STRUCTURE OF PENTA-O-ACETYLSUCROSES FORMED BY DEACETYLATION OF OCTA-O-ACETYLSUCROSE. REACTION OF 2,3,4,6,6'-PENTA-O-ACETYLSUCROSE*

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Dedicated to Academician J. Mostecký on the occasion of his 65th birthday.

Chromatographic separation of penta-O-acetylsucrose fraction from deacetylation of octa-O-acetylsucrose by treatment with aluminum oxide impregnated by potassium carbonate gave 1',3,4,6,6'-penta-O-acetylsucrose (*XII*), 1,2,3,4,6-penta-O-acetylsucrose (*XIII*), and the prevailing 2,3,4,6,6'-penta-O-acetylsucrose (*XIV*). Reaction of compound *XIV* with two equivalents of *p*-toluenesulfonyl chloride in pyridine produced besides the 1'-O-*p*-toluenesulfonyl derivative *XXI* and 1',3',4'-tri-O-tosyl derivative *XXII* also 1',3'-di-O-tosyl derivative *XXIII* and 1',4'di-O-tosyl derivative *XX*. 1',2-anhydro-(3,4,6-tri-O-acetyl-α-D-glucopyranosyl 6'-O-acetyl-3',4'-anhydro-β-D-*ribo*-hexulofuranoside) (*X*) and 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl 1,6-di-O-acetyl-3,4-anhydro-β-D-*ribo*-hexulofuranoside (*VIII*) were prepared from compound *XXIII* by two minutes boiling with 1M sodium methoxide, evaporation of the reaction mixture, and acetylation (method *A*). Compound *XX* gives under reaction conditions of method *A* 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl 1,6-di-O-acetyl-3,4-anhydro-β-D-*lyxo*-hexulofuranoside (*IX*) only. However, upon 24 h boiling with 1M sodium methoxide, neutralization, evaporation, and acetylation of the reaction mixture (method *B*), we obtained 3,3',4,6,6'-penta-O-acetyl-1',2-anhydro-4'-O-methylsucrose (*XXIV*), 1',2,3,3',4,6,6'-hepta-O-acetyl-4'-O-methylsucrose (*XXV*), and 1',2-anhydro-(3,4,6-tri-O-acetyl-α-D-glucopyranosyl 3',4',6'-tri-O-acetyl-β-D-*xylo*-hexulofuranoside) (*XXVI*). Compounds *XXV* and *XXVI* are also formed by reaction of epoxide *IX* with sodium methoxide according to method *B*. Compound *XXVI* can be prepared by hydrolysis of the dianhydro derivative *X* followed by acetylation. A reaction mechanism for compound *XXVI* formation from the epoxide *IX* is proposed. It assumes an intramolecular opening of the oxirane ring in compound *IX* under formation of α-D-glucopyranosyl 1,3-anhydro-β-D-*xylo*-hexulofuranoside (*XLVI*). The 1'-O-tosyl derivative *XXI* reacts with sodium methoxide according to method *B* to give 3,3',4,4',6,6'-hexa-O-acetyl-1',2-anhydrosucrose (*XXVIII*), octa-O-acetylsucrose, and 2,3,3',4,6,6'-hexa-O-acetyl-1',4'-anhydrosucrose *XL*.

Recently, we have found that the action of aluminum oxide impregnated with potassium carbonate[1] on methanolic solution of octa-O-acetylsucrose leads to

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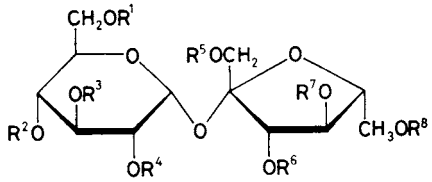
a mixture of O-acetylsucroses with acetylation degree 1 – 8 (ref.[2]). Octa-O-acetylsucrose is deacetylated exclusively on fructose part of the molecule providing the mixture of four hepta-O-acetylsucroses *I* – *IV* in which the isomer *III* having an OH group in the position 4′ dominates. The last mentioned compound and the compound *II* give further 1′,2,3,4,6,6′-hexa-O-acetylsucrose (*V*). Compound *I* si deacetylated to 2,3,4,4′,6,6′-hexa-O-acetylsucrose (*VI*). Compound *IV* is transformed into hexa-O-acetylsucrose(s) that are deacetylated to penta-O-acetylsucrose(s) so quickly (in comparison with compounds *V* and *VI*) that its abundance in hexa-O--acetylsucrose fraction is negligible[3]. We have subjected this fraction to tosylation and upon crystallization we have obtained[4] 1′,2,3,4,6,6′-hexa-O-acetyl-3′,4′-di-O--*p*-toluenesulfonylsucrose (*VII*) in 70% yield. By its reaction with sodium methoxide under conditions already described[5] (2 minutes boiling, evaporation of the reaction mixture, and acetylation; further referred as method *A*) we obtained 2,3,4,6-tetra-O--acetyl-α-D-glucopyranosyl 1,6-di-O-acetyl-3,4-anhydro-β-D-*ribo*-hexulofuranoside (*VIII*) and its corresponding *lyxo*- isomer *IX*. We subjected the mother liquors after crystallization of compound *VII* to the same reaction sequence and we isolated besides the epoxides *VIII* and *IX* also 1′,2-anhydro-(3,4,6-tri-O-acetyl-α-D-glucopyranosyl 6′-O-acetyl-3′,4′-anhydro-β-D-*ribo*-hexulofuranoside (*X*, ref.[4]). Compound *X* was evidently formed from the ditosyl derivative *XI* so that the minor hexa-O--acetylsucrose was assigned the structure *VI*.

This paper is devoted to the analysis of the penta-O-acetylsucrose fraction formed in deacetylation of octa-O-acetylsucrose and to the exploitation of the dominant penta-O-acetylsucrose. Re-chromatography of this fraction on silica gel yielded compounds *XII*, *XIII*, and *XIV* in the ratio 1 : 3 : 7. Their reaction with deuterioacetanhydride in pyridine provided the corresponding tri-O-deuterioacetyl derivatives *XV*–*XVII*. The ions *m*/*z* 289 and 247 or 334 and 337, respectively, were present in the mass spectra of compounds *XII* and *XV*. That indicated an absence of one O-acetyl group on the glucose moiety and two O-acetyl groups on the fructose part of the molecule[6]. The ions *m*/*z* 331 and 205 or 331 and 340, respectively, observed in the spectra of compounds *XIII* or *XIV*, and *XVI* or *XVII*, respectively, indicated an absence of three O-acetyl groups on the fructose part. The missing signals of protons H-2, H-3′, and H-4′ in the 4·7 – 5·7 ppm region of ^{1}H NMR spectrum of compound *XII* indicate deacetylation in these positions. This deduction is confirmed by comparison of ^{13}C NMR spectra of octa-O-acetylsucrose[7], compound *XII*, and the product of its in situ reaction with trichloroacetyl isocyanate (TAI)[8,9]. The most diagnostic is the effect on C-1 (+2·9 and −1·9 ppm, respectively). Signals of H-3′ and H-4′ are also missing in the region under discussion of the ^{1}H NMR spectra of compounds *XIII* and *XIV*. Downfield shifts of one of the methylene carbons in ^{13}C NMR spectra of TAI derivatives of compounds *XIII* and *XIV* indicate again an absence of the O-acetyl group in one of these positions. Since the chemical shifts of glucose carbons are virtually unchanged in both cases, it must be

evidently either position 1′ or 6′. With compound *XIII*, a marked effect on C-5′ (+3·0 or −3·9 ppm, respectively) was observed so that we assigned the structure of 1′,2,3,4,6-penta-O-acetylsucrose (*XIII*) to this compound. Compound *XIV* in which a similar effect was observed on C-2′ (+0·3 or −1·4 ppm, respectively) was assigned the structure of 2,3,4,6,6′-penta-O-acetylsucrose.



I, R^5= H ; R^1= R^2= R^3= R^4= R^6= R^7= R^8= Ac
II, R^6= H ; R^1= R^2= R^3= R^4= R^5= R^7= R^8= Ac
III, R^7= H ; R^1= R^2= R^3= R^4= R^5= R^6= R^8= Ac
IV, R^8= H ; R^1= R^2= R^3= R^4= R^5= R^6= R^7= Ac
V, R^6= R^7= H ; R^1= R^2= R^3= R^4= R^5= R^8= Ac
VI, R^5= R^6= H ; R^1= R^2= R^3= R^4= R^7= R^8= Ac
VII, R^6= R^7= Ts ; R^1= R^2= R^3= R^4= R^5= R^8= Ac
XI, R^5= R^6= Ts ; R^1= R^2= R^3= R^4= R^7= R^8= Ac
XII, R^4= R^6= R^7= H ; R^1= R^2= R^3= R^5= R^8= Ac
XIII, R^6= R^7= R^8= H ; R^1= R^2= R^3= R^4= R^5= Ac
XIV, R^5= R^6= R^7= H ; R^1= R^2= R^3= R^4= R^8= Ac
XV, R^4= R^6= R^7= C^2H_3CO ; R^1= R^2= R^3= R^5= R^8= Ac
XVI, R^6= R^7= R^8= C^2H_3CO ; R^1= R^2= R^3= R^4= R^5= Ac
XVII, R^5= R^6= R^7= C^2H_3CO ; R^1= R^2= R^3= R^4= R^8= Ac
XVIII, R^6= R^8= H ; R^1= R^2= R^3= R^4= R^5= R^7= Ac
XIX, R^7= R^8= H ; R^1= R^2= R^3= R^4= R^5= R^6= Ac
XX, R^5= R^7= Ts ; R^6= H ; R^1= R^2= R^3= R^4= R^8= Ac
XXI, R^5= Ts ; R^6= R^7= H ; R^1= R^2= R^3= R^4= R^8= Ac
XXII, R^5= R^6= R^7= Ts ; R^1= R^2= R^3= R^4= R^8= Ac
XXIII, R^5= R^6= Ts ; R^7= H ; R^1= R^2= R^3= R^4= R^8= Ac
XXV, R^7= CH_3; R^1= R^2= R^3= R^4= R^5= R^6= R^8= Ac
XXIX, R^1= R^2= R^3= R^4= R^5= R^6= R^7= R^8= CH_3
XXXV, R^5= Ts ; R^7= CH_3; R^1= R^2= R^3= R^4= R^6= R^8= H
XXXVIII, R^7= CH_3; R^1= R^2= R^3= R^4= R^5= R^6= R^8= H
XLII, R^5= Tr ; R^6= R^7= H ; R^1= R^2= R^3= R^4= R^8= Ac
XLIII, R^5= Tr ; R^1= R^2= R^3= R^4= R^6= R^7= R^8= Ac
XLIV, R^5= Ms ; R^1= R^2= R^3= R^4= R^6= R^7= R^8= Ac
XLV, R^6= Ms ; R^1= R^2= R^3= R^4= R^5= R^7= R^8= Ac

Taking the relative proportion of compounds *XII*–*XIV* in the reaction mixture into account, it can be stated that the dominant penta-O-acetylsucrose *XIV* is formed

by regiospecific deacetylation of the minor hexa-O-acetylsucrose *VI* at the position 4′ whereas the dominant hexa-O-acetylsucrose *V* is deacetylated at C-1′. The later hexa-O-acetylsucrose is also deacetylated at C-2 providing compound *XII* and probably also at the position 6′ under formation of compound *XIII*. This compound is also formed by deacetylation of hexa-O-acetylsucrose that must have the structure *XVIII* or *XIX*. With respect to octa-O-acetylsucrose the deacetylation is highly specific. Among 56 possible isomers, only three are formed, with compound *XIV* prevailing.

Compound *XIV* offers several possibilities of chemical exploitation. Our first idea was to try whether the treatment of its 1′,4′-di-O-tosyl derivative *XX* with sodium methoxide will give the isomer of compound *X* having *lyxo*-configuration on the furanose part of the molecule. Therefore, we treated the compound *XIV* with two equivalents of *p*-toluenesulfonyl chloride in pyridine. We isolated besides the 1′-O--tosyl derivative *XXI* and 1′,3′,4′-tri-O-tosyl derivative *XXII* the 1′,3′-di-O-tosyl derivative *XXIII* and 1′,4′-di-O-tosyl derivative *XX* in equal yields. The structures of compounds *XX*–*XXIII* were derived from their NMR spectra. Number of tosyloxy groups followed directly from ^{1}H NMR spectra. Their position was inferred from the downfield shift of the corresponding protons and carbons caused by tosylation of a hydroxy group (pronounced effect for the primary alcoholic groups) that is usually accompanied by an upfield shift of the neighbour carbons.

The reaction of sodium methoxide with 1′,4′-di-O-tosyl derivative *XX* according to method *A* gave epoxide *IX* whereas with 1′,3′-di-O-tosyl derivative *XXIII* epoxide *VIII* (57%) and dianhydro derivative *X* (32%) were obtained. Because of high yield of 1′,2-anhydro ring clossure obtained by British authors[10] with 1′-O-*p*-toluenesulfonyl-6,6′-di-O-triphenylmethylsucrose upon 24 h heating with sodium methoxide, neutralization of the reaction mixture, and acetylation (method *B*), we subjected the compounds *XX* and *XXIII* to this procedure. With compound *XXIII*, we again obtained the mixture of dianhydro derivative *X* and epoxide *VIII*, now with compound *X* prevailing (52%). On the contrary, three compounds *XXIV*–*XXVI* were isolated from the reaction of *XX*. The compound *XXIV* (60% yield) contains a methoxyl group according to its NMR spectra. The signals of protons H-1′a, H-1′b, and H-2 in its ^{1}H NMR spectrum are shifted upfield in comparison with those of corresponding protons in octa-O-acetylsucrose. Therefore, the presence of a 1′,2-anhydro ring is inferred. The methoxyl is located at C-4′ since the proton H-4′ is shifted upfield from its "normal" region 4·7–5·7 ppm and the signals of C-4′ and C-5′ are both shifted downfield. Deacetylation of compound *XXIV* followed by treatment with methyl iodide and silver oxide in N,N-dimethylformamide yielded the hexa-O-methyl derivative *XXVII* identical with the product of deacetylation and methylation of 3,3′,4,4′,6,6′-hexa-O-acetyl-1′,2-anhydrosucrose (*XXVIII*, ref.[10]). Therefore, compound *XXIV* has the structure of 3,3′,4,6,6′-penta-O-acetyl-1′,2-anhydro-4′-O-methylsucrose. Compound *XXV* exhibited in its mass spectrum ions at

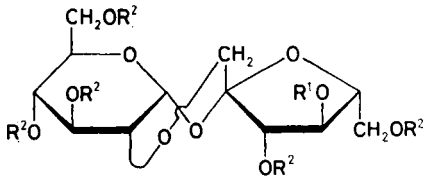
m/z 331 and 303. Its deacetylation and methylation led to octa-O-methylsucrose (*XXIX*, ref.[11]). It contains a methoxyl group according to its NMR spectra; H-4' resonates at higher field (3·88 ppm) and C-4' at lower field ($\Delta\delta$ = 8·2 ppm) in comparison with octa-O-acetylsucrose. Therefore, the compound *XXV* is 1',2,3,3',4,6,6'--hepta-O-acetyl-4'-O-methylsucrose. Compound *XXVI* exhibited in its ^{1}H NMR spectrum the presence of six acetyl groups. Signals of H-1'a, H-1'b, and H-2 were shifted upfield – a diagnostic feature for the 1',2-anhydro ring. Its ^{13}C NMR spectrum was similar but not identical to that of 1',2-anhydro derivative *XXVIII*. Also the hexa-O-methyl derivative *XXX* obtained from *XXVI* by deacetylation and methylation was different from the compound *XXVII*, as judged from the NMR spectra. Since the epoxide *IX* is formed in the reaction of 1',4'-di-O-tosyl derivative *XX* with sodium methoxide according to method *A*, we expected that it may be an intermediate also in the reaction of *XX* according to method *B*. We subjected the epoxide *IX** to this procedure and we obtained compounds *XXVI* and *XXV* in 40% and 36% yield, respectively. The 1',2-anhydro derivative *XXVI* formation (besides the expected derivative *XXV*) can be most plausibly explained by an intramolecular attack of the oxirane ring of compound *XXXVII* by the hydroxyl group at the position 1'. Most probably the α-D-glucopyranosyl 1,3-anhydro-β-D-*xylo*-hexulofuranoside (*XLVI*) is formed at the beginning and its oxetane ring** is subsequently opened by the OH group from the position 2. In that case the compound *XXVI* should have a *xylo*- configuration on the fructose part. The same product might be also formed by hydrolysis of compound *X* if the opening of the oxirane ring occurs in the preferred[14] position 4'. We treated the compound *X* with boiling sodium hydroxide. After acetylation, we obtained the compound *XXVI* in 70% yield. This compound has therefore the structure 1',2-anhydro-(3,4,6-tri-O-acetyl-α--D-glucopyranosyl 3',4',6'-tri-O-acetyl-β-D-*xylo*-hexulofuranoside).

From the above given facts it follows that with both di-O-tosyl derivatives *XX* and *XXIII* the formation of the oxirane ring in the reaction with sodium methoxide is easy, producing tosylanhydro derivatives *XXXI* or *XXXII*, respectively. With compound *XXXII*, the accessibility of position 4' for the methoxide ion is diminished by its interaction with the hydroxymethyl group at the position 5' so that the oxirane ring remains unchanged even upon 24 h boiling with sodium methoxide. Compound *XXXII* is cyclized to the dianhydro derivative *XXXIII* or it is solvolyzed to the epoxide *XXXIV*. On the contrary, with compound *XXXI*, the oxirane ring is opened at the position 4' under formation of compound *XXXV* that is further cyclized to compound *XXXVI*. As a side reaction, part of the compound *XXXI* is solvolyzed to epoxide *XXXVII* that is either opened at the position 4' under formation of compound *XXXVIII* or transformed to the 1',2-anhydro derivative *XXXIX* by the above

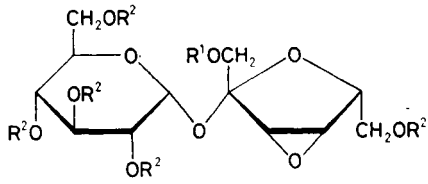
* Compound *IX* described[4,5,12,13] as a sirup was obtained in crystalline form.

** For oxetane ring formation in hydrolysis of methyl 2,3-anhydro-β-D-*ribo*-furanoside see ref.[15].

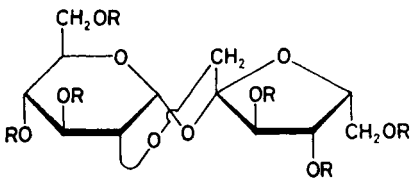
proposed mechanism. The possibility of compound *XXXVIII* formation by solvolysis of tosyloxy group in *XXXV* can be rejected as improbable because of equal ratio



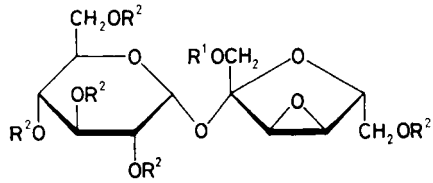
XXIV, $R^1 = CH_3$; $R^2 = Ac$
XXVII, $R^1 = R^2 = CH_3$
XXVIII, $R^1 = R^2 = Ac$
XXXVI, $R^1 = CH_3$; $R^2 = H$



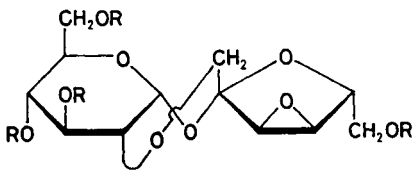
IX, $R^1 = R^2 = Ac$
XXXI, $R^1 = Ts$; $R^2 = H$
XXXVII, $R^1 = R^2 = H$
XLI, $R^1 = H$; $R^2 = Ac$



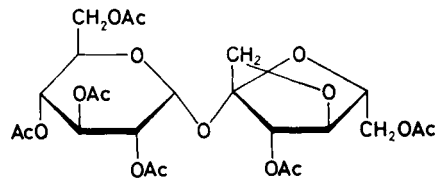
XXVI, R = Ac
XXX, $R = CH_3$
XXXIX, R = H



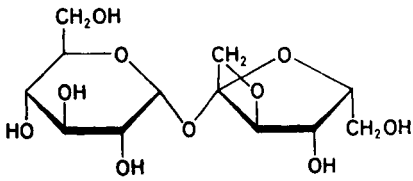
VIII, $R^1 = R^2 = Ac$
XXXII, $R^1 = Ts$; $R^2 = H$
XXXIV, $R^1 = R^2 = H$



X, R = Ac
XXXIII, R = H



XL



XLVI

Ac = acetyl
Ts = 4-toluenesulfonyl
Ms = methanesulfonyl
Tr = trityl

of compounds *XXV* and *XXVI* isolated from the reaction of 1',4'-di-O-tosyl derivative *XX* and epoxide *IX* with sodium methoxide. The question why the anhydro derivative *XXXII* is transformed to dianhydro derivative *XXXIII* in the reaction with sodium methoxide and the anhydro derivative *XXXI* is not, remains unanswered.

Our attempt to cyclize 1'-O-tosyl derivative *XXI* to 1',2-anhydro derivative *XXVIII* lead to surprise. The reaction of *XXI* with sodium methoxide according to method *B* followed by acetylation gave besides the expected 1',2-anhydro derivative *XXVIII* (32%, ref.[10]) and octa-O-acetylsucrose (16%) the compound *XL* (16%). The ions *m/z* 331 and 229 present in its mass spectrum indicated the presence of four O-acetyl groups on the pyranose moiety and two O-acetyl groups and an anhydro ring on the furanose part of the molecule. There are signals of six O-acetyl groups in its ^{1}H NMR spectrum. Signals of H-1'a, H-1'b, and H-4' are shifted upfield in comparison with octa-O-acetylsucrose; geminal coupling J(1'a, 1'b) is reduced to 7·9 Hz. The downfield shift of one methylene carbon (72·7 ppm) indicates participation of this group on the anhydro ring formation. Compound *XL* has evidently the structure of 2,3,3',4,6,6'-hexa-O-acetyl-1',4'-anhydrosucrose.

The compound of this structure was described[13] (but with NMR spectra different from ours) besides the epoxide *IX* as a product of the reaction of sucrose with diethyl azodicarboxylate and triphenylphosphine followed by acetylation. Since in the reaction of sucrose with this reagent other anhydro derivatives might be also formed (e.g. those with 3,6- or 3',6'-anhydro ring), we performed the same reaction with penta-O-acetylsucrose *XIV*. In that case the formation of anhydro derivatives other than 1',4' or 3',4' is highly improbable. We obtained the 2,3,4,6-tetra-O-acetyl--α-D-glucopyranosyl 6-O-acetyl-3,4-anhydro-β-D-*lyxo*-hexulofuranoside (*XLI*) as the only product. It was identical with the product of partial deacetylation of epoxide *IX* (ref.[4]). On the basis of these facts and the comparison[16] of ^{1}H NMR spectrum of "1',4'-anhydrosucrose[13]" with that of 3',6'-anhydrosucrose[17], we came to the conclusion that our compounds *XL* contained a 1',4'-anhydro ring an that the product of sucrose reaction with diethyl azodicarboxylate–triphenylphosphine mixture[13] should be assigned the structure of 3',6'-anhydrosucrose.

Formation of 1',4'-anhydro derivative *XL* and a relatively low yield of 1',2'-anhydro derivative *XXVIII* from 1'-O-tosyl derivative *XXI* are rather striking since the 1'-O-*p*-toluenesulfonyl-6,6'-di-O-triphenylmethylsucrose gives under the same conditions the corresponding 1',2-anhydro derivative in a high yield and probably as the only product[10]. Since the presence of any group at the position 6 can hardly have any effect on the substitution of tosyl group at the position 1', the observed difference is evidently due to the triphenylmethyl group at the position 6'. It is possible that this bulky group forces a certain flattening of the original $_3T^4$ conformation of the furanose ring that moves the hydroxyl group at the position 4' away from the tosyloxy group at the position 1'. That may have such an effect that this hydroxyl group will be substituted exclusively by the hydroxyl group at the position 2

whereas with compound *XXI* there will be a competition with the hydroxyl group in the position 4'.

Penta-O-acetylsucrose *XIV* was also used to prepare the hepta-O-acetylsucrose *I* that we have previously isolated[3] as the mixture with hepta-O-acetylsucrose *II*. Reaction of *XIV* with triphenylchloromethane provided the corresponding 1'-O--triphenylmethyl derivative *XLII* that was transformed to 2,3,3',4,4',6,6'-hepta-O--acetyl-1'-O-triphenylmethylsucrose (*XLIII*)[18] by acetylation. Hepta-O-acetylsucrose *II* was prepared from hexa-O-acetylsucrose *V*. Its partial acetylation with acetic anhydride in pyridine afforded besides octa-O-acetylsucrose the hepta-O-acetylsucroses *II* and *III* well separable on silica gel. Comparison of ^{13}C NMR spectra of compounds *I* and *II* and their mixture in 2 : 1 ratio (ref.[3]) has justified our interpretation. Compounds *I* and *II* were also transformed to their mesyl derivatives *XLIV* and *XLV*, respectively, that were identical with the compounds obtained[3] by separation of their mixture.

EXPERIMENTAL

Melting points were determined on a Kofler apparatus and were not corrected. Optical rotations were determined with an Opton instrument at 20°C in 20 cm cuvette using chloroform (*c* 1 ± 0·3). Thin-layer chromatography (TLC) was performed on silica gel according to Stahl (Merck, Darmstadt). Detection was achieved by spraying with 1% cerium(IV) sulfate in 10% sulfuric acid and heating. Silica gel (Lachema, Brno) of particle size 100—250 μm was used for preparative chromatography. Solvents were removed on a rotary evaporator in vacuo at temperatures below 50°C. NMR spectra were recorded with a Jeol FX-60 spectrometer (15·036 MHz for ^{13}C, 59·797 MHz for ^{1}H, respectively). When not given otherwise, the spectra were measured in deuteriochloroform containing tetramethylsilane as an internal standard. Chemical shifts are reported in the δ-scale with accuracy ±0·005 and ±0·06 ppm for ^{1}H and ^{13}C, respectively. Signal assignments are based on homonuclear decoupling and multiplicity (^{1}H NMR) and on off-resonance, noise off-resonance and selective heteronuclear decoupling (^{13}C NMR). Mass spectra were measured with a Jeol JMS DX-200 instrument (70 eV).

Isolation of Penta-O-acetylsucroses *XII*, *XIII*, and *XIV*

Penta-O-acetylsucrose portion (6·77 g) obtained by deacetylation of octa-O-acetylsucrose (differences from ref.[4]: reaction time 26 h, yield 24%) was subjected to column chromatography on silica gel (300 g) in the system chloroform–ethanol 100 : 2; TLC of chromatographic fractions in the same system 100 : 5, three times developed. Re-chromatography of mixed fractions gave 1·62 g of *XIII*, 0·62 g of *XII*, and 4·53 g of *XIV*.

Compound *XII* was recrystallized from the mixture ethyl acetate–petroleum ether, m.p. 176—177°C, $[\alpha]_D$ +60°. For $C_{22}H_{32}O_{16}$ (552·5) calculated: 47·82% C, 5·84% H; found: 48·05% C, 5·93% H. ^{1}H NMR: 2·03 s, 3 H (OAc); 2·05 s, 3 H (OAc); 2·09 s, 3 H (OAc); 2·11 s, 3 H (OAc); 2·13 s, 3 H (OAc); 4·99 dd, 1 H (H-4, J(3, 4) = 10·0, J(4, 5) = 9·2); 5·31 t, 1 H (H-3, J(2, 3) = = J(3, 4) = 10·0); 5·51 d, 1 H (H-1, J(1, 2) = 3·7). ^{13}C NMR: 20·8 q (5 C), 62·4 t, 62·9 t, 64·6 t, 68·4 d, 68·5 d, 70·4 d, 73·3 d, 74·6 d, 77·8 d, 79·1 d, 92·5 d, 102·9 s, 169·6 s, 170·5 s, 171·0 s, 171·4 s, 171·8 s. Mass spectrum: *m/z* 289, 247. Deuterioacetyl derivative *XV*: m.p. 86—88°C (ethanol), mass spectrum: *m/z* 337, 334.

Compound *XIII* was crystallized from the mixture ethyl acetate–petroleum ether, m.p. 152 to 153°C, change of modification at 90°C, $[\alpha]_D$ +80·1°. For $C_{22}H_{32}O_{16}$ (552·5) calculated: 47·82% C, 5·84% H; found: 47·58% C, 6·04% H. ^{1}H NMR: 2·02 s, 3 H (OAc); 2·04 s, 3 H (OAc); 2·11 s, 9 H (3 × OAc); 4·87 dd, 1 H (H-2, $J(1, 2)$ = 3·7, $J(2, 3)$ = 9·8); 5·21 t, 1 H (H-3, $J(2, 3)$ = $J(3, 4)$ = 9·8); 5·50 dd, 1 H (H-4, $J(3, 4)$ = 9·8, $J(4, 5)$ = 10·4); 5·71 d, 1 H (H-1, $J(1, 2)$ = 3·7). ^{13}C NMR: 20·7 q (5 C), 60·2 t, 61·6 t, 63·9 t, 68·2 d, 68·6 d, 69·5 d, 70·4 d, 73·0 d, 78·1 d, 81·6 d, 89·3 d, 103·3 s, 169·9 s, 170·2 s (2 C), 171·0 s (2 C). Mass spectrum: *m/z* 331, 205. Deuterioacetyl derivative *XVI*: m.p. 85–87°C (ethanol), mass spectrum: *m/z* 340, 331.

Compound *XIV*, amorphous, $[\alpha]_D$ +60°. For $C_{22}H_{32}O_{16}$ (552·5) calculated: 47·82% C, 5·84% H; found: 47·79% C, 5·91% H. ^{1}H NMR: 2·02 s, 3 H (OAc); 2·04 s, 3 H (OAc); 2·11 s, 9 H (3 × OAc); 4·92 dd, 1 H (H-2, $J(1, 2)$ = 3·9, $J(2, 3)$ = 9·8); 5·05 dd, 1 H (H-4, $J(3, 4)$ = = 9·8, $J(4, 5)$ = 9·3); 5·51 t, 1 H (H-3, $J(2, 3)$ = $J(3, 4)$ = 9·8); 5·62 d, 1 H (H-1, $J(1, 2)$ = 3·9). ^{13}C NMR: 20·4 q (5 C), 62·0 t, 63·4 t, 64·2 t, 67·8 d, 68·2 d, 69·9 d, 70·1 d, 74·9 d, 77·5 d, 78·6 d, 88·8 d, 104·1 s, 169·3 s, 169·6 s, 170·4 s, 170·8 s, 171·0 s. Mass spectrum: *m/z* 331, 205. Deuterioacetyl derivative *XVII*: m.p. 85–87°C (ethanol), mass spectrum: *m/z* 340, 331.

Reaction of 2,3,4,6,6′-Penta-O-acetylsucrose (*XIV*) with Two Equivalents of *p*-Toluenesulfonyl Chloride

p-Toluenesulfonyl chloride (3·00 g, 2·15 equiv.) was added under cooling to 0° to the solution of compound *XIV* (4·04 g, 7·32 mmol) in pyridine (25 ml) and the reaction mixture was left standing 65 h at room temperature. Then it was decomposed with water, chloroform was added, and extracted with cold 10% sulfuric acid, water, 5% hydrogen carbonate, and water. The extract was dried over magnesium sulfate and the solvent was removed. The residue was chromatographed on silica gel column (200 g) in the system benzene–acetone 90 : 10 to 80 : 20. After re-chromatography of mixture fractions, following compounds were obtained: 1′,3′,4′-tri-O-tosyl derivative *XXII* (0·86 g, 12%), 1′,4′-di-O-tosyl derivative *XX* (1·5 g, 24%), 1′,3′-di-O-tosyl derivative *XXIII* (1·52 g, 24%), and 1′-O-tosyl derivative *XXI* (1·51 g, 29%). In another experiment with shorter reaction time the yields were: 3% of *XXII*, 13% of *XX*, 16% of *XXIII*, and 43% of *XXI*.

Compound *XX*: amorphous, $[\alpha]_D$ +64·2°. For $C_{36}H_{44}O_{20}S_2$ (860·8) calculated: 50·23% C, 5·15% H, 7·45% S; found: 50·37% C, 5·24% H, 7·69% S. ^{1}H NMR*: 1·982 s, 3 H (OAc); 2·010 s, 3 H (OAc); 2·031 s, 3 H (OAc); 2·034 s, 3 H (OAc); 2·107, 3 H (OAc); 2·468 s, 6 H (2 × CH_3); 3·168 d, 1 H (3′-OH, $J(3', OH)$ = 6·8); 3·913 d, 1 H (H-1′b, $J(1'a, 1'b)$ = 10·7); 4·090 d, 1 H (H-1′a, $J(1'a, 1'b)$ = 10·7); 4·192 dd, 1 H (H-6a, $J(5, 6a)$ = 4·8, $J(6a, 6b)$ = 13·2); 4·317 ddd, 1 H (H-5, $J(4, 5)$ = 10·3, $J(5, 6a)$ = 4·8, $J(5, 6b)$ = 2·4); 4·418 dd, 1 H (H-3′, $J(3', 4')$ = 8·0, $J(3', OH)$ = 6·8); 4·834 dd, 1 H (H-2, $J(1, 2)$ = 3·9, $J(2, 3)$ = 10·4); 4·870 dd, 1 H (H-4′, $J(3', 4')$ = 8·0, $J(4', 5')$ = 7·7); 5·065 dd, 1 H (H-4, $J(3, 4)$ = 9·4, $J(4, 5)$ = 10·3); 5·392 dd, 1 H (H-3, $J(2, 3)$ = 10·4, $J(3, 4)$ = 9·4); 5·668 d, 1 H (H-1, $J(1, 2)$ = 3·9); 7·638 and 7·830 AA′BB′, 4 H (J(A, B) + J(A, B′) = 8·25); 7·384 and 7·805 AA′BB′, 4 H (J(A, B) + J(A, B′) = = 8·25). ^{13}C NMR: 20·7 q (5 C), 21·9 q (2 C), 61·7 t, 62·1 t, 68·1 t, 68·5 d, 68·7 d, 69·7 d, 69·9 d, 75·0 d, 76·7 d, 80·4 d, 89·0 d, 103·3 s, 128·1 d (4 C), 130·2 d (4 C), 132·3 s, 134·6 s, 145·7 s (2 C), 169·2 s, 169·7 s, 170·1 s (3 C).

Compound *XXI*: sirup, $[\alpha]_D$ +46·7°. For $C_{29}H_{38}O_{18}S$ (706·7) calculated: 49·28% C, 5·42% H, 4·54% S; found: 49·27% C, 5·51% H, 4·65% S. ^{1}H NMR: 1·98 s, 3 H (OAc); 2·01 s, 3 H (OAc); 2·03 s, 3 H (OAc); 2·09 s, 3 H (OAc); 2·12 s, 3 H (OAc); 2·47 s, 3 H (CH_3); 4·86 dd, 1 H (H-2, $J(1, 2)$ = 3·9, $J(2, 3)$ = 10·3); 4·98 t, 1 H (H-4, $J(3, 4)$ = $J(4, 5)$ = 9·8); 5·47 dd, 1 H (H-3,

* Varian XL-200, 200 MHz

$J(2, 3) = 10{\cdot}3$, $J(3, 4) = 9{\cdot}8$); 5·57 d, 1 H (H-1, $J(1, 2) = 3{\cdot}9$); 7·37 and 7·80 AA'BB', 4 H ($J(A, B) + J(A, B') = 8{\cdot}1$). ^{13}C NMR: 20·5 q, 20·6 q, 20·7 q (3 C), 21·7 q, 62·2 t, 63·1 t, 68·1 t, 68·5 d, 68·6 d, 69·8 d, 69·9 d, 74·4 d, 76·8 d, 79·2 d, 88·9 d, 102·7 s, 128·1 s (2 C), 130·1 d (2 C), 132·5 s, 145·4 s, 169·5 s, 169·8 s, 170·2 s, 170·6 s, 171·2 s.

Compound *XXII*: sirup, $[\alpha]_D$ +50·5°. For $C_{43}H_{50}O_{22}S_3$ (1 015·0) calculated: 50·88% C, 4·97% H, 9·48% S; found: 50·78% C, 4·90% H, 9·38% S. ^{1}H NMR: 1·95 s, 3 H (OAc); 2·01 s, 3 H (OAc); 2·03 s, 3 H (OAc); 2·05 s, 3 H (OAc); 2·10 s, 3 H (OAc); 2·10 s, 3 H (OAc); 2·47 s, 9 H (3 × CH_3); 4·79 dd, 1 H (H-2, $J(1, 2) = 3{\cdot}9$, $J(2, 3) = 9{\cdot}8$); 5·06 m, 3 H (H-3', H-4, H-4'); 5·39 dd, 1 H (H-3, $J(2, 3) = 9{\cdot}8$, $J(3, 4) = 8{\cdot}8$); 5·72 d, 1 H (H-1, $J(1, 2) = 3{\cdot}9$); 7·20 m, 6 H; 7·87 m, 6 H. ^{13}C NMR: 20·5 q (2 C), 20·7 q (3 C), 21·8 q (3 C), 60·8 t, 61·2 t, 67·8 t, 68·5 d, 68·8 d, 69·9 d, 70·0 d, 75·8 d, 76·2, 78·4 d, 88·8 d, 101·0 s, 128·2 d (4 C), 128·7 d (2 C), 130·1 d (4 C), 130·2 d (2 C), 131·6 s, 132·4 s, 132·6 s, 145·5 s, 146·1 s (2 C), 169·7 s, 170·0 s (3 C), 170·5 s.

Compound *XXIII*: sirup, $[\alpha]_D$ +37·2°. For $C_{36}H_{44}O_{20}S_2$ (860·8) calculated: 50·24% C, 5·15% H, 7·45% S; found: 50·45% C, 5·45% H, 7·44% S. ^{1}H NMR: 1·94 s, 3 H (OAc); 2·01 s, 3 H (OAc); 2·03 s, 3 H (OAc); 2·06 s, 3 H (OAc); 2·10 s, 3 H (OAc); 2·48 s, 6 H (2 × CH_3); 4·74 d, 1 H (H-3', $J(3', 4') = 8{\cdot}8$); 4·78 dd, 1 H (H-2, $J(1, 2) = 3{\cdot}9$, $J(2, 3) = 10{\cdot}3$); 5·04 dd, 1 H (H-4, $J(3, 4) = 9{\cdot}7$, $J(4, 5) = 9{\cdot}3$); 5·38 dd, 1 H (H-3, $J(2, 3) = 10{\cdot}3$, $J(3, 4) = 9{\cdot}7$); 5·68 d, 1 H (H-1, $J(1, 2) = 3{\cdot}9$); 7·39—7·81 m, 8 H. ^{13}C NMR: 20·47 q, 20·55 q, 20·63 q, 20·71 q (2 C), 21·68 q, 21·77 q, 61·6 t, 61·7 t, 68·1 d, 68·4 t, 68·5 d, 69·9 d, 70·0 d, 71·2 d, 78·4 d, 81·5 d, 88·3 d, 101·2 s, 128·0 d (2 C), 128·3 d (2 C), 130·4 d (2 C), 131·7 s, 132·5 s, 145·3 s, 146·2 s, 169·6 s, 169·7 s, 170·0 s, 170·6 s, 170·9 s.

Reaction of 2,3,4,6,6'-Penta-O-acetyl-1',3'-di-O-*p*-toluenesulfonylsucrose (*XXIII*) with Sodium Methoxide

A) Solution of compound *XXIII* (1·08 g, 1·25 mmol) in 1M sodium methoxide (18 ml) was boiled 2 min, evaporated to dryness and the residue dried in vacuo. Pyridine (40 ml) and acetic anhydride (20 ml) were added, the mixture was allowed to stand 17 h at room temperature and then it was poured on ice and extracted with chloroform. Solvent was removed and the residue was chromatographed on silica gel column (160 g) in the system benzene–acetone 9 : 1. Dianhydro derivative *X* (191 mg, 32%), m.p. 151—152°C (ethanol) and epoxide *VIII* (400 mg, 55%), identical according to NMR with an authentic sample[4], were obtained.

B) Solution of compound *XXIII* (900 mg, 1·04 mmol) in 1M sodium methoxide (16 ml) was boiled 24 h. Carbon dioxide was bubbled through the reaction mixture, inorganic precipitate was filtered off and the filtrate was evaporated to dryness. Acetylation of the residue (30 ml of pyridine, 6 ml of acetic anhydride) and the work-up as under *A*) gave compound *X*, m.p. 150 to 152°C (ethanol) (257 mg, 52%) and compound *VIII* (236 mg, 38%).

Reaction of 2,3,4,6,6'-Penta-O-acetyl-1',4'-di-O-*p*-toluenesulfonylsucrose (*XX*) with Sodium Methoxide

A) Solution of compound *XX* (580 mg, 0·67 mmol) in 1M sodium methoxide (10 ml) was boiled 2 min, evaporated to dryness, and the residue dried in vacuo. Pyridine (20 ml) and acetic anhydride (10 ml) were added and the mixture was left stading 17 h at room temperature. It was then poured on ice and the product was extracted with chloroform. Solvent was removed and the residue was chromatographed on silica gel column (120 g) in the system benzene–acetone 9 : 1. Anhydro derivative *IX* (238 mg, 60%) was obtained besides the small amount of chromatographically nonhomogeneous substances. Upon standing, crystalls were obtained, m.p. 114 to 116°C (ethyl acetate–petroleum ether).

B) Mixture of compound *XX* (915 mg, 1·06 mmol) and 1M sodium methoxide (15 ml) was boiled for 24 h, then diluted with methanol (20 ml) and neutralized with stream of carbon dioxide. Inorganic precipitate was filtered off, solvent removed and the residue was acetylated (30 ml of pyridine, 7 ml of acetic anhydride). After 15 h standing at room temperature, the mixture was poured on ice and extracted with chloroform. Solvent was removed and the product chromatographed on silica gel column (150 g) in the system ether–petroleum ether 4 : 1. TLC of chromatographic fractions was performed in the system ether–petroleum ether 2 : 1 (twice developed).

Compound *XXIV* (350 mg, 60%) and a sirup (190 mg), according to TLC in the above mentioned system homogeneous but containing two compounds according to TLC in the system benzene–acetone 95 : 5 (twice developed) were obtained. Re-chromatography of this fraction on silica gel column (50 g) in the system benzene–acetone 9 : 1 provided compounds *XXVI* (96 mg, 15·7%) and *XXV* (89 mg, 12·9%). Both these compounds were according to their NMR spectra identical with the products of methanolysis of epoxide *IX*.

Compound *XXIV* was recrystallized from ethanol, m.p. 109—111°C, $[\alpha]_D$ +53·6°. For $C_{23}H_{32}O_{15}$ (548·5) calculated: 50·36% C, 5·88% H; found: 50·28% C, 5·90% H. ^{1}H NMR: 2·05 s, 3 H (OAc); 2·06 s, 3 H (OAc); 2·09 s, 3 H (OAc); 2·13 s, 3 H (OAc); 2·22 s, 3 H (OAc); 3·40 s, 3 H (OCH_3); 3·47 d, 1 H (H-1'b, J(1'a, 1'b) = 13·4); 3·78 dd, 1 H (H-2, J(1, 2) = 3·7, J(2, 3) = 10·0); 3·98 dd, 1 H (H-1'a, J(1'a, 1'b) = 13·4); 5·06 dd, 1 H (H-4, J(3, 4) = 9·3, J(4, 5) = 10·0); 5·11 d, 1 H (H-3', J(3', 4') = 6·1); 5·49 d, 1 H (H-1, J(1, 2) = 3·7); 5·60 dd, 1 H (H-3, J(2, 3) = 10·0, J(3, 4) = 9·3). ^{13}C NMR: 20·7 q (5 C), 58·2 q, 61·7 t, 61·8 t, 64·3 t, 67·1 d, 67·6 d, 69·7 d, 71·8 d, 77·1 d, 79·7 d, 82·8 d, 90·5 d, 103·7 s, 169·4 s, 169·8 s, 170·2 s, 170·6 s, 170·8 s.

Reaction of 2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl 1,6-di-O-acetyl-3,4-anhydro-β-D-*lyxo*-hexulofuranoside (*IX*) with Sodium Methoxide

Mixture of compound *IX* (1·16 g, 2·01 mmol) (m.p. 114—116°C, $[\alpha]_D$ +72°, for $C_{24}H_{32}O_{16}$ (576·5) calculated: 50·00% C, 5·60% H; found: 49·73% C, 5·56% H, ^{1}H NMR spectrum identical with that of an authentic sample[4]) and 1M sodium methoxide (24 ml) was boiled 24 h, diluted with methanol, neutralized with stream of carbon dioxide, filtered, and evaporated to dryness. The residue was acetylated with pyridine (70 ml) and acetic anhydride (20 ml) 16 h at room temperature. The mixture was then poured on ice, extracted with chloroform and this extract chromatographed on silica gel (100 g, benzene–acetone 95 : 5). Compounds *XXVI* (464 mg, 40%) and *XXV* (474 mg, 36%) were obtained.

Compound *XXV*: sirup, $[\alpha]_D$ +47°. For $C_{27}H_{38}O_{18}$ (650·6) calculated: 49·84% C, 5·89% H; found: 50·11% C, 6·09% H. ^{1}H NMR: 2·01 s, 3 H (OAc); 2·04 s, 3 H (OAc); 2·08 s, 3 H (OAc); 2·10 s, 6 H (2 × OAc); 2·11 s, 3 H (OAc); 2·19 s, 3 H (OAc); 3·41 s, 3 H (OCH_3); 3·88 t, 1 H (H-4', J(3', 4') = J(4', 5') = 5·5); 4·84 dd, 1 H (H-2, J(1, 2) = 3·7, J(2, 3) = 9·8); 5·07 t, 1 H (H-4, J(3, 4) = J(4, 5) = 9·2); 5·38 d, 1 H (H-3', J(3', 4') = 5·5); 5·47 dd, 1 H (H-3, J(2, 3) = = 9·8, J(3·4) = 9·2); 5·64 d, 1 H (H-1, J(1, 2) = 3·7). ^{13}C NMR: 20·7 q (7 C), 58·2 q, 61·9 t, 63·5 t, 64·1 t, 68·4 d (2 C), 69·7 d, 70·4 d, 76·6 d, 79·5 d, 83·2 d, 89·8 d, 104·0 s, 169·5 s, 170·4 s (2 C), 171·6 s (4 C). Mass spectrum: m/z 331, 303.

Compound *XXVI*: sirup, $[\alpha]_D$ +69°. For $C_{24}H_{32}O_{16}$ (576·5) calculated: 50·00% C, 5·60% H; found: 49·96% C, 5·43% H. ^{1}H NMR: 2·05 s, 3 H (OAc); 2·08 s, 9 H (3 × OAc); 2·11 s, 3 H (OAc); 2·13 s, 3 H (OAc); 3·50 d, 1 H (H-1'b, J(1'a, 1'b) = 12·2); 3·81 dd, 1 H (H-2, J(1, 2) = = 3·7, J(2, 3) = 9·2); 3·88 dd, 1 H (H-1'a, J(1'a, 1'b) = 12·2); 5·07 t, 1 H (H-4, J(3, 4) = = J(4, 5) = 9·2); 5·36 m, 2 H (H-3', H-4'); 5·50 d, 1 H (H-1, J(1, 2) = 3·7); 5·64 t, 1 H (H-3, J(2, 3) = J(3, 4) = 9·2). ^{13}C NMR: 20·6 q (2 C), 20·7 q (4 C), 60·8 t, 61·7 t, 62·6 t, 66·4 d,

67·4 d, 69·7 d, 71·9 d, 75·6 d, 78·5 d, 81·0 d, 90·3 d, 106·2 s, 169·5 s, 170·2 s, 170·6 s (2 C), 170·9 s, 171·0 s.

Hydrolysis of 1′,2-Anhydro-(3,4,6-tri-O-acetyl-α-D-glucopyranosyl 6′-O-Acetyl-3′,4′-anhydro-β-D-*ribo*-hexulofuranoside) (*X*)

Mixture of compound *X* (160 mg, 0·34 mmol) and 1M sodium hydroxide (7 ml) was boiled 42 h, neutralized with hydrochloric acid (phenolphtalein) and evaporated to dryness. Pyridine (10 ml) and acetic anhydride (3 ml) were added to the residue and the mixture was left standing 15 h at room temperature. It was then diluted with chloroform, washed with 10% sulfuric acid, water, 5% sodium hydrogen carbonate, and water. The extract was dried over magnesium sulfate, chloroform was evaporated and the residue chromatographed on silica gel column (100 g, benzene–acetone 95 : 5). Compound *XXVI* (136 mg, 70%) was obtained, $[\alpha]_D$ +68·4°, NMR spectrum identical with those of *XXVI* obtained using the above mentioned procedures.

1′,2-Anhydro-3,3′,4,4′,6,6′-hexa-O-methylsucrose (*XXVII*)

A) Two drops of 1M sodium methoxide were added to the solution of 1′,2-anhydro-3,3′,4,6,6′-penta-O-acetyl-4′-O-methylsucrose (*XXIV*) (90 mg, 0·164 mmol) in methanol (5 ml). After 1·5 h standing at room temperature when the compound *XXIV* was according to TLC (benzene–ethanol 10 : 1) deacetylated, the mixture was neutralized with stream of carbon dioxide and evaporated to dryness. N,N-Dimethylformamide (2 ml), methyl iodide (1 ml), and silver oxide (300 mg) were added to the residue. The mixture was shaken 8 h and then left standing 48 h at room temperature. It was extracted several times with chloroform (total amount 50 ml), extracts were combined, solvent removed and the residue was purified by column chromatography on silica gel (20 g, benzene–ethanol 100 : 1). Sirupy product (72 mg) formed crystals upon standing. Twice repeated crystallization from petroleum ether gave compound *XXVII* (43 mg, 64%), m.p. 85–87°, $[\alpha]_D$ +68·6°. For $C_{18}H_{32}O_{10}$ (408·4) calculated: 52·93% C, 7·90% H; found: 52·61% C, 7·66% H. ^{1}H NMR: 3·40 s, 9 H (3 × CH_3O); 3·51 s, 3 H (CH_3O); 3·56 s, 3 H (CH_3O); 3·64 s, 3 H (CH_3O); 5·40 d, 1 H (H-1, $J(1, 2) = 3·7$). ^{13}C NMR: 58·1 q, 59·0 q, 59·2 q, 59·3 q, 60·2 q, 60·5 q, 62·0 t, 70·5 t, 72·1 d, 74·0 d, 74·6 t, 77·0 d, 78·6 d, 80·6 d, 86·3 d, 87·2 d, 90·7 d, 103·5 s.

B) Same procedure as in *A*) was applied to 3,3′,4,4′,6,6′-hexa-O-acetyl-1′,2-anhydrosucrose (*XXVIII*, 70 mg) and provided 37 mg of compound *XXVII*, m.p. 85–87° (petroleum ether) identical (NMR) with compound *XXVII* obtained from *XXIV*.

1′,2,3,3′,4,4′,6,6′-Octa-O-methylsucrose (*XXIX*)

Using the same procedure as given above for preparation of compound *XXVII*, we obtained from 73 mg of compound *XXV* 28 mg of compound *XXIX*, $[\alpha]_D$ 71·3°, identical according to NMR spectra with compound *XXIX*, prepared[11] by methylation of sucrose.

1′,2-Anhydro-(3,4,6-tri-O-methyl-α-D-glucopyranosyl 3′,4′,6′-tri-O-methyl-β-D-*xylo*-hexulofuranoside) (*XXX*)

Applying the procedure for preparation of *XXVII* to 91 mg of compound *XXVI*, we obtained 35 mg of compound *XXX*, $[\alpha]_D$ +46°. For $C_{18}H_{32}O_{10}$ (408·4) calculated: 52·93% C, 7·90% H; found: 52·94% C, 8·20% H. ^{1}H NMR: 3·38 s, 3 H (CH_3O); 3·40 s, 6 H (2 × CH_3O); 3·44 s, 3 H (CH_3O); 3·56 s, 3 H (CH_3O); 3·65 s, 3 H (CH_3O); 5·42 d, 1 H (H-1, $J(1, 2) = 3·4$). ^{13}C NMR: 58·3 q, 58·4 q, 59·3 q (2 C), 60·2 q, 60·6 q, 61·2 t, 70·7 t, 71·7 t, 72·1 d, 74·1 d, 77·2 d, 78·7 d, 79·6 d, 84·1 d, 89·8 d, 90·9 d, 106·1 s.

Reaction of 2,3,4,6,6′-Penta-O-acetyl-1′-O-*p*-toluenesulfonylsucrose (*XXI*) with Sodium Methoxide

Mixture of compound *XXI* (490 mg, 0·69 mmol) and 1M sodium methoxide (12 ml) was refluxed 24 h, diluted with methanol, neutralized with stream of carbon dioxide, and evaporated to dryness. Pyridine (20 ml) and acetic anhydride (5 ml) were added to the residue and the mixture was allowed to stand overnight at room temperature. It was then poured on ice and extracted with chloroform. Solvent was removed and the residue was chromatographed on silica gel (70 g, ether–petroleum ether 2 : 1). Re-chromatography of the mixture fractions gave compounds *XL* (70 mg, 17·6%), *XXVIII* (127 mg, 32%), and octa-O-acetylsucrose (76 mg, 16·2%), m.p. 84—85°C (ethanol).

Compound *XXVIII* was recrystallized from ether and had a m.p. 138—140°C, $[\alpha]_D$ 79·1°. Ref.[10] gives m.p. 141°C, $[\alpha]_D$ +79°.

Compound *XL* was recrystallized from the mixture ether–petroleum ether and had a m.p. 105—107°C, $[\alpha]_D$ +142·5°. For $C_{24}H_{32}O_{10}$ (576·5) calculated: 50·00% C, 5·60% H; found: 50·08% C, 5·53% H. ^{1}H NMR ($C_6{}^2H_6$): 1·62 s, 3 H (OAc); 1·69 s, 9 H (3 × OAc); 1·75 s, 3 H (OAc); 1·82 s, 3 H (OAc); 3·60 d, 1 H (H-1′b, J(1′a, 1′b) = 7·9); 3·72 d, 1 H (H-1′a, J(1′a, 1′b) = = 7·9); 3·87 d, 1 H (H-4′, J(3′, 4′) = 2·2); 5·07 dd, 1 H (H-2, J(1, 2) = 3·7, J(2, 3) = 10·4); 5·26 d, 1 H (H-3′, J(3′, 4′) = 2·2); 5·28 dd, 1 H (H-4, J(3, 4) = 9·3, J(4, 5) = 9·6); 5·70 dd, 1 H (H-3, J(2, 3) = 10·4), J(3, 4) = 9·3); 5·99 d, 1 H (H-1, J(1, 2) = 3·7). ^{13}C NMR: 20·7 q (6 C), 61·5 t, 62·3 t, 68·3 t, 68·7 d, 69·5 d, 70·0 d, 71·1 d, 72·8 d, 76·4 d, 81·3 d, 90·9 d, 104·9 s, 169·5 s (2 C), 170·2 s (3 C), 170·6 s. Mass spectrum: *m/z* 331, 229.

Reaction of 2,3,4,6,6′-Penta-O-acetylsucrose (*XIV*) with Triphenylphosphine–Diethyl Azodicarboxylate Mixture

Triphenylphosphine (1·1 g, 2·8 equiv.) was added to the solution of compound *XIV* (820 mg, 1·48 mmol) in chloroform devoid of ethanol (20 ml) at 0°C under stirring; after 10 min was added diethyl azodicarboxylate (0·73 g, 2·8 equiv.). The mixture was allowed to warm-up to the room temperature and was stirred for 16 h. Then it was evaporated to dryness and the residue was chromatographed on silica gel column (200 g). N,N′-bis(ethoxycarbonyl) hydrazine and triphenylphosphine oxide were eluted with mixture ether–petroleum ether 4 : 1; elution with mixture benzene–acetone 95 : 5 provided epoxide *XLI* (255 mg, 32%). Compound *XLI*, $[\alpha]_D$ +77·9° had ^{1}H and ^{13}C NMR spectra identical with those of compound *XLI* obtained[4] by partial deacetylation of compound *IX*. Acetylation of *XLI* (50 mg) by acetic anhydride (0·3 ml) in pyridine (3 ml) at room temperature (16 h) followed by evaporation to dryness gave the epoxide *IX* (m.p. 114—116°C, ethyl acetate–petroleum ether) in quantitative yield.

2,3,4,6,6′-Penta-O-acetyl-1′-O-triphenylmethylsucrose (*XLII*)

Triphenylchloromethane (2·0 g, 2·9 equiv.) was added to the solution of compound *XIV* (1·38 g, 2·5 mmol) in pyridine (15 ml). The mixture was heated to 50°C for 30 h, another 1 g of triphenylchloromethane was added and heating was prolonged for another 20 h. The mixture was diluted with chloroform, washed with 10% sulfuric acid, water, 5% sodium hydrogen carbonate, and water. Chloroform extract was dried over $MgSO_4$, solvent removed and the residue was chromatographed on silica gel (150 g, benzene–acetone 9 : 1 and 8 : 2). Amorphous compound *XLII*, $[\alpha]_D$ +52° (1·23 g, 62%) was obtained. For $C_{41}H_{46}O_{16}$ (794·8) calculated: 61·95% C, 5·83% H; found: 61·67% C, 6·09% H.

2,3,3′,4,4′,6,6′-Hepta-O-acetyl-1′-O-triphenylmethylsucrose (*XLIII*)

Acetic anhydride (1 ml) was added to the solution of compound *XLII* (330 mg, 0·41 mmol) in pyridine (5 ml) and the reaction mixture was allowed to stand overnight at room temperature. Then it was evaporated to dryness, some toluene was added and evaporated again. The residue was purified by column chromatography on silica gel (20 g, benzene–ethanol 100 : 1). Compound *XLIII* (356 mg, 100%), $[\alpha]_D$ +62·2° was obtained. Ref.[18] gives $[\alpha]_D$ +76·5° (chloroform). ^{1}H NMR spectrum of compound *XLIII* was identical with that published[18]. ^{13}C NMR: 20·7 q (7 C), 61·5 t, 63·3 t, 63·8 t, 68·1 d, 68·3 d, 70·1 d (2 C), 75·0 d, 75·7 d, 78·3 d, 89·6 d, 105·1 s, 127·2 d (3 C), 127·9 d (6 C), 128·7 d (6 C), 140·3 s (3 C), 169·5 s, 169·8 s (2 C), 170·0 s (2 C), 170·6 (2 C).

2,3,3′,4,4′,6,6′-Hepta-O-acetylsucrose (*I*)

Mixture of compound *XLIII* (285 mg, 0·32 mmol) and 80% acetic acid (8 ml) was heated 14 h to 40°C and then evaporated to dryness. The residue was chromatographed on silica gel (30 g, benzene–ethanol 100 : 1 and 100 : 2). Besides triphenylmethanol were isolated starting compound *XLIII* (61 mg) and *I* (120 mg, 74% conversion), $[\alpha]_D$ +38·5°. For $C_{26}H_{36}O_{18}$ (636·5) calculated: 49·06% C, 5·70% H; found: 48·81% C, 5·77% H. ^{1}H NMR: 2·02 s, 3 H (OAc); 2·04 s, 3 H (OAc); 2·08 s, 3 H (OAc); 2·09 s, 6 H (2 × OAc); 2·11 s, 3 H (OAc); 2·19 s, 3 H (OAc); 3·65 s, 1 H (OH); 4·90 dd, 1 H (H-2, $J(1, 2) = 3·7$, $J(2, 3) = 9·8$); 5·08 t, 1 H (H-4, $J(3, 4) = J(4, 5) = 9·8$); 5·44 m, 2 H (H-3′, H-4′); 5·48 t, 1 H (H-3, $J(2, 3) = J(3, 4) = 9·8$); 6·08 d, 1 H (H-1, $J(1, 2) = 3·7$). ^{13}C NMR: 20·5 q (7 C), 61·8 t, 63·5 t (2 C), 68·2 d, 68·4 d, 69·6 d, 70·2 d, 74·8 d, 76·4 d, 78·9 d, 89·7 d, 105·1 s, 169·7 s, 170·0 s (2 C), 170·3 s (2 C), 170·4 s (2 C).

Reaction of *I* (30 mg) with methanesulfonyl chloride (0·05 ml) in pyridine (2 ml) followed by usual work-up yielded mesyl derivative *XLIV* (32 mg) that was purified by column chromatography on silica gel (10 g, benzene–ethanol 100 : 2). This product was identical with compound *XLIV* obtained by chromatographic separation[3] of mixture of compounds *XLIV* and *XLV*.

1′,2,3,4,4′,6,6′-Hepta-O-acetylsucrose (*II*)

Solution (2·1 ml) of acetic anhydride (1 ml) and pyridine (9 ml) was added to the solution of compound *V* (1·32 g, 2·07 mmol) in pyridine (10 ml) at −70°C. The mixture was kept 17 h at −15°C and then 24 h at room temperature. Then it was evaporated to dryness, some toluene was added and evaporation was repeated. The residue was chromatographed on silica gel (100 g, chloroform–ethanol 100 : 0 and 100 : 2); chromatographic fractions were analysed by TLC (chloroform–ethanol 100 : 1, three times developed). Isolated were: octa-O-acetylsucrose, m.p. 85—86°C (ethanol) (360 mg, 26%), compound *II* (87 mg, 7%), compound *III*, $[\alpha]_D$ +53·5° (559 mg, 43%) for which ref.[19] gives $[\alpha]_D$ +54·3°, ref.[3] gives $[\alpha]_D$ 53·2°, and starting compound *V* (294 mg, 24%).

Compound *II*: sirup, $[\alpha]_D$ +58°. For $C_{26}H_{35}O_{18}$ (636·5) calculated: 49·06% C, 5·70% H, found: 49·33% C, 5·70% H. ^{1}H NMR: 2·01 s, 3 H (OAc); 2·04 s, 3 H (OAc); 2·09 s, 6 H (2 × OAc); 2·13 s, 3 H (OAc); 4·94 dd, 1 H (H-2, $J(1, 2) = 3·7$, $J(2, 3) = 10·4$); 5·20 t, 1 H (H-4, $J(3, 4) = J(4, 5) = 9·2$); 5·48 dd, 1 H (H-3, $J(2, 3) = 10·4$, $J(3, 4) = 9·2$); 5·72 d, 1 H (H-1, $J(1, 2) = 3·7$). ^{13}C NMR: 20·7 q (7 C), 62·2 t, 63·4 t, 63·7 t, 68·6 d (2 C), 69·7 d, 70·0 d, 76·5 d, 76·6 d, 77·6 d, 89·7 d, 103·9 s, 169·6 s (2 C), 170·1 s (3 C), 170·6 s (2 C). Mesylation of compound *II* (45 mg) by the procedure described for *I* produced compound *XLV* (49 mg), $[\alpha]_D$ +51·5°, identical with compound prepared earlier[3].

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