PARTIAL TOSYLATION OF METHYL 6-DEOXY-β-D-GLUCOPYRANOSIDE

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Received December 19th, 1974

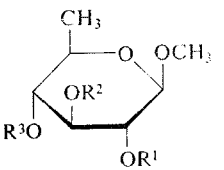
All three possible mono-O-*p*-toluenesulfonyl derivatives *IX*, *X* and *XI*, as well as the three di--O-*p*-toluenesulfonyl derivatives *VI*, *VII* and *VIII* have been prepared by tosylation of methyl 6-deoxy-β-D-glucopyranoside (*I*) with one equivalent of *p*-toluenesulfonyl chloride in pyridine. In order to enable the assignment of structures to compounds *IX*—*XI* they were converted to di--O-benzoyl derivatives *XII*—*XIV*. The first two di-O-benzoyl derivatives were also obtained on reaction of methyl 3-O-benzoyl-4,6-O-benzylidene-2-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XVII*) or of its 2-O-benzoyl-3-O-*p*-toluenesulfonyl isomer *XVIII* with N-bromosuccinimide and subsequent dehalogenation of compounds *XV* and *XVI*. The structures of di-O-*p*-toluenesulfonyl derivatives *VI*—*VIII* were assigned on the basis of the results of further tosylation of mono-O-*p*-toluenesulfonyl derivatives *IX*—*XI*, affording in all instances in addition to tri-O-*p*-toluenesulfonyl derivative *XXVI* both possible di-O-*p*-toluenesulfonyl derivatives, and they were confirmed by ^{1}H-NMR spectra of corresponding benzoyl derivatives *XXVII*—*XXIX*. On reaction of mono-O-*p*-toluenesulfonyl derivatives *IX* and *XI* with Amberlite IRA-400 (OH^-) corresponding methyl 2,3-anhydro-6-deoxy-β-D-mannopyranoside (*XXI*) or methyl 3,4-anhydro--6-deoxy-β-D-galactopyranoside (*XX*) were prepared. The reaction takes place without migration of epoxides. Under the effect of the ion exchanger tosyl derivative *X* gave a mixture of both possible epoxides which were separated in the form of their acetyl derivatives *XXIV* and *XXV*. From the results of the reactions of substances *I*, *IX*, *X* and *XI* with *p*-toluenesulfonyl chloride in pyridine it is evident that the tosylation is slowed down in the case of β-D-*gluco* configuration by the presence of the *p*-toluenesulfonyloxy group in the saccharide molecule, especially so if the group is vicinal to the reacting hydroxyl group.

Partial tosylation of saccharides is interesting both from the point of view of the preparation of important intermediates for further syntheses and from that of the investigation of the differences in reactivity of single hydroxyl groups on the pyranoside skeleton[1,2]. As we needed in connection with the study of partial esterification of amino sugars (ref.[3] and the references therein) to prepare a larger amount of all three mono-O-*p*-toluenesulfonyl derivatives of methyl 6-deoxy-β-D-glucopyranoside (*I*) as starting material for the syntheses of other model substances[4], we used such opportunity in order to investigate more thoroughly the partial tosylation of compound *I* with *p*-toluenesulfonyl chloride in pyridine as well. The results are presented in this paper.

For the preparation of the starting methyl 6-deoxy-β-D-glucopyranoside[5,6] (*I*) we modified the described reaction of methyl 4,6-O-benzylidene-β-D-glucopyranoside

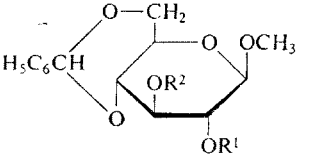
(*II*) with N-bromosuccinimide, giving rise to 4-O-benzoyl-6-bromo-6-deoxy derivative[7]. By benzoylation of compound *II* (ref.[8]) to corresponding 2,3-di-O-benzoyl derivative[9] *III* prior to the reaction with N-bromosuccinimide we were able to improve substantially the yield of the cleavage of the 1,3-dioxan ring. The benzoylation increases the solubility of the starting benzylidene derivative and of the reaction product in non-polar solvent, which substantially decreases the losses during the working up of the reaction mixture by extraction, in addition to a shortening of the reaction time. The subsequent hydrogenation of methyl 2,3,4-tri-O-benzoyl-6-bromo--6-deoxy-β-D-glucopyranoside[10] (*IV*) afforded methyl 2,3,4-tri-O-benzoyl-6-deoxy--β-D-glucopyranoside (*V*) which had considerably different properties from the preparation obtained recently by another route[11]. On catalytic debenzoylation of compound *V* derivative *I* was obtained. A practically quantitative conversion in the sequence *II*→*III*→*IV*→*V*→*I* now makes this procedure as efficient as the preparation of compound *I* described[6] earlier.

Reaction of methyl 6-deoxy-β-D-glucopyranoside (*I*) with one equivalent of *p*-toluenesulfonyl chloride in pyridine gave a mixture of three di-O-*p*-toluenesulfonyl derivatives *VI* (1·8%), *VII* (7·3%) and *VIII* (2·5%), three mono-O-*p*-toluenesulfonyl derivatives *IX* (17·8%), *X* (18·2%) and *XI* (25·7)%, and 26% of the unreacted glucoside *I*, which we separated by repeated chromatography on silica gel to individual components.

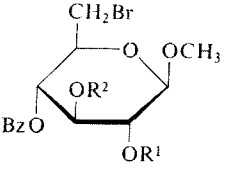


I, $R^1 = R^2 = R^3 = H$
V, $R^1 = R^2 = R^3 =$ Bz
VI, $R^1 = R^2 =$ Ts; $R^3 = H$
VII, $R^1 = R^3 =$ Ts; $R^2 = H$
VIII, $R^2 = R^3 =$ Ts; $R^1 = H$
IX, $R^2 = R^3 = H$; $R^1 =$ Ts
X, $R^1 = R^3 = H$; $R^2 =$ Ts
XI, $R^1 = R^2 = H$; $R^3 =$ Ts
XII, $R^2 = R^3 =$ Bz; $R^1 =$ Ts
XIII, $R^1 = R^3 =$ Bz; $R^2 =$ Ts
XIV, $R^1 = R^2 =$ Bz; $R^3 =$ Ts
XIX, $R^2 = R^3 =$ Ac; $R^1 =$ Ts
XXVI, $R^1 = R^2 = R^3 =$ Ts
XXVII, $R^1 = R^2 =$ Ts; $R^3 =$ Bz
XXVIII, $R^1 = R^3 =$ Ts; $R^2 =$ Bz
XXIX, $R^2 = R^3 =$ Ts; $R^1 =$ Bz

For the determination of the position of *p*-toluenesulfonyloxy group in mono-O-*p*-toluenesulfonyl derivatives *IX*, *X* and *XI* we converted each of these substances to corresponding di-O-benzoyl derivative *XII*, *XIII* and *XIV* under the effect of benzoyl chloride in pyridine. The last mentioned derivative had identical properties with methyl 2,3-di-O-benzoyl-6-deoxy-4-O-*p*-toluenesulfonyl-β-D-glucopyranoside described in literature[11,12]. Derivative *XII*, or *XIII*, was identical with the product of catalytic hydrogenation of methyl 3,4-di-O-benzoyl-6-bromo-6-deoxy-2-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XV*), or methyl 2,4-di-O-benzoyl-6-bromo-6-deoxy-3-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XVI*), respectively, which we prepared on reaction of methyl 3-O-benzoyl-4,6-O-benzylidene-2-O-*p*-toluenesulfonyl-β-D-glucopyranoside[13] (*XVII*) or methyl 2-O-benzoyl-4,6-O-benzylidene-3-O-*p*-toluenesulfonyl-β-D-glucopyranoside[13] (*XVIII*), respectively, with N-bromosuccinimide in tetrachloromethane. We also confirmed the structure of methyl 6-deoxy-2-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*IX*) by converting it to methyl 3,4-di-O-acetyl-6-deoxy-2-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XIX*) which was prepared[14] by a different procedure. The proposed structures of mono-O-*p*-toluenesulfonyl derivatives *IX*, *X* and *XI* are in agreement both with the reactivity of these compounds during epoxide formation[15,16] and with the structures of products formed by this reaction. While 4-O-*p*-toluenesulfonyl derivative *XI* affords in reaction with Amberlite IRA-400 (OH^-) in anhydrous methanol methyl 3,4-anhydro-6-deoxy-β-D-galactopyranoside (*XX*)[12,14,17] in an almost quantitative yield[17] within several minutes, 2-O-*p*-toluenesulfonyl derivative *IX* requires about 3 hours for a quantitative conversion to methyl 2,3-anhydro-6-deoxy-β-D-mannopyranoside[14] (*XXI*). According to ^{1}H-NMR spectra and thin-layer chromatography in neither case did the reaction mixture contain the product of the migration of the oxiran ring, *i.e.* methyl 2,3-anhydro-6-deoxy-β-D-gulopyranoside (*XXII*) or methyl 3,4-anhydro-6-deoxy-β-D-altropyranoside (*XXIII*). It should be noted that the common procedure for the preparation of anhydro derivatives, *i.e.* the reaction with sodium methylate, gives only a mixture of anhydro derivatives[14] in the case of methyl 6-deoxy-2-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*IX*); with 1·5 equivalents of sodium methylate we obtained



II, $R^1 = R^2 = H$
III, $R^1 = R^2 = Bz$
XVII, $R^1 = Ts$; $R^2 = Bz$
XVIII, $R^1 = Bz$; $R^2 = Ts$



IV, $R^1 = R^2 = Bz$
XV, $R^1 = Ts$; $R^2 = Bz$
XVI, $R^1 = Bz$; $R^2 = Ts$

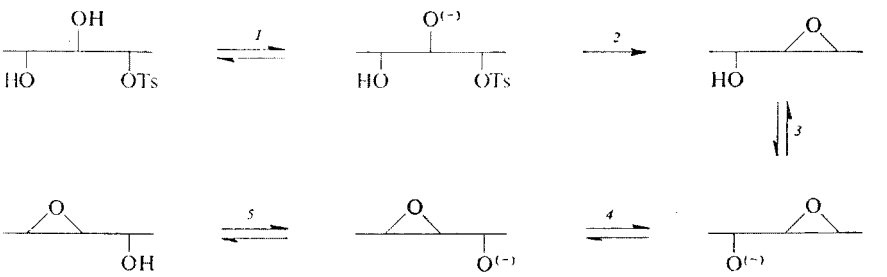
a mixture composed of *XXI* and *XXIII* in a 2 : 1 ratio (determined by integration of the doublets of methyls on $C_{(5)}$ in ^{1}H-NMR spectrum). The same composition has been described for the equilibrium mixture of compounds *XXI* and *XXIII* in aqueous medium[14].

The above mentioned, different behaviour of bases indicates that in common mechanism of formation and migration of epoxides[15] (Scheme 1) it will be necessary also to consider in the case of the quaternary ammonium base on the ion exchanger surface the effect of the bulky cation on the reactivity of alkoxide (*cf.*, for instance, the effect of sodium methoxide[15,16,18]). Its participation could cause the difference in sterical requirements of the transition states of the reactions (*2*) and (*4*) to increase to such an extent as would cause the reaction (*4*) practically not to take place under the effect of the ion exchanger in OH^- cycle. It is improbable that the difference in the cation would cause substantial changes in the equilibrium constant values of the reactions (*1*) and (*3*), or (*5*).

However, it should be mentioned that on prolonged effect of Amberlite IRA-400 (OH^-) on substance *XXI* another product begins to appear in the reaction mixture, probably under the effect of the amine set free by standing of the ion exchanger, which gives a positive reaction with Buchanan's reagent for epoxides[19], and which has identical R_F value as anhydroaltroside *XXIII*. The same effect was also observed when a small amount of ion exchanger was used where the attainment of a quantitative conversion of 2-O-*p*-toluenesulfonyl derivative *IX* required an excessively long reaction time.

Methyl 6-deoxy-3-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*X*) gave two anhydro derivatives on reaction with the ion exchanger which were separable with difficulty. Therefore we converted them first to corresponding O-acetyl derivatives *XXIV* and *XXV*, and we isolated by column chromatography on silica gel 64% of methyl 2-O-acetyl-3,4-anhydro-6-deoxy-β-D-allopyranoside (*XXIV*) and 13·5% of methyl 4-O-acetyl-2,3-anhydro-6-deoxy-β-D-allopyranoside (*XXV*).

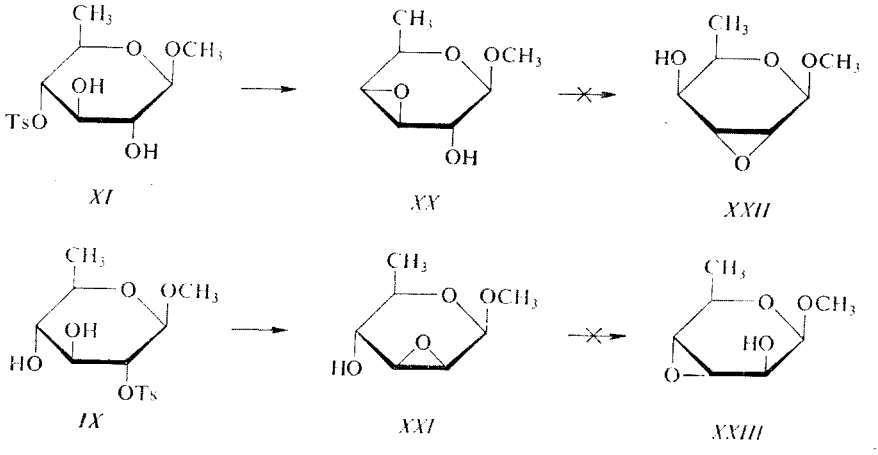
The structures of anhydro derivatives *XXIV* and *XXV* were determined from



SCHEME 1

^{1}H-NMR spectra. In the spectrum of the minor derivative *XXV* a one-proton singlet is present at δ 4·63, attributable only to the hydrogen atom $H_{(1)}$ of 2,3-anhydro derivative. For methyl 4-O-acetyl-2,3-anhydro-6-deoxy-β-D-gulopyranoside the measured[14] coupling constant $J_{1,2}$ was 0·5 Hz. The "singlet" appeared[14] in the *trans* arrangement of the oxiran ring and the methoxy group on the pyranoside skeleton both in $^0H_5$ and $^5H_0$ conformation. In our case the magnitude of the coupling constant $J_{4,5}$ = 0·9 Hz indicates unambiguously that compound *XXV* exists preferably in half-chair conformation $^0H_5$. The spectrum of compound *XXIV* enables the assignment of all protons; in this case $J_{4,5}$ = 0 Hz, and the coupling constant value $J_{2,3}$ = 1·8 Hz corresponds to the coupling constant value $J_{3,4}$ of the isomer *XXV*. The value $J_{1,2}$ = 7·2 Hz indicates an *anti*-periplanar arrangement of the hydrogen atoms, which means that methyl 2-O-acetyl-3,4-anhydro-6-deoxy-β-D-allopyranoside (*XXIV*) exists in chloroform solution almost exclusively in the $^0H_1$ conformation. In both acetyl derivatives the proton on the carbon atom carrying the acetoxyl group resonates at the lowest field.

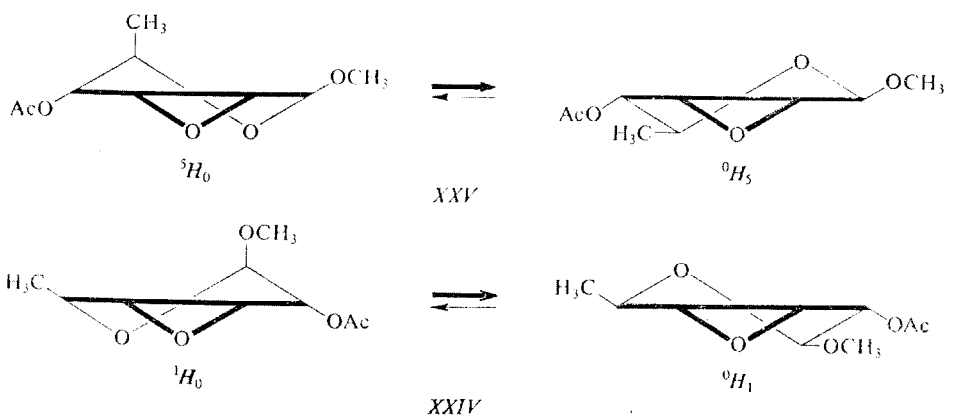
The fact that in the reaction of 3-O-*p*-toluenesulfonyl derivative *X* with ion exchanger more 3,4-anhydro derivative was obtained than 2,3-anhydro derivative differs from the result of the reaction of hydroxymethyl analogue, *i.e.* methyl 3-O-*p*-toluenesulfonyl-β-D-glucopyranoside, with sodium methoxide, where evidently slightly more 2,3-anhydro derivative[20–22] is formed. In order to exclude the possibility that this difference is caused by a different character of the reagent we prepared a mixture of 3,4-anhydroalloside *XXIV* and 2,3-anhydroalloside *XXV* from 3-O-*p*-toluenesulfonyl derivative *X* also on reaction with sodium methoxide. The ratio observed *XXIV* : *XXV* = 5 : 1 does not practically differ from the result obtained by the above given procedure with Amberlite IRA-400 (OH^-). It should be mentioned that in the reaction with sodium hydroxide[16] 1,6-anhydro-3-O-*p*-toluen-



sulfonyl-β-D-glucopyranose also gives more (2·3 times) 3,4-anhydro derivative than 2,3-anhydro derivative; a similar ratio was also found in the reaction of 1,6-anhydro--2,4-di-O-benzyloxycarbonyl-3-O-methanesulfonyl-β-D-glucopyranose[23,24].

For the determination of the position of *p*-toluenesulfonyloxy group in derivatives *VI*, *VII* and *VIII* we submitted each of the mono-O-*p*-toluenesulfonyl derivatives *IX*, *X* and *XI* to further reaction with *p*-toluenesulfonyl chloride in pyridine. As the reactions almost did not take place when one equivalent of *p*-toluenesulfonyl chloride was used, we applied five equivalents of *p*-toluenesulfonyl chloride. In the reaction of 2-O-*p*-toluenesulfonyl derivative *IX* at room temperature and for 48 hours 37·6% of 2,4-di-O-*p*-toluenesulfonyl derivative *VII* and 30% of 2,3-di-O-*p*-toluenesulfonyl derivative *VI* were formed in addition to 5·1% of methyl 6-deoxy-2,3,4-tri-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XXVI*). The same reaction with 3-O-*p*-toluenesulfonyl derivative *X* afforded 5·4% of compound *XXVI*, 34·3% of 3,4-di-O-*p*-toluenesulfonyl derivative *VIII* and 23·8% of 2,3-di-O-*p*-toluenesulfonyl derivative *VI*, while with 4-O-*p*-toluenesulfonyl derivative *XI* 8·3% of substance *XXVI*, 45·4% of 2,4-di-O--*p*-toluenesulfonyl derivative *VII* and 19·5% of 3,4-di-O-*p*-toluenesulfonyl derivative *VIII* were obtained. As after the tosylation of both 2-O-*p*-toluenesulfonyl derivative *IX* and 3-O-*p*-toluenesulfonyl derivative *X* the same di-O-*p*-toluenesulfonyl derivative *VI* was present in the reaction mixture, this must possess the structure of methyl 2,3-di-O-*p*-toluenesulfonyl-6-deoxy-β-D-glucopyranoside. For the same reason the identical tosylation product of compounds *IX* and *XI*, *i.e.* derivative *VII*, must possess the structure of 2,4-di-O-*p*-toluenesulfonyl derivative, and derivative *VIII* must correspond to methyl 6-deoxy-3,4-di-O-*p*-toluenesulfonyl-β-D-glucopyranoside.

^{1}H-NMR spectra of derivatives *XXVII*, *XXVIII* and *XXIX* (see Table I) which we prepared on benzoylation of single di-O-*p*-toluenesulfonyl derivatives *VI* – *VIII* with benzoyl chloride in pyridine agree with the proposed structures; the signal



of the proton on the carbon carrying the benzoyloxy group is always shifted downfield in comparison with the chemical shift value of a corresponding proton on the carbon atom substituted with the *p*-toluenesulfonyloxy group. The considerable upfield shift of the methoxyl group signal in the case of 2,3-di-O-*p*-toluenesulfonyl derivative *XXVII* or 2,3,4-tri-O-*p*-toluenesulfonyl derivative *XXVI* is caused evidently by the shielding with the aromatic nucleus of the *p*-toluenesulfonyloxy group; a similar upfield shift was also observed in 2,3-di-O-*p*-toluenesulfonyl derivative of methyl 4,6-O-benzylidene-β-D-glucopyranoside (δ 3·08), but not in its 2,3-di-O--methanesulfonyl derivative[25] (δ 3·52). The conformation of the *p*-toluenesulfonyloxy group on carbon atom $C_{(2)}$, necessary for the explanation of this upfield shift, requires such an orientation of the aromatic nucleus as would exclude simultaneously any attracting interaction (π-overlap) of the benzene nuclei of the substituents in the positions 2 and 3. On the other hand, in benzoyloxy analogues, *i.e.* in tri-O-benzoyl derivative *V*, or 2,3-di-O-benzoyl derivative *XIV*, an attracting interaction of this type (ref.[26]) is evidently so important that the population of the conformation necessary for the upfield shift of the methoxyl group is negligible. Similarly, no shift is produced by the *p*-toluenesulfonyloxy group in the neighbourhood of which a benzoyloxy group is present (compound *XII*). A possible repulsion of two equatorial *p*-tolu-

TABLE I

Chemical Shifts (δ) and Coupling Constants (Hz) of Derivatives of Methyl 6-Deoxy-β-D-glucopyranoside (*I*; $R^1 = R^2 = R^3 = H$) in Deuteriochloroform

	V[a]	*XXVI*	*XII*	*XIII*	*XIV*	*XXVII*	*XXVIII*	*XXIX*
R^1	Bz	Ts	Ts	Bz	Bz	Ts	Ts	Bz
R^2	Bz	Ts	Bz	Ts	Bz	Ts	Bz	Ts
R^3	Bz	Ts	Bz	Bz	Ts	Bz	Ts	Ts
C—CH_3	1·40	1·19	1·31	1·32	1·50	1·19	1·44	1·31
C_6H_4—CH_3	—	2·43 (3×)	2·21	2·07	2·07	2·22; 2·40	2·10; 2·23	2·10; 2·43
O—CH_3	3·53	2·98	3·43	3·49	3·49	3·03	3·35	3·39
$H_{(1)}$	4·75	4·24	4·49	4·57	4·56	4·26	4·36	4·40
$H_{(2)}$	5·53	4·38	4·78	5·1—5·4	5·29	4·52	4·65	5·23
$H_{(3)}$	5·91	4·81	5·66	5·1—5·4	5·62	5·0—5·2	5·48	4·96
$H_{(4)}$	5·38	4·45	5·18	5·1—5·4	4·70	5·0—5·2	4·60	4·58
$H_{(5)}$	3·93	3·59	3·75	3·75	3·76	3·59	3·64	3·62
$J_{1,2}$	7·7	~7	7·7	7·0	7·8	7·6	7·6	7·5
$J_{2,3}$	9·4	7·0	9·4	—	9·4	—	9·4	9·0
$J_{3,4}$	9·4	8·2	9·4	—	9·4	—	9·4	9·0
$J_{4,5}$	9·4	8·2	9·4	8·6	9·4	9·0	9·4	9·0
$J_{5,6}$	6·1	6·2	6·1	6·2	6·1	6·1	6·1	6·2

[a] In all substances measured signals due to aromatic protons appear in the 7·0—8·0 region.

enesulfonyloxy groups, which is indicated by the above mentioned methoxyl group shift to higher fields, should not remain without effect on the partial reactivity in such a system and may represent one of the causes of the deceleration of the reactivity during the tosylation of methyl 6-deoxy-β-D-glucopyranoside (*I*) to the second or third stage (see below).

From the composition of the reaction mixture after partial tosylation of compound *I* with one equivalent of *p*-toluenesulfonyl chloride it is evident that in the reaction to the first stage the differences in the reactivities of the individual hydroxyl groups are not too substantial; in addition to this the amount of disubstituted derivatives is so high (11·5%) that the yields of monosubstituted derivatives need not be quite parallel with the reactivity of the individual hydroxyl groups[27] in substance *I*. Nevertheless, keeping in mind that further tosylation takes place in all three mono-O--*p*-toluenesulfonyl derivatives *IX*, *X* and *XI* at a comparable rate, it is probable that in the tosylation of compound *I* the hydroxyl group in the position 4 is indeed the most reactive one. This finding is in agreement with the result of dimolar methanesulfonylation of methyl β-D-glucopyranoside[28] even though the yield of the major 4,6-di-O-methanesulfonyl derivative (13%) together with the 4% of 2,6-di-O-methanesulfonyl derivative and 4% of further disubstituted derivative need not be quite convincing with respect to the low total yield (28%). The greater reactivity of $C_{(4)}$—OH in comparison with $C_{(2)}$—OH must be due to the only difference between these hydroxyl groups, *i.e.* the difference between the methoxyl and the methyl groups on the neighbouring carbon atom; substitution of the methyl group by the methoxyl group probably rather manifests itself by inductive effect (decrease of the reactivity in the position 2), than by the effect of a possible intramolecular hydrogen bond, because the bond of the hydroxyl group in the position 2 to the *trans*-oriented anomeric methoxyl group is rather weak[29].

Much more unambiguous is, however, the finding that in monomolar tosylation of methyl 6-deoxy-β-D-glucopyranoside (*I*) the hydroxyl groups react to the second stage much slower; the yield 11·5% of disubstituted derivatives and 61·7% of monosubstituted derivatives is far from corresponding to the statistical distribution. This fact is also evident from further tosylation of mono-O-*p*-toluenesulfonyl derivatives *IX*, *X* or *XI*, where practically no reaction took place with one equivalent of *p*-toluenesulfonyl chloride at room temperature for 18 hours. Even with five equivalents the conversion degrees after 48 hours are about 0·8; 2-O-*p*-toluenesulfonyl derivative reacts slightly more easily. From the minimum amounts of trisubstituted derivative *XXVI* isolated from the mentioned tosylations of compounds *IX*, *X* or *XI* it is evident that the tosylation of each subsequent hydroxyl group is further hampered. This slowing down, caused by sterical and polar effect of the vicinal *p*-toluenesulfonyloxy group, probably reflects itself also in the fact that from 4-O-*p*-toluenesulfonyl derivative *XI* 2·3 times more 2,4-di-O-*p*-toluenesulfonyl derivative *VII* than 3,4-isomer *VIII* is formed. In the case of 2-O-*p*-toluenesulfonyl derivative *IX* this difference in reactivity

is smaller, but it becomes distinct in the attempt at the preparation of tri-O-*p*-toluenesulfonyl derivative *XXVI* from methyl 6-deoxy-2,4-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*VII*). Only after 13 days of reaction with 9 equivalents of *p*-toluenesulfonyl chloride in pyridine at 30°C did the starting compound *VII* disappear. These findings are in contradiction to the statement[25] that the tosylation of methyl 4,6-O--benzylidene-β-D-glucopyranoside in the position 2 accelerates the tosylation in the neighbouring position 3. A larger amount of 3,4-di-O-*p*-toluenesulfonyl derivative *VIII* (34·3%) obtained on tosylation of 3-O-*p*-toluenesulfonyl derivative *X*, compared with the 23·8% of 2,3-di-O-*p*-toluenesulfonyl derivative *VI* indicates that the substitution of $C_{(3)}$—OH by $C_{(3)}$—OTs has no substantial effect on the somewhat higher reactivity of the hydroxyl group in the position 4.

The isolation of a larger amount of 2,4-di-O-*p*-toluenesulfonyl derivative *VII* after tosylation of compound *I*, or after tosylation of mono-O-*p*-toluenesulfonyl derivatives *IX* and *XI* (caused by a slightly higher reactivity of the hydroxyl group in the position 4, and mainly by the sterical and polar hindrance of the esterification of the hydroxyl group by the vicinal *p*-toluenesulfonyloxy group), does not correspond to the result[11] of dimolar benzoylation of compound *I*, from which 2,4-di-O-benzoyl derivative was isolated in 1·1% yield only (in addition to 28·5% of 2,3-di-O-benzoyl- and 4·1% of 3,4-di-O-benzoyl derivative). Although these percentages need not necessarily correspond to the reactivity of the hydroxyloxy groups in mono-O-benzoyl derivatives (in view of the unknown percentage of the transitorily formed mono-O--benzoyl derivatives, of which totally 21·3% were isolated[11]), the prevalence of 2,3--di-O-benzoyl derivative will surely not be changed.* This means that the slowing down of the reactivity of the secondary hydroxyl group under the effect of the vicinal *p*-toluenesulfonyloxy group will be substantially higher than in the case of the benzoyloxy group; it is even possible that the vicinal benzoyloxy group will, on the contrary, increase the reactivity of the hydroxyl group in the case of β-D-*gluco* configuration. This statement together with the fact that $C_{(4)}$—OH in methyl-6-deoxy--β-D-glucopyranoside (*I*) is evidently[11] the least reactive with benzoyl chloride in pyridine, while with *p*-toluenesulfonyl chloride the opposite is true, would represent the first substantial difference observed in the selectivity of the reactivity of polyols with these reagents[31].

EXPERIMENTAL

The melting points were measured on a Kofler block and they are not corrected. Optical rotations were determined with an instrument of the firm Opton, at 20°C, and 0·5—1·0 g/100 ml concentration. Chromatography was carried out on silica gel of Lachema (Brno), 70—200 μm, thin-layer chromatography on silica gel G according to Stahl (Merck, Darmstadt), 10—40 μm. Dimension

* Methyl 2,3,6-tri-O-benzoyl-β-D-glucopyranoside is the major product of partial benzoylation of methyl β-D-glucopyranoside[30].

of the plates was 25 . 75 mm, layer thickness was 0·2—0·3 mm. The substances were detected by spraying with 1% cerium sulfate in 10% sulfuric acid and subsequent mineralization by heating. The solvents were evaporated on a rotatory evaporator at maximum temperature 50°C and in a water-pump vacuum. The light petroleum used for crystallization had b.p. 45—60°C. Samples for analysis were dried at 20—50°C and 0·1 Torr. ^{1}H-NMR spectra were measured in deuteriochloroform on a Varian XL-100-15 and Varian EM-300 instruments. Chemical shifts (δ) are referred to tetramethylsilane as internal standard, coupling constants values (Hz) are read from the first order analyses of the spectra.

Methyl 2,3,4-Tri-O-benzoyl-6-bromo-6-deoxy-β-D-glucopyranoside (*IV*)

N-Bromosuccinimide (5 g) and 12 g of barium carbonate were added to a solution of 14·4 g of methyl 2,3-di-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside[8,13] (*III*) in 250 ml of tetrachloromethane and the mixture was refluxed for 2·5 hours. After filtration and washing of the residue twice with 50 ml portions of tetrachloromethane the filtrates were combined and evaporated and the residue shaken between water and chloroform. After drying over magnesium sulfate chloroform was evaporated and the residue crystallized from methanol, affording 15·6 g (93·5%) of compound *IV* the properties of which were identical with the properties of the described substance[10], m.p. 160—162°C, $[\alpha]_D$ −5° (chloroform).

Methyl 2,3,4-Tri-O-benzoyl-6-deoxy-β-D-glucopyranoside (*V*)

A mixture of 18 g of derivative *IV*, 400 ml of methanol, 12·5 ml of a 3·4M diethylamine solution in methanol, and 50 ml of Raney nickel was hydrogenated at normal pressure for 4 hours. The catalyst was filtered off, washed with three 100 ml portions of acetone and the combined filtrates were evaporated. After dissolution of the residue in 200 ml of chloroform and washing twice with 50 ml portions of water the chloroform layer was dried over calcium chloride, filtered with active charcoal, and evaporated. The 15 g (97%) of the syrup obtained were crystallized from ether–light petroleum, m.p. 90—93°C. After repeated crystallization from ethanol, substance *V* melted at 92—94°C, $[\alpha]_D$ −5° (chloroform), $[\alpha]_D$ −38° (pyridine). For $C_{28}H_{26}O_8$ (490·5) calculated: 68·56% C, 5·34% H; found: 68·42% C, 5·48% H.

Methyl 6-Deoxy-β-D-glucopyranoside (*I*)

A mixture of 14·9 g of compound *V*, 400 ml of methanol, and 0·1 ml of 1M sodium methanolate was allowed to stand at room temperature overnight. The sodium ions were removed with Amberlite IR-120 (H^+), the methanolic filtrate was decolorized with charcoal and evaporated to a syrup from which methyl benzoate was evaporated at 0·1 Torr and 25°C within two hours. The residue was crystallized from ethyl acetate, yield 4·9 g (91%) of compound *I*, m.p. 130—132°C, $[\alpha]_D$ −55° (water), *cf*[5,6].

Partial Tosylation of Methyl 6-Deoxy-β-D-glucopyranoside (*I*)

p-Toluenesulfonyl chloride (1·1 g; 1·03 equivalents) was added to a solution of 1·0 g of compound *I* in 20 ml of pyridine and the mixture allowed to stand at room temperature for 48 hours. Water (5 ml) was then added and the acid eliminated with sodium hydrogen carbonate, and the mixture was evaporated. The residue was extracted with four 10 ml portions of acetone, the combined extracts were dried over magnesium sulfate, filtered and evaporated. The residual syrup (1·9 g) was put on a silica gel column (50 g) and eluted with benzene–acetone (17 : 1); 200 mg (7·3%)

of methyl 6-deoxy-2,4-di-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*VII*) were eluted first, followed by 50 mg (1·8%) of methyl 6-deoxy-2,3-di-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*VI*) and 70 mg (2·5%) of methyl 6-deoxy-3,4-di-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*VIII*). Benzene–acetone 12 : 1 eluted 340 mg (18·2%) of methyl 6-deoxy-3-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*X*), then 332 mg (17·8%) of methyl 6-deoxy-2-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*IX*), and 480 mg (25·7%) of methyl 6-deoxy-4-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XI*). Benzene–ethanol mixture (10 : 1) eluted 260 mg (26%) of the unreacted starting substance. Mixed fractions, containing compounds *VI* and *VII*, or *IX* and *XI* were rechromatographed under the same conditions and the results were included in the above given values. Syrupy 2,3-di-O-*p*-toluenesulfonyl derivative *VI* would not crystallize; after dissolution in ethanol and filtration with charcoal the analytically pure syrup had $[\alpha]_D$ +4° (chloroform). For $C_{21}H_{26}O_9S_2$ (486·6) calculated: 51·84% C, 5·39% H; found: 51·63% C, 5·50% H.

2,4-*Di*-O-p-*toluenesulfonyl derivative* VII was crystallized from ethanol, m.p. 97—99°C, $[\alpha]_D$ −36° (chloroform). For $C_{21}H_{26}O_9S_2$ (486·6) calculated: 51·84% C, 5·39% H; found: 51·78% C, 5·54% H.

3,4-*Di*-O-p-*toluenesulfonyl derivative* VIII was crystallized from a mixture of ethanol, ether and light petroleum, m.p. 139—140°C, $[\alpha]_D$ −16° (chloroform). For $C_{21}H_{26}O_9S_2$ (486·6) calculated: 51·84% C, 5·39% H; found: 51·73% C, 5·49% H.

2-O-p-*Toluenesulfonyl derivative* IX was obtained in the form of a syrup, $[\alpha]_D$ −40° (methanol), which crystallizes as a hydrate from a mixture of water-saturated ethyl acetate and light petroleum, m.p. 55—58°C, $[\alpha]_D$ −42° (methanol). For $C_{14}H_{20}O_7S.H_2O$ (350·4) calculated: 47·99% C, 6·33% H, 9·15% S; found: 47·93% C, 6·37% H, 9·19% S.

3-O-p-*Toluenesulfonyl derivative* X was crystallized from acetone–light petroleum mixture, m.p. 154—156°C (decomp.), $[\alpha]_D$ −6° (methanol). For $C_{14}H_{20}O_7S$ (332·4) calculated: 50·58% C, 6·08% H; found: 50·83% C, 6·22% H.

4-O-p-*Toluenesulfonyl derivative* XI was obtained in the form of a syrup which crystallized on standing. The crystals were washed with ether and they melted then at 85—92°C. However, this product could not be recrystallized, $[\alpha]_D$ −37° (methanol). For $C_{14}H_{20}O_7S$ (332·4) calculated: 50·58% C, 6·08% H; found: 50·59% C, 6·19% H. Only derivatives *IX* and *XI* could be detected by Bonner's reagent[31] for vicinal diols on thin layers.

Methyl 3,4-Di-O-benzoyl-6-deoxy-2-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XII*)

a) Benzoyl chloride (0·1 ml) was added to a solution of compound *IX* (51 mg) in 3 ml of pyridine and the mixture was allowed to stand at room temperature overnight. After decomposition of the mixture with water the separated syrup was shaken between water and chloroform; evaporation of the chloroform layer gave 75 mg (90%) of a syrup which was purified by filtration with charcoal. On standing for several months the syrup crystallized. The crystallized product had m.p. 127—135°C and it was recrystallized from ether. The derivative *XII* obtained had m.p. 138—140°C, $[\alpha]_D$ −65° (chloroform). For $C_{28}H_{28}O_9S$ (540·6) calculated: 62·22% C, 5·22% H; found: 62·31% C, 5·42% H.

b) A mixture of 24 mg of substance *XV*, 3 ml of methanol, 15 ml of diethylamine, and 0·2 ml of Raney nickel was stirred under hydrogen for 4 hours. The catalyst was filtered off, the filtrate evaporated, and the residue freed from diethylamine hydrobromide by filtration through a layer of silica gel. The substance *XII* obtained (16 mg; 76%) was identical with the substance prepared under *a*).

Methyl 2,4-Di-O-benzoyl-6-deoxy-3-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XIII*)

a) Substance *X* (49 mg) was benzoylated with benzoyl chloride in pyridine in the same manner as substance *IX*. After decomposition of the mixture with water the separated crystals of *XIII* were filtered off under suction, washed with water and light petroleum. After drying 50 mg (63%) of crude compound *XIII* were obtained, which had after several crystallizations from ethanol m.p. 203–204°C (decomp.), $[\alpha]_D$ ±0°, $[\alpha]_{365}$ +23° (chloroform). For $C_{28}H_{28}O_9S$ (540·6) calculated: 62·22% C, 5·22% H; found: 62·41% C, 5·43% H.

b) A mixture of 20 mg of compound *XVI*, 3 ml of methanol, 15 mg of diethylamine and 0·3 ml of Raney nickel was hydrogenated at normal pressure for one hour. The reaction course was controlled by thin-layer chromatography in benzene–acetone 33 : 1 (the substances also differ in colour changes during carbonization). The mixture was worked up in the same manner as described for the analogous reaction of derivative *XV*, and it yielded 15 mg (86%) of 2,4-di-O-benzoyl derivative *XIII*, identical with the substance prepared under *a*).

Methyl 2,3-Di-O-benzoyl-6-deoxy-4-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XIV*)

Substance *XI* was benzoylated in the same manner as substance *IX*; after decomposition with water a syrup separated which crystallized on standing. After filtration and washing with water the crystals weighed 70 mg (96%). The crude derivative *XIV* had m.p. 154–158°C and it was dissolved in chloroform filtered with charcoal, evaporated, and the residue crystallized from ethanol. Even after 6 crystallizations from ethanol the melting point would not be better than 157–159°C, $[\alpha]_D$ +23° (methanol). Literature[11] gives m.p. 158–159°C, $[\alpha]_D$ +20° (methanol), or[12] m.p. 162°C, $[\alpha]_D$ +19·9° (methanol). For $C_{28}H_{28}O_9S$ (540·6) calculated: 62·22% C, 5·22% H; found: 62·48% C, 5·38% H.

Methyl 3,4-Di-O-acetyl-6-deoxy-2-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XIX*)

Acetic anhydride (1 ml) was added to a solution of anhydrous 2-O-tosyl derivative *IX* (436 mg; 1·31 mmol) in 5 ml of pyridine and the mixture was allowed to stand overnight. After decomposition with water it was diluted with chloroform and the chloroform solution was extracted gradually with cold 10% sulfuric acid, water, 1% sodium hydrogen carbonate and water. The chloroform solution was then dried over magnesium sulfate, filtered and evaporated. The residue was crystallized from ethyl acetate–light petroleum; yield 423 mg (78%) of derivative *XIX*, m.p. 141–142°C, $[\alpha]_D$ +13° (chloroform). Literature[14] gives m.p. 136°C, $[\alpha]_D$ +10·7° (chloroform).

Methyl 2,4-Di-O-benzoyl-6-bromo-6-deoxy-3-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XVI*)

A mixture of 40 mg of methyl 2-O-benzoyl-4,6-O-benzylidene-3-O-*p*-toluenesulfonyl-β-D-glucopyranoside[13] (*XVIII*), 25 mg of N-bromosuccinimide, 50 mg of barium carbonate, and 4 ml of tetrachloromethane was refluxed for one hour, then evaporated and the residue shaken between water and chloroform. The chloroform layer was dried over magnesium sulfate, evaporated, dissolved in benzene and filtered through a layer of silica gel (8 g). Elution with benzene gave 22 mg (48%) of substance *XVI* which crystallized out on addition of ether. After three crystallizations from acetone–light petroleum the substance *XVI* melted at 187–189°C (decomp.), $[\alpha]_D$ +7° (chloroform). For $C_{28}H_{27}BrO_9S$ (619·5) calculated: 54·28% C, 4·40% H; found: 54·14% C, 4·44% H.

Methyl 3,4-Di-O-benzoyl-6-bromo-6-deoxy-2-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XV*)

A mixture of 64 mg of compound *XVII*, 36 mg of N-bromosuccinimide, 72 mg of barium carbonate, and 4 ml of tetrachloromethane was refluxed for 1·5 hours. After evaporation the residue was applied directly on a column of 10 g of silica gel and eluted with benzene; evaporation of the combined chromatographic fractions gave (after filtration with charcoal) 41 mg (56%) of compound *XV*, which after crystallization from methanol had m.p. 131—132·5°C, $[\alpha]_D$ —48° (chloroform). For $C_{28}H_{27}BrO_9S$ (619·5) calculated: 54·28% C, 4·40% H; found: 54·43% C, 4·26% H.

Methyl 4-O-Benzoyl-6-deoxy-2,3-di-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XXVII*)

A solution of 587 mg of substance *VI* in 5·7 ml of pyridine was cooled at —70°C, 0·6 ml of benzoyl chloride were added to it and the mixture allowed to stand at room temperature. The reaction course was followed by thin-layer chromatography (benzene–acetone 5 : 1). After one hour about 5% conversion was achieved, after 16 hours the conversion was about 80%; after two days the reaction mixture was decomposed with water, the separated syrup was shaken between water and chloroform, the chloroform solution was evaporated and the residue chromatographed on a column of silica gel (20 g) with benzene–acetone 10 : 1. The obtained 620 mg (87%) of compound *XXVII* were crystallized from acetone–ether–light petroleum mixture, m.p. 147—149°C, $[\alpha]_D$ —63° (chloroform). $C_{28}H_{30}O_{10}S_2$ (590·7) calculated: 56·94% C, 5·11% H, 10·86% S; found: 57·12% C, 5·07% H, 10·62% S.

Methyl 3-O-Benzoyl-6-deoxy-2,4-di-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XXVIII*)

A mixture of 455 mg of di-O-*p*-toluenesulfonyl derivative *VII* and 5 ml of pyridine was cooled at —70°C, additioned with 0·45 ml of benzoyl chloride, and allowed to stand at room temperature. According to thin-layer chromatography (benzene–acetone 5 : 1) 5% of the starting compound had reacted only after one hour, while after 16 hours the conversion was 50%; even after 48 hours the conversion was not higher than 95%. After four days the reaction mixture was decomposed with water, the separated crystals were filtered off under suction, dissolved in acetone and filtered with charcoal. Acetone was evaporated and the obtained residue crystallized from a mixture of ethanol and light petroleum. Yield 359 mg (73%), m.p. 199—200°C, $[\alpha]_D$ —25° (chloroform). For $C_{28}H_{30}O_{10}S_2$ (590·7) calculated: 56·94% C, 5·11% H, 10·86% S; found: 56·80% C, 5·10% H, 11·08% S.

Methyl 2-O-Benzoyl-6-deoxy-3,4-di-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XXIX*)

Benzoylation of 455 mg of compound *VIII* with 0·5 ml of benzoyl chloride in 5 ml of pyridine was carried out in the same manner as in the preceding case. According to thin-layer chromatography the reaction mixture already contained after one hour's reaction about 60% of compound *XXIX*. After 24 hours the mixture was decomposed with water, the crystals were filtered off and crystallized from ethanol–acetone–light petroleum mixture. Yield 482 mg (82%), m.p. 184—184·5°C (decomp.), $[\alpha]_D$ +46° (chloroform). For $C_{28}H_{30}O_{10}S_2$ (590·7) calculated: 56·94% C, 5·11% H, 10·86% S; found: 56·87% C, 5·22% H, 10·96% S.

Methyl 6-Deoxy-2,3,4-tri-O-*p*-toluenesulfonyl-β-D-glucopyranoside (*XXVI*)

A mixture of 100 mg of derivative *X*, 2 ml of pyridine, and 460 mg (8 equivalents) of *p*-toluenesulfonyl chloride was heated at 60°C for 100 hours and then decomposed with water. The separat-

ed crystals were filtered off, washed with water, dried and purified by filtration of an acetone solution with charcoal. After crystallization from ethanol 144 mg (75%) of compound *XXVI* were obtained, m.p. 174–175°C, $[\alpha]_D$ −23° (chloroform). For $C_{28}H_{32}O_{11}S_3$ (640·8) calculated: 52·49% C, 5·03% H, 15·01% S; found: 52·64% C, 5·08% H, 14·82% S.

Partial Tosylation of Mono-O-*p*-toluenesulfonyl Derivatives of Methyl 6-Deoxy-β-D-glucopyranoside (*I*)

a) A mixture of 100 mg of 3-O-*p*-toluenesulfonyl derivative *X*, 287 mg (5 equivalents) of *p*-toluenesulfonyl chloride, and 2 ml of pyridine was allowed to stand at room temperature for 30 hours. The reaction course was followed by thin-layer chromatography in benzene–acetone 5 : 1. The mixture was decomposed with ice and evaporated, eventually with toluene. After drying *in vacuo* (oil pump) the residue was dissolved in chloroform and applied onto a column of silica gel (30 g). The column was washed with 100 ml of benzene and then eluted with benzene–acetone (17 : 1); 17 mg (8·3%) of 2,3,4-tri-O-*p*-toluenesulfonyl derivative *XXVI* came out first, followed by 35·7 mg (23·8%) of derivative *VI*, 54·1 mg (34·3%) of derivative *VIII*, and 35·3 mg (33·3%) of the unreacted compound *X*.

b) A mixture of 120 mg of 2-O-*p*-toluenesulfonyl derivative *IX*, 380 mg of *p*-toluenesulfonyl chloride, and 2 ml of pyridine, was allowed to stand at room temperature for 23 hours and worked up as under *a*). Chromatography gave 11·8 mg (5·1%) of compound *XXVI*, 66·0 mg (37·6%) of derivative *VII*, 52·7 mg (30·0%) of derivative *VI*, and 31·9 mg (26·6%) of the starting substance *IX*.

c) A mixture of 116 mg of 4-O-*p*-toluenesulfonyl derivative *XI*, 292 mg of *p*-toluenesulfonyl chloride, and 2 ml of pyridine was allowed to stand at room temperature for 20 hours and worked up as under *a*). Chromatography gave 12 mg (5·4%) of compound *XXVI*, 76·5 mg (45·4%) of derivative *VII*, 32·9 mg (19·5%) of derivative *VIII*, and 34·0 mg (29·6%) of the starting compound *XI*.

Methyl 2,3-Anhydro-6-deoxy-β-D-mannopyranoside (*XXI*)

a) Amberlite IRA 400 (OH^-) converted to its OH form immediately before use and washed with methanol[17] was added (100 mg) to a solution of 3·34 g of syrupy compound *IX* in 100 ml of methanol. The mixture was shaken for 3 hours, the ion exchanger was filtered off, washed with methanol (3 times with 100 ml) and the combined methanolic filtrates were evaporated. The obtained residue was chromatographically pure according to TLC in benzene–acetone 4 : 1, or benzene–ether 1 : 1, in the ^{1}H-NMR spectrum of the sample, measured in D_2O and with sodium 2,2-dimethyl-2-silapentane-5-sulfonate as internal reference, a single doublet was observed in the $C_{(5)}$ methyl group resonance region (δ 1·27; ref.[14]). The same group in methyl 3,4-anhydro-6-deoxy-β-D-altropyranoside (*XXIII*) gives a signal[14] at δ 1·44. The syrupy product was filtered immediately through a column of silica gel (30 g) with benzene–acetone 3 : 1. Evaporation of the filtrate gave 1·59 g (99%) of chromatographically pure compound *XXI* which crystallized after addition of ether. Alternatively, the residue after elimination of ion exchanger can be dissolved in water, additioned with Amberlite IR 120 (H^+) in order to eliminate traces of basic impurities, and filtered with charcoal. 2,3-Anhydro derivative *XXI* was sublimated at 70°C/0·01 Torr, m.p. 78–80°C, $[\alpha]_D$ −40° (methanol). Literature[14] gives m.p. 72–74°C, $[\alpha]_D$ −27·5° (water), ^{1}H-NMR data of the compound prepared by us agree with the described values[14]. Substance *XXI* was converted to 4-O-acetyl derivative, identical with the described substance[14].

b) 0·5 ml of 1M sodium methanolate (1·5 equivalent) were added to a solution of 106 mg of 2-O-*p*-toluenesulfonyl derivative *IX* in 2 ml methanol and the reaction course followed by TLC in benzene–ether 1 : 1. After 20 hours, when all starting material had disappeared the mixture was evaporated and the residue dissolved in deuterated water (0·5 ml) and the ratio of anhydro derivative *XXI* and *XXIII* determined (see procedure *a*)) by integrating the doublets of the methyl groups on carbon atoms $C_{(5)}$ at SW 100 Hz. The ratio was 2 : 1 in favour of substance *XXI*. The obtained mixture of epoxides may be chromatographed in benzene–ether 19 : 1 in the described manner[14].

Methyl 2-O-Acetyl-3,4-anhydro-6-deoxy-β-D-allopyranoside (*XXIV*)
and Methyl 4-O-Acetyl-2,3-anhydro-6-deoxy-β-D-allopyranoside (*XXV*)

a) A mixture of 1·00 g (3·01 mmol) of 3-O-*p*-toluenesulfonyl derivative *X*, 40 ml of methanol, and 15 ml of Amberlite IRA 400 (OH^-) was shaken at room temperature for 1·5 hours, the ion exchanger was filtered off, washed with methanol and the combined filtrates were evaporated. The syrupy residue contained according to thin-layer chromatography (benzene–acetone 10 : 4) two substances of which the minor component had identical R_F value with the starting material, but could be detected with a reagent for substances with oxiran ring[19]. After short drying in a vacuum (oil pump) the residue was dissolved in 5 ml of pyridine and 0·5 ml of acetic anhydride were added to it. After 24 hours the mixture was decomposed with water, mixed with 60 ml of chloroform and the organic layer washed gradually with 15% cold sulfuric acid, water, 1% sodium hydrogen carbonate solution, and again with water. The chloroform layer was dried over magnesium sulfate and evaporated. The residue was chromatographed on 20 g of silica gel; light petroleum–ethyl acetate mixture (20 : 1) eluted first anhydro derivative *XXV*, followed by anhydro derivative *XXIV*. Chromatographic fractions containing compound *XXV* were combined, evaporated and the residue was sublimated at 35°C and 0·01 Torr; yield 82 mg (13·5%) of compound *XXV*, m.p. 33–36°C, $[\alpha]_D$ +74° (chloroform). For $C_9H_{14}O_5$ (202·2) calculated: 53·46% C, 6·98% H; found: 53·73% C, 7·12% H. ^{1}H-NMR data: 1·09 (3 H, d, $J_{5,6} = 6·2$, CH_3CH), 2·03 (3 H, s, CH_3COO), 3·43 (3 H, s, CH_3O), 4·63 (1 H, s, $H_{(1)}$), 4·79 (1 H, q, $J_{3,4} = J_{4,5} = 9·0$, $H_{(4)}$), 3·26 (1 H, d, $J_{2,3} = 4·1$, $H_{(2)}$), 3·47 (1 H, o, $J_{5,6} = 6·2$, $H_{(5)}$), ~6·63 ($H_{(3)}$). Chromatographic fractions containing anhydro derivative *XXIV* were worked up in the same manner (sublimation at 65°C/0·01 Torr); the 388 mg (63·8%) of compound *XXIV* obtained had m.p. 64–66°C, $[\alpha]_D$ −190° (chloroform). For $C_9H_{14}O_5$ (202·2) calculated: 53·46% C, 6·98% H; found: 53·51% C, 7·11% H. ^{1}H-NMR data: 1·31 (3 H, d, $J_{5,6} = 6·8$, CH_3CH), 2·04 (3 H, s, CH_3COO), 3·34 (3 H, s, CH_3O), 4·35 (1 H, d, $J_{1,2} = 7·2$, $H_{(1)}$), 4·85 (1 H, q, $J_{1,2} = 7·2$, $J_{2,3} = 1·8$, $H_{(2)}$), 4·00 (1 H, q, $J_{4,5} = 6·8$, $H_{(5)}$), 3·44 (1 H, q, $J_{2,3} = 1·8$, $J_{3,4} = 4·2$, $H_{(3)}$), 3·11 (1 H, d, $J_{3,4} = 4·2$, $H_{(4)}$).

b) Two ml of 1M sodium methanolate were added to a solution of 332 mg of 3-O-*p*-toluenesulfonyl derivative *X* in 2 ml of methanol and allowed to stand at room temperature. After one hour TLC showed that the result is similar to that obtained under *a*). The mixture was titrated with 1M hydrochloric acid and evaporated. The residue was extracted with acetone, the acetone extract was evaporated to a syrup (162 mg) which was acetylated with acetic anhydride in pyridine and chromatographed in the same manner as under *a*). Total yield, 26 mg (12·96%) of compound *XXV* and 130 mg (64·4%) of compound *XXIV*.

The analyses were carried out in the Department of Organic Analysis of the Central Laboratories of the Institute of Chemical Technology (head Dr L. Helešic), ^{1}H-NMR *spectra were measured in the Department of* NMR *Spectroscopy of the same Laboratories (head Professor V. Dědek); our thanks are due to the staff of these departments. Further we thank Miss E. Kvapilová and Mrs B. Hanousková for carrying out some of the experiments.*

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Translated by Ž. Procházka.