PREPARATION OF 2-AMINO-1,6-ANHYDRO-2-DEOXY-β-D-MANNOPYRANOSE BY INTRAMOLECULAR SUBSTITUTION OF THE TOSYLOXY GROUP IN STERICALLY HINDERED POSITION OF 1,6-ANHYDRO-2-O-*p*-TOLYLSULFONYL-β-D-GLUCOPYRANOSE*

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1,6 : 3,4-Dianhydro-2-O-*p*-tolylsulfonyl-β-D-galactopyranose (*I*) was converted to 1,6-anhydro-4-O-benzyl-2-O-*p*-tolylsulfonyl-β-D-glucopyranose (*II*) and then reacted with benzylisocyanate to give 3-O-(N-benzylcarbamoyl) derivative *III*. The cyclization of this substance under the effect of potassium tert-butoxide in tert-butanol gave 3-benzyl-(1,6-anhydro-4-O-benzyl-2,3-dideoxy-β-D-mannopyrano) [2,3-*d*]oxazolidin-2-one (*IV*) which was hydrolysed to 1,6-anhydro-4-O-benzyl-2-benzylamino-2-deoxy-β-D-mannopyranose (*VIII*). Catalytic debenzylation of *VIII* on palladium on charcoal in the presence of hydrochloric acid gave the hydrochloride of 2-amino-1,6-anhydro-2-deoxy-β-D-mannopyranose (*IX*), which was acetylated to triacetate *XI*. Depending on the conditions during catalytic debenzylation of the oxazolidine derivative *IV* either O-debenzylated derivative *VI* alone was obtained, or the completely debenzylated oxazolidine derivative *VII*.

Recently published papers[1-3] showed that some 2-aminodeoxy derivatives of 1,6-anhydro-β-D-hexopyranoses were used as intermediates in the preparation of biologically interesting aminodeoxyhexoses and their N- or O-substituted derivatives, and corresponding oligosaccharides.

While 2-aminodeoxy derivatives of 1,6-anhydro-β-D-hexopyranoses of D-*gluco* and D-*galacto* configuration can easily be obtained today by ammonolysis of 1,6 : 2,3-dianhydro-β-D-manno-[4] or D-talopyranose[5] respectively, 2-amino-1,6-anhydro-2-deoxy-β-D-mannopyranose is difficult to obtain. The only method known so far[6] for its preparation consists in the isomerization of 1,6-anhydro-2,3-dideoxy-2,3-epimino-β-D-mannopyranose in alkaline medium; this procedure is time-consuming, however, and its disadvantage is that it does not permit a direct preparation of 4-substituted derivatives of 2-amino-2-deoxy-D-mannose.

In view of the occurrence of 2-amino-2-deoxy-D-mannose in natural polysaccharides[7-10] and with respect to its importance in the biogenesis of neuraminic

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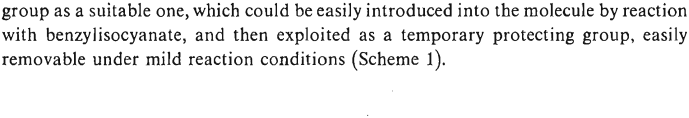
acid[11] we tried to work out a more feasible synthesis of its 1,6-anhydro derivative which might display a broader applicability. The most commonly used method of synthesis of aminodeoxy derivatives of 1,6-anhydrohexopyranoses[12] is the ammonolysis of the oxirane ring in 1,6 : 2,3- or 1,6 : 3,4-dianhydrohexopyranoses, which – however, does not bring about a *cis*-opening of the ring. Neither the conversion of 1,6-anhydro-β-D-*arabino*-hexopyranos-2-ulose nor its derivatives to oximes and subsequent reduction[13], nor the S_N2 substitution of the *p*-tolylsulfonyloxy group, as described in the case of the derivatives of methyl 2-O-*p*-tolylsulfonyl-D-glucofuranoside[14] came into consideration. In the first case the preparation of the starting components would be very difficult[15], while in the second it is known that the substitution of *exo*-axial oriented sulfonyloxy group in the position $C_{(2)}$ of 1,6-anhydrohexopyranoses does not practically take place for sterical reasons and owing to the unfavourable polar effect of the 1,6-anhydride bond[16,17]. The reactivity of the *p*-tolylsulfonyloxy group in the *endo* position is somewhat higher. Thus, for example, in the case of 1,6-anhydro-3,4-dideoxy-2-O-*p*-tolylsulfonyl-β-D-*threo*-hexopyranose it may exchange for the azido group[18].

Therefore we tried to use for our synthesis the reaction taking place under participation of the neighbouring group, which – in comparison with the analogous intermolecular reaction – decreases the activation entropy of the transition state. Basing our considerations on the papers studying the participation of the neighbouring acylamido[19] and thiocarbamoyl[20] group we selected the N-benzylcarbamoyl group as a suitable one, which could be easily introduced into the molecule by reaction with benzylisocyanate, and then exploited as a temporary protecting group, easily removable under mild reaction conditions (Scheme 1).



SCHEME 1

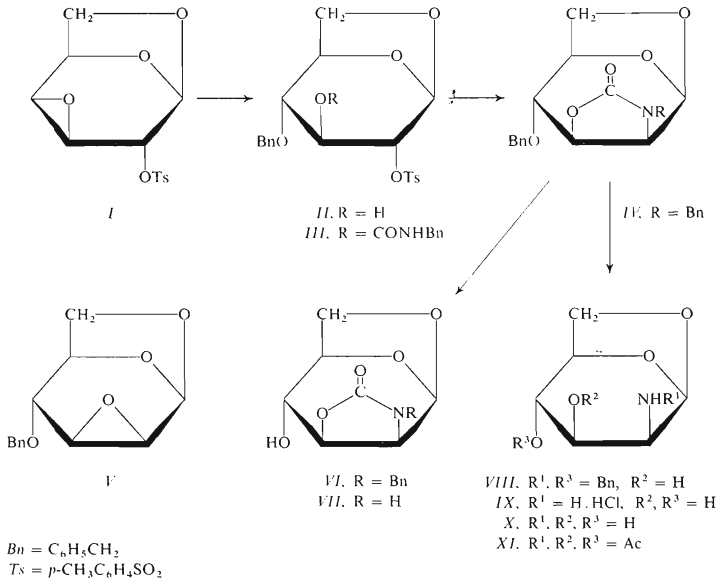
As the starting substance for our synthesis[21] 1,6 : 3,4-dianhydro-2-O-*p*-tolylsulfonyl-β-D-galactopyranose (*I*) served which was converted by a known procedure[22] to 1,6-anhydro-4-O-benzyl-2-O-*p*-tolylsulfonyl-β-D-glucopyranose (*II*). On reaction of *II* with benzylisocyanate in toluene the corresponding urethan *III* was prepared in about 85% yield, the ν(N—C=O) at 1734 and 1520 cm^{-1} and ν(NH) at 3458 cm^{-1} in chloroform and the elemental analysis were in agreement with the assumed structure. In the reaction mixture a small amount of trimer of benzyliso-

cyanate[23] was always present, which is poorly soluble in organic solvents and therefore it does not complicate the workup of the reaction mixture. The use of polar solvents 2-butanone or acetonitrile, and basic catalysis with traces of triethylamine or pyridine, was not advantageous in the present case, although it enhanced the formation of urethans in many other cases[24].

The key reaction of our synthesis is the cyclization of urethan *III* to 3-benzyl-(1,6-anhydro-4-O-benzyl-2,3-dideoxy-β-D-mannopyrano) [2,3-*d*]oxazolidin-2-one (*IV*) which took place most successfully under the effect of potassium tert-butoxide in tert-butanol at room temperature and gave an approximately 60% yield. The experiments aimed at the cyclization under solvolytic conditions, such as heating with sodium acetate in acetic acid or with aqueous pyridine at 180°C in a sealed tube, remained unsuccessful, and only the starting substance was isolated. Parallelly with oxazolidinone *IV* 4-O-benzyl-1,6 : 2,3-dianhydro-β-D-mannopyranose (*V*) was also obtained the formation of which could not be suppressed by changing the reaction conditions either (for example by using sodium isopropoxide in isopropyl alcohol, sodium hydride in toluene, *etc.*). A further possible cyclization product, derivative of iminocarbonic acid, which could be formed under participation of the carbonyl group during the leaving of the *p*-tolylsulfonyloxy group, was not found. The structure of oxazolidinone *IV* was confirmed by IR spectroscopy, analysis and a sequence of further reactions. The wave-number ν(C=O) 1 761 cm^{-1} of oxazolidinone *IV* is 27 cm^{-1} higher than the corresponding wave-number of the starting urethan *III*, which is comparable with the difference $\Delta\nu = 35\ cm^{-1}$ found[25] for ethyl urethan (ν(C=O) 1 689 cm^{-1}) and 1,3-oxazolidin-2-one (ν(C=O) 1 724 cm^{-1}). Catalytic debenzylation of compound *IV* on 10% palladium on charcoal in ethanol gave O-debenzylated product *VI*, the further debenzylation of which on palladium in acetic acid and in the presence of hydrochloric acid (or under the same conditions from compound *IV* directly) gave (1,6-anhydro-2,3-dideoxy-β-D-mannopyrano) [2,3-*d*]oxazolidin-2-one (*VII*). The structure of this compound was proved by ^{1}H-NMR spectroscopy: the D-*manno*-configuration follows from the coupling constants values $J_{1,2} \sim 2 - 2{\cdot}5$, $J_{2,3} \sim 7$ and $J_{3,4} \sim 1{\cdot}5$ Hz; the presence of a 1,6-anhydride bond was proved by the typical ABX system formed by —CH_2—O— and H-5 with corresponding values $J_{5,6endo} \sim 1{\cdot}5$, $J_{5,6exo} \sim 6$ and $J_{6,6} \sim 7{\cdot}5$ Hz.

Hydrolysis of oxazolidinone *IV* with sodium hydroxide in aqueous ethanol took place under heating within 1·5 h and gave 1,6-anhydro-4-O-benzyl-2-benzylamino-2-deoxy-β-D-mannopyranose (*VIII*) in practically quantitative yield. In a better way than from pure oxazolidinone *IV* obtained chromatographically, benzylamino derivative *VIII* can be prepared under the same conditions on hydrolysis of the reaction mixture after cyclization of compound *III*, which contains compound *IV* and epoxide *V*. Only compound *IV* is hydrolysed while the epoxide remains unchanged. The product of hydrolysis of compound *IV*, benzylamino derivative *VIII*, is then isolated from the mixture by crystallization. The structure of compound *VIII* was confirmed

by elemental analysis and IR spectra. On catalytic debenzylation of compound *VII* on palladium on charcoal in ethanolic hydrogen chloride the hydrochloride of 2-amino-1,6-anhydro-2-deoxy-β-D-mannopyranose (*IX*) was obtained the identity of which with the authentic sample[6] followed from a comparison of physical constants. Using Amberlite IRA-400 (in OH^- cycle) the base *X* was set free from the hydro-



I

II, R = H
III, R = CONHBn

IV, R = Bn

V

VI, R = Bn
VII, R = H

VIII, R^1, R^3 = Bn, R^2 = H
IX, R^1 = H.HCl, R^2, R^3 = H
X, R^1, R^2, R^3 = H
XI, R^1, R^2, R^3 = Ac

Bn = $C_6H_5CH_2$
Ts = *p*-$CH_3C_6H_4SO_2$

chloride *IX*. Its acetylation in pyridine gave the corresponding triacetyl derivative *XI*, the IR spectrum of which displays characteristic vibrations of the acetamido group and the acetoxy group. Hydrolysis of compounds *IX* according to literature[6] in 6M hydrochloric acid at 100°C, monitored with an amino acid analyzer, gave the hydrochloride of 2-amino-2-deoxy-D-mannose.

To our knowledge the substitution described in this paper is the first case of a successful substitution of an *exo*-axial group in the position $C_{(2)}$ in 1,6-anhydrohexoses. As shown by preliminary experiments this method also comes into consideration for the preparation of 4-substituted derivatives of 2-amino-1,6-anhydro-2-deoxy-β-D--mannopyranose from corresponding 4-substituted derivatives of 1,6-anhydro-2-O--*p*-tolylsulfonyl-β-D-glucopyranose.

EXPERIMENTAL

The melting points were determined on a Boëtius micromelting point apparatus. Optical rotation was measured on an automatic polarimeter, Bendix–Ericsson ETL 143A, at 23–25°C. The IR spectra were measured on the spectrophotometers UR 10 and UR 20. The ^{1}H-NMR spectra were measured on a Varian HA-100 instrument. The signals of individual protons were assigned on the basis of the double resonance method. For column chromatography silica gel of 100 to 160 μm particle size (Lachema, Brno) was used, and for thin-layer chromatography silica gel according to Stahl, layer thickness 0·2–0·3 mm; detection was carried out with 50% sulfuric acid and carbonization. The solvents were evaporated on a rotary vacuum evaporator at 50°C (bath temperature). Samples for analysis were dried over phosphorus pentoxide at 13·3 Pa.

Benzyl Isocyanate

Benzyl isocyanate (19·6 g; 65%) was prepared according to literature[26] from 26·5 ml of phenylacetyl chloride. B.p. of the product 84°C/1·33 kPa. IR spectrum (toluene): a single strong band of ν(N=C=O) at 2260 cm^{-1} in the 1600–2800 cm^{-1} region.

1,6-Anhydro-4-O-benzyl-3-O-(N-benzylcarbamoyl)-2-O-*p*-tolylsulfonyl-β-D-glucopyranose (*III*)

A mixture of tosyl derivative[22] *II* (18·4 g) and benzylisocyanate (6·63 g) in 180 ml of toluene (dried over sodium) was refluxed and the reaction followed using thin-layer chromatography in benzene–acetone (9 : 1); for the starting compound *II* R_F = 0·36, for the product *III* R_F = 0·46. After 7 h refluxing the mixture was filtered with charcoal and concentrated to a syrup which was dissolved twice in a small amount of chloroform and evaporated. Crystallization of the residue from ether–light petroleum mixture afforded 20·75 g (85%) of product *III* of m.p. 106–108°C, $[\alpha]_D$ +25° (*c* 0·69; chloroform). IR spectrum (chloroform): ν(—SO_2—O—) 1177, 1191, 1374 cm^{-1}, ν(N—C=O) 1520, 1734 and ν(NH) 3458 cm^{-1}. For $C_{28}H_{29}NO_8S$ (539·6) calculated: 62·33% C, 5·42% H, 2·60% N, 5·94% S; found: 62·08% C, 5·57% H, 2·65% N, 6·20% S.

3-Benzyl-(1,6-anhydro-4-O-benzyl-2,3-dideoxy-β-D-mannopyrano) [2,3-*d*]oxazolidin-2-one (*IV*)

A solution of 0·1 g of potassium in 10 ml of tert-butanol was added to a solution of urethan *III* (0·4 g) in 20 ml of tert-butanol. The mixture was allowed to stand at room temperature and the reaction course was followed using thin-layer chromatography in ether–light petroleum (7 : 3). R_F of the starting substance *III* was 0·46, of the product *IV* 0·29 and of epoxide *V* 0·62; on detection with 50% sulfuric acid the product *IV* gave yellow to blue spots. After 1·5 h standing of the mixture the starting compound could no longer be detected; the pH of the solution was adjusted to pH 7 with 5% hydrochloric acid and the solution was concentrated. The residue was repeatedly extracted between water and chloroform, the chloroform solutions were combined and dried

over anhydrous magnesium sulfate and evaporated to a syrup. On column chromatography on silica gel with ether–light petroleum (1 : 1) as eluent 1,6 : 2,3-dianhydro-4-O-benzyl-β-D-mannopyranose (*V*) was eluted first in a 25% yield (49 mg), identical with an authentic specimen[27] according to their m.p., R_F and IR spectra. As the main product oxazolidinone *IV* was eluted next, in a 58% yield (150 mg), m.p. 84–85°C, $[\alpha]_D$ −56° (*c* 0·72; chloroform). IR spectrum (chloroform): ν(CO) 1761 cm^{-1}. For $C_{21}H_{21}NO_5$ (367·4) calculated: 68·65% C, 5·76% H, 3·81% N; found: 68·99% C, 5·68% H, 4·00% N.

3-Benzyl-(1,6-anhydro-2,3-dideoxy-β-D-mannopyrano) [2,3-*d*]oxazolidin-2-one (*VI*)

A solution of oxazolidinone *IV* (250 mg) in 10 ml of ethanol was hydrogenated on 10% palladium on charcoal (80 mg) at about 40°C. The reaction course was followed by thin-layer chromatography in chloroform–methanol (10 : 1). The R_F value of the starting compound *IV* was 0·80, of the product *VI* 0·50. After 12 h the mixture was filtered and evaporated. Crystallization of the residue from ethanol–ether gave 135 mg (72%) of product *VI*, m.p. 167–169°C, $[\alpha]_D$ −111° (*c* 0·65; chloroform). IR spectrum (chloroform): ν(CO) 1765 cm^{-1}, ν(OH) 3400–3500, 3600 cm^{-1}. For $C_{14}H_{15}NO_5$ (277·3) calculated: 60·64% C, 5·45% H, 5·05% N; found: 60·51% C, 5·37% H, 4·90% N.

(1,6-Anhydro-2,3-dideoxy-β-D-mannopyrano) [2,3-*d*]oxazolidin-2-one (*VII*)

A solution of oxazolidinone *IV* (975 mg) in a mixture of acetic acid and 2·8 ml of 6M hydrochloric acid was hydrogenated on 230 mg of 30% palladium on charcoal at 40–50°C for 2 days. The reaction was followed using thin-layer chromatography in chloroform–methanol (10 : 1). The mixture was filtered, evaporated with 3 ml of methanol and the residue deionized with Amberlite IR 45 (in OH^- cycle). Chromatography of the residue on silica gel in chloroform–methanol (15 : 1) and crystallization from ethanol–ether mixture gave 176 mg (35%) of product *VII*, m.p. 171–172°C, $[\alpha]_D$ −125° (*c* 0·7; water). IR spectrum (dioxane): ν(CO) 1782 cm^{-1}. ^{1}H-NMR spectrum (hexadeuteriodimethyl sulfoxide, δ-scale, coupling constants *J* in Hz): 5·23 (H-1), 3·59 (H-2), 3·77 (H-3), 3·80 (H-4), 4·51 (H-5), 4·30 ($H\text{-}6_{endo}$), 3·61 ($H\text{-}6_{exo}$), 5·55 (OH), 7·59 (NH); $J_{1,2} \sim 2$–2·5, $J_{2,3} \sim 7$, $J_{3,4} \sim 1·5$, $J_{5,6endo} \sim 1·5$, $J_{5,6exo} \sim 6$, $J_{6,6} \sim 7·5$, $J_{4,OH} \sim$ ~ 5 Hz. For $C_7H_9NO_5$ (187·2) calculated: 44·92% C, 4·85% H, 7·48% N; found: 44·57% C, 4·88% H, 7·23% N. Compound *VII* was prepared from N-benzyloxazolidinone *VI* in 52% yield in a similar manner.

1,6-Anhydro-4-O-benzyl-2-benzylamino-2-deoxy-β-D-mannopyranose (*VIII*)

A solution of sodium hydroxide (1·5 g in 5 ml of water) was added to a solution of oxazolidinone *IV* (240 mg) in ethanol (25 ml) and the mixture refluxed for 1·5 h. The course of hydrolysis was followed by thin-layer chromatography in benzene–acetone (9 : 1); R_F of the starting compound is 0·46, R_F of product *VIII* is 0·31. The mixture was concentrated, extracted with chloroform, the extract was dried over anhydrous magnesium sulfate, filtered and evaporated. Crystallization of 210 mg of the product from ether–ethanol mixture gave 183 mg (84%) of pure *VIII*, m.p. 86 to 87°C, $[\alpha]_D$ −33° (*c* 0·72; chloroform). IR spectrum (chloroform): ν(NH) 3350 cm^{-1}, ν(OH, NH) 3200–3600 cm^{-1}. For $C_{20}H_{23}NO_4$ (341·4) calculated: 70·36% C, 6·80% H, 4·10% N; found: 70·59% C, 6·82% H, 4·45% N.

A mixture of oxazolidinone *IV* and epoxide *V*, prepared from 0·9 g of urethan *III* in the above described manner, was hydrolysed directly, without previous chromatographic separation, and worked up as described here. Yield 290 mg (51%) of benzylamino derivative *VIII*.

Hydrochloride of 2-Amino-1,6-anhydro-2-deoxy-β-D-mannopyranose (*IX*)

6M Hydrochloric acid (0·18 ml) and 64 mg of 10% palladium on charcoal were added to a solution of benzylamino derivative *VIII* (120 mg) in 3 ml of ethanol and the mixture was hydrogenated at 40–50°C. The reaction course was followed using thin-layer chromatography in the system chloroform–isopropyl alcohol–ammonia–water (10 : 10 : 1 : 1). Hydrogenolysis was terminated after 4 h (product *IX* was formed, with R_F 0·23), the mixture was filtered, the filtrate evaporated and the free hydrochloric acid eliminated by triple evaporation with methanol (3 × 2 ml). Hydrochloride *IX* crystallized from an ethanol–acetone–water mixture as hydrate; yield 59 mg (77%), m.p. 203–205°C (crystal water is lost at 100°C, at 160°C sublimation sets on), $[\alpha]_D$ −91° (*c* 0·92; water). For a sample of *IX* dried under reduced pressure over phosphorus pentoxide at 100°C to constant weight the melting point was 203–205°C and $[\alpha]_D$ −99° (*c* 0·99; water). An authentic sample prepared according to lit.[6] had m.p. 200–203°C, $[\alpha]_D$ −98° (*c* 0·47; water) and an identical ^{1}H-NMR spectrum.

2-Acetamido-3,4-di-O-acetyl-1,6-anhydro-2-deoxy-β-D-mannopyranose (*XI*)

Pyridine (1·5 ml) and acetic anhydride (0·5 ml) were added to 91 mg of 2-amino-1,6-anhydro-β-D-mannopyranose (*X*) prepared from hydrochloride *IX* by means of Amberlite IRA-400 (in OH^- cycle) and the mixture was allowed to stand for 4 h. Methanol (1 ml) was then added to the mixture, which was evaporated and the residue was treated several times with small amounts of methanol–toluene mixture (1 : 3), and evaporated. The residue was dissolved in ethanol, filtered with charcoal and evaporated. Crystallization of the residue from an ethanol–ether mixture gave; 77 mg (47%) of acetyl derivative *XI*, m.p. 182–183°C (sublimes at 140°C), $[\alpha]_D$ −98° (*c* 0·80 chloroform). IR spectrum (chloroform): ν(N—C=O) 1 505, 1 680 cm^{-1}, ν(CO) 1 748 cm^{-1} and ν(NH) 3 458 cm^{-1}. For $C_{12}H_{17}NO_7$ (287·3) calculated: 50·17% C, 5·96% H, 4·88% N; found: 50·36% C, 5·97% H, 4·83% N.

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