

Studies of Tritylated Sucrose. I. Mono-*O*-tritylsucroses

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Two isomeric mono-*O*-tritylsucroses were isolated from a mixture of tritylated sucrose which had been obtained by the reaction of sucrose and trityl chloride in the ratio of 1 : 1.2 by mole. The structures of these two isomers were established by the application of gas chromatography and NMR spectroscopy to appropriate derivatives. One of the two substances is 6'-mono-*O*-tritylsucrose, and the other is 6-mono-*O*-tritylsucrose, which is crystallized as white needles. The detritylation of mono-*O*-trityl-*O*-acetylsucroses yielded hepta-*O*-acetylsucroses, which were confirmed by a study of their NMR spectra to be 2,3,4,6,1',3',4'- and 2,3,4,1',3',4',6'-hepta-*O*-acetylsucrose. No migration of the acetyl group on the sucrose molecule was observed during the detritylation procedure.

Several works on tritylated sucrose have been reported during the past forty years. Josephson<sup>1)</sup> in 1929 reported the synthesis of "tri-*O*-tritylsucrose" with 3 mol of trityl chloride. Later, McKeown and his co-workers<sup>2)</sup> described that the product obtained by the Josephson's route was a mixture of tri-*O*-tritylsucrose, products with a lower trityl content, reducing sugar, and tritanol. McKeown reported also that tri-*O*-trityl-penta-*O*-acetylsucrose was conveniently prepared in a crystalline form, after the tritylation of sucrose in pyridine, by acetylation in the same solution. The detritylation of this crystalline substance by graded hydrolysis with acetic acid, followed by methylation and deacetylation, yielded 1',6',4-tri-*O*-methylsucrose. The structure of this tri-*O*-methylsucrose was established by the production of the corresponding *O*-methyl ethers of glucose and fructose.

However, according to McKeown,<sup>3)</sup> his deacetylation of the same crystalline substance, followed by methylation and detritylation, gave a syrupy penta-*O*-methylsucrose, which was concluded to consist of 2,3,4,3',4'-penta-*O*-methyl derivatives of sucrose by the specific rotation measurement and by the paper chromatography of the corresponding *O*-methyl ethers of glucose and fructose. Accordingly, McKeown and his co-workers concluded that the original positions of trityl groups were at the three primary carbons in the sucrose molecule and that the acetyl migration from C<sub>4</sub> to C<sub>6</sub> occurred during the detritylation or methylation reaction.

Subsequently, Bredreck and his co-workers<sup>4)</sup> reported a crystalline tri-*O*-trityl-penta-*O*-acetylsucrose with a melting point equal with that of the crystalline substance prepared by McKeown. The mild detritylation of the tri-*O*-trityl-penta-*O*-acetylsucrose with hydrobromic acid in a cold acetic acid solution yielded 2,3,4,3',4'-penta-*O*-acetylsucrose, which turned into 2,3,6,3',4'-penta-*O*-acetyl derivative when treated with sodium bicarbonate. The structure of the penta-*O*-acetylsucrose was established by periodate oxidation.

Scanning through these reports, one cannot help noticing how often treacherous conclusions were obtained from chemical reactions alone; thus, McKeown and his co-workers were first beguiled with the position of trityl groups and speculated on migration during deacetylation or methylation, and later confirmed the structure through a complex reaction route and a purely chemical determination, leaving ambiguities inherently connected with the chemical analyses.

Our present objective is the synthesis and structural determination of mono- and di-*O*-tritylsucroses obtained through various separation techniques. Studies of these products with a lower trityl content by a direct physical method such as NMR spectroscopy will give a further confirmation of the structure of the tri-*O*-trityl derivative of sucrose by eliminating the ambiguity which would otherwise arise from the analysis of the chemical procedures. The hepta-*O*-acetylsucroses prepared from the mono-*O*-tritylsucroses will be compounds for the synthesis of oligosaccharides, such as raffinose and planteose. This paper will deal with two isomeric mono-*O*-tritylsucroses and hepta-*O*-acetylsucroses derived from these isomers.

1) K. Josephson, *Ann. Chem.*, **472**, 230 (1929).

2) G. McKeown, R. Serenius and L. Hayward, *Can. J. Chem.*, **35**, 28 (1957).

3) G. McKeown and L. D. Hayward, *ibid.*, **35**, 992 (1957).

4) H. Bredreck, H. Zimmer, A. Wagner, G. Faber, W. Greiner and W. Huber, *Chem. Ber.*, **91**, 2824 (1958).

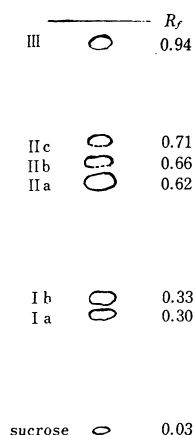


Fig. 1. The thin layer chromatogram of a reaction mixture of tritylation, effected on silica gel G with 20 : 20 : 3 : 57 (V/V/V/V) methanol-acetone-water-chloroform. Zones were located with 50% sulfuric acid.

## Results and Discussion

The thin-layer chromatogram of a reaction mixture obtained from the treatment of sucrose with slightly overdosed trityl chloride in a pyridine solution is shown in Fig. 1. The chromatogram, which was detected by spraying with 50% sulfuric acid and by subsequent heating at 120°C, shows at least six kinds of tritylated sucroses, observable in the form of dark green spots. The tritylated sucroses, Ia and Ib, corresponding to the  $R_f$  values of 0.30 and 0.33 respectively, have been identified as mono-*O*-tritylated sucroses by UV spectroscopy, as will be described later. The tritylated sucroses, IIa, IIb and IIc, corresponding to the  $R_f$  values of 0.62, 0.66, and 0.71, are confirmed to be di-*O*-tritylated sucroses by UV spectroscopy.

Of the total tritylated sucroses obtained, 47% by weight consisted of the combined yields of the di- and tri-*O*-tritylated sucroses, this was quite a large figure in comparison with the overdosage of trityl chloride, in the molar ratio of 1.2 : 1, used for the treatment of sucrose. It is also noteworthy that the reaction mixture was about 10% free sucrose.

The reaction mixture was resolved in 1-butanol, and the butanol solution was washed with water to remove the free sucrose; the subsequent evaporation of the organic layer produced a mixture of tritylated sucroses as colorless glass. It was found that this mixture could conveniently be separated into mono-*O*-tritylsucrose and a mixture of substances with higher trityl contents by a counter-current distribution using a solvent system such as trichloroethylene - methanol - water; thus, the evaporation of the polar layer, consisting of methanol and water, yielded the mono-*O*-tritylsucrose 53% of the total tritylated sucroses, while the non-polar layer contained the

remaining 47% the di- and tri-*O*-tritylsucroses.

Mono-*O*-tritylsucrose, Ib, was separated as white needles from a solution of 80% ethanol (mp 99—101°C;  $[\alpha]_D^{25} + 51.7^\circ$  ( $c$  4, *N,N*-dimethylformamide). The other isomeric mono-ether, Ia, was obtained as an amorphous powder from the concentrate of the mother liquid after Ib had been removed by means of recycling column chromatography.<sup>5)</sup> The amorphous powder Ia softens at 149°C and has  $[\alpha]_D^{25} + 31.9^\circ$  ( $c$  4, *N,N*-dimethylformamide). A small amount of Ib was further recovered in a crystalline form from a fraction with a higher Ib content by recycling column chromatography; the total yield for the crystalline Ib was 35% as against 36% for Ia, relative to a mixture of mono-*O*-tritylsucroses.

The IR spectra of Ia and Ib, while each shows essentially the same pattern as that of free sucrose between 1400 and 800  $\text{cm}^{-1}$ , both exhibited characteristic phenyl absorptions at 1600, 1495, and 1450  $\text{cm}^{-1}$ . On the UV spectra of trityl chloride, Ia and Ib have also identical absorption patterns ( $\lambda_{\text{max}} = 260 \text{ m}\mu$ ) and assume almost the same values in the molar extinction coefficients ( $\epsilon_{\text{max}}$ : Ia, 725; Ib 715; trityl chloride, 720). These spectroscopic observations confirm that Ia and Ib are mono-*O*-tritylsucroses.

The tritylated sucroses with higher  $R_f$  values, IIa, IIb, and IIc, take molar extinction coefficients of 1415—1460, which are twice as much as those of mono-*O*-tritylsucroses; this proves that IIa, IIb, and IIc, are di-*O*-trityl derivatives.

The methylation of both the mono-*O*-tritylsucroses according to the Kuhn procedure,<sup>6)</sup> followed by column-chromatographic purification, produced mono-*O*-trityl-hepta-*O*-methylsucroses, IVa and IVb, in 77% and 83% yields respectively. Both the products were colorless glass, and IVb was crystallized from 80% ethanol as white plates, melting at 84°C. They showed a single spot of a dark green color in a thin-layer chromatogram and no hydroxy absorption in IR spectra, revealing that the methylation was completed in both IVa and IVb.

The NMR spectrum of IVa shows all seven methoxyl-group signals separately defined ( $\delta$  3.33 (3H), 3.36(3H), 3.41(3H), 3.43(3H), 3.47(3H), 3.54(3H), and 3.56(3H)). In IVb, two of the methoxyl-group signals overlap to give five 3-proton singlets and a coincident resonance of six protons ( $\delta$  3.30(3H), 3.32(6H), 3.39(3H), 3.42(3H), 3.50 (3H) and 3.62(3H)). These spectra further confirm that both products are hepta-*O*-methyl derivatives. The IVa and IVb products were then detritylated by Brederick's procedure.<sup>4)</sup> After column-chromatographic purification, hepta-*O*-methylsucroses, Va and Vb, were obtained as a colorless oil in yields

5) T. Otake and E. Tamate, *Nippon Kagaku Zasshi*, **90**, 388 (1969).

6) R. Kuhn, H. Trischmann and I. Low, *Angew. Chem.*, **67**, 32 (1955).

of 74% and 78% respectively. The phenyl absorptions were not observed, but the absorptions due to the hydroxy group were noticed in the IR spectra and the thin-layer chromatograms showed a single black spot each.

The detritylated products, Va and Vb, were subjected to methanolysis with 5% methanolic hydrochloric acid to yield a mixture of the fully and the partially-methylated methyl fructoside and methyl glucoside. These methanolysis products did not reduced Fehling's solution, and unreacted hepta-*O*-methylsucrose was not observed by thin-layer chromatography. The products of methanolysis were subsequently analyzed by gas chromatography, using the diethyleneglycol succinate polyester as the liquid phase. The gas chromatogram of the methanolysate of Va (Fig. 2) showed six peaks. Among

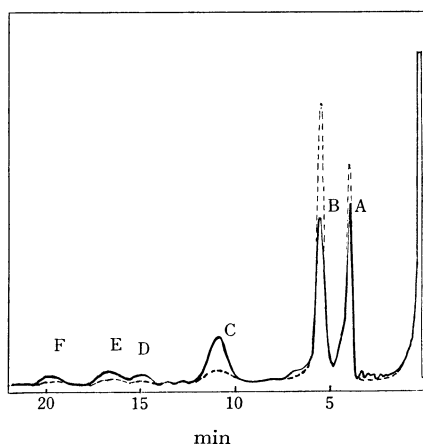


Fig. 2. The gas chromatogram of the methanolysis products of the hepta-*O*-methylsucrose derived from Ia. Conditions: 5' × 1/8", 20% diethyleneglycol succinate polyester on Chromosorb W 100/120 mesh at 170°, N<sub>2</sub> at 20 ml/min. Detector: FID. —, methanolysis products; ----, methanolysis products + permethylglucose.

these peaks, A and B were assigned to methyl 2,3,4,6 tetra-*O*-methyl β- and α-*D*-glucopyranoside respectively, for they had the same retention volumes as authentic samples. The peaks with higher retention volumes, C, D, E, and F, may be assumed to be partially-methylated fructosides, but the assignment of each peak still remains to be done. The gas-chromatographic analysis reveals, however, that the trityl group of the original compound, Ia, is at the fructose moiety of the sucrose molecule.

All five peaks were observed in a gas chromatogram of the methanolysis product of Vb (Fig. 3). The peaks A' and B' which did not correspond to the permethyl glucose, were identified as methyl 1,3,4,6-tetra-*O*-methyl α- and β-*D*-fructofuranoside respectively by referring to Gee's data.<sup>7)</sup> The D'

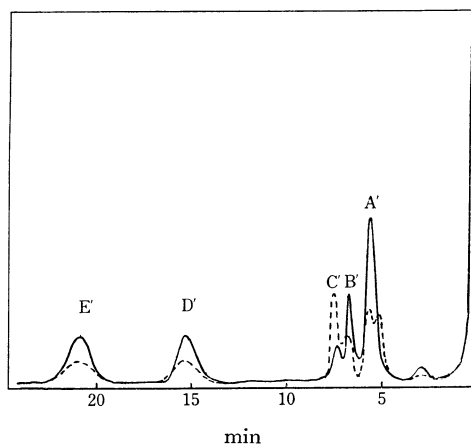


Fig. 3. The gas chromatogram of the methanolysis products of the hepta-*O*-methylsucrose derived from Ib. Conditions are same as for Fig. 2, except the column temperature, which is 108°C. —, methanolysis product; ----, methanolysis product + permethylglucose.

and E' peaks were assigned to methyl 2,3,4-tri-*O*-methyl β- and α-*D*-glucopyranoside respectively by comparing them with authentic samples.

The relatively low peak, C', was assigned to methyl 1,3,4,5-tetra-*O*-methyl-α-*D*-fructopyranoside, again by referring to Gee's results, in which both the anomeric isomers were assumed to be contained in the peak E'.

The two methyl glucosides of the peak E' were actually separated into compounds by gas chromatography using a Chromosorb W-neopentyl-glycol-succinate-polyester (10% W/W) glass column. Though the route of the formation of the minor fructopyranosides is not clear, it may be concluded that the original compound, Ib, has a trityl group combined at the glucose moiety of the sucrose molecule. Mono-*O*-tritylsucroses (Ia and Ib) were acetylated with acetic anhydride in pyridine at room temperature; these products were then purified by chromatography on silica gel to obtain mono-*O*-trityl-hepta-acetylsucroses (VIa and VIb). The product VIb was crystallized from 80% ethanol as white prisms (mp 103–104°C). The thin-layer chromatograms of the products (VIa and VIb) showed a single spot of a dark green color on each, and no hydroxy absorption was observed in the IR spectra.

The mass spectra of the two products were identical on all the fragments with respect to the mass numbers. Both parent peaks were of a very low intensity, and the only prominent peaks appearing close to the parent peaks were at *m/e* 801 (M–77). There were, however, some differences in the mass spectra as regards the pattern coefficients of the two products; for example, the intensities of the M–77 ions of VIa and VIb relative to the peak

7) M. Gee and H. G. Wilker, Jr., *Anal. Chem.*, **34**, 650 (1962).

at  $m/e$  243 were 2.4% and 0.8% respectively. It should be remembered that  $m/e$  243 and  $M-77$  are considered as coming mainly from the trityl cation and from the phenyl radical dissociation of the products respectively.

Turning to NMR spectroscopy, the integrated intensities of the acetyl, trityl, and other protons of VIa and VIb agreed with the theoretical values of the assumed mono-*O*-trityl-hepta-*O*-acetyl-derivatives.

The observed chemical shifts of the acetyl-group protons of VIa and VIb have low  $\delta$  values, with certain differences between them (VIa:  $\delta$  1.93(3H), 1.99(3H), 2.00(3H), 2.07(9H) and 2.10(3H); VIb:  $\delta$  1.75(3H), 2.01(6H), 2.09(3H), and 2.12(9H), while the signals arising from the methine and the methylene protons fall in the region between  $\delta$  2.8–5.9; each spectrum can be subdivided into three non-overlapping regions, the region A ( $\delta$  2.7–3.5, 2H), the region B ( $\delta$  3.6–4.5, 6H), and the region C ( $\delta$  4.5–5.8, 6H).

The NMR spectrum of octa-*O*-acetylsucrose<sup>8)</sup> shows no signal in the region A, but it does show signals in the region B which arise from eight protons assigned to the overlapped signal of H-5, of H-5', and of the protons of the methylene groups to which *O*-acetyl groups are attached. The signals in the region C correspond to six protons, the number of protons in the region C of VIa and VIb, all of which can be assigned to the ring protons of sucrose other than H-5 and H-5'.

When we compare the NMR spectra of mono-*O*-trityl-hepta-*O*-acetylsucroses and octa-*O*-acetylsucrose, the signals of the region A in the spectra of VIa and VIb may be assigned to the protons of the methylene group to which an *O*-trityl group is directly attached. The acetyl derivatives, VIa and VIb, show apparent seven-line and eight-line signals respectively in the region A. Each of these

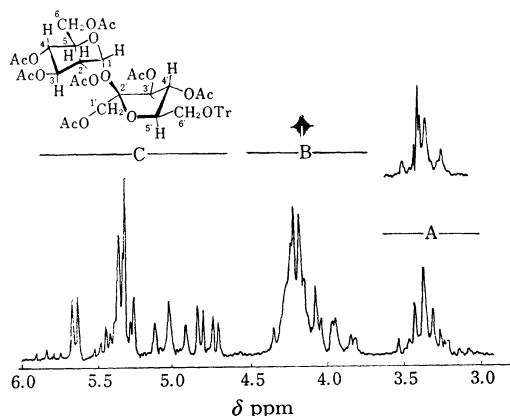


Fig. 4. Partial NMR spectra at 100 MHz of VIa in  $\text{CDCl}_3$ .

8) W. W. Binkly, D. Horton and N. S. Bhacca, *Carbohydr. Res.*, **10**, 245 (1969).

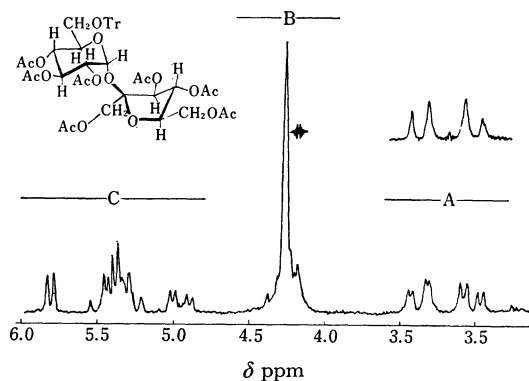


Fig. 5. Partial NMR spectra of 100 MHz of VIb in  $\text{CDCl}_3$ .

signals is considered to consist of the AB part in an ABX system. This assumption has been confirmed for both the products by irradiating them near  $\delta$  4.0 and by then observing the perturbation of the signals in the region A as it gives rise to the signals with four transitions, as is shown in Figs. 4 and 5. The following simulation spectra were obtained by a computer, thus confirming the proposed spin systems defined thus: for VIa  $\delta$  (1) 3.30, (2) 3.43, (3) 4.16 and (4) 5.36 with  $J(1,2) -10.2$ ,  $J(1,3) 5.4$ ,  $J(2,3) 6.0$  and  $J(3,4) 5.5\text{Hz}$ ; for VIb  $\delta$  (1) 3.01, (2) 3.36, (3) 4.16 and (4) 5.28 with  $J(3,4) -10.6$ ,  $J(1,4) 3.6$ ,  $J(2,3) 2.0$  and  $J(3,4) 10.0\text{Hz}$ .

	1	2	3	4	5	6	7	8
VIa								
Observed	3.21	3.27	3.31	3.37	3.43	3.47	3.53	
Generated	3.20	3.26	3.30	3.36	3.42	3.47	3.53	
VIb								
Observed	2.93	2.97	3.04	3.07	3.31	3.33	3.41	3.43
Generated	2.94	2.98	3.05	3.08	3.31	3.33	3.42	3.43

On the basis of these observations, the signals in the region A can be assigned to the methylene protons of H-6 and H-6'. Combined with the data of gas chromatography, it can be concluded that the original compounds, Ia and Ib, are 6'-mono-*O*-trityl-sucrose and 6-mono-*O*-tritylsucrose respectively.

The products VIa and VIb were detritylated by Brederick's method, using hydrobromic acid in an acetic acid solution. The oily chloroform extracts then separated from the trityl bromide and the unreacted mono-*O*-trityl-hepta-*O*-acetyl derivatives by column chromatography on silica gel, thus producing hepta-*O*-acetylsucroses, VIIa and VIIb, as colorless glass in 69% and 63% yields respectively. The product VIIa was crystallized from 80% ethanol as white prisms which melted at 93–94°C.

The thin-layer chromatogram confirmed that both products were homogeneous and untritylated com-

pounds generating a single black spot. Their IR spectra noted to have absorptions in the O-H stretching region, and no phenyl absorption was observed. The NMR spectra of each of the products showed acetyl-group signals of the anticipated 21 protons (VIIa:  $\delta$  2.01(3H), 2.04(3H), 2.11(9H), 2.13(3H) and 2.21(3H); VIIb:  $\delta$  2.02(3H), 2.06(3H), 2.09(3H), 2.10(3H), 2.21(6H) and 2.20(3H)). The NMR spectrum of VIIa shows an apparent 2-proton octet between  $\delta$  3.5–4.0. The chemical shift of the octet consists of directly connecting the methylene group to the hydroxy group. The irradiation at  $\delta$  4.1 brings about the collapse of the octet to a four-line pattern (one line showing beat perturbation), as Fig. 6 shows. This 8-line pattern may be recognized as the AB part of an ABX system. The spectrum of VIIb appeared as a wide doublet of 2-protons, between  $\delta$  3.55–3.75, which reduces to a wide singlet with a half-width of 7Hz upon irradiation at  $\delta$  4.0 (Fig. 7).

Inasmuch as the chemical shift is almost iden-

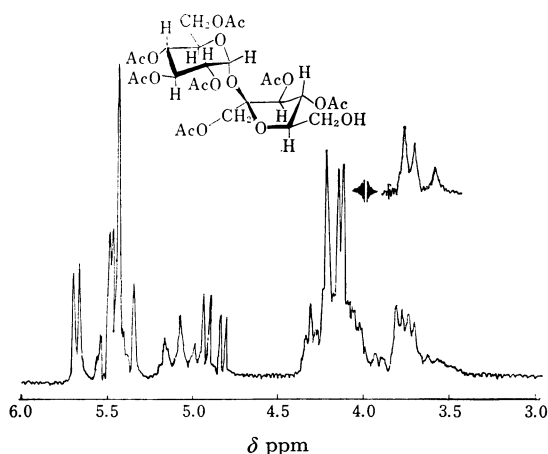


Fig. 6. Partial NMR spectra at 100 MHz of VIIa in  $\text{CDCl}_3$ .

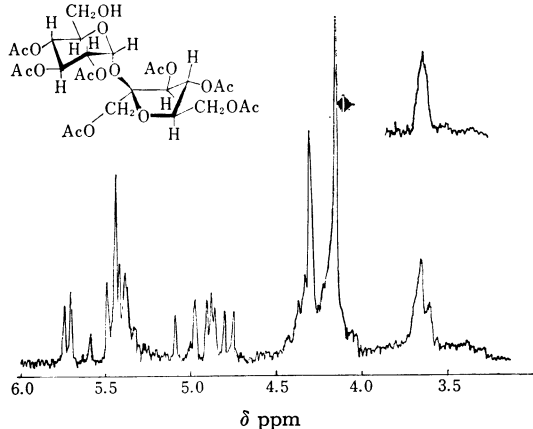


Fig. 7. Partial NMR spectra at 100 MHz of VIIb in  $\text{CDCl}_3$ .

tical to that of the above-mentioned octet, the observed wide doublet can also be assigned to the methylene protons of the hydroxymethyl group. Because the protons of the methylene group are practically equivalent, there are no other signals which appear on both sides of the wide doublet.

On the basis of the NMR data, the hydroxymethyl groups of VIIa and VIIb may be said to be those of the 6'- and 6-positions respectively. Thus, the detritylated products, VIIa and VIIb, must be 2,3,4,6,1',3',4'- and 2,3,4,1',3',4',6'-hepta-*O*-acetylsucrose respectively.

## Experimental

**General Methods.** Thin-layer chromatography was effected using Merck silica gel G as the adsorbent in a thickness of 0.25 mm and with these solvent systems: (A) methanol - water - acetone - chloroform (20 : 4 : 20 : 56) for tritylated sucrose and (B) methyl ethyl ketone (MEK)-toluene for the *O*-methyl and *O*-acetyl derivatives of sucrose. The developed plates were sprayed with 50% sulfuric acid and heated at 120°C. The column chromatography was performed using silica gel, 60–80 mesh, prepared by the Kanto Chemical Co., Japan.

The IR and the UV spectra were measured with a Hitachi EPI-II IR spectrometer and a Cary Model 14R recording spectrophotometer respectively. The mass spectra were recorded with a Varian M-66 mass spectrometer. The gas-liquid chromatography were performed with a Varian-Aerograph Model 1200 instrument with a hydrogen-flame ionization detector. The NMR spectra were recorded with a Varian HA-100D (100 MHz) spectrometer using chloroform- $d$ , with tetramethylsilane as an internal lock; the signal positions were expressed in  $\delta$  values. The NMR simulations were accomplished by a Varian Spectro System SS-100 equipped with a Varian 620/i computer.

**Tritylation of Sucrose.** Commercial granulated sucrose (34.2 g) was reacted with recrystallized trityl chloride (33.4 g) in dry pyridine (1 l) at room temperature. The reaction was assisted by the agitation of the reaction solution on a magnetic stirrer for 96 hours. At the end of the reaction period, the solution was dried *in vacuo* on a rotary evaporator. The residue was dissolved in 1-butanol (200 ml) and then washed with a McKirvin buffer (pH 7.0) and water in order to remove the free sucrose. The evaporation of the butanol solution under reduced pressure left 59.5 g of tritylated sucrose as colorless glass.

**6-Mono-*O*-tritylsucrose (Ib).** A mixture of tritylated sucrose (55.1 g) was subjected to a counter-current distribution of six steps using an equilibrated system with methanol (1.75 l), a McKirvin buffer (pH 7.0) (0.75 l), and trichloroethylene (2.5 l).

The polar layer, consisting of methanol and water, was dried *in vacuo* to yield 28.54 g of a mixture of mono-*O*-tritylsucroses. The evaporation of the combined polar layer under reduced pressure yielded 24.98 g of a glassy product which contained di- and tri-*O*-tritylsucrose.

A mixture of mono-*O*-tritylsucroses (25.92 g) was dissolved in 50% ethanol (200 ml); 7.5 g of 6-mono-*O*-tritylsucrose (Ib) were crystallized from this solution as white needles. Further, 2.8 g of Ib were separated

from the evaporated residue of the mother liquid by recycling column chromatography. After repeated recrystallizations from 70% ethanol, Ib had a mp of 99–101°C,  $[\alpha]_D^{20} +51.7^\circ$  (*c* 4, dimethylformamide (DMF)). The thin-layer chromatogram developed by the A solvent showed the crystalline product to be homogeneous with the  $R_f$  value of 0.33.

Found: C, 63.23; H, 6.62%. Calcd for  $C_{31}H_{36}O_{17}$ : C, 63.78; H, 6.16%.

**6'-Mono-O-tritylsucrose (Ia).** After the crystallization of Ib, the mother liquid was dried *in vacuo* to yield 16.56 g of the residue, which contained Ia as the major component.

The residue was chromatographed on silica gel (160 g) by means of graded elution with 1.6-l portion of 8, 12, and 16% methanol/chloroform solutions. The eluent was divided into twelve 400-ml fractions; after all the solvent had then passed through the column, the fractions were gradually returned to the column. The column was then washed with 800 ml of the 16% methanol/chloroform solution. The recycling procedure was repeated again to give 16 fractions of the eluent.

Each of the fractions was dried *in vacuo*, and each residue was chromatographed on thin-layer plates; this indicated that the residues of the 13th, 14th, 15th, and 16th fractions consisted of almost pure Ia. The admixture of the residues from those four fractions weighed 9.06 g and had a softening point of 149°C and  $[\alpha]_D^{20} +31.9^\circ$  (*c* 4, DMF). The spots on a thin-layer chromatogram (solvent A) of the combined residues were very faint for a  $R_f$  value of 0.33, while they were distinct for a  $R_f$  value of 0.30.

Found: C, 63.00; H, 6.58%. Calcd for  $C_{31}H_{36}O_{17}$ : C, 63.70; H, 6.16%.

**6- and 6'-Mono-O-trityl-hepta-O-methylsucrose (IVa and IVb).** Each of the mono-O-tritylsucroses, Ia and Ib (0.584 g) was methylated in dry *N,N*-dimethylformamide (DMF) (10 ml) with methyl iodide (10 ml) and silver oxide (5 g). Finely-divided anhydrous barium oxide (5 g) was added to each of the reaction solutions to ensure anhydrous conditions, and the reaction was assisted by the vigorous agitation of the reaction solution on a magnetic stirrer for 24 hr. At the end of the reaction period, the solution was filtered to remove any solids, and the residues were washed with an admixture of toluene and DMF (1 : 1 vol/vol) (10 ml). The combined filtrate and washings were then evaporated to yield a syrupy product. The product was resolved in an admixture of methyl ethyl ketone (MEK) and toluene (1 : 1 vol/vol) (20 ml), after which the solution was filtered to remove any insoluble matter. The filtrate was then dried *in vacuo* to yield a colorless glass.

Each of the products was resolved in 5 ml of toluene and chromatographed on a column of silica gel (5 g). The column was eluted with 5% MEK/toluene (100 ml) and 8% MEK/toluene (100 ml). The evaporation of the latter solvent yielded 0.447 g of IVa and 0.480 g of IVb in both cases as colorless glass. The IVb was crystallized from 90% methanol as white plates which melted at 84°C.

A thin-layer chromatogram with MEK/toluene (3 : 7 vol/vol) showed both IVa and IVb to be homogeneous, and both  $R_f$  values were 0.50.

Found, IVa: C, 65.72; H, 7.76%. Found, IVb: C, 66.10; H, 7.28%. Calcd for  $C_{38}H_{50}O_{17}$ : C, 66.90; H, 7.34%.

**2,3,4,6,1',3',4'- and 2,3,4,1',3',4',6'-Hepta-O-methylsucrose (Va and Vb).** Each of the methylation products (IVa and IVb) (200 mg) was detritylated in 0.6 ml of acetic acid with hydrogen bromide, which was added as a saturated acetic acid solution (0.06 ml) under ice cooling. The reaction solution was then allowed to remain for two minutes while being vigorously agitated. At the end of the reaction period, the solution was poured into iced water (10 ml) and the detritylation products were extracted from the suspension with 10 ml of chloroform. The chloroform solution was allowed to stand for three hours after calcium chloride (1 g) had been added, and then it was filtered to remove any solids. The filtrate was evaporated under reduced pressure, and the residue was chromatographed on 5 g of silica gel to free it from trityl bromide and the unreacted IVa or IVb.

The column was washed with 10 ml of 10% MEK/toluene and then with 100 ml of 15% MEK/toluene to elute the hepta-O-methylsucrose. The evaporation of the latter washing *in vacuo* yielded 103 mg of Va and 108 mg of Vb as colorless oil. A thin-layer chromatogram with MEK/toluene (6 : 4) showed both products, Va and Vb, to be homogeneous; they had  $R_f$  values of 0.25 and 0.21 respectively.

**Methanolysis of Hepta-O-methylsucroses.** Approximately 100 mg of each hepta-O-methylsucrose was methanolized at 60°C with 3 ml of 5% methanolic hydrochloric acid in a sealed tube for one hour. At the end of the reaction period, the reaction solution was passed through an anion exchanger column, *e.g.*, IRA 410 (Amberlite Rohm & Haas) (5 ml). Then the column was washed with approx. 50 ml methanol. The combined mixture of the eluent and the washing was dried, and the evaporation residue was submitted to gas chromatography.

**Mono-O-trityl-hepta-O-acetylsucroses (VIa and VIb).** Each of the mono-O-tritylsucrose (Ia and Ib) (1.168 g, each) was dissolved in 10 ml of dry pyridine and then acetylated with acetic anhydride (2.8 ml). The solution was allowed to stand for 24 hr and then evaporated to yield a syrupy product. Each of the products was chromatographed on silica gel (10 g) column; the column was washed with 200 ml of toluene and then with 200 ml of 10% MEK/toluene to elute mono-O-trityl-hepta-O-acetylsucroses. The evaporation of the MEK-toluene fractions yielded 1.39 g of VIa and 1.42 g of VIb respectively, as both a white amorphous powder. Thin-layer chromatography with MEK/toluene (9 : 6) showed both products, VIa and VIb, to be homogeneous and to have  $R_f$  values of 0.55. One of the acetyl derivatives, VIb, was crystallized from 80% ethanol as white prisms with a mp of 103–104°C.

Found, VIa: C, 62.01; H, 6.08%. Found, VIb: C, 59.49; H, 5.86%. Calcd for  $C_{45}H_{50}O_{24}$ : C, 61.49; H, 5.69%.

**Hepta-O-acetylsucroses (VIIa and VIIb).** 0.878 g portions of VIa and VIb were dissolved in 3 ml of glacial acetic acid saturated with hydrogen bromide under ice cooling. The reaction solution was allowed to stand with vigorous agitation for 5 min and then poured into cold water (20 ml). The reaction products were extracted twice with 20 ml of chloroform from the water suspension by washing the chloroform layers with water after which the combined chloroform solution was dried. The

evaporation residue was chromatographed on a silica-gel (10 g) column. The column was then washed with 200 ml of 10% MEK/toluene to elute trityl bromide and unreacted mono-*O*-trityl derivatives, and each hepta-*O*-acetylsucrose sample was eluted with 200 ml of the 20% MEK/toluene from the column. The evaporation of the 20% MEK/toluene fractions yielded 439 mg of VIIa and 401 mg of VIIb respectively, in both cases as colorless glass. Thin-layer chromatography with MEK/toluene (4 : 6) showed the final products to be

homogeneous, with a  $R_f$  value of 0.25. VIIa was crystallized from 80% ethanol as white prisms which melted at 93—94°C.

Found, VIIa: C, 49.19; H, 5.80%. Found, VIIb: C, 49.16; H, 5.66%. Calcd for  $C_{26}H_{36}O_{18}$ : C, 49.06; H, 5.66%.

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