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Note

Synthesis of 6,6′-dideoxysucrose (6-deoxy-α-D-glucopyranosyl 6-deoxy-β-D-fructofuranoside)*

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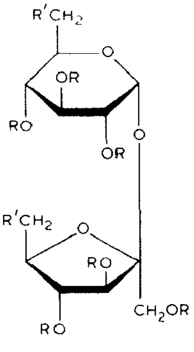
6,6′-Dideoxysucrose (**5**) has been reported by Bragg and Jones[1], who prepared a tri-*O*-tosylsucrose that they thought to be 6,1′,6′-tri-*O*-tosylsucrose. This compound was reduced with lithium aluminum hydride in oxolane to give a solid, characterized as **5**, by enzymic hydrolysis with invertase. The enzymic products co-chromatographed with authentic 6-deoxy-D-fructose and 6-deoxy-D-glucose. The identity of the tri-*O*-tosylsucrose has been questioned[2–4] and Khan[4] showed that the so-called "tri-*O*-tosylsucrose" is a mixture of penta-, tetra-, tri-, and di-*O*-tosylsucrose in the molar ratios of 0.05:0.33:1:1, respectively[4,5].

Lemieux and Barrette[5] reported an improved method for the preparation of 6,1′,6′-trideoxysucrose by way of 6,1′,6′-tri-*O*-mesylsucrose. Treatment of the pentaacetate of the trimesyl derivative with lithium chloride in *N*,*N*-dimethylformamide containing a trace of iodine yielded the trichloride, which was deacetylated and dechlorinated with Raney nickel to give 6,1′,6′-trideoxysucrose.



1 R = H, R′ = OH
2 R = H, R′ = Cl
3 R = OAc, R′ = Cl
4 R = OAc, R′ = H
5 R = H, R′ = H

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We now report a simpler method for the preparation of 6,6′-dideoxysucrose (**5**) from 6,6′-dichloro-6,6′-dideoxysucrose (**2**). Compound **2** was easily prepared by use of carbon tetrachloride, triphenylphosphine, and pyridine solvent[6]. Acetylation of **2** gave **3**, which was readily reduced by tributyltin hydride[7,8] to yield **4** and, apparently, some partially deacetylated products of **4**, as indicated by t.l.c. examination (9:1, v/v, chloroform–acetone). The mixture was deacetylated to give **5** as a single product.

The structure of **5** was confirmed by ^{13}C-n.m.r. spectroscopy. The ^{13}C-n.m.r. spectrum of **5** was recorded with a Varian XL-200 spectrometer, operated at 50.3 MHz, with decoupling of all of the protons and without the proton decoupler. The concentration of the solution was 90 mg/3 mL of deuterium oxide, with 1,4-($^{2}H_4$)dioxane added as internal reference. The chemical shifts relative to the signal for tetramethylsilane were obtained by adding 66.487 p.p.m. (the chemical shift of 1,4-($^{2}H_4$) dioxane relative to that of Me_4Si) to the experimentally obtained values. The ^{13}C-n.m.r. spectrum of sucrose was recorded under the same conditions (see Table I).

Except for the three signals for C-2,-3, and -5, the other signals observed for sucrose have been assigned to specific carbon atoms[9–11]. In the case of 6,6′-dideoxysucrose, except for the signals for C-1,-6,-1′,-2′, and 6′, which are fairly certainly based on comparison with those for sucrose, and the data from one- and two-bond carbon–hydrogen coupling, the assignment of the signals for other carbon atoms are only tentative.

The three primary carbons (C-6, -1′, and -6′) were readily distinguished by the high-field locations of their signals. The replacement of a hydroxyl group by a proton at C-6 and -6′ is evident from the chemical shift of the signals for two *C*H$_2$OH by ~44 p.p.m. to higher field (at δ 18.099 p.p.m. and 16.546)[12]. With the

TABLE I

^{13}C-CHEMICAL SHIFTS OF SUCROSE (**1**) AND 6,6′-DIDEOXYSUCROSE (**5**)[a]

Atom	*Sucrose* (**1**)	*6,6′-Dideoxysucrose* (**5**)
C-2′	103.595	103.272
C-1	92.072	91.824
C-4′	81.283	78.765
C-3′	76.333	77.314
C-5′	73.912	76.096
C-2	72.472	75.071
C-3	72.311	72.305
C-5	70.979	71.340
C-4	69.135	68.186
C-6′	62.260	18.099
C-1′	61.262	60.852
C-6	60.033	16.546

[a]Values (δ) downfield from the signal of Me_4Si.

proton decoupler turned off, the primary carbon atoms (δ 18.099 and 16.546) coupled with three protons to give a quartet (${}^1J_{C-6',H-6'}$ 123 and ${}^1J_{C-6,H-6}$ 126 Hz). Each peak in the quartet was further split owing to the two-bond, carbon-hydrogen coupling of C-6′–H-5′ and C-6–H-5. These data indicate that the two primary carbon atoms are C-6′ and -6. The primary carbon (δ 60.852) gave a triplet (${}^1J_{C-1',H-1'}$ 143 Hz) with no further splitting. Thus, the third primary carbon atom (C-1) is linked to a hydroxyl group, and deoxy groups are, therefore, unequivocally at C-6 and -6′.

EXPERIMENTAL

6,6′-Dichloro-6,6′-dideoxysucrose (**2**). — A solution of sucrose (4.3 g) in pyridine (250 mL) was cooled to 25°, and triphenylphosphine (20 g) and carbon tetrachloride (20 mL) were added. The mixture was heated at 65–70° for 0.5 h. Methanol (20 mL) was added and, after 1 h at 50°, the mixture was evaporated. The residue was partitioned between chloroform and water, and the aqueous phase was washed three times with chloroform. The aqueous layer was evaporated and the residue chromatographed on a silica gel column. Elution with chloroform and then with 54:5:3 (v/v) ethyl acetate–ethanol–water, gave a hygroscopic, amorphous powder (3.4 g, 71%), $[\alpha]_D^{25}$ +58° (*c* 0.5, water); R_F (t.l.c. on silica gel in 4:1:0.7, v/v ethyl acetate–methanol–water) 0.65; lit.[7], $[\alpha]_D^{25}$ +60°, water.

Anal. Calc. for $C_{12}H_{20}Cl_2O_9$: C, 37.9; H, 5.3; Cl, 18.7. Found: C, 37.9; H, 5.5; Cl, 18.7

2,3,4,1′,3′,4′-Hexa-O-acetyl-6,6′-dichloro-6,6′-dideoxysucrose (**3**). — Acetic anhydride (50 mL) was added to a solution of **2** (10 g) in pyridine (50 mL). After being kept overnight at room temperature, the mixture was evaporated. The trace amount of pyridine in the residue was removed by co-evaporation with toluene. The residue was dissolved in chloroform, and the solution washed with water, dried (Na_2SO_4) and evaporated to yield a syrup (14.9 g, 89.5%).

6,6′-Dideoxysucrose (**5**) — Tributyltin hydride (3.69 g) was added to a solution of **3** (2 g) in dry toluene (10 mL). The mixture was boiled under reflux and nitrogen for 4 days. After the removal of toluene, the residue was dissolved in acetonitrile (40 mL), and the solution washed with dry hexane (5 × 40 mL). The acetonitrile layer was evaporated to a syrup (**4**, 1.75 g, 98%), which was dissolved in methanol (20 mL). The pH was adjusted to ~10 with a methanolic solution of sodium methoxide. After being kept overnight at room temperature, the mixture was made neutral with solid carbon dioxide, and then evaporated. The syrupy residue was de-ionized with a column of Amberlite MB-1 ion-exchange resins, and eluted with water. The effluent was concentrated to a syrup that crystallized from ethanol (0.71 g, 73.5%). Recrystallization from ethanol gave **5**, m.p 205–206°, $[\alpha]_D^{25}$ +54° (*c* 1.5, water); ^{1}H-n.m.r. (D_2O): δ 5.3 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 3.6 (m, 9 H), and 1.5–1.1 (m, 6 H_3, H-6 and -6′); ^{13}C-n.m.r.: see Table I.

Anal. Calc. for $C_{12}H_{22}O_9$: C, 46.45; H, 7.15. Found: C, 46.58; H, 7.35.

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