Fluorination Reactions at C-5 of 3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidenehexofuranoses

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Fluorination reactions of 2-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-α-D-gluco-, β-L-ido-, α-D-allo-, and β-L-talo-furanoses (**1**, **2**, **3**, and **4**) were investigated. The reaction of **1** with diethylaminosulfur trifluoride (DAST) predominantly produced 2-*O*-benzyl-5,6-dideoxy-5-fluoro-1,2-*O*-isopropylidene-α-D-glucofuranose with the retention of the configuration at C-5. Both of the fluorides with retained and inverted configurations were obtained in the fluorination of **2** with DAST. In contrast, only the inversion of the configuration occurred when **3** and **4** were reacted with DAST. The reactions of the methanesulfonates of **3** and **4** with tetrabutylammonium fluoride (TBAF) and those of their trifluoromethanesulfonates with tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) gave the 5-deoxy-5-fluoro derivatives with the inversion of each configuration and the 5,6-unsaturated derivative. However, the reactions of the sulfonates of **1** and **2** overwhelmingly produced the 4,5- and 5,6-eliminated derivatives. For the reaction in which the steric hindrance of the benzyloxyl group at C-3 and the electronic repulsion of ring oxygen to the S_N2 displacement with fluoride anion are significant, such as the fluorination of **1** with DAST, the S_Ni mechansim is reasonable.

Although the incorporation of fluorine into carbohydrates has been widely investigated,[1—3] a smaller number of 5-deoxy-5-fluorofuranose derivatives was reported.[2] Our first attempted fluorination at C-5 of 6-deoxyhexofuraoses with tetrabutylammonium fluoride (TBAF) to the 5-*O*-methanesulfonates (mesylates) gave the 4,5- and 5,6-unsaturated derivatives as the major products, instead of the 5-fluorides.[4]

Among the procedures for the fluorination exploited so far, tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) was successfully utilized for the S_N2 fluorination of the trifluoromethanesulfonates (triflates) of carbohydrates.[5] For the direct displacement of a hydroxyl group by fluorine, diethylaminosulfur trifluoride (DAST)[6] has frequently been used, even though the use of DAST sometimes provided unexpected products[2] through rearrangement, ring-transformation,[7] and fluorination with a retention of the configuration.[8]

Thus, we now describe the results of fluorination at C-5 of 6-deoxyhexofuranose derivatives by using such reagents as TASF and DAST, and discuss the reaction mechanisms.

Results and Discussion

All of the compounds reacted and produced in the reactions, which are mentioned in the following, are listed in Chart 1.

The fluorination reaction of 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-5-*O*-methylsulfonyl-α-D-glucofuranose (**5**)[9] with TBAF in *N*,*N*-dimethylformamide (DMF) gave (*E*)-3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-β-L-*threo*-hex-4-enofuranose (**17**)[4] and 3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-β-L-*threo*-hex-5-enofuranose (**19**)[10] as the major products, along with only 5% yield of 3-*O*-benzyl-5,6-dideoxy-5-fluoro-1,2-*O*-isopropylidene-β-L-idofuranose (**14**).[4] Similarly, the reaction of the 5-epi mesylate **6**[11] afforded the 5-deoxy-5-fluoro compound **13**[4] of the α-D-gluco configuration in 8% yield, though the *Z*-isomer of the 4,5-unsaturated compound **18**[4,12] and **19** were predominantly formed.[4]

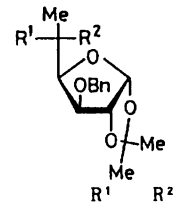
Thus, fluorination of triflates **9** and **10**, prepared from **1** and **2**, respectively, with TASF in dichloromethane was first attempted in order to improve the yields of the fluorinated derivatives. The result of the reaction of **9**, however, was almost equivalent to that of **5**; in the reaction of **10**, the yield of the fluoride **13** was slightly improved (Table 1).

A drastic change in the product distribution was observed in the fluorination of **1**[13] with DAST in dichloromethane; compound **13** with a retained configuration at C-5 was obtained in 61% yield, along with **14** in 3% yield. The reaction of **2**[11] with DAST gave **13** and **14** in 9 and 12% yields, respectively. In each reaction, only small quantities of the unsaturated derivatives were obtained.

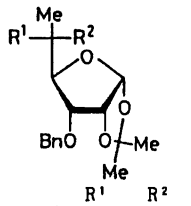
3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-5-*O*-methylsulfonyl-α-D-allo- and β-L-talofuranoses (**7** and **8**) were prepared by the mesylation of **3**[14] and **4**, respectively. Compound **4** was derived by the reduction using lithium aluminum hydride from the 5,6-anhydro compound **24**, which was prepared from 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-allofuranose[15] through successive reactions with triphenylmethyl chloride, mesyl chloride, aqueous acetic acid, and sodium methoxide.

Both the reaction of **7** with TBAF and that of **11** with TASF afforded the configuration-inverted fluoride **16** in approximately 20% yields and the 5,6-unsaturated derivative **20**[16] in approximately 70% yields (Table 2). The fluorination of **8** and **12** gave **15** and **20**; the yield of **15** from **12** was better than that from **8**.

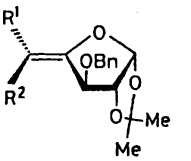
The fluorination of **3** and **4** with DAST also proceeded with an inversion of the configuration to give **16** and **15** in 39 and 61% yields, respectively. This is obviously different from the results concerning the flu-



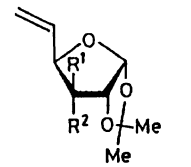
	R¹	R²
1	OH	H
2	H	OH
5	OMs	H
6	H	OMs
9	OTf	H
10	H	OTf
13	F	H
14	H	F



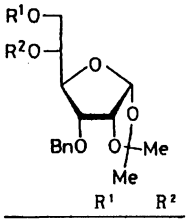
	R¹	R²
3	OH	H
4	H	OH
7	OMs	H
8	H	OMs
11	OTf	H
12	H	OTf
15	F	H
16	H	F



	R¹	R²
17	H	Me
18	Me	H



	R¹	R²
19	OBn	H
20	H	OBn



	R¹	R²
21	Tr	H
22	Tr	Ms
23	H	Ms

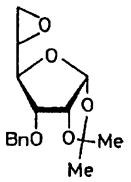


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Chart 1.

Table 1. Fluorination of **1**, **2**, and Their Sulfonates (**5**, **6**, **9**, and **10**)

Substrate	Reagent	Yield/%				
		13	**14**	**17**	**18**	**19**
1	DAST	61	3	5		8
5	TBAF		5	54		37
9	TASF		3	58		35
2	DAST	9	12		3	2
6	TBAF	8			43	32
10	TASF	23			25	37

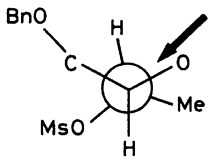
orination of **1** and **2**, of which the benzyloxyl groups at C-3 are oriented to the same side as C-5.

The above-mentioned results are summarized in Tables 1 and 2.

The preferred conformation around the C-4–C-5 bond of each mesylate is illustrated in Fig. 1. The dihedral angles were roughly estimated from the coupling constants between H-4 and H-5 observed in $CDCl_3$. All of the ^1H NMR data are shown in Table 5.

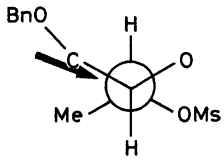
Table 2. Fluorination of **3**, **4**, and Their Sulfonates (**7**, **8**, **11**, and **12**)

Substrate	Reagent	Yield/%		
		15	**16**	**20**
3	DAST		39	2
7	TBAF		20	69
11	TASF		23	72
4	DAST	61		2
8	TBAF	44		45
12	TASF	59		21



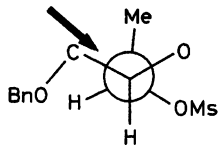
$J_{4,5}$ = 7.9 Hz

5



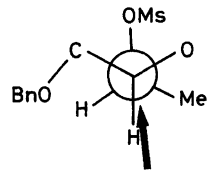
$J_{4,5}$ = 8.9 Hz

6



$J_{4,5}$ = 2.4 Hz

7



$J_{4,5}$ = 4.0 Hz

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Fig. 1. Preferred conformation for the C-4–C-5 bonds of 5—8 presumed from $J_{H\text{-}4,H\text{-}5}$.

The access of a fluoride anion (F^-) to **5** for the S_N2 reaction (depicted as a bold arrow) is hindered by both the electronic repulsion with ring oxygen and the bulkiness of a benzyloxyl group at C-3. The steric hindrance of a benzyloxyl group is also significant in the reaction of **6**. The obstruction to the attack of F^- to **7** is much less than that to **6**, though the directions of the incoming of F^- in both cases are not so different. The attack of F^- may not be appreciably hindered in the reaction of **8**. Considering the results concerning the fluorination of the triflates, the shapes of their reactions are quite similar to those of the mesylates.

The yields of the configuration-inverted fluorides from the sulfonates were consistent with the extent of the obstruction predicted from each preferred conformation. Instead, the low nucleophilicity and high basicity of F^- liberated from TBAF or TASF caused an elimination reaction by pulling out H-4 and H-6 from the sulfonates (**5**, **6**, **9**, and **10**) to produce **17** or **18**, and **19**. In the reactions of **7**, **8**, **11**, and **12**, only the 5,6-unsaturated derivative **20** was formed, because pulling out of H-4 by F^- would be extremely restricted by the benzyloxyl

group at C-3.

When DAST was used for the fluorination of **1**—**4**, the formation of the eliminated products was considerably diminished. This is because DAST is not a good source of F^-, but reacts with an alcohol to generate hydrogen fluoride,[6] which hardly dissociates in dichloromethane.

In order to rationalize the reason why the reaction of **1** with DAST in dichloromethane predominantly gave the configuration-retained fluoride **13**, the solvent dependence of the reaction was surveyed (Table 3). When the reaction was conducted in toluene or acetonitrile, the retention of the configuration still predominated. In tetrahydrofuran, both **13** and **14** were formed in almost the same amounts, and the yield of **19** increased. No configuration-retained fluoride **13** was obtained, but the eliminated derivatives **17** and **19** were mainly produced in pyridine.

In additon, the influence of molar amounts of DAST on the reaction of **1** in dichloromethane was examined; Table 4 reveals that an excess amount of DAST is unnecessary for fluorination.

The reaction mechanism of fluorination with DAST is not simply likened as S_N2 when the restriction to the accessing F^- is significant. For retaining the configuration, the S_Ni mechanism via an ion-pair intermediate in a solvent cage (Fig. 2) is most reasonable, considering the following discussion. In an electron-donating solvent like pyridine, released HF gives highly ionized pyridinium fluoride,[17] which increases the probability of elimination. Tetrahydrofuran may have an effect similar to that of pyridine to increase the concentration of F^-, and may also have an effect to separate the components of the ion-pair in Fig. 2 to form both fluorides.

In the reaction of **2** with DAST, the lesser restriction to the accessing F^- would increase the S_N2 character. Moreover, only an inversion of the configuration of **3** and **4** occurred, even in their reactions with DAST, because of the absence of a steric hindrance.

Table 3. Solvent Dependence of the Reaction of **1** with DAST[a]

Solvent	Reaction Time/h		Yield/%			
	at −10 °C,	at r.t.	**13**	**14**	**17**	**19**
CH_2Cl_2	0.5	1.0	61	3	5	8
C_6H_5Me	0.5	1.5	35	3	1	7
MeCN	1.5	–	30	1	4	6
THF[b]	1.5	–	7	9	1	16
C_5H_5N	0.5	1.0[c]	0	3	11	35

a) 1.5 Molar amounts of DAST were used. b) THF= tetrahydrofuran. c) Reacted at 60 °C.

Table 4. Influence of the Molar Amount of DAST on the Reaction of **1** in CH_2Cl_2

DAST	Reaction Time/h		Yield/%			
mol	at −10 °C,	at r.t.	**13**	**14**	**17**	**19**
1.2	0.5	1.0	59	4	2	9
1.5	0.5	1.0	61	3	5	8
2.0	0.5	1.0	54	3	0	6
2.0	3.0	–	54	2	0	9
3.0	1.5	–	52	2	0	4

Experimental

The melting points were determiend with a Yanagimoto MP-500D melting-point apparatus and are uncorrected. The optical rotations were measured with a Horiba SEPA-200 polarimeter at 20 °C. The NMR spectra were recorded with a Varian VXR-300 specrometer at 300 MHz for ^1H NMR and at 75.4 MHz for ^{13}C NMR in $CDCl_3$. The assignment of all of the proton and carbon signals was performed based on H–H and C–H COSY measurements. The chemical shifts of the protons were calculated from that of the satellite peak of $CDCl_3$ at $\delta=7.26$, and those of the carbons are relative to the central peak of $CDCl_3$ at $\delta=77.0$. The ^1H and ^{13}C NMR spectral data for the prepared compounds are summarized in Tables 5 and 6, respectively. The chemical shifts for ^{19}F NMR are relavtive to hexafluorobenzene as an internal standard. Silica gel (Wakogel C-300) was used for column chromatography.

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-5-*O*-methylsulfonyl-α-D-allofuranose (7). To a cooled solution of **3** (409 mg, 1.39 mmol) in pyridine (3.3 ml), methanesulfonyl chloride (0.16 ml, 2.08 mmol) was added dropwise at −10 °C. After the reaction temperature was raised to room temperature, stirring was continued for 1 h. Several drops of water were added to the reaction mixture, which was then evaporated. The residue was made up to a chloroform solution, which was washed with 2% aqueous hydrogen chloride, 5% aqueous sodium hydrogencarbonate, and water, successively, and dried over anhydrous sodium sulfate. Column chromatography using a mixed solvent of toluene and ethyl acetate (5 : 1) gave **7** (508 mg, 98%); $[\alpha]_D$ +111.6° (*c* 1, $CHCl_3$).

Found: C, 54.94; H, 6.60; S, 8.36%. Calcd for $C_{17}H_{24}O_7S$: C, 54.82; H, 6.50; S, 8.61%.

3-*O*-Benzyl-1,2-*O*-isopropylidene-5-*O*-methylsulfonyl-6-*O*-triphenylmethyl-α-D-allofuranose (22). A solution of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-allofuranose (5.50 g, 17.7 mmol) and chlorotriphenylmethane (5.92 g, 21.2 mmol) in pyridine (44.0 ml) was stirred overnight at 55 °C. To the cooled solution, methanesulfonyl chloride (2.74 ml, 35.4 mmol) was added at −10 °C. The mixture was stirred at room temperature for 3 h, poured into ice blocks under good stirring, and extracted with chloroform. The organic layer was washed with 2% aqueous hydrogen chloride, 5% aqueous sodium hydrogencarbonate, and water, successively, and dried over anhydrous sodium sulfate. Column chromatography using a mixed solvent of toluene and ethyl acetate (10 : 1) provided **22** as foams (9.22 g, 83%); $[\alpha]_D$ +39.6° (*c* 1, $CHCl_3$).

Found: C, 68.66; H, 6.23; S, 5.03%. Calcd for $C_{36}H_{38}O_8S$: C, 68.55; H, 6.07; S, 5.08%.

5,6-Anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-talofuranose (24). A mixture of **22** (9.00 g, 14.3 mmol) and 80% aqueous acetic acid (270 ml) was stirred at 50 °C for 3 h. Upon cooling the reaction mixture at 0

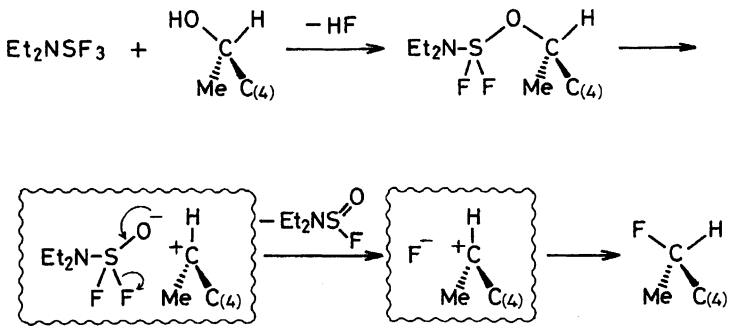

Fig. 2. Plausible mechanism for fluorination with the retention of the configuration at C-5.

Table 5. ^{1}H NMR Spectral Data[a)]

Compd	δ/ppm $J_{H,H}$/Hz ($J_{F,H}$/Hz)									
	H-1	H-2	H-3	H-4	H-5	H-6	H-6′	Me_2C	MeS	$PhC\underline{H}_2$
4	5.73	4.58	3.80	3.92	3.82	1.28		1.36, 1.59		4.58, 4.77
	3.7	4.2	8.8	3.0	6.4					(J_{AB}=12.0)
5	5.90	4.61	4.06	4.16	5.14	1.56		1.32, 1.51	2.93	4.60, 4.65)
	3.8	0	3.1	7.9	6.3					(J_{AB}=11.5)
6	5.96	4.65	3.88	4.16	4.90	1.28		1.33, 1.50	3.08	4.42, 4.67
	3.8	0	3.2	8.9	6.4					(J_{AB}=11.6)
7	5.71	4.57	3.94	4.14	4.93	1.45		1.36, 1.59	2.97	4.58, 4.75
	3.7	4.4	8.8	2.4	6.7					(J_{AB}=11.7)
8	5.75	4.58	3.72	4.05	4.86	1.50		1.36, 1.58	3.00	4.58, 4.75
	3.7	4.4	8.9	4.0	6.5					(J_{AB}=11.5)
15	5.75	4.57	3.88	4.11	4.87	1.37		1.36, 1.60		4.59, 4.77
	3.8	4.5	8.9	2.2	6.7					(J_{AB}=11.9)
				(22.3)	(48.8)	(23.8)				
16	5.76	4.58	3.86	3.97	4.74	1.44		1.38, 1.59		4.59, 4.77
	3.8	4.4	8.9	2.3	6.4					(J_{AB}=12.0)
				(24.5)	(47.0)	(24.0)				
20	5.74	4.56	3.51	4.47	5.81	5.26	5.45	1.36, 1.61		4.62, 4.75
	3.8	4.4	8.8	6.9	10.7	1.8				(J_{AB}=12.7)
					17.0					
22	5.72	4.60	3.86	4.18	5.20	3.38	3.48	1.36, 1.60	3.06	4.39, 4.56
	3.7	4.3	8.8	2.5	3.5	10.9				(J_{AB}=11.6)
					8.3					
23	5.76	4.61	3.99	4.27	4.92	3.85		1.37, 1.59	3.03	4.56, 4.77
	3.8	4.4	8.8	2.7	5.1					(J_{AB}=11.0)
24	5.70	4.56	3.79	4.03	3.08	2.79	2.87	1.35, 1.58		4.62, 4.79
	3.7	4.1	8.9	3.9	4.2	5.1				(J_{AB}=11.9)
					2.6					

a) Data for protons of phenyl groups are not shown.

°C, pale-yellow crystals precipitated. After filtering off the precipitates, the filtrate was evaporated below 50 °C, and chromatographed using a mixed solvent of chloroform and methanol (12 : 1) to afford **23** (5.36 g, 97%); $[\alpha]_D$ +90.3° (*c* 0.6, $CHCl_3$). To a solution of **23** (5.14 g, 13.2 mmol) in methanol (87.0 ml), 1.5 equiv methanolic sodium methoxide (16.0 ml) was added, and the resulting mixture was stirred at room temperature for 2 h. Neutralization of the solution with acetic acid, followed by evaporation, left a syrup, which was then chromatographed using a mixed solvent of toluene and ethyl acetate (7 : 1) to give **24** (3.43 g, 89%); $[\alpha]_D$ +96.4° (*c* 0.8, $CHCl_3$).

Found: C, 65.53; H, 6.98%. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90%.

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-β-L-talofuranose (4). A mixture of **24** (3.34 g, 11.4 mmol), lithium aluminum hydride (1.08 g, 28.5 mmol), and diethyl ether (67.0 ml) was refluxed under efficient stirring for 0.5 h. Excess reagent was decomposed by the additon of ethyl acetate. After diluting with diethyl ether, the mixture was washed with aqueous potassium sodium tartarate, and the aqueous layer was extracted with diethyl ether two times. The ether extracts were combined, dried, and evaporated. Column chromatography using a mixed solvent of toluene and ethyl acetate (3 : 1) afforded crystalline **4** (3.25 g, 97%). recrystallization from diisopropyl ether–hexane (4 : 1) fur-

Table 6. ^{13}C NMR Spectral Data[a)]

Compd	δ/ppm ($J_{C,F}$/Hz)									
	C-1	C-2	C-3	C-4	C-5	C-6	$\underline{Me}_2C$	$Me_2\underline{C}$	MeS	$Ph\underline{C}H_2$
4	104.1	77.8	77.9	81.9	66.5	20.3	26.6 26.9	113.1		72.3
5	105.1	81.7	81.1	81.5	75.2	18.7	26.2 26.8	112.0	39.0	72.1
6	105.1	81.4	81.3	82.1	79.2	17.8	26.2 26.7	112.0	38.3	71.8
7	103.9	77.5	77.2	79.8	78.0	17.1	26.6 26.9	113.3	38.1	72.2
8	104.0	77.3	78.1	80.2	77.4	18.2	26.5 26.8	113.2	38.8	72.3
15	104.1	77.6	77.0	80.2	88.9	16.4	26.6 26.9	113.0		72.1
			(5.7)	(20.4)	(172.5)	(22.5)				
16	104.2	77.4	77.1	80.2	87.3	17.3	26.5 26.8	113.0		72.4
			(5.7)	(18.3)	(174.1)	(23.3)				
20	103.7	77.6	81.8	79.1	134.8	118.8	26.5 26.7	112.9		72.2
22	104.1	77.2	77.1	77.1	80.7	62.4	26.5 26.9	113.3	38.9	72.1
23	104.1	77.1	77.0	77.5	80.6	61.8	26.5 26.8	113.5	38.2	72.3
24	104.1	77.4	79.1	77.1	51.0	44.2	26.5 26.8	113.2		72.4

a) Data for carbons of phenyl groups are not shown.

nished an analytical sample of **4**; mp 68.1—68.9 °C, $[\alpha]_D$ +120.7° (*c* 1, $CHCl_3$).

Found: C, 65.14; H, 7.54%. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53%.

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-5-*O*-methylsulfonyl-β-L-talofuranose (8). To a solution of **4** (270 mg, 0.918 mmol) in pyridine (2.2 ml), mesyl chloride (0.11 ml, 1.40 mmol) was added dropwise at −10 °C, and the resulting solution was stirred at room temperature for 3 h. A work-up and chromatography were performed in the same manner as described for the preparation of **7**. Crystalline **8** (328 mg, 96%) obtained was recrystallized from diisopropyl ether containing a small amount of ethyl acetate to form prisms; mp 135.1—136.2 °C, $[\alpha]_D$ +90.0° (*c* 0.95, $CHCl_3$).

Found: C, 55.01; H, 6.59; S, 8.37%. Calcd for $C_{17}H_{24}O_7S$: C, 54.82; H, 6.50, S, 8.16%.

Fluorination of the Mesylates with TBAF. A solution of a mesylate (372 mg, 1.00 mmol) and TBAF (1.58 g, 5.00 mmol) in DMF (3.0 ml) was stirred at 120 °C for 18 h. DMF was removed by evaporation, and the residue was dissolved in chloroform. The solution was washed with water, drived over anhydrous sodium sulfate, and evaporated. Column chromatography was performed by using a gradient mixed-solvent system of toluene–ethyl acetate (30 : 1→8 : 1) to isolate the products.

Fluorination of the Triflates with TASF. To a solution of a 5-hydroxy compound such **1**, **2**, **3**, or **4** (320 mg, 1.09 mmol) in dichloromethane (8.0 ml) and pyridine (0.53 ml, 6.55 mmol), triflic anhydride (0.46 ml, 2.73 mmol) was slowly added under efficient stirring at 0 °C, and the stirring was continued for 1 h. The mixture was diluted with dichloromethane, washed with 2% aqueous hydrogen chloride and then water, and dried over anhydrous sodium sulfate. Evaporation left a residue, which was dissolved in dichloromethane (8.0 ml). TASF (900 mg, 3.27 mmol) was added to the solution at 0 °C, and the soluton was stirred at 40 °C for 1 h. The mixture was diluted with dichloromethane, washed with water, and dried over anhydrous sodium sulfate. Evaporation left a residue, which was chromatographed using a gradient mixed-solvent system of toluene–ethyl acetate (30 : 1→8 : 1) to isolate the products.

Fluorination of 5-Hydroxy Compounds with DAST. To a cooled solution of a 5-hydroxy compound (350 mg, 1.19 mmol) in dichloromethane (7.0 ml), DAST (0.24 ml, 1.80 mmol) was added dropwise at −10 °C. The solution was stirred at −10 °C for 0.5 h, and then at room temperature for 1 h. 5% Aqueous sodium hydrogencarbonate (30 ml) was added to the reaction mixture at 0 °C under vigorous stirring. After stirring for 0.5 h, the mixture was extracted with chloroform, and the organic layer was washed with water and dried over anhydrous sodium sulfate. Column chromatography using a grandient mixed-solvent system of toluene–ethyl acetate (30 : 1→8 : 1) was used to isolate the products.

3-*O*-Benzyl-5,6-dideoxy-5-fluoro-1,2-*O*-isopropylidene-α-D-allofuranose (15) and 3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hex-5-enofuranose (20). The reaction of the mesylate **8** with TBAF was conducted as described aobve. Column chromatography provided **15** (131 mg, 44%) and **20** (125 mg, 45%). The

reactions of **12** with TASF and of **4** with DAST analogously produced **15** and **20**.

15: $[\alpha]_D$ +103.8° (*c* 1, $CHCl_3$). ^{19}F NMR ($CDCl_3$) δ=−23.35 (ddq, $J_{F,H\text{-}4}$=22 Hz, $J_{F,H\text{-}5}$=49 Hz, $J_{F,H\text{-}6}$=24 Hz, F-5).

Found: C, 64.21; H, 7.20%. Calcd for $C_{16}H_{21}FO_4$: C, 64.85; H, 7.14%.

20: $[\alpha]_D$ +63.2° (*c* 1.5, $CHCl_3$) (lit,[16] $[\alpha]_D$ +64±0.5° (*c* 1, $CHCl_3$)).

Found: C, 69.71; H, 7.41%. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30%.

3-*O*-Benzyl-5,6-dideoxy-5-fluoro-1,2-*O*-isopropylidene-β-L-talofuranose (16) and 20. The reaction of **7** with TBAF was conducted as described above. Column chromatography provided **16** (59.4 mg, 20%) and **20** (190 mg, 69%). Analogously, the reactions of **11** with TASF and of **3** with DAST produced **16** and **20**.

16: $[\alpha]_D$ +108.0° (*c* 2, $CHCl_3$). ^{19}F NMR ($CDCl_3$) δ=−28.39 (ddq, $J_{F,H\text{-}4}$=25 Hz, $J_{F,H\text{-}5}$=47 Hz, $J_{F,H\text{-}6}$=24 Hz, F-5).

Found: C, 64.67; H, 7.09%. Calcd for $C_{16}H_{21}FO_4$: C, 64.85; H, 7.14%.

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