlet, CH_3O—) were assigned to compound *V* and the bands at 1·39 (3 H, doublet, $J_{5,6} = 6{\cdot}5$, CH_3—CH), 2·06 (3 H, singlet, CH_3CONH—), 3·02 (3 H, singlet, CH_3SO_2O—), and 3·55 (3 H, singlet, CH_3O—) to compound *VI*. By integration of the acetamido group bands the ratio *V* : *VI* was found to be 1·52 ± 0·1, *i.e.* in the mixture of compounds *V* and *VI* there are 60% of compound *V* and 40% of compound *VI*. The same result is achieved when the values of optical rotations of the mixture of *V* and *VI* ($[\alpha]_D$ −96·3° (methanol)) and of authentic samples were used for calculations.

Deacetylation of Di-O-acetyl Derivative *III*

Substance *III* (300 mg; 0·99 mmol) dissolved in benzene was poured onto a column of alkaline alumina (40 g) and the solution was allowed to enter the column and stand for 30 hours. The column was then eluted with a mixture of benzene and ethanol (100 : 2·5). From single fractions the following material was isolated: 126 mg (42%) of compound *III*, 18 mg (0·07 mmol; 7·0% of 2-O-acetyl derivative *XIII*, and 129 mg (0·49 mmol; 50%) of 4-O-acetyl derivative *XV*.

Deacetylation of Di-O-acetyl Derivative *IV*

a) *On alkaline alumina*: A benzene solution of 400 mg (1·32 mmol) of di-O-acetyl derivative *IV* was allowed to enter a column of 60 g of alumina and the column was slowly eluted over 4 hours with 250 ml of benzene and then with benzene–ethanol 100 : 3 mixture which eluted 330 mg of the starting compound *IV* and 53 mg (0·203 mmol; 15·4%) of 4-O-acetyl derivative *VIII*. Benzene–ethanol mixture 10 : 1 eluted 2 mg of acetamidomannoside *II*; 2-O-acetyl derivative *VII* was not detected. In another experiment a solution of 24 mg of di-O-acetyl derivative *IV* in 1·5 ml of benzene was allowed to stand under occassional stirring with 1 g of the same alkaline alumina for 26 hours. Alumina was filtered off and washed with 50 ml of a mixture of benzene and ethanol 5 : 1, the combined filtrates were evaporated; according to thin-layer chromatography in benzene–ethanol 10 : 1 the residue contained substances *IV* and *VIII* and traces of compound *II*. In the PMR spectrum of this mixture the ratio of the areas of the acetyl groups and the methyl groups was $G = 2{\cdot}48$; hence, the mixture contained approx. 46% of compound *IV* and 54% of compound *VIII*. In contrast to this when alkaline alumina acted on a solution of 23 mg of compound *IV* in a mixture of benzene and ethanol (100 : 5; 1·5 ml) for 26 hours, deacetylation did not take place.

b) *Under the effect of sodium hydroxide*: A solution of derivative *IV* (20 mg) in 4 ml of 0·05M-NaOH was allowed to stand at 23°C for 5 minutes, then neutralised with Amberlite IR-120 (H^+) and evaporated. From the residue which contained according to thin-layer chromatography in addition to 4-O-acetyl derivative *VIII* also traces of compounds *IV*, *VII* and *II*, 15 mg of compound *VIII* were obtained on chromatography on a column of silica gel (8 g). In an experiment where the reaction time was prolonged to 60 minutes acetamidomannoside *II* was isolated exclusively.

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

a) *From* 2-O-*acetyl derivative* XIII: 25 µl of methanesulfonyl chloride were added at −70°C to a mixture of 33 mg of compound *XIII* and 1 ml of pyridine and the mixture allowed to stand at −17°C overnight. After decomposition with water the mixture was diluted with chloroform and extracted consecutively with dilute hydrochloric acid, water, 5% sodium hydrogen carbonate

and water. After drying of the chloroform extract over magnesium sulfate and filtration with charcoal chloroform was evaporated and the solid residue (30 mg, 70%) crystallised from acetone–ether–light petroleum mixture, m.p. 165–167°C, $[\alpha]_D$ −48° (chloroform). For $C_{12}H_{21}NO_8S$ (339·4) calculated: 42·47% C, 6·24% H, 4·13% N; found: 42·52% C, 6·48% H, 4·16% N. PMR spectrum: 1·38 (3 H, doublet, $J_{5,6}$ = 6·0, CH_3—CH), 1·96 (3 H, singlet, CH_3CONH—), 2·07 (3 H, singlet, CH_3COO—), 3·04 (3 H, singlet, CH_3SO_2O—), 3·48 (3 H, singlet, CH_3O—), 3·64 (1 H, octet, $J_{5,6}$ = 6·0, $J_{4,5} \cong$ 9·0, H-5), 4·29 (1 H, multiplet, $J_{4,5} \cong$ 9·0, $J_{3,4} \cong$ 9·0, H-4), ~4·35 (1 H, multiplet, $J_{2,3}$ = 9·8, $J_{3,4} \cong$ 9·0, $J_{NH,3}$ = 8·5, H-3), 4·42 (1 H, doublet, $J_{1,2}$ = 7·4, H-1), 4·79 (1 H, quartet, $J_{2,2}$ = 7·4, $J_{2,3}$ = 9·8, H-2), 6·18 (1 H, doublet, $J_{NH,3}$ = 8·5, NH).

b) *From* 4-O-*mesyl derivative* XI: Acetic anhydride (0·5 ml) was added to a solution of 64 mg of compound *XI* in 1 ml of pyridine and the mixture was allowed to stand at room temperature for 48 hours. After decomposition with water it was evaporated with water and then with toluene. The residue was dissolved in acetone, filtered with charcoal and crystallised from a mixture of acetone, ether and light petroleum. Yield 70 mg (96%) of compound *XIV*.

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

Methanesulfonyl chloride (40 µl) was added at −70°C to a mixture of 48 mg of 4-O-acetyl derivative *XV* and 2 ml of pyridine and the mixture was allowed to stand at −17°C overnight. After decomposition with water and evaporation with water and toluene the residue was transferred onto a column of silica gel (10 g) and compound *XVI* was eluted from it with benzene–ethanol 100 : 5. After two crystallisations from a mixture of ethanol and light petroleum 35 mg (57%) of compound *XVI* were obtained, m.p. 179–180·5°C, $[\alpha]_D$ +3° (chloroform), identical with an earlier described preparation[7]. PMR spectrum: 1·23 (3 H, doublet, $J_{5,6}$ = 6·0, CH_3—CH), 1·97 (3 H, singlet, CH_3CONH—), 2·06 (3 H, singlet, CH_3COO—), 3·06 (3 H, singlet, CH_3SO_2O—), 3·55 (3 H, singlet, CH_3O—), 3·63 (1 H, octet, $J_{5,6}$ = 6·0, $J_{4,5} \cong$ 9·3, H-5), ~4·35 (1 H, multiplet, $J_{1,2}$ = 7·5, H-2), ~4·42 (1 H, multiplet, $J_{3,4}$ = 9·3, $J_{NH,3}$ = 8·0, H-3), 4·48 (1 H, doublet, $J_{1,2}$ = 7·5, H-1), 4·64 (1 H, triplet, $J_{3,4} \cong$ 9·3, $J_{4,5} \cong$ 9·3, H-4), 5·90 (1 H, doublet, $J_{NH,3}$ = 8·0, NH).

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

Methanesulfonyl chloride (40 µl) was added to a mixture of 33 mg of 2-O-acetyl derivative *VII* and 2 ml of pyridine at −70°C and the mixture was allowed to stand at −17°C overnight. After decomposition with water and evaporation with water and toluene the residue was chromatographed on a column of silica gel (10 g); benzene–ethanol 100 : 5 eluted 41 mg (95%) of compound *IX*; after three crystallisations from chloroform–light petroleum the m.p. was 160–164°C, $[\alpha]_D$ −66° (chloroform). For $C_{12}H_{21}NO_8S$ (339·4) calculated: 42·47% C, 6·24% H; found: 42·68% C, 6·30% H. PMR spectrum: 1·44 (3 H, doublet, $J_{5,6}$ = 6·2, CH_3—CH), 1·99 (3 H, singlet, CH_3CONH—), 2·19 (3 H, singlet, CH_3COO—), 3·07 (3 H, singlet, CH_3SO_2O—), 3·51 (3 H, singlet, CH_3O—), 3·66 (1 H, octet, $J_{5,6}$ = 6·2, $J_{4,5}$ = 9·0, H-5), 4·32–4·53 (2 H, multiplet, H-3, H-4), 4·55 (1 H, doublet, $J_{1,2}$ = 1·2, H-1), 5·41 (1 H, quartet, $J_{1,2}$ = 1·2, $J_{2,3}$ = 2·6, H-2), 6·07 (1 H, doublet, $J_{NH,3}$ = 8·0, NH).

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

In the same manner as in the case of the preparation of compound *IX*, 38 mg of 4-O-acetyl derivative *VIII* and 60 µl of methanesulfonyl chloride gave 40 mg (81%) of derivative *X*. After repeated crystallisation from ethyl acetate–light petroleum the m.p. was 142–144°C, $[\alpha]_D$ −61° (chloro-

form). For $C_{12}H_{21}NO_8S$ (339·4) calculated: 42·47% C, 6·24% H, 4·13% N; found: 42·50% C, 6·16% H, 4·30% N. PMR spectrum: 1·28 (3 H, doublet, $J_{5,6} = 6·0$, CH_3—CH), 1·98 (3 H, singlet, CH_3CONH—), 2·07 (3 H, singlet, CH_3COO—), 3·13 (3 H, singlet, CH_3SO_2O—), 3·56 (3 H, singlet, CH_3O—), 3·62 (1 H, octet, $J_{5,6} = 6·0$, $J_{4,5} = 9·1$, H-5), 4·31 (1 H, octet, $J_{2,3} = 3·0$, $J_{3,4} = 10·6$, $J_{NH,3} = 8·5$, H-3), 4·55 (1 H, doublet, $J_{1,2} = 1·0$, H-1), 4·75 (1 H, quartet, $J_{3,4} = 10·6$, $J_{4,5} = 9·1$, H-4), 4·92 (1 H, quartet, $J_{1,2} = 1·0$, $J_{2,3} = 3·0$, H-2), 5·99 (1 H, doublet, $J_{NH,3} = 8·5$, NH).

Methyl 3-Acetamido-3,6-dideoxy-4-O-methanesulfonyl-β-D-mannopyranoside (*VI*)

A drop of 1M sodium methoxide was added to a solution of 40 mg of substance *IX* in 5 ml of methanol and the mixture was allowed to stand overnight. After shaking with Amberlite 1R-120 (H^+) the mixture was filtered and the filtrate evaporated. The residue was crystallised from ethanol–light petroleum, m.p. 167—170°C (decomposition), $[\alpha]_D$ −49° (methanol). For $C_{10}H_{19}NO_7S$ (297·3) calculated: 40·40% C, 6·44% H, 4·71% N; found: 40·62% C, 6·48% H, 4·56% N.

Methyl 3-Acetamido-3,6-dideoxy-2-O-methanesulfonyl-β-D-mannopyranoside (*V*)

Compound *V* (22 mg) of m.p. 178—180°C (after crystallisation from ethanol–light petroleum) was obtained from 30 mg of compound *X* in the same manner as described for the preparation of *VI*; $[\alpha]_D$ of the product was −128° (methanol). For $C_{10}H_{19}NO_7S$ (297·3) calculated: 40·40% C, 6·44% H, 4·71% N; found: 40·56% C, 6·64% H, 4·57% N.

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

Benzoyl chloride (50 µl) was added to a solution of 43 mg od 2-O-acetyl derivative *VII* in 0·5 ml of pyridine under cooling with water and the mixture was allowed to stand at room temperature overnight. After decomposition with water it was extracted several times with chloroform. The combined chloroform extracts were washed consecutively with dilute hydrochloric acid, water, 5% sodium hydrogen carbonate and water. After drying over sodium sulfate and evaporation of the solvent 70 mg of a syrup were obtained which crystallised out after addition of acetone, ether and light petroleum. After crystallisation from the same mixture 56 mg (93%) of compound *XVII* were obtained, m.p. 106—108°C, $[\alpha]_D$ −64° (chloroform), identical with a preparation described earlier[7].

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

On benzoylation of 4-O-acetyl derivative *VIII* (40 mg) in the same manner as described under the preparation of compound *XVII* 50 mg of syrupy derivative *XVIII* were obtained which was purified for analysis by chromatography on a column of silica gel (8 g) with benzene–ethanol 100 : 2. The pure product (47 mg) had $[\alpha]_D$ −117° (chloroform). For $C_{18}H_{23}NO_7$ (365·4) calculated: 59·17% C, 6·34% H, 3·83% N; found: 59·10% C, 6·12% H, 3·96% N.

Reaction of 4-O-Mesylglucoside *XI* with Sodium Acetate

A mixture of 25 mg of compound *XI*, 1·5 ml of 2-methoxyethanol, 0·1 ml of water and 100 mg of sodium acetate trihydrate was refluxed for 3·5 hours. After evaporation the residue was chromatographed on a column of 8 g of silica gel. Benzene–ethanol mixture (10 : 1) eluted 15 mg

of acetamidogalactoside *XIX*, m.p. 246–248°C, $[\alpha]_D$ +48° (water), identical with a preparation described earlier[6].

Reaction of a Mixture of 2-O-Mesylmannoside *V* and 4-O-Mesylmannoside *VI* with Sodium Acetate

A mixture of 130 mg of mono-O-mesyl derivative *V* and *VI* (6 : 4), 8 ml of 2-methoxyethanol, 0·8 ml of water and 0·8 g of sodium acetate trihydrate was refluxed for 5 hours, then evaporated to dryness and the residue chromatographed on a column of 10 g of silica gel. Benzene–ethanol 100 : 5 mixture eluted 61 mg of 2-O-mesyl derivative *V*. Benzene–ethanol mixture 10 : 1 eluted 30 mg of acetamidotaloside[6] *XX* which was characterised as 2,4-di-O-acetyl derivative[6] (m.p. 204–205°C, $[\alpha]_D$ −28° (chloroform)).

The analyses were carried out in the Central Laboratories, Department of Organic Analysis, Institute of Chemical Technology (head Dr L. Helešic), the PMR spectra were measured in the Department of NMR Spectroscopy of the same Laboratories (head Professor Dr V. Dědek); we thank the members of the departments mentioned for their help.

REFERENCES

1. Čapek K., Šteffková J., Jarý J.: This Journal *31*, 1854 (1966).
2. Čapek K., Šteffková J., Jarý J.: This Journal *32*, 2491 (1967).
3. Čapek K., Šteffková J., Jarý J.: This Journal *33*, 781 (1968).
4. Čapek K., Šteffková J., Jarý J.: This Journal *33*, 1750 (1968).
5. Čapek K., Šteffková J., Jarý J.: This Journal *35*, 107 (1970).
6. Čapek K., Staněk J. jr, Jarý J.: This Journal *39*, 1462 (1974).
7. Staněk J. jr, Čapek K., Jarý J.: This Journal *39*, 1479 (1974).
8. Lichtenthaler F. W.: Chem. Ber. *102*, 994 (1969).
9. Lichtenthaler F. W., Emig P.: Carbohydrate Res. *7*, 121 (1968).
10. Staněk J. jr, Chuchvalec P., Čapek K., Kefurt K., Jarý J.: Carbohydrate Res., in press.

Translated by Ž. Procházka.