PARTIALLY ACETYLATED SUCROSE. PREPARATION OF 3-O-ACETYLSUCROSE AND 3,6'-DI-O-ACETYLSUCROSE AND THE ANALYSIS OF MIXTURES OF O-ACETYL DERIVATIVES OF SUCROSE OF VARIOUS DEGREES OF ACETYLATION BY THIN-LAYER CHROMATOGRAPHY WITH FLAME-IONIZATION DETECTION

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Partial deacetylation of 3,3',4',6'-tetra-O-acetyl-1',2 : 4,6-di-O-isopropylidene sucrose (*V*) with aluminum oxide impregnated with potassium carbonate gave a mixture of 3,6'-di-O-acetyl-1',2:4,6-di-O-isopropylidenesucrose (*VI*) and 3-O-acetyl-1',2:4,6-di-O-isopropylidenesucrose (*VII*). 3,6'-di-O-acetylsucrose (*IX*) and 3-O-acetylsucrose (*X*) were prepared on deacetalation of compounds *VI* and *VII*, respectively. The structure of compounds *IX* and *X* was proved by ^{13}C NMR and mass spectra of their deuterioacetyl derivatives *XI* and *XII*. Using procedures described in literature 3,3',4',6'-tetra-O-acetylsucrose (*IV*), 2,3,3',4',6-penta-O-acetylsucrose (*III*), 1',2,3,3',4',6'-hexa-O-acetylsucrose (*II*) and 1',2,3,3',4,4',6-hepta-O-acetylsucrose (*I*) were prepared. These acetyl derivatives, sucrose and their octa-O-acetyl derivative were analysed by thin-layer chromatography with flame-ionization detection either separately or in mixtures. A chromatogram of the mixture was identical with a chromatogram of a mixture of O-acetyl derivatives of sucrose formed on deacetylation of octa-O-acetylsucrose with aluminum oxide impregnated with potassium carbonate; from this it follows that under the conditions of analysis O-acetyl derivatives of sucrose are separated on the basis of the degree of acetylation.

O-Acetyl derivatives of sucrose are much-sought-for intermediates in chemical conversions of sucrose in laboratories[1] and potentially on an industrial scale as well[2-4]. They are prepared by partial acetylation of sucrose[3,5], its transesterification[6] and multistep syntheses[1] in which first some hydroxyl groups of sucrose are protected by suitable substituents, then acetylation is carried out and finally the protecting groups are eliminated. The disadvantage of these procedures consists in high-boiling toxic solvents which are needed for the dissolution of sucrose; the last mentioned method is also usually time-consuming. In our laboratory we pre-

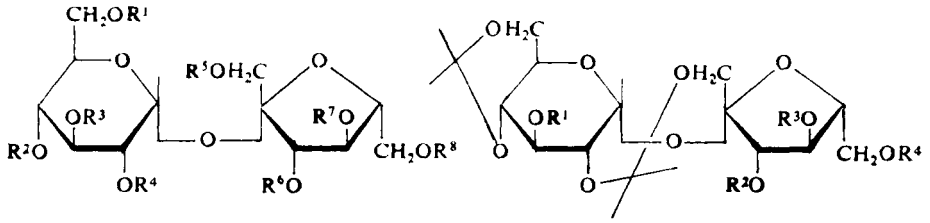
pared partially acetylated derivatives of acetamidodeoxysaccharides[7-12] and deoxysaccharides[13] by partial deacetylation of their per-O-acetyl derivatives with aluminum oxide. This procedure was applied to octa-O-acetylsucrose by British authors[14,15] who found that octa-O-acetylsucrose is deacetylated in a poor yield to a mixture of hepta-O-acetylsucrose in which the isomer with the free hydroxyl group in the position 6' predominates. We used aluminum oxide impregnated with potassium carbonate[16]. Chromatography on thin layers showed that octa-O-acetylsucrose is deacetylated to a rich mixture of substances the population of which depends on the reaction time. However, on chromatograms from thin-layer chromatography with flame-ionization detection (TLC-FID) we detected maximally 9 peaks. The R_F value of the first and the last peak agreed well with the R_F value of octa-O-acetylsucrose and sucrose, respectively (Fig. 1). This indicated that under the conditions of TLC-FID analysis the products of the deacetylation of octa-O-acetyl sucrose are separated according to the degree of acetylation, *i.e.* that each of the remaining 7 peaks indicates the presence of all potential isomers with an equal number of O-acetyl groups. Since this method of analysis is very suitable* for the monitoring of the deacetylation course of octa-O-acetylsucrose we decided to check in this study whether the above-mentioned assumption is correct.

For the preparation of O-acetyl derivatives of sucrose with a higher degree of acetylation literature[1] offers a number of procedures leading to the isomers with a defined position of the O-acetyl groups on the sucrose skeleton. Using these procedures we prepared 1',2,3,3',4,4',6-hepta-O-acetylsucrose[17] (*I*), 1',2,3,3',4',6'-hexa-O-acetylsucrose[18] (*II*), 2,3,3',4',6-penta-O-acetylsucrose[17] (*III*) and 3,3',4',6'-tetra-O-acetylsucrose[19] (*IV*). In contrast to this, the mono and di-O-acetyl derivatives of sucrose, if mentioned in the literature at all[5,6,20-22], are not sufficiently characterized.** For the preparation of mono- and di-O-acetylsucrose with a defined position of the O-acetyl groups we chose 3,3',4',6'-tetra-O-acetyl-1',2:4,6-di-O-isopropylidenesucrose[19] (*V*) as starting material. Kahn and co-workers[23] found that this substance is deacetylated to 3,6'-di-O-acetyl-1',2:4,6-di-O-isopropylidenesucrose (*VI*), 3-O-acetyl-1',2:4,6-di-O-isopropylidenesucrose (*VII*) and 1',2:4,6-di-O-isopropylidenesucrose (*VIII*) under the effect of ammonia in methanol. Hence, the possibility of comparing the method of deacetylation of compound *V* used in ref.[23] with our own method[16] was provided, and – in the case that equal or similar result was obtained – of preparing the required O-acetyl derivatives of sucrose from compounds *VI* and *VII*. We found that the deacetylation of tetraacetyl derivative *V* with aluminum oxide

* On deacetylation of octa-O-acetylsucrose up to 254 O-acetyl derivatives may be formed theoretically; however, for their possible industrial use the degree of acetylation will be the most important factor.

** 3-O-Acetylsucrose is only mentioned in ref.[22].

impregnated with potassium carbonate[16] also gave a mixture of mono- and di-O-acetyl derivatives; we did not observe deacetylation to compound *VIII*. On comparison



I, $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^7 = CH_3CO$, $R^8 = H$

II, $R^3 = R^4 = R^5 = R^6 = R^7 = R^8 = CH_3CO$, $R^1 = R^2 = H$

III, $R^1 = R^3 = R^4 = R^6 = R^7 = CH_3CO$, $R^2 = R^5 = R^8 = H$

IV, $R^3 = R^6 = R^7 = R^8 = CH_3CO$, $R^1 = R^2 = R^4 = R^5 = H$

V, $R^1 = R^2 = R^3 = R^4 = CH_3CO$

VI, $R^1 = R^4 = CH_3CO$, $R^2 = R^3 = H$

VII, $R^1 = CH_3CO$, $R^2 = R^3 = R^4 = H$

VIII, $R^1 = R^2 = R^3 = R^4 = H$

IX, $R^3 = R^8 = CH_3CO$, $R^1 = R^2 = R^4 = R^5 = R^6 = R^7 = H$

X, $R^3 = CH_3CO$, $R^1 = R^2 = R^4 = R^5 = R^6 = R^7 = R^8 = H$

XI, $R^3 = R^8 = CH_3CO$, $R^1 = R^2 = R^4 = R^5 = R^6 = R^7 = C^2H_3CO$

XII, $R^3 = CH_3CO$, $R^1 = R^2 = R^4 = R^5 = R^6 = R^7 = R^8 = C^2H_3CO$

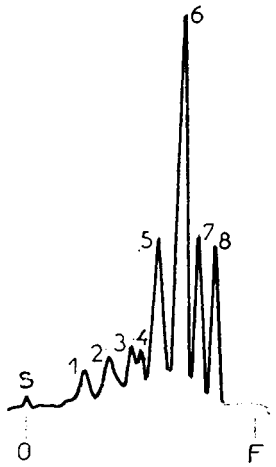


FIG. 1

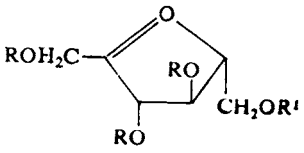
Chromatogram from TLC-FID analysis of a mixture of O-acetylated sucroses prepared by partial deacetylation of octa-O-acetylsucrose with aluminum oxide impregnated with potassium carbonate[16] (for experimental conditions see Experimental). S sucrose, 1 mono-O-acetylsucrose(s), 2 di-O--acetyl sucrose (s), 3 tri-O-acetylsucrose(s), 4 tetra-O-acetylsucrose (s), 5 penta-O-acetylsucrose (s), 6 hexa-O-acetylsucrose(s), 7 hepta-O-acetylsucrose(s), 8 octa-O-acetylsucrose

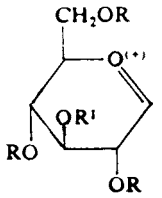
of the ^{1}H NMR spectra of mono- and di-O-acetyl derivatives with the published data[23] and from the ^{13}C NMR spectra of these substances we found that they have the structure of *VI* or *VII*, respectively. Hence, the deacetylation of tetra-O-acetyl derivative *V* with impregnated aluminum oxide[16] proceeds in principle in the same way as the deacetylation with ammonia[23] and its regioselectivity is not due to the method of deacetylation, but to the substrate.

Diisopropylidene derivative *VI* or *VII* was deacetalated with aqueous acetic acid, affording 3,6'-di-O-acetylsucrose (*IX*) or 3-O-acetylsucrose (*X*), respectively. Both substances were obtained in the form of strongly hygroscopic syrups from which water could not be eliminated completely even after several days' drying over phosphorus pentoxide.* The ^{1}H NMR and ^{13}C NMR spectra of compounds *IX* and *X* confirm that they are di-O-acetyl- or mono-O-acetyl derivative, respectively. From the chemical shift H-3 (5·02 or 5·00 ppm, resp.) it follows that in both substances the acetyl group is in position 3. A correlation of the ^{13}C NMR spectra measured in deuterium oxide with the assigned sucrose spectrum[24–26] shows that in mono-O-acetyl derivative *X* the $C_{(3)}$ signal is shifted by 2·4 ppm downfield (the α-effect) and the signal $C_{(2)}$ or $C_{(4)}$ by 2·0 or 1·9 ppm, respectively, upfield (β-effects). This demonstrates the substitution on $C_{(3)}$. In the ^{13}C NMR spectrum of di-O-acetyl derivative *IX* the signal of the primary hydroxyl group on $C_{(6')}$ is shifted downfield by 3·5 ppm in comparison with *X* (α-effect), while the chemical shift of the neighbouring atom ($C_{5'}$) is less by 3·0 ppm. This means that the second O-acetyl group in compound *IX* is in position 6'. On acylation of compound *IX* or *X* with deuterioacetic anhydride in pyridine we obtained hexadeuterioacetyl derivative *XI* or heptadeuterioacetyl derivative *XII*, respectively. Their ^{1}H NMR spectra in the 3·8–5·5 ppm region do not differ from the spectrum of octa-O-acetylsucrose. The acetyl group methyls resonate in diacetyl derivative *XI* at 2·02 and 2·12 ppm, in monoacetyl derivative *XII* at 2·01 ppm. For chemical shifts of these groups in deuteriochloroform in derivatives of monosaccharides the values 2·16 ± 0·05 ppm are given[27] for axially oriented and 2·01 ± 0·08 ppm for equatorially oriented O-acetyl groups. The methyl of the acetyl group in position 3 of the α-D-glucopyranose gives a chemical shift of 2·01 ppm (ref.[28]). The chemical shifts of the acetyl methyls in the 100 MHz ^{1}H NMR spectrum of octa-O-acetylsucrose[29] do not differ from the values in a 60 MHz spectrum: 2·18 (3 H), 2·12–2·10 (15 H), 2·05 (3 H) and 2·02 (3 H). According to our results in octa-O-acetylsucrose the acetyl group on $C_{(3)}$ resonates at 2·02 ppm and on $C_{(6')}$ in the 2·10–2·12 ppm region. The structure proposed for compounds *IX* and *X* is also suggested by the mass spectra of their deuteroacetyl derivatives *XI* and *XII*. In the spectrum of heptadeuterioacetyl derivative *XII* intensive ions are present with *m/z* 343 (31%) and 340 (25%), of which the more abundant evidently belongs[1,15] to the fructofuranosyloxonium ion *A* ($R^1 = C^2H_3CO$) and the less

* A similar finding is quoted in ref.[5].

abundant to glucopyranosyloxonium ion *B*. The same as in 4-O-acetyl-1',2,3,3'.4',6,6'--hepta-O-deuterioacetylsucrose[15] a weak peak of the ion m/z 280 (< 5%) is present in the spectrum, which is evidently formed by the cleavage of acetic acid from ion *B*.





A, R = C^2H_3CO, *B*, R = C^2H_3CO, R^1 = CH_3CO

All the more important ions in the spectrum satisfy the fragmentation scheme according to which acetic acid, deuterioacetic acid, CH_2CO and C^2H_2CO are split from the ion *B* or also *A*. The ratio of the intensities of the ions m/z 46 (100%) and 43 (13·5%) shows an about 7-fold number of deuterioacetyl groups in comparison with the acetyl ones. In the spectrum of hexadeuterioacetyl derivative *XI* an abundant ion of m/z 340 (65%) is present, corresponding evidently to ion *A* (R^1 = CH_3CO—) and ion *B*, which both contain one O-acetyl group; the ratio of the intensities of the ions m/z 46 (100%) and 43 (26·5%) indicates a 3–4 fold excess of deuterioacetyl groups in comparison with the acetyl groups.

We analysed octa-O-acetylsucrose, hepta-O-acetylsucrose *I*, hexa-O-acetylsucrose *II*, penta-O-acetylsucrose *III*, tetra-O-acetylsucrose *IV*, di-O-acetylsucrose *IX*, mono-O-acetylsucrose *X* and surcose separately and in mixtures by TLC-FID. We found that each of these substances gives one peak only; the R_F values (octa--O-acetylsucrose 0·67, compound *I* 0·60, compound *II* 0·54, compound *III* 0·46, compound *IV* 0·37, compound *IX* 0·21, compound *X* 0·07, sucrose 0·04) correspond to the R_F values of the substances from partial deacetylation of octa-O-acetylsucrose[16] (Fig. 1). The response coefficient of individual substances was almost identical and equal to one, the variation coefficient of the percentual content was lower than 5% and of the R_F values lower than 3%. Since we have also found that on partial acetylation of octa-O-acetylsucrose at least three hepta-O-acetylsucroses, two hexa-O-acetylsucroses and three penta-O-acetylsucroses[30] are formed, it may be stated that under the conditions of analysis by TLC-FID the O-acetyl derivatives of sucrose separate according the degree of acetylation.

EXPERIMENTAL

The melting points were determined on a Kofler block and they are not corrected. Optical rotations were measured on an Opton instrument at 20°C and 1 ± 0·2 concentration. For analysis

the substances were dried in a vacuum (10 Pa) and at room temperature for 8 h. Chromatography on thin layers of silica gel was carried out on silica gel G plates according to Stahl (Merck, Darmstadt), of 10–40 μm particle size and 25 × 75 mm dimension, layer thickness 0·2–0·3 mm. The substances were detected by spraying with 1% of a cerium sulfate solution in 10% sulfuric acid and heating. TLC-FID was carried out on a Iatroscan TH-10 (Iatron, Tokyo) instrument under the following conditions: Chromarod S II sticks, 150 mm long, 0·9 mm diameter, eluent benzene–methanol–n-hexane 62 : 19 : 19, elution time 25 min, drying time 7 min at 105°C, hydrogen flow 180 ml min^{-1}, air flow 2 100 ml min^{-1}, combusion rate 0·31 cm s^{-1}. Preparative chromatography was carried out on a silica gel column, Lachema, Brno, particle size 100–160 μm. The solvents were evaporated in a vacuum (water pump) at maximally 50°C. The ^1H and ^{13}C NMR spectra were measured on an FT NMR spectrometer Jeol FX-60 (FT mode, 59·797 and 15·036 MHz) in deuteriochloroform, hexadeuteriobenzene and deuterium oxide at 25°C. The deuterium signal of the solvent was used for the stabilization of the field (deuterium internal lock). The chemical shifts are given in δ-scale with a $\pm 0{\cdot}005$ and $\pm 0{\cdot}06$ ppm accuracy for ^1H and ^{13}C NMR spectra, respectively. Tetramethylsilane and dimethyl sulfoxide (δ_H 2·54, δ_C 39·6) were used as internal standards. The assignment of the signals is based on mononuclear decoupling and the multiplicity of the signals (^1H NMR) and on off-resonance, noise off-resonance and selective heteronuclear decoupling experiments (^{13}C NMR). The mass spectra were measured on a Jeol JMS-DX 200 instrument with a JMA 2000 computer.

Compounds *I* – *V*

Using a procedure described in literature the following compounds were prepared: 1′,2,3,3′,4,4′,6-hepta-O-acetylsucrose (*I*) with m.p. 159–160°C, $[\alpha]_D$ +53·5° (chloroform), lit.[17] gives m.p. 160°C, $[\alpha]_D$ +49·5° (chloroform), lit.[14] gives $[\alpha]_D$ +52·5° (chloroform); 1′,2,3,3′,4′,6′-hexa-O-acetylsucrose (*II*), syrup, $[\alpha]_D$ +49° (chloroform), lit.[18,31] gives a syrup with $[\alpha]_D$ +28·4° (chloroform); 2,3,3′,4′,6-penta-O-acetylsucrose (*III*), m.p. 154–155°C, $[\alpha]_D$ +27° (chloroform), lit.[17] gives m.p. 154–156°C, lit.[32] gives $[\alpha]_D$ +22° (chloroform); 3,3′,4′,6′-tetra-O-acetylsucrose (*IV*), m.p. 137–138°C, $[\alpha]_D$ +30·1°, lit.[19] gives m.p. 121–123°C, $[\alpha]_D$ +58·6 (chloroform), lit.[33] gives m.p. 128–130°C; 3,3′,4′,6′-tetra-O-acetyl-1′,2:4,6-di-O-isopropylidenesucrose (*V*), m.p. 135–137°C, $[\alpha]_D$ +13·1 (chloroform), lit.[19] gives m.p. 85–87°C, $[\alpha]_D$ +12·8° (chloroform), lit.[23] gives m.p. 135–137°C. ^{13}C NMR (deuteriochloroform): 18·8 q, 20·8 q (3 C), 21·0 q, 23·8 q, 25·4 q, 29·7 q, 62·1 t, 64·3 d, 65·2 t, 65·9 t, 70·5 d, 71·4 d, 71·8 d, 76·9 d, 77·1 d, 79·7 d, 91·4 d, 99·7 s, 101·5 s, 104·5 s, 170·0 s (2 C), 170·6 s (2 C). The ^1H NMR spectra of compounds *I* to *V* were identical with those published.

3,6-Di-O-Acetyl-1′,2:4,6-di-O-isopropylidenesucrose (*VI*)
and 3-O-Acetyl-1′,2:4,6-di-O-isopropylidenesucrose (*VII*)

Aluminum oxide impregnated with potassium carbonate (11 g; procedure: 5 g of potassium carbonate in 50 ml of water was added to 1 000 g of alumina, activity II according to Brockmann, under occasional shaking, and the mixture was allowed to stand at room temperature at least for 5 days) was added to a solution of 4·61 g (7·81 mmol) of tetraacetyl derivative *V* in 35 ml of methanol and the reaction mixture was shaken on a laboratory shaker. The reaction was checked by TLC in benzene–ethanol 5 : 1 After 1 h 2 compounds could be detected in the mixture, having very close R_F values (0·75), after 5 h di-O-acetyl derivative *VI* was present in the mixture (R_F 0·7), after 20 h derivative *VI* predominated, but mono-O-acetyl derivative *VII* (R_F 0·6) also appeared. After 48 h all starting material has vanished, as well as the minor components with R_F 0·75. After 80 h only derivatives *VI* and *VII* were present in the mixture. It was filtered and the

material on the filter washed with methanol (50 ml), and the combined filtrates were evaporated. Chromatography of the residue on a column of 120 g of silica gel gave 1·86 g (47%) of di-O-acetyl derivative *VI* and 1·56 g (43%) of mono-O-acetyl derivative *VII*, both in the form of syrups. Derivative *VI* had $[\alpha]_D$ +46·5° (chloroform), lit.[23] gives $[\alpha]_D$ +49·5° (chloroform), the ^{1}H NMR data were in agreement with the published data[23]. ^{13}C NMR (deuteriochloroform): 19·0 q 20·9 q (2 C), 24·0 q, 25·2 q, 29·0 q, 62·1 t, 63·8 t, 65·8 d, 65·9 t, 71·0 d, 71·5 d, 71·7 d, 77·8 d, 79·5 d, 79·8 d, 91·1 d, 99·8 s, 101·4 s, 104·0 s, 170·6 s, 171·1 s. Derivative *VII* had $[\alpha]_D$ +30·1 (chloroform), lit.[23] gives $[\alpha]_D$ +28° (chloroform), ^{1}H NMR data were identical with the literature data[23], ^{13}C NMR (deuteriochloroform): 18·8 q, 20·9 q, 24·0 q, 25·1 q, 28·9 q, 61·2 t, 61·9 t, 63·9 d, 66·1 t, 70·7 d, 71·3 d (2 C), 73·3 d, 79·7 d, 82·9 d, 91·1 d, 99·9 s, 101·6 s, 103·2 s, 170·1 s.

3,6′-Di-O-acetylsucrose (*IX*)

A solution of 780 mg of compound *VI* in 15 ml of 60% acetic acid was heated at 60°C for 40 min. According to TLC (chloroform–ethanol 5 : 1) the starting material had completely reacted. The mixture was evaporated, finally with toluene, and the syrupy residue chromatographed on a silica gel column with chloroform ethanol 10 : 1. In addition to a small amount of ballasts 583 mg (89%) of a syrupy compound *IX* were obtained, which was first dried in a vacuum (10 Pa, 20°C) for 8 h and then over phosphorus oxide for 3 days; $[\alpha]_D$ +72° (water), on a chromatogram from TLC-FID analysis the R_F value was 0·21, without admixtures. For $C_{16}H_{26}O_{13}$ (426·3) calculated: 45·07% C, 6·15% H; found: 45·14% C, 6·65% H. ^{1}H NMR (deuterium oxide): 1·98 s (3 H), 2·02 s (3 H), 2·98-4·33 mt (12 H), 5·02 dd ($J_{2,3}$ = 9·8 Hz, $J_{3,4}$ 8·6 Hz, H-3), 5·26 dd ($J_{1,2}$ = 3·7 Hz, H-1). ^{13}C NMR (deuterium oxide): 21·2 q (2 C), 60·7 t ($C_{(6)}$), 61·9 ($C_{(1')}$), 66·4 t ($C_{(6')}$), 68·1 d ($C_{(4)}$), 70·0 d ($C_{(2)}$), 73·0 d ($C_{(5)}$), 75·1 d ($C_{(4')}$), 75·9 d ($C_{(3)}$), 76·9 d ($C_{(3')}$), 79·1 d ($C_{(5')}$), 92·9 d ($C_{(1)}$), 104·8 s ($C_{(2')}$), 174·8 s (2 C).

3-O-Acetylsucrose (*X*)

A solution of 710 mg of compound *VII* in 15 ml 60% acetic acid was heated at 50°C for 30 min. According to TLC (in chloroform–ethanol 5 : 1) the starting material was no longer present. The mixture was evaporated, finally with toluene. After chromatographic purification of the residue (on 25 g of silica gel, with chloroform–ethanol 5 : 1) 528 mg (90%) of chromatographically pure compound *X* were obtained, with R_F 0·07 on chromatogram from TLC-FID, which was dried for analysis in the same manner as compound *IX* (see above); $[\alpha]_D$ +70·5° (water). For $C_{14}H_{24}O_{12}$ (384·3) calculated: 43·75% C, 6·29% H; found: 43·58% C, 6·83% H. ^{1}H NMR (deuterium oxide): 2·00 s (6 H), 3·14–4·22 mt (12 H), 5·00 dd ($J_{2,3}$ = 9·8 Hz, $J_{3,4}$ = 8·5 Hz, H-3), 5·29 d ($J_{1,2}$ = 3·7 Hz, H-1). ^{13}C NMR (deuterium oxide): 21·2 q, 60·6 t ($C_{(6)}$), 62·0 t ($C_{(1')}$), 63·0 t ($C_{(6')}$), 68·1 d ($C_{(4)}$), 70·0 d ($C_{(2)}$), 72·9 d ($C_{(5)}$), 74·7 d ($C_{(4')}$), 75·9 d ($C_{(3)}$), 77·1 d ($C_{(3')}$), 82·1 d ($C_{(5')}$), 92·8 d ($C_{(1)}$), 104·6 s ($C_{(2')}$), 174·8 s.

3,6′-Di-O-acetyl-1′,2,3′,4,4′,6-hexa-O-deuterioacetylsucrose (*XI*)

Deuterioacetic anhydride (0·4 ml) was added to a solution of 108 mg of compound *IX* in 2 ml of pyridine and the mixture was allowed to stand overnight at room temperature. After decomposition with water the mixture was evaporated, finally with toluene. After double crystallization of the residue from ethanol 103 mg of compound *XI* were obtained, m.p. 83–84°C, $[\alpha]_D$ +60·4° (chloroform). For $C_{28}H_{20}{}^2H_{18}O_{19}$ (696·7) calculated: 48·27% C, 8·10% H + ^{2}H; found: 48·00% C, 7·92% H + ^{2}H. Mass spectrum: *m/z* 341 (11%), 340 (65%), 280 (7%), 218 (8%), 217 (71%), 216 (6%), 214 (20%), 173 (43%), 172 (92%), 171 (7%), 170 (18%), 129 (6%), 128 (9%), 127 (6%), 118 (5%), 110 (8%), 109 (87%), 104 (8%), 98 (8%), 46 (100%), 43 (26·5%).

3-O-Acetyl-1′,2,3′,4,4′,6,6′-hepta-O-deutarioacetylsucrose (*XII*)

Deuterioacetic anhydride (0·3 ml) was added to a solution of 57 mg of compound *X* in 1·5 ml of pyridine and the mixture was allowed to stand at room temperature overnight. After working up in the same manner as described for compound *XI*, 70 mg of compound *XII* were obtained, m.p. 83–84°C, $[\alpha]_D$ +61° (chloroform). For $C_{28}H_{17}{}^2H_{21}O_{19}$ (699·7) calculated: 48·06% C, 8·50% H + ^{2}H; found: 48·27% C, 8·64% H + ^{2}H. Mass spectrum: *m/z* 344 (5%), 343 (31%), 340 (25%), 280 (<5%), 218 (8%), 217 (68%), 173 (44%), 172 (70)%, 128 (7%), 118 (5%), 110 (6%), 109 (70%), 104 (6%), 98 (7%), 46 (100%), 43 (13·5%).

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REFERENCES

1. Khan R.: Advan. Carbohyd. Chem. Biochem. *33*, 235 (1976).
2. Mufti K. S., Khan R.: Eur. Pat. Appl. EP 43, 649; Chem. Abstr. *96*, 163 112 (1982).
3. Mieth G., Weiss A., Behrens H., Pohl J., Brueckner J.: Ger. DD. 156, 263; Chem. Abstr. *98*, 161 106 (1983).
4. Musso S., Pages-Xatart-Pares W., Bouvron C.: Eur. Pat. Appl. EP 62, 565; Chem. Abstr. *98*, 161 105 (1983).
5. Kononenko O. K., Kestenbaum I. L.: J. Appl. Chem. *11*, 7 (1961).
6. Hass H. B., Snell F. D., York W. C., Osipow L. I.: U.S. 2, 893, 990; Chem. Abstr. *53*, 19 422 (1959).
7. Čapek K., Šteffková J., Jarý J.: This Journal *31*, 1854 (1966).
8. Čapek K., Šteffková J., Jarý J.: This Journal *32*, 2491 (1967).
9. Čapek K., Šteffková J., Jarý J.: This Journal *33*, 781 (1968).
10. Čapek K., Šteffková J., Jarý J.: This Journal *33*, 1750 (1968).
11. Čapek K., Šteffková J., Jarý J.: This Journal *35*, 107 (1970).
12. Čapek K., Jarý J.: This Journal *38*, 2518 (1973).
13. Čapek K., Čapková-Šteffková J., Jarý J.: This Journal *35*, 321 (1970).
14. Ballard J. M., Hough L., Richardson A. C.: Carbohyd. Res. *24*, 152 (1972).
15. Ballard J. M., Hough L., Richardson A. C.: Carbohyd. Res. *34*, 184 (1974).
16. Čapek K., Čapková J., Kvapilová E., Vydra T., Bláhová M., Ranný M.: Czech 223 440.
17. Buchanan J. G., Cummerson D. A., Turner D. M.: Carbohyd. Res. *21*, 283 (1972).
18. Khan R., Mufti K. S., Jenner M. R.: Carbohyd. Res. *65*, 109 (1978).
19. Khan R., Mufti K. S.: Carbohyd. Res. *43*, 247 (1975).
20. Frohwein Y. Z., Leibowitz J.: Bull. Res. Council Israel. Sci. A *11*, 330 (1963); Chem. Abstr. *59*, 15 363 (1963).
21. Frohwein Y. Z., Leibowitz J.: Enzymologia *26*, 193 (1963).
22. Avela E., Aspelund S., Holmbom B., Melander B., Jalonen H., Peltonen C.: ACS Symp. 1977, 41, Sucrochem. Symp. 1976, 62; Chem. Abstr. *87*, 136 200 (1977).
23. Khan R., Jenner M. R., Lindseth H.: Carbohyd. Res. *65*, 99 (1978).
24. Jones A. J., Hanisch P., Mc Phail A. K.: Aust. J. Chem. *32*, 2763 (1979).
25. Pfeffer P. E., Valentine K. M., Parrish F. W.: J. Amer. Chem. Soc. *101*, 1265 (1979).
26. Bax A., Freeman R., Frenkiel T. A., Lewitt M. H.: J. Magn. Resonance *43*, 478 (1981).
27. Hirano S.: Org. Magn. Resonance *3*, 353 (1971).

28. Casu B., Reggiani M., Gallo G. G., Vigevani A.: Carbohyd. Res. *12*, 157 (1970).
29. Binkley W. W., Horton D., Bhacca N. S.: Carbohyd. Res. *10*, 245 (1969).
30. Čapek K., Vydra T., Vodrážková M.: Unpublished results.
31. Khan R.: Carbohyd. Res. *32*, 375 (1974).
32. Mc Keown G. G., Serenius R. S. E., Hayward L. D.: Can. J. Chem. *35*, 28 (1957).
33. Khan R., Lindseth H.: Carbohyd. Res. *71*, 327 (1979),

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