the degradation product yielded from the *E* isomer and was 6.12×10^5 cpm for that obtained from the *Z* isomer.

Derivatization and Separation of the Degradation Products. Redissolved in 2 mL of water, the degradation products were mixed with excess α-bromophenylacetophenone (60 mg) in 40 mL of acetone. The resulting milky white solution was refluxed overnight. After being cooled to room temperature and concentrated in vacuo, the yellow solid residue was purified by preparative TLC ($CHCl_3$). For the sample derived from (*E*)-[3,4-$^2H_2$]vinylglycine (**12**), 4.5 mg of the *p*-phenylphenacyl acetate having a total activity of 2.24×10^5 cpm was obtained; whereas, in the case of (*Z*)-[4-$^2H_2$]vinylglycine (**11**), 8.4 mg of the *p*-phenylphenacyl acetate having a total activity of 1.38×10^5 cpm was collected. Since acetate accounts for only 23% of the total mass in each sample, the specific activity can be estimated to be 2.13×10^5 cpm/mg (1.28×10^7 cpm/mmol) and 7.04×10^4 cpm/mg (4.22×10^6 cpm/mmol) for the expected chiral acetate derived from *E* and *Z* isomer, respectively.

Conversion of Phenylphenacyl Acetate to Acetate. Each of the p-phenylphenacyl acetates was redissolved in 1 mL of acetone and then mixed with 1 g of *p*-toluenesulfonic acid and 10 mL of water. Refluxing was maintained overnight, during which time a considerable amount of brown precipitate was formed. Steam distillation followed by basification to pH 8 with 0.1 N NaOH of the collected distillate was carried out, and the resulting clear solution was concentrated to dryness in vacuo. Total ^3H activity was 2.06×10^5 cpm for the chiral acetate derived from *E* isomer and was 1.24×10^5 cpm for its analogue obtained from the *Z* isomer. To allow more sensitive counting of the $^3H/^{14}C$ ratio in the subsequent analyses, 4.58×10^4 cpm and 2.76×10^4 of [U-^{14}C]acetate were mixed with the acetate samples derived from *E*- and *Z*-[4-^{2}H]-vinylglycine, respectively, to make the $^3H/^{14}C$ ratio 4.5/1 in both cases.

Sample Preparation for C-4 Chirality Determination. Conversion of 1-Amino-2-methylcyclopropane-1-carboxylate (10) to 2-Keto[4-$^2H_1$]pentanoate (19). 2-Me-ACPC (**10**) (12 mg) and ACPC deaminase (200λ, 0.4 mg/mL) were incubated in deuterated potassium pyrophosphate buffer (50 mM, pD 8.8, 3 mL) for 2 days at 37 °C. The reaction mixture was loaded onto a Dowex-50 (H^+) column (1.5 × 5 cm) and the column was then eluted with water. The aqueous eluate was concentrated and the white residue was redissolved in NaOH solution (8 mL) and incubated at 40 °C for 24 h. The resulting clear solution was again loaded on a Dowex-50 (H^+) column 1.5 × 5 cm) and washed with water. The eluate was collected and concentrated in vacuo to afford the 2-keto-pentanoate sodium salt (**19**) as a white solid. ^1H NMR (D_2O) δ 2.93 (d, 7.3, 3-H's, keto form), 1.88 (d, 7.9, 3-H's, hydrated form), 1.65 (m, 4-H, keto form), 1.25 (m, 4-H, hydrated form), 0.95 (d, 7.9, Me).

Decarboxylation of 2-Keto[4-$^2H_1$]pentanoate (19). To a clear solution of 2-keto[4-$^2H_1$]pentanoate (**19**) in 3% H_2O_2 (10 mL, pH adjusted to 7.8 with 0.1 N NaOH) was added 200λ of catalase over a period of 10 min. After being stirred vigorously for 5 h at room temperature, the resulting cloudy solution was subjected to Dowex-50 (H^+) cation exchange chromatography (1.5 × 5 cm) and eluted with water. The aqueous eluate was saturated with sodium chloride and extracted thoroughly with ether. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated to give [3-$^2H_1$]butyric acid (**20**).

Derivatization of Enzymically Produced [3-$^2H_1$]Butyric Acid (20). The residual colorless oil **20** obtained from the preceding reaction was dissolved in DMF (2 mL). To this solution was added 2-naphthol (28.8 mg, 0.2 mmol), (dimethylamino)pyridine (6 mg), and dicyclohexylcarbodiimide (20.6 mg, 0.1 mmol). The reaction mixture was kept stirring at room temperature overnight. After the mixture was diluted with ether and quenched with water, the aqueous layer was separated and further extracted with ether. The pooled ether extracts were dried ($MgSO_4$), concentrated, and purified by HPLC (C_{18} column, 30% H_2O/MeOH). CD (MeOH), $\Delta\epsilon$ (276 nm) = −0.36.

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Registry No. 1, 22059-21-8; **3**, 87480-58-8; **4**, 84392-07-4; **5**, 91366-02-8; **6**, 35356-70-8; **7**, 91366-03-9; **8**, 91366-04-0; **9**, 91366-05-1; **10**, 91366-06-2; **11**, 75538-79-3; **12**, 75549-36-9; **13**, 1462-12-0; **14**, 16783-17-8; **15**, 91366-07-3; **16**, 91366-08-4; **17**, 91366-09-5; **19**, 91366-10-8; **20**, 91366-11-9; **21**, 66311-24-8; **22**, 66311-25-9; **23**, 3976-69-0; **24**, 53562-86-0; **25**, 91366-12-0; **26**, 91366-13-1; **27**, 91366-14-2; **28**, 91366-15-3; **29**, 91366-16-4; **30**, 91366-17-5; **31**, 91366-18-6; **32**, 927-74-2; **33**, 40365-61-5; **34**, 91366-19-7; **35**, 91366-20-0; **36**, 91366-21-1; **37**, 91366-22-2; **38**, 91366-23-3; **39**, 91366-24-4; **40**, 91366-25-5; **41**, 91366-26-6; **42**, 91366-27-7; **43**, 91366-28-8; ethyl cyanoacetate, 105-56-6; [1,1,2,2-$^2H_4$]-1,2-dibromoethane, 22581-63-1; ethyl malonate, 105-53-3; ethyl 1-cyano[2,2,3,3-$^2H_4$]cyclopropane-1-carboxylate, 91366-29-9; 1-carboxy[2,2,3,3-$^2H_4$]cyclopropane-1-carboxamide, 91366-30-2; 1-aminocyclopropane-1-carboxylate deaminase, 69553-48-6.

Synthesis of 1′-Deoxy-1′-fluorosucrose via Sucrose Synthetase Mediated Coupling of 1-Deoxy-1-fluorofructose with Uridine Diphosphate Glucose

Peter J. Card* and William D. Hitz

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Abstract: 1′-Deoxy-1′-fluorosucrose (**1**) has been synthesized by a sucrose synthetase mediated coupling of 1-deoxy-1-fluoro-D-fructose with UDP-glucose. 1-Deoxy-1-fluoro-D-fructose (**2**) was prepared from 2,3:4,5-di-*O*-isopropylidene-D-fructopyranose via tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) reaction upon the corresponding trifylate followed by hydrolysis. Fluorosucrose **1** is stable to hydrolysis by invertase and is recognized by the sucrose carrier protein.

Sucrose is the predominant carbohydrate transported from photoautotrophic organs to heterotrophic organs in most plant species. Such long-distance transport, in the absence of a fluid pumping mechanism, requires the establishment of a steep sucrose concentration gradient between exporting and importing organs. This gradient is apparently established by a sucrose carrier protein in the membranes of certain cells within leaf vascular tissue and in some other organs, which is capable of moving sucrose across the membrane against a large concentration gradient.[1] Study of this carrier protein and of the physiology of sucrose transport is complicated by the metabolic lability of sucrose, especially its susceptibility to extracellular hydrolysis by invertase. To further

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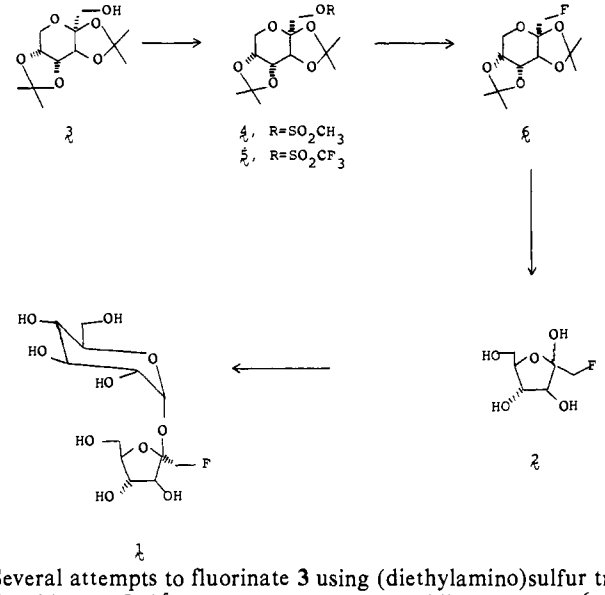
our studies in this area, we have sought substituted sucrose derivatives that are not substrates for invertase but are transported by sucrose-specific carriers.

Since it has been shown that methyl 1-deoxy-1-fluoro-β-D-fructofuranoside is not an invertase substrate,[2] we assumed that 1′-deoxy-1′-fluorosucrose (**1**) would likewise be inactive as a substrate. Further, since fluorine is isosteric with a hydroxyl group and capable of accepting H bonds, it seemed likely that **1** might be recognized by the sucrose carrier protein.

A successful sucrose analogue would need to be made radiolabeled as well, and since synthetic chemical couplings of glucose and fructose to give sucrose are tedious and proceed in extremely low yield (<9%),[3] we decided to investigate a preparative, sucrose synthetase catalyzed coupling of 1-deoxy-1-fluoro-D-fructose (**2**) with UDP-glucose to give **1**.

1-Deoxy-1-fluoro-D-fructose (**2**) was prepared from the readily available 2,3:4,5-di-O-isopropylidene-D-fructopyranose (**3**).[4]



3 **4**, R=SO_2CH_3 **5**, R=SO_2CF_3 **6** **2** **1**

Several attempts to fluorinate **3** using (diethylamino)sulfur trifluoride (DAST)[5] were unsuccessful. In addition, Barnett[6] reported that tetrabutylammonium fluoride reacted with mesylate **4** to give only a low yield (<9%) of impure **6**. We have found that tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF)[7] reacts with trifylate **5** to afford good yields of **6**. Trifylate **5** was prepared from **3** via a standard procedure.[8] Reaction of **5** with 1.1 equiv of TASF in refluxing tetrahydrofuran gave an 80% yield of distilled **6**. The structure of **6** follows from its 360-MHz ^{1}H NMR spectrum, which exhibits a typical geminal H–F coupling (48 Hz) between the H-1 protons and the fluorine atom. Hydrolysis of **6** with an acidic ion-exchange resin afforded **2** (81%) as a syrup.

A crude preparation of sucrose synthetase was easily obtained from barley seeds (see Experimental Section). When equimolar quantitites of **2** and UDP-glucose were incubated with the sucrose synthetase preparation at 35 °C and pH 8.2 by using a pH stat, **1** was obtained in 59–83% yield via simple isolation techniques. The structure of **1** was assigned on the basis of its mode of synthesis and comparison of its ^{13}C NMR spectrum with that of sucrose. The bottom spectrum in Figure 1 is that of sucrose which

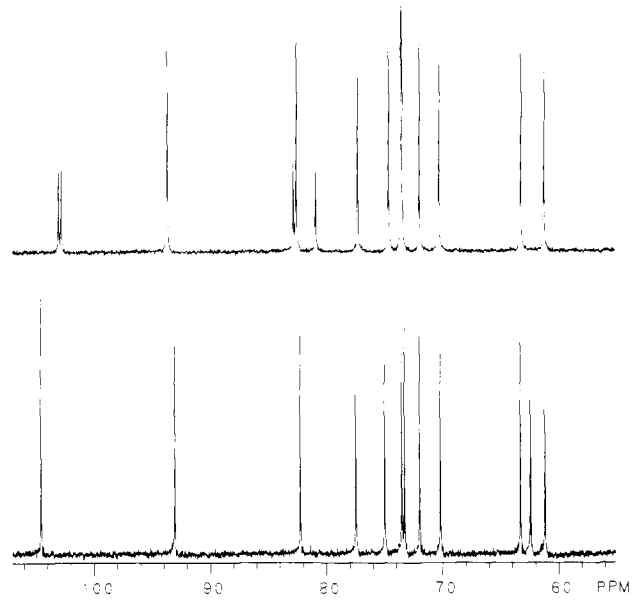


Figure 1. (Top) ^{13}C NMR spectrum of **1** in D_2O. (Bottom) ^{13}C NMR spectrum of sucrose in D_2O.

exhibits three hydroxymethylene resonances (δ 61–64) and C-2′ at δ 104. The ^{13}C NMR spectrum of **1** (Figure 1, top) is superimposable with that of sucrose with the exception of C-1′, which is shifted downfield (δ 81.7, $J_{C,F}$ = 172.9 Hz), and C-2′, which exhibits a β C–F coupling of 20 Hz.

To the best of our knowledge this is the first reported preparative-scale enzymatic synthesis of an unnatural disaccharide.

Incubation of **1** with invertase preparations from yeast[9] or plant tissue (protein extract from corn roots) at pH 6.5 gave no hydrolysis as measured by glucose appearance. Further, **1** at equimolar concentrations to sucrose did not inhibit hydrolysis by these invertase preparations, indicating that **1** is not recognized or is very poorly recognized by invertase.

Sucrose is actively accumulated by protoplasts prepared from immature soybean cotyledon tissue.[10] When such protoplast preparations were incubated with ^{14}C-labeled **1** (0.5 mm, 3.3 μCi/μ mol) a linear rate of accumulation by the protoplasts occurred for at least 1 h. The uptake rate for **1** was 1.4 times the sucrose uptake rate into similar preparations. Addition of ^{12}C-**1** to uptake solutions of [^{14}C]sucrose or of [^{12}C]sucrose to ^{14}C-**1** uptake solutions resulted in decreased ^{14}C accumulation by the protoplasts in both cases, indicating recognition of both substrates by a single carrier.

Enzymatic coupling of UDP-glucose and **2** provides a simple method of producing **1** and for introducing ^{14}C into the molecule. The single hydroxyl substitution in **1** eliminates invertase hydrolysis and allows a slightly enhanced recognition by the sucrose carrier protein in at least one biological system.

Experimental Section

General Methods. All chemical reactions were performed under a nitrogen atmosphere. Melting points were determined with a Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were determined on a Nicolet 7199 FT-IR spectrometer. Optical rotations were determined on a Perkin-Elmer 241 MC polarimeter. 360-MHz ^{1}H NMR and 90.78-MHz ^{13}C NMR spectra were obtained on a Nicolet NT WB 360 spectrometer and are referenced to internal tetramethylsilane unless stated otherwise. The ^{19}F NMR spectra were obtained on a Varian XL-100 spectrometer and are referenced to internal trichlorofluoromethane. Uridine-5′-diphosphoglucose was obtained from Sigma.

2,3:4,5-Di-*O*-isopropylidene-1-[(trifluoromethylsulfonyl)oxy]-*D*-fructopyranose (5). A solution of **3** (26.8 g, 103 mmol) in anhydrous dichloromethane (1470 mL) and pyridine (52 mL) at −15 °C was treated

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(7) (a) Middleton, W. J. *U.S.* Patent 3 940 402, describes the use of TASF as a fluoride ion source. (b) For a preparation of TASF, see: Farnham, W. B.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4608, ref 3. (c) Aldrich Chemical Co.
(8) Binkley, R. W.; Ambrose, M. G.; Hehemann, D. G. *J. Org. Chem.* **1980**, *45*, 4387. In contrast to this report, we have found that **5** is completely stable at room temperature for weeks at a time.
(9) Sigma Chemical Co.
(10) Hitz, W. D.; Schmitt, M. R.; Giaquinta, R. T.; Card, P. J. *Plant Phisol.*, in press.

dropwise with a solution of trifluoromethanesulfonic anhydride (19.5 mL, 117.6 mmol) in dichloromethane (100 mL). After it was stirred for 90 min at −15 °C, the mixture was poured into ice-cold saturated $NaHCO_3$ solution (1470 mL), and the organic layer was withdrawn. The aqueous layer was extracted with dichloromethane, and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure using toluene to remove the last traces of pyridine. The residue was dissolved in petroleum ether, filtered, and concentrated under reduced pressure to afford a colorless syrup which eventually solidified (38.3 g, 95%): mp 36–38.5 °C; 360-MHz ^1H NMR ($CDCl_3$) δ 1.35 (s, 3 H), 1.42 (s, 3 H), 1.47 (s, 3 H), 1.56 (s, 3 H), 3.7 ($^1/_2$AB, H-6_{eq}, $J_{6,6'}$ = 13 Hz), 3.93 (dd, $^1/_2$ AB, H-6_{ax}, J = 13, 1.9 Hz), 4.25 (dd, H-5, $J_{4,5}$ = 7.9, $J_{5,6_{ax}}$ = 1.9 Hz), 4.32 (d, H-3, $J_{3,4}$ = 2.7 Hz), 4.41 ($^1/_2$AB, H-1, $J_{1,1'}$ = 10 Hz), 4.53 ($^1/_2$AB, H-1′), 4.64 (dd, H-4); ^{19}F NMR (^1H decoupled) ($CDCl_3$) ϕ −75.1 (s); IR (KBr) 1418, 1246, 1208, 1145, 1071, 980, 609 cm^{-1}; $[\alpha]_D$ −28.5° (*c* 1.03, $CHCl_3$).

Anal. Calcd for $C_{13}H_{19}F_3O_8S$: C, 39.80; H, 4.88. Found: C, 39.94; H, 4.89.

1-Deoxy-1-fluoro-2,3:4,5-di-*O*-isopropylidene-D-fructopyranose (6). TASF (16.5 g, 60 mmol) was loaded into a flask, and the flask was capped with a rubber septum in a drybox. The flask was removed from the box, and a solution of **5** (21.56 g, 55 mmol) in anhydrous tetrahydrofuran (50 mL) was added via syringe. The septum was removed, and the flask was fitted with a reflux condenser and a positive pressure of N_2. The mixture was then heated at reflux overnight. The mixture was poured into water and extracted with ether. The ether layer was dried and concentrated under reduced pressure. Chromatography of the residue on silica gel (2:1 hexane/EtOAc) afforded **6** as a colorless syrup: Kugelröhr distillation gave 11.58 g (80%) of **6**; bp 85–95 °C (0.1 mmHg); 360-MHz ^1H NMR ($CDCl_3$) δ 1.35 (s, 3 H), 1.40 (s, 3 H), 1.46 (s, 3H), 1.56 (s, 3 H), 3.74 ($^1/_2$AB, H-6, $J_{6,6'}$ = 12 Hz), 3.92 ($^1/_2$AB, H-6_{ax}, $J_{6_{ax},5}$ = 2 Hz), 4.25 (dd, H-3, $J_{3,4}$ = 8, $J_{H,F}$ = 1.5 Hz), 4.37 (d of AB, H-1 and H-1′ $J_{H-1,F}$ = 48, $J_{1,1'}$ = 10 Hz), 4.39 (m, H-5), 4.64 (dd, H-4, $J_{4,5}$ = 3 Hz); ^{13}C NMR (acetone-d_6) δ 23.6 (s, CH_3), 24.7 (d, CH_3, $J_{C,F}$ = 2.9 Hz), 25.5 (s, CH_3), 26.0 (s, CH_3), 61.1 (d, C-6, $J_{C,F}$ = 1 Hz), 69.9 (d, C-3, $J_{C,F}$ = 2 Hz), 70.2 (s, C-4), 70.9 (s, C-5), 82.2 (d, C-1, $J_{C,F}$ = 174 Hz), 101.2 (d, C-2, $J_{C,F}$ = 21.5 Hz), 108.7 (s, acetonide quaternary), 108.8 (s, acetonide quarternary); ^{19}F NMR (acetone-d_6) ϕ −230.1 (s, ^1H decoupled; ^1H coupled, t, $J_{H,F}$ = 48 Hz); $[\alpha]_D$ −19.2 (*c* 0.63, $CHCl_3$).

Anal. Calcd for $C_{12}H_{19}FO_5$: C, 54.95; H, 7.30. Found: C, 54.99; H, 7.28.

1-Deoxy-1-fluoro-D-fructose (2). A solution of **6** (11.05 g, 42 mmol) in EtOH (50 mL) and water (150 mL) was treated with Bio-Rad AG 50W-X8 (21 g; hydrogen form), and the mixture was heated at 60–70 °C for 3 h. The reaction mixture was filtered, decolorized, and then extracted with ether. The aqueous layer was partially concentrated on a rotatory evaporator to remove the EtOH and then lyophilized to afford **2** (6.23 g, 81%) as a colorless syrup which eventually solidified, $[\alpha]_D$ −93.1 (*c* 1.23, H_2O).

Anal. Calcd for $C_6H_{11}FO_5$: C, 39.56; H, 6.09. Found: C, 39.76; H, 5.84.

Sucrose Synthetase Preparation. Barley (Hordeum Vulgare L., cv. (CM-72) was grown in a commercial medium (Metro Mix, W. R. Grace & Co., Cambridge, MA) in a controlled environment chamber (16 h day, day temperature 25 °C, night temperature 18 °C, 50% relative humidity). Photosynthetically active radiation was 800 μmol photons m^{-2} s^{-1}. Immature seeds were removed from the heads during mid-grainfill (40–45 days after planting). The awn and outer glume were removed, and the remaining grain was frozen in liquid N_2, then maintained frozen at −20 °C until use.

Protein was extracted from 10 g of frozen seed into 50 mL of grinding buffer containing 100 mM tris(hydroxymethyl)aminomethane hydrochloride (Tris HCl), 10 mM $MgCl_2$, 10 mM EDTA, and 1 mM dithiothreitol (DTT) at pH 8.2 by homogenizing for 1 min at 4 °C in a Waring blender. The homogenate was filtered through cheesecloth, and the filtrate was centrifuged (15 min, 12000xG) to yield a clear extract. The protein extract was brought to 30% saturation at 4 °C with solid $(NH_4)_2SO_4$ (176 g/L), stirred for 30 min, and then centrifuged as before. The pellet was discarded, and the supernatant brought to 50% saturation in $(NH_4)_2SO_4$ (313 g/L), stirred for 30 min, and again centrifuged. The pellet was redissolved in 7.5 mL of reaction buffer containing 20 mM Tris HCl, 0.1 mM EDTA, 10 mM $MgCl_2$, and 1 mM DTT at pH 8.2 and then desalted by passage through Sephadex G-25 equilibrated with the same buffer.

1′-Deoxy-1′-fluorosucrose (1). 1-Deoxy-1-fluorofructose (**2**, 455 mg, 2.5 mmol) in 1 mL of reaction buffer and UDP-glucose (2.5 mmol) in 3 mL of buffer were added to 8 mL of the above sucrose synthetase preparation in a pH Stat at 35 °C. Reaction progress was monitored by the rate of H^+ appearance (~6 h) and was terminated by heating to 100 °C for 10 min. Precipitated protein was removed from the reaction mixture by centrifugation, and the cleared solution was applied to two ion-exchange columns run in series (4.2 cm × 5 cm each column; top Dow-50 × 8 H^+ form, bottom Dow-1 × 8 ^-OH form). The columns were eluted with 750 mL of water that was reduced under vacuum at 40 °C to about 20 mL then lyophylized. The dried, white solid was dissolved in 20 mL of dry MeOH with warming and slowly crystallized in the cold to give 507 mg (59%) of **1** as a colorless solid: mp 192–193 °C; 360-Hz ^1H NMR (D_2O) δ 3.35 (t, H-4, J = 9.5 Hz, collapses to a d upon irradiation at δ 3.7), 3.47 (dd, H-2, $J_{1,2}$ = 3.5, $J_{2,3}$ = 10 Hz), 3.62 (t, H-3, collapses to a d upon irradiation at δ 3.35), 3.68–3.75 (m, H-5), 3.81 (m, 1 H), 3.95 (t, 1 H), 4.11 (dd, 1 H, J = 1.5, 9 Hz), 4.36 (m, H-1′, $J_{H,F}$ = 47, $J_{H-1'H-1'}$, = 10.5 Hz), 4.43 (m, H-1′, J = 47, 10 Hz), 5.29 (d, H-1, $J_{1,2}$ = 3.5 Hz); ^{19}F NMR (D_2O) ϕ −225 (t, $J_{H,F}$ = 47 Hz); ^{13}C NMR (D_2O) δ 60.9 (s, C-6), 62.7 (s, C-6′), 69.9 (s, C-4), 71.5 (s, C-2), 73.0 (s, C-5), 73.1 (s, C-3), 74.5 (s, C-4′), 77.2 (s, C-3′), 81.7 (d, C-1′, $J_{C,F}$ = 172.9 Hz), 82.0 (s, C-5′), 93.2 (s, C-1), 102.5 (d, C-2′, $J_{C,F}$ = 20 Hz); $[\alpha]_D$ +56.3 (*c* 0.99, H_2O).

Anal. Calcd for $C_{12}H_{21}FO_{10}$: C, 41.86; H, 6.15. Found: C, 41.76; H, 6.07.

[*glucosyl*-U-^{14}C]-1′-Deoxy-1′-fluorosucrose (7). **7** was prepared as above by using 0.9 mL of the sucrose synthetase preparation with 5 μmol each of **2** and UDP-glucose uniformly labeled in the glucose moiety with ^{14}C (25 μCi). After 19 h at 35 °C, workup was as for **1** using ion-exchange column volumes of 1 mL (Dow 50×8) and 1.5 mL (Dow 1×8). The purified product was better than 99% radiochemically pure as determined by HPLC (Bio-Rad Aminex HPX-87 [300 × 7.8 mm], 85 °C, flow rate 1.3 mL/min, H_2O).

Membrane Transport of 1. Protoplasts from immature soybean cotyledons[10] were incubated in 0.5 mM **7** (3.3 μCi/μmol) for up to 60 min and ^{14}C in the protoplasts was determined by described techniques.[10]

Registry No. 1, 77453-90-8; **2**, 40614-94-6; **3**, 20880-92-6; **5**, 74925-15-8; **6**, 40614-93-5; **7**, 91266-00-1; tris(dimethylamino)sulfonium difluorotrimethylsilicate, 59218-87-0; sucrose synthetase, 9030-05-1; UDP-glucose, 133-89-1; trifluoromethanesulfonic anhydride, 358-23-6.