STRUCTURES OF HEXA-O-ACETYLSUCROSES FORMED BY DEACETYLATION OF SUCROSE OCTA-O-ACETATE

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A fraction corresponding to hexa-O-acetylsucrose was isolated in 34% yield from the reaction mixture after deacetylation of sucrose octa-acetate by aluminum oxide impregnated by potassium carbonate. Its subsequent reaction with *p*-toluenesulfonyl chloride in pyridine provided crystalline 1′,2,3,4,6,6′-hexa-O-acetyl-3′,4′-di-O-*p*-toluenesulfonylsucrose (*III*). With triphenylphosphine–diethyl azodicarboxylate reagent, 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl 1,6-di-O-acetyl-3,4-anhydro-β-D-*lyxo*-hexulofuranoside (*VI*) was obtained. Treatment of ditosyl derivative *III* with sodium methoxide followed by acetylation gave besides the anhydro derivative *VI* also the anhydro derivative *V* with *ribo* configuration. The same reaction carried out with mother liquors after crystallization of ditosyl derivative *III* yielded in addition to anhydro derivatives *V* and *VI* the crystalline 1′,2-anhydro(3,4,6-tri-O-acetyl-α-D-glucopyranosyl 6′-O-acetyl-3′,4′-anhydro-β-D-*ribo*-hexulofuranoside) (*VII*). From these results and the analysis of NMR and mass spectra of the hexa-O-acetylsucrose, it follows that the deacetylation of sucrose octa-acetate is highly regioselective, providing the mixture of 1′,2,3,4,6,6′-hexa-O-acetylsucrose (*I*) and 2,3,4,4′,6,6′-hexa-O-acetylsucrose (*XIII*) with markedly prevailing the former component. The structure of dianhydro derivative *VII* (except the oxirane ring configuration) was determined by NMR spectroscopy. The configuration of this ring follows from the fact that the treatment of 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl 6-O-acetyl-3,4-anhydro-1-O-methanesulfonyl-β-D-*lyxo*-hexulofuranoside (*IX*) with sodium methoxide followed by acetylation does not give the dianhydro derivative *VII*. However, this compound is formed from the anhydro derivative *V* by its partial deacetylation, mesylation, reaction with sodium methoxide, and acetylation.

We have already prepared partially acetylated derivatives of acetamidodideoxyhexosides[1–5] and dideoxyhexosides[6] by partial deacetylation of corresponding per-O-acetyl derivatives on aluminum oxide. A British group had applied this method to sucrose octa-acetate[7,8]. They have found three hepta-O-acetylsucroses with hydroxyl groups in positions 4, 4′, and 6′. The last mentioned compound, 1′,2,3,3′,4,4′,6-hepta-O-acetylsucrose, is formed in 9% yield which is comparable with the yield of several step synthesis carried out by Otake[9] and then by Buchanan's group[10] in connection

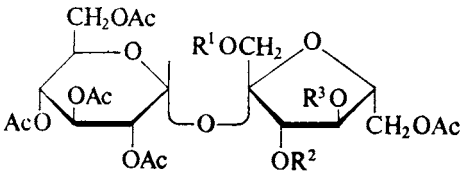
with the synthesis of sucrose 6'-phosphate. The O-acetylsucroses with lower degree of acetylation* are sometimes intermediates in chemical transformations of sucrose[11]. Therefore, we sought the way how to make these compounds by deacetylation of sucrose octa-O-acetate. We have found that such deacetylation takes place in methanolic solution of sucrose octa-O-acetate on aluminum oxide impregnated by potassium carbonate[12]. The course of deacetylation can be followed by thin-layer chromatography with flame-ionization detection (TLC-FID) in which the O-acetylsucroses are separated according to their degree of acetylation[13]. The TLC-FID analysis showed that after 21 hours the preponderant components (c. 34 mass %) are hexa-O-acetylsucroses. We become interested in the selectivity of the octa-O-acetylsucrose deacetylation to hexa-O-acetylsucroses that can affect the use of the reaction products in sucrose transformations. This paper is devoted to these problems.

Hexa-O-acetylsucroses were isolated from the reaction mixture by extraction and silica gel chromatography. Thin layer chromatography suggested a two-component mixture with one compound prevailing. Mass spectrum displayed ions at m/z 247 and 331. The more intense among them, evidently due to the fructofuranosyloxonium ion[8,11], indicates that both hydroxyl groups are located in the fructose moiety. The same conclusion was reached on the basis of the mass spectrum of bis-(deuterioacetyl) derivative, obtained from hexa-O-acetylsucrose by reaction with deuterioacetanhydride in pyridine. Besides the ion m/z 331, there was a more intense ion m/z 337 in this mass spectrum. The result of TLC analysis (two compounds, one prevailing) was confirmed by NMR spectroscopy. Signals of H-1, H-2, H-3, and H-4 were identified in the ^{1}H NMR spectrum of the major component between 4·8 and 5·8 ppm on the basis of their multiplicities and coupling constants. The comparison with spectrum of sucrose octa-O-acetate[14] shows that signals of H-3' and H-4' are missing in this region. Therefore, these positions were deacetylated. The addition of trichloroacetyl isocyanate (TAI) (refs[15-17]) to the measured sample increased the number of proton signals from four to six in the region under discussion and two new signals of NH protons appeared at 8·72 and 9·61 ppm. Thus, the major component is most probably 1',2,3,4,6,6'-hexa-O-acetylsucrose (*I*). ^{13}C NMR spectra of compound *I* and its TAI-derivative are in a good agreement with the structure derived from ^{1}H NMR. However, the interpretation of the observed changes in ^{13}C chemical shifts is rather difficult owing to the compensation of effects caused by the spatial proximity and by conformational changes forced by the bulky groups.

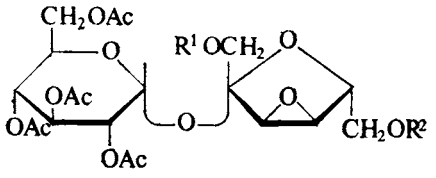
Hexa-O-acetylsucrose *I* was hitherto known as its di-O-mesyl derivative *II* and crystalline di-O-tosyl derivative *III* (ref.[18]). These compounds were prepared from 3,6'-di-O-acetyl-1',2:4,6-di-O-isopropylidenesucrose (*IV*) (ref.[19]) by its mesylation (or tosylation, respectively), deacetalization, and acetylation. By treatment of our

* The degree of acetylation means here the number of O-acetyl groups in the molecule of partially acetylated sucrose.

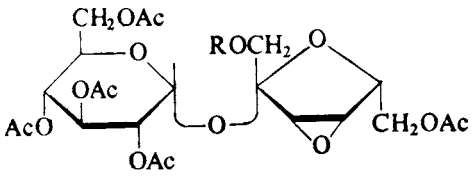
hexa-O-acetylsucrose with *p*-toluenesulfonyl chloride we obtained a di-tosyl derivative *III* identical with the di-tosyl derivative prepared from the diisopropyl derivative *IV* (refs[13,19]) by the above mentioned procedure. It has been also described[18] that the reaction of dimesyl derivative *II* with sodium methoxide followed by acetylation produced a mixture of 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl 1,6-di-O-acetyl--3,4-anhydro-β-D-*ribo*-hexulofuranoside (*V*) and 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl 1,6-di-O-acetyl-3,4-anhydro-β-D-*lyxo*-hexulofuranoside (*VI*) with the



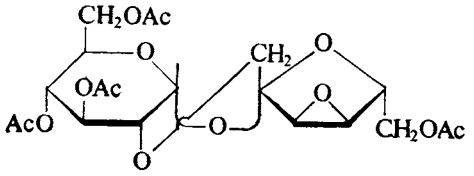
I, R^1 = Ac, R^2 = R^3 = H
II, R^1 = Ac, R^2 = R^3 = CH_3SO_2—
III, R^1 = Ac, R^2 = R^3 = $CH_3C_6H_4SO_2$ —
XIII, R^1 = R^2 = H, R^3 = Ac



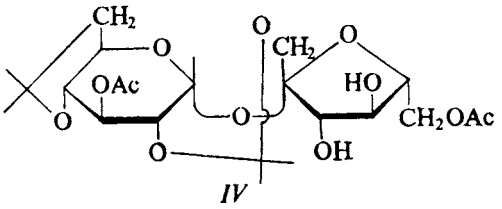
V, R^1 = R^2 = Ac
VIII, R^1 = CH_3SO_2—, R^2 = Ac
XI, R^1 = Ac, R^2 = H
XII, R^1 = H, R^2 = Ac



VI, R = Ac
IX, R = CH_3SO_2
X, R = H



VII



IV

Ac = CH_3CO—

later one prevailing. We obtained the same results when this reaction sequence was applied to the ditosyl derivative *III*. When the mother liquors after crystallization of ditosyl derivative *III* or the product of mesylation of hexa-O-acetylsucrose were used, the dianhydro derivative *VII* was isolated besides the anhydro derivative *V* and *VI*. From its ^1H NMR spectrum it was deduced that this compound contains an 3',4'

oxirane ring and four O-acetyl groups; no hydroxyl group is present. Proton H-2 resonates at higher field than in the anhydro derivatives *V* and *VI*. Its chemical shift is similar to that of H-2 in 3,3',4,4'-tetra-O-acetyl-1',2-anhydro-6,6'-di-O-triphenylmethyl-sucrose[20]. There is also a notable magnetic nonequivalence (0·59 ppm) of $C_{(1')}$ protons. The chemical shifts of carbon atoms $C_{(2)}$ to $C_{(5)}$ in ^{13}C NMR spectrum of *VII* are also different from those in the anhydro derivatives *V* and *VI*; the resonance of $C_{(2)}$ is markedly shifted downfield. All that indicates that there is an additional anhydro ring at the position 1',2 besides the 3',4' anhydro ring. We tried to solve the problem of the oxirane ring configuration by chemical transformation. According to the literature[20], the 1',2-anhydro ring is evidently formed by a nucleophilic substitution of the sulfonyloxy group at the position 1' by hydroxyl group at the position 2. Thus, the dianhydro derivative *VII* should be formed from that 1'-O-mesyl-3',4'-anhydro derivative which has the same oxirane ring configuration as the anhydro derivative *VII*, *i.e.* from the derivative *VIII* or *IX*.

To prepare the compound *IX*, we treated the hexaacetyl derivative *VI* with impregnated aluminum oxide. Chromatography of the reaction mixture on silica gel afforded the compound *X*. Its ^1H NMR spectrum allows the identification of five O-acetyl groups, two oxirane protons H-3' and H-4', and protons H-1 to H-4. A one-proton singlet appears at 9·01 ppm upon addition of TAI. In the ^{13}C NMR spectrum of *X*, there is one OCH_2 carbon shifted upfield with respect to *VI* and the $C_{(2')}$ resonance is moved downfield. Comparison of ^{13}C NMR spectra of *X* and its TAI-derivative shows that one OCH_2 resonance is shifted 2·4 ppm downfield and, on the other hand, that of $C_{(2')}$ appears 2·1 ppm upfield. From that it follows that the hydroxyl group in *X* is at carbon atom 1'. Therefore, *X* possesses the structure of 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl 6-O-acetyl-3,4-anhydro-β-D-*lyxo*-hexulofuranoside (*X*). Reaction of *X* with methanesulfonyl chloride gives *IX*. The signal of $C_{(1')}$ in its NMR spectrum is shifted 3·2 ppm downfield and that of $C_{(2')}$ 2·2 ppm upfield with respect to *X*. That finding also agrees with the proposed structure. By reaction of derivative *IX* with sodium methoxide and acetylation we obtained the hexa-O-acetylanhydro derivative *VI*. We did not detect any dianhydro derivative *VII* in the reaction mixture.

On the contrary, partial deacetylation of hexa-O-acetylanhydro derivative *V* by impregnated aluminum oxide yielded a mixture of two compounds with close R_F values. The signals of $C_{(1)}$ to $C_{(5)}$ in its ^{13}C NMR spectrum for both compounds were identical. One OCH_2 signal of each compound was shifted downfield upon addition of TAI. That suggest a mixture of penta-O-acetyl derivatives *XI* and *XII*. This mixture was converted into a mixture of mesyl derivatives by its treatment with methanesulfonyl chloride in pyridine and then subjected to reaction with sodium methoxide and acetylation. We isolated two compounds. The former was identical with dianhydro derivative *VII*, the later with hexaacetylanhydro derivative *V*. From this fact and from the result of the reaction of compound *IX* with sodium methoxide,

it follows that the dianhydro derivative *VII* has structure of 1′,2-anhydro-(3,4,6-tri--O-acetyl-α-D-glucopyranosyl 6′-O-acetyl-3′,4′-anhydro-β-D-*ribo*-hexulofuranoside). The minor hexa-O-acetylsucrose formed by deacetylation of octa-O-acetylsucrose should then have the structure of 2,3,4,4′,6,6′-hexa-O-acetylsucrose *XIII* since only from its 1′,3′-di-O-mesyl (tosyl) derivative the formation of dianhydro derivative *VII* is possible.

In agreement with these conclusions we obtained the hexa-acetylanhydro derivative *VI* by treatment of the mixture of hexa-acetylsucroses *I* and *XIII* with triphenylphosphine–diethyl azodicarboxylate mixture[21]. This compound has been recently prepared in the same way[22,23] from various sucrose derivatives having hydroxyl groups in positions 3′ and 4′.

Therefore, deacetylation of octa-O-acetylsucrose on impregnated aluminum oxide is highly specific. Among 28 possible isomers, hexa-O-acetylsucrose *I* is formed as the major product and hexa-O-acetylsucrose *XIII* as a minor one. The presence of minor components having free hydroxyl groups in positions 1′ and 4′, 3′ and 6′, and 4′ and 6′ in the reaction mixture from the deacetylation of octa-O-acetylsucrose cannot be excluded with respect to the behaviour of compound *IX* and the 1′-O-mesyl derivative of compound *XII*. However, our chromatographic and spectroscopic results do not support this alternative. Our finding that hexa-O-acetylsucrose *I* with hydroxyl groups at positions 3′ and 4′ is the main product of octa-O-acetylsucrose deacetylation is in agreement with results of partial deacetylation of 3,3′,4′,6′--tetra-O-acetyl-1′,2:4,6-di-O-isopropylidenesucrose. Deacetylation of this compound both by methanolic ammonia[18] and by impregnated aluminum oxide[13] also furnishes a product with free hydroxyl groups at positions 3′ and 4′. That casts some doubt on the possibility considered by British authors[8] who suggested that the O-acetyl groups attached to primary hydroxyls are removed first and then the migration of O-acetyl groups from the positions 4 and 4′ takes place. However, we cannot reject their hypothesis entirely.

EXPERIMENTAL

Melting points were determined on a Kofler apparatus and are uncorrected. Optical rotations were measured on a Opton instrument at 20°C in concentrations 1 ± 0·2. Analytical samples were dried 8 h *in vacuo* (10 Pa) at room temperature. Thin-layer chromatography was performed on silica gel according to Stahl (Merck, Darmstadt), particle size 10—40 μm, dimensions 25 × 75 mm, thickness 0·2—0·3 mm. Compounds were detected by spraying the plates with 1% cerium(IV) sulfate in 10% sulfuric acid followed by heating. Preparative chromatography was done on a silica gel column of particle size 100—160 μm (Lachema, Brno). Solvents were removed *in vacuo*; the temperature was kept below 50°C. ^{1}H and ^{13}C NMR spectra were measured on a Jeol FX-60 spectrometer (FT mode, 59·797 and 15·036 MHz) in deuteriochloroform at 25°C. Solvent deuterium resonance was used as an internal lock. Chemical shifts are given in the δ-scale with accuracy ±0·005 and 0·06 ppm for ^{1}H and ^{13}C NMR spectra, respectively. Tetramethylsilane was employed as an internal standard. Signals were assigned using homo-

nuclear decoupling and multiplicity pattern (^{1}H NMR) or using off-resonance, noise off-resonance, and selective heteronuclear decoupling experiments (^{13}C NMR). ^{1}H NMR spectra of anhydro derivatives *V*, *VI*, and *VII* were measured on a Varian XL-200 (200 MHz) NMR spectrometer. Mass spectra were recorded on a Jeol JMS DX-300 spectrometer equipped with JMA 200 computer.

Deacetylation of Octa-O-acetylsucrose

Impregnated aluminum oxide (210 g) was added to the solution of octa-O-acetylsucrose (86 g, 127 mmol) in methanol (650 ml). The mixture was stirred 12 h, allowed to stand 9 h at ambient temperature and then filtered. Filtration cake was washed with methanol. Combined filtrates were evaporated. Sirupy residue contained at least 10 components according to TLC in benzene–ethanol 5 : 1. The residue was dissolved in chloroform (200 ml) and extracted by water (200 ml). The evaporation of chloroform extract furnished a sirup (62 g) containing 5 compounds according to TLC (benzene–ethanol 5 : 1). TLC-FID (ref.[13]) results were: 15% octa-O-acetylsucrose, 16% hepta-O-acetylsucrose, 43% hexa-O-acetylsucroses, and 21% penta-O-acetylsucrose. This mixture was separated by column chromatography on silica gel (200 g, benzene–ethanol 100 : 2 to 100 : 7). The yield after re-chromatography of mixture containing fractions was: 10·2 g (16·4% of chloroform portion, yield 11·8%) of octa-O-acetylsucrose, 11·2 g of hepta-O-acetylsucroses (18·0% of chloroform portion, yield 13·9%), 25·7 g of hexa-O-acetylsucroses (41·4% of chloroform portion, yield 34·1%), and 13·0 g of a mixture of at least two penta-O-acetylsucroses (21% of chloroform portion, yield 18·5%). These two compounds were different on TLC but their R_F-values on TLC–FID were identical.

Hexa-O-acetylsucroses: a sirup, $[\alpha]_D$ +65·6° (chloroform). For $C_{24}H_{34}O_{17}$ (594·5) was calculated 48·48% C, 5·76% H; found 48·21% C, 5·90% H. ^{1}H NMR spectrum: 2·02 s (3 H), 2·04 s (3 H), 2·08 s (3 H), 2·10 s (6 H), 2·13 s (3 H), 4·91 dd ($J_{1,2}$ = 3·7 Hz, $J_{2,3}$ = 9·8 Hz, H-2), 5·02 t ($J_{2,3} = J_{3,4}$ = 9·8 Hz, H-3), 5·48 dd ($J_{3,4}$ = 9·8 Hz, $J_{4,5}$ = 9·2 Hz, H-4), 5·63 d ($J_{1,2}$ = = 3·7 Hz, H-1). ^{13}C NMR spectrum: 20·7 q (6C), 62·1 t, 63·4 t, 63·8 t, 68·4 d, 68·6 d, 69·8 d, 70·0 d, 74·9 d, 77·8 d, 79·1 d, 89·3 d, 103·2 s, 169·8 s, 170·2 s (2C), 170·8 s, 171·3 s. Mass spectrum, *m/z*: 331, 271, 247, 211, 187, 169, 127, 109, 73, 43.

Di-O-deuterioacetyl Derivatives of Hexa-O-acetylsucroses

Perdeuterioacetanhydride (0·15 ml) was added to the solution of hexa-O-acetylsucroses (60 mg) in 3 ml of pyridine and the mixture was allowed to stand overnight at room temperature. Water (1 ml) was added and the mixture was evaporated; then toluene was added and the evaporation was repeated. The residue was crystallized from ethanol. The yield was 68 mg, m.p. 85—88°C. Mass spectrum, *m/z*: 337, 331, 271, 214, 211, 170, 169, 127, 109, 46, 43.

Di-O-methanesulfonyl Derivatives of Hexa-O-acetylsucroses

Methanesulfonyl chloride (3 ml, 1·3 equivalents) was added at −40°C to the solution of hexa-O-acetylsucroses (9·07 g, 15·27 mmol) in 50 ml of pyridine. The mixture was kept 48 h at −15°C and then decomposed by 0·5 ml of water and diluted by chloroform (100 ml). The chloroform layer was extracted by 10% sulfuric acid, water, 5% sodium hydrogen carbonate, and water. It was dried over magnesium sulfate. The sirupy residue was purified by column chromatography on silica gel (200 g, elution with benzene–ethanol 100 : 2). The product (9·6 g, 85%) contained a small amount of some admixture with slightly higher R_F-value according to TLC (benzene–ethanol 10 : 1). Optical rotation $[\alpha]_D$ +42·5° (chloroform). For $C_{26}H_{38}O_{21}S_2$ (750·2) was calculated 41·60% C, 5·10% H, 8·64% S; found 41·73% C, 5·34% H, 8·54% S. Mass spectrum, *m/z*: 403,

347, 331, 271, 211, 169, 109, 127. Literature reports[18] for compound *I* optical rotation $[\alpha]_D$ +47° (chloroform) and the same mass spectrum.

1′,2,3,4,6,6′-Hexa-O-acetyl-3′,4′-di-O-*p*-toluenesulfonylsucrose (*III*)

A) *p*-Toluenesulfonyl chloride (3·85 g, 4 equivalents) was added to the solution of hexa--O-acetylsucroses (3·01 g, 5·07 mmol) in pyridine (15 ml). The mixture was left 48 h at room temperature and then worked-up as described under di-O-methanesulfonyl derivatives of hexa--O-acetylsucroses. Ether (50 ml) was added to the chloroform extract. Precipitated crystals (3·5 g, m.p. 160—162°C, change of modification occurs at 147—149°C) contained a small amount of impurity according to TLC (benzene–ethanol 10 : 1). Recrystallization from ethyl acetate–-light petroleum provided 3·25 g (71%) of chromatographically pure *III*, m.p. 163—165°C, $[\alpha]_D$ +52·3° (chloroform). The residue after evaporation of mother liquors weighted 868 mg. ^{13}C NMR spectrum: 20·7 q (6C), 21·7 q (2C), 61·5 t, 61·9 t, 63·4 t, 68·0 d, 68·6 d, 69·5 d, 69·7 d, 76·7 d, 77·5 d, 78·8 d, 89·0 d, 101·8 s, 128·3 d (4C), 130·1 d (4C), 132·3 s (2C), 145·9 s (2C), 169·5 s, 170·0 s (4C), 170·6 s. ^1H NMR spectrum was in a good agreement with ref.[18]. M.p. reported for *III* was 150—152°C, $[\alpha]_D$ +54° (chloroform).

B) Mixture of 3,6′-di-O-acetyl-1′,2:4,6-di-O-isopropylidene-3′,4′-di-O-*p*-toluenesulfonylsucrose[18] (204 mg, 0·25 mmol) (sirup, $[\alpha]_D$ −14·6°, chloroform, prepared[13] by tosylation of compound *IV*) and 60% aqueous acetic acid (5 ml) was boiled for 8 min and then evaporated. Pyridine (5 ml) and acetanhydride (1 ml) were added and after 15 h standing all solvents were removed by evaporation. Crystallization from the mixture ethyl acetate – light petroleum yielded compound *III* (200 mg, 89%, m.p. 163°C, $[\alpha]_D$ +52° (chloroform)). Its IR and ^1H NMR spectra were identical with those of *III* prepared by the method *A*.

Reaction of Ditosyl Derivative *III* with Sodium Methoxide

Compound *III* (1·8 g, 2 mmol) and methanolic solution of sodium methoxide (20 ml, 1 mol l^{-1}) were boiled 2 min. Then it was evaporated to dryness and pyridine (50 ml) and acetanhydride (20 ml) were added. After 15 h standing at room temperature, the mixture was poured onto crushed ice and extracted by chloroform. The solvent was evaporated and the residue subjected to column chromatography on silica gel (50 g, system ether – light petroleum 4 : 1). Together 356 mg (31%) of compound *V*, $[\alpha]_D$ +59·7° (chloroform) and 637 mg (55%) of compound *VI*, $[\alpha]_D$ +70·2° (chloroform) were obtained. ^{13}C NMR spectrum of compound *V*: 20·7 q (6C), 57·8 d, 58·6 d, 61·7 t, 63·2 t (2C), 68·3 d, 68·4 d, 69·8 d, 70·3 d, 78·1 d, 90·3 d, 105·0 s, 169·5 s, 170·1 s (3C), 170·5 (2C). ^1H NMR spectra, mass spectra, and optical rotations of compounds *V* and *VI* as well as the ^{13}C NMR spectrum of compound *VI* were identical to those published[18,22,23].

Reaction of Mother Liquors after Crystallization of Compound *III* with Sodium Methoxide

The work-up of residue from mother liquors after crystallization of compound *III* (868 mg) by the above described procedure produced 96 mg of compound *VII*, 136 mg of compound *V*, and 163 mg of compound *VI*. Dianhydro derivative *VII* re-crystallized from ethanol had m.p. 152—153°C, $[\alpha]_D$ +82° (chloroform). For $C_{20}H_{26}O_{13}$ (474·4) was calculated 50·63% C, 5·52% H; found 50·33% C, 5·47% H. ^1H NMR spectrum: 2·042 s (3 H), 2·075 s (3 H), 2·085 s (3 H), 2·099 s (3 H), 3·550 d ($J_{1'a,1'b}$ = 12·6 Hz, H-1′b), 3·721 d ($J_{3',4'}$ = 2·9 Hz, H-3′), 3·804 d

($J_{3',4'}$ = 2·9 Hz, H-4'), 4·098 d ($J_{1'a,1'b}$ = 12·6 Hz, H-1'a), 4·099 dd ($J_{1,2}$ = 3·7 Hz, $J_{2,3}$ = = 9·8 Hz, H-2), 5·082 dd ($J_{3,4}$ = 9·8 Hz, $J_{4,5}$ = 10·0 Hz, H-4), 5·718 t ($J_{2,3}$ = $J_{3,4}$ = 9·8 Hz, H-3), 5·440 d ($J_{1,2}$ = 3·7 Hz, H-1). ^{13}C NMR spectrum 20·7 q (4C), 54·7 d, 57·3 d, 61·3 t, 61·6 t, 63·0 t, 66·1 d, 67·6 d, 71·7 d, 77·7 d, 90·6 d, 103·8 s, 169·3 s, 170·1 s, 170·5 s (2C).

Reaction of Hexa-O-acetylsucroses with Triphenylphosphine – Diethyl Azodicarboxylate Mixture

Triphenylphosphine (2·2 g, 2·5 equivalents) was added to the solution of hexa-O-acetylsucroses (2·06 g, 3·47 mmol) in 40 ml of N,N-dimethylformamide at 0°C. Diethyl azodicarboxylate (1·48 g, 2·5 equivalents) was added stepwise during 15 min. The mixture was allowed to warm to the room temperature and then left standing for 60 h. N,N-Dimethylformamide was distilled off and the residue was chromatographed on a silica gel column (100 g, system ether–light petroleum 4 : 1). N,N'-Bis(ethoxycarbonyl) hydrazine was eluted first followed by partly crystallizing mixture of anhydro derivative *VI* and triphenylphosphine oxide (2·1 g). Addition of ether (10 ml) precipitated another triphenylphosphine oxide (1·2g) that was filtered off. The filtrate was evaporated and the residue chromatographed on a silica gel column (100 g). Mixture benzene–acetone 9 : 1 has eluted anhydro derivative *VI* (1·08 g, 54%), identical according to optical rotation, IR, and NMR spectra with anhydro derivative *VI* prepared from the ditosyl derivative *III*. A comparable yield (50%) was obtained when N,N-dimethylformamide was replaced by chloroform.

2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl 6-O-acetyl-3,4-anhydro-β-D-*lyxo*-hexulofuranoside (*X*)

Impregnated aluminum oxide (1·3 g) was added to the solution of anhydro derivative *VI* (523 mg, 0·91 mmol) in methanol (11 ml). The suspension was shaken for 4·5 h. Then it was filtered off and filtrate was washed with methanol. Combined filtrates were evaporated. Column chromatography (silica gel 60 g, system benzene–ethanol 100 : 3) of the residue (460 mg) yielded unreacted starting compound *VI* (197 mg, 37·5%) and compound *X* (149 mg, 30·5%), $[\alpha]_D$ +78·3° (chloroform). ^{1}H NMR spectrum: 2·03 s (12 H), 2·08 s (3 H), 3·77 d ($J_{3',4'}$ = 3·1 Hz, H-3'), 3·85 d ($J_{3',4'}$ = 3·1 Hz, H-4'), 4·83 dd ($J_{1,2}$ = 3·7 Hz, $J_{2,3}$ = 9·8 Hz, H-2), 5·05 dd ($J_{3,4}$ = 9·8 Hz, $J_{4,5}$ = 9·2 Hz, H-4), 5·52 t ($J_{2,3}$ = $J_{3,4}$ = 9·8 Hz, H-3), 5·75 d ($J_{1,2}$ = 3·7 Hz, H-1). ^{13}C NMR spectrum: 20·6 q (5C), 54·9 d, 56·6 d, 62·1 t, 62·3 t, 64·9 t, 67·9 d, 68·7 d, 69·7 d, 70·2 d, 74·9 d, 89·4 d, 104·0 s, 169·3 s, 169·7 s, 170·1 s, 170·4 s, 170·5 s.

2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl 6-O-acetyl-3,4-anhydro-1-O-methanesulfonyl-β-D-*lyxo*-hexulofuranoside (*IX*)

Methanesulfonyl chloride (0·15 ml) was added at −30°C to the solution of compound *X* (180 mg, 0·34 mmol) in pyridine (5 ml). The mixture was kept 15 h at −15°C, decomposed by water and diluted by chloroform. The chloroform layer was washed with 10% sulfuric acid, water, 5% sodium hydrogen carbonate, and again with water. The extract was dried over magnesium sulfate, solvent evaporated and the residue was purified by column chromatography on silica gel (20 g, system benzene–ethanol 100 : 1). Compound *IX* was obtained (174 mg, 84%), $[\alpha]_D$ +61·8° (chloroform). For $C_{23}H_{32}O_{17}S$ (612·5) was calculated 45·09% C, 5·27% H, 5·23% S; found: 44·96% C, 5·44% H, 5·04% S. ^{1}H NMR spectrum: 2·03 s (6 H), 2·04 s (3 H), 2·08 s (3 H), 2·09 s (3 H), 3·12 s (3 H), 3·82 mt (2 H, H-3' and H-4'), 4·81 dd ($J_{1,2}$ = 3·9 Hz, $J_{2,3}$ = 9·8 Hz, H-2), 5·05 t ($J_{3,4}$ = $J_{4,5}$ = 9·8 Hz, H-4), 5·49 t ($J_{2,3}$ = $J_{3,4}$ = 9·8 Hz, H-3), 5·81 d ($J_{1,2}$ = = 3·9 Hz, H-1). ^{13}C NMR spectrum: 20·4 q (4C), 37·6 q, 54·7 d, 56·0 d, 61·8 t, 61·9 t, 68·1 t, 68·4 d, 69·3 d, 69·7 d, 75·1 d, 89·5 d, 101·8 s, 169·3 s, 169·6 s (2C), 170·4 s.

Reaction of Compound *IX* with Sodium Methoxide

Solution of *IX* (108 mg, 0·176 mmol) in 3 ml (1 mol l^{-1}) of sodium methoxide was boiled 2 min and then evaporated to dryness. Pyridine (5 ml) and acetanhydride (2 ml) were added. After 15 h standing at room temperature, the mixture was poured onto crushed ice and extracted with chloroform. The residue after evaporation was chromatographed on a silica gel column (20 g, system ether–light petroleum 4 : 1). Compound *VI* was obtained (56 mg, 55%), $[\alpha]_D$ +68·3° (chloroform). Its NMR spectra were identical with those of an authentic sample. The side product (27 mg) was a mixture of 4 components. None of them was the dianhydro derivative *VII*, according to TLC (ether–light petroleum 4 : 1).

Transformation of Anhydro Derivative *V* to Dianhydro Derivative *VII*

Impregnated aluminum oxide (3 g) was added to the solution of *V* (1·2 g) in methanol (25 ml). The suspension was shaken for 9 h, filtered, the filtration cake washed with methanol and the combined filtrates evaporated. Column chromatography of the residue on silica gel (60 g, benzene–acetone 9 : 1) gave 389 mg (32%) of two-component mixture (close R_F, probably *XI* and *XII*). A part of this mixture (102 mg) was mesylated as described above for *IX* (3 ml of pyridine, 0·15 ml of methanesulfonyl chloride). The product (97 mg) contained two compounds, according to TLC (benzene–acetone 8 : 2). It was allowed to react (as described for *IX*) with sodium methoxide (2 min heating with 3 ml of 1 ml l^{-1} solution) and then it was acetylated (5 ml of pyridine, 2 ml of acetanhydride). Resulting sirup (92 mg) consisted of *VII* and *V* (major component), according to TLC (benzene–acetone 4 : 1). Chromatography of this mixture (silica gel 15 g, system benzene–acetone 95 : 5) has provided 10 mg of *VII*, $[\alpha]_D$ +81·7° (chloroform) that crystallized upon standing, m.p. 146–150°C. Its IR and NMR spectra were identical with those of compound *VII* prepared by the above mentioned procedure from hexa-O-acetylsucroses. Furthermore, we isolated 20 mg of the mixture *VII* and *V* and 31 mg of compound *V*, $[\alpha]_D$ +57·6° (chloroform), identical according to NMR spectra with the authentic sample.

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REFERENCES

1. Čapek K., Šteffková J., Jarý J.: This Journal *31*, 1854 (1966).
2. Čapek K., Šteffková J., Jarý J.: This Journal *32*, 2491 (1967).
3. Čapek K., Šteffková J., Jarý J.: This Journal *33*, 781 (1968).
4. Čapek K., Šteffková J., Jarý J.: This Journal *33*, 1750 (1968).
5. Čapek K., Šteffková J., Jarý J.: This Journal *35*, 107 (1970).
6. Čapek K., Šteffková-Čapková J., Jarý J.: This Journal *35*, 321 (1970).
7. Ballard J. M., Hough L., Richardson A. C.: Carbohyd. Res. *24*, 152 (1972).
8. Ballard J. M., Hough L., Richardson A. C.: Carbohyd. Res. *34*, 184 (1974).
9. Otake T.: Bull. Chem. Soc. Jap. *43*, 3199 (1970).
10. Buchanan J. G., Cummerson D. A., Turner D. M.: Carbohyd. Res. *21*, 283 (1972).
11. Khan R.: Advan. Carbohyd. Chem. Biochem. *33*, 235 (1976).
12. Čapek K., Čapková J., Kvapilová E., Vydra T., Bláhová M., Ranný M.: Czech 223 440.
13. Čapek K., Vydra T., Čapková J., Ranný M., Bláhová M., Sedmera P.: This Journal *50*, 1039 (1985).
14. De Bruyn A., Anteunis M., Verhegge G.: Carbohyd. Res. *42*, 157 (1975).

15. Goodlet V. W.: Anal. Chem. *37*, 431 (1965).
16. Trehan I. R., Monder C., Bose A. K.: Tetrahedron Lett. *1968*, 67.
17. Bose A. K., Srivanasan P. R.: Tetrahedron *30*, 3025 (1975).
18. Khan R., Jenner M. R., Lindseth H.: Carbohyd. Res. *65*, 99 (1978).
19. Khan R., Mufti K. S.: Carbohyd. Res. *43*, 247 (1975).
20. Chiu A. K. B., Gurjar M. K., Houhg L., Sincharoenkul L. V., Richardson A. C.: Carbohyd. Res. *100*, 247 (1982).
21. Mitsunobu O., Kimura J., Ihzumi K., Yanagida N.: Bull. Chem. Soc. Jap. *49*, 510 (1976).
22. Guthrie R. D., Jenkins I. D., Yamasaki R.: Carbohyd. Res. *85*, C5 (1980).
23. Guthrie R. D., Jenkins I. D., Thang S., Yamasaki R.: Carbohyd. Res. *121*, 109 (1983).

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