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Fluorination by anchimeric assistance of a diallylamino group: application to the synthesis of some methyl aminofluoropentofuranosides

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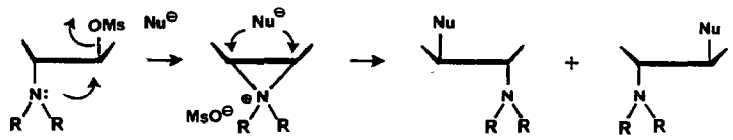
ABSTRACT

Methyl 2,3-*trans*-dialkylaminofluoro-α(or β)-D-pentofuranosides were prepared by fluorination wherein the dialkylamino group assists the replacement of a *trans*-vicinal mesylate. Whatever the location of the dialkylamino group (α or β face of the ring), the regioselectivity of fluorination depends mainly on the α or β orientation of the anomeric methoxyl group. The use of a diallylamino substituent led to methyl 3-amino-2,3-dideoxy-2-fluoro-β-D-xylofuranoside, methyl 2-amino-2,3-dideoxy-3-fluoro-α-D-arabinofuranoside, methyl 2-amino-2,3-dideoxy-3-fluoro-β-D-xylofuranoside, and methyl 3-amino-2,3-dideoxy-2-fluoro-α-D-arabinofuranoside. Attempts to obtain 2(or 3),5-difluoro analogues starting from corresponding dimesylates gave only disappointing results.

INTRODUCTION

In a preceding paper[1], we showed that methyl glycopyranosides having dialkylamino and mesylate groups in a *trans* relationship undergo an intramolecular reaction in which the amino group assists the replacement of the mesylate by a nucleophile such as fluoride ion (Scheme 1). 3-Amino-2-fluoro-2,3,6-trideoxy-L-galactose (2α-fluoro-L-daunosamine) was synthesised by using this reaction[2]. Some recent reports on antiviral nucleosides described syntheses of fluorofuranoses[3],

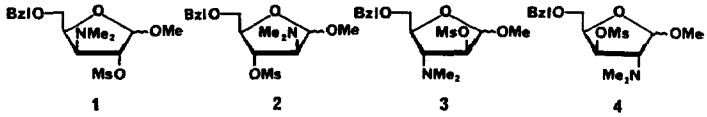


Scheme 1.

and we wished to apply this fluorination reaction to furanoside synthesis. Because of the formation of an intermediary aziridinium ion, the regioselectivity of fluorination of pyranosides is governed by the preference for diaxial opening of the aziridinium ring. In furanosides, there is no bias from axial and equatorial orientations, but attack of the fluoride anion (usually solvated or chelated) is expected to favor the ring face that is not hindered by bulky groups at C-1 or C-4.

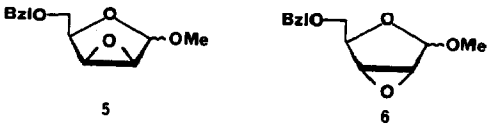
RESULTS AND DISCUSSION

Fluorination at C-2 or C-3.—In previous work[4], we recorded synthesis of the eight furanosides **1**–**4** (α and β, Scheme 2) and showed that they were in pairwise equilibrium (**1** ⇆ **2** and **3** ⇆ **4**) with an intermediate aziridinium ion, the formation of which is generally the slow step in slightly polar solvents. Furthermore, we



Scheme 2.

observed that, unlike chlorination, fluorination of **1**β with[5] $Et_3N \cdot 2HF$ led to the two aminofluorofuranosides **15**β + **16**β, the ratio of which reflects the ease of approach of the fluoride ion at C-2 or C-3. The intermediacy of an aziridinium ion explains the identical results obtained with any pair of starting materials (**1** or **2**, and **3** or **4**). For example, yields, reaction time, and regioselectivity are the same when **1**β or **2**β are fluorinated. On the other hand, the free-energy difference between the two transition states for **1**α and **2**α explains the different reaction times (9 and 2 h, respectively), for these two stereoisomers; it is more difficult to form the cyclic ion from **1**α. This accords with Richardson's work[6], in which substitution of a mesylate at C-2 was more difficult (in pyranosides) when the directions of the approaching nucleophile and the anomeric methoxyl group are antiperiplanar. In order to utilize the procedure for the preparation of fluorinated primary amines, we decided to examine the reaction in corresponding *N*,*N*-diallylamines which could subsequently be *N*,*N*-dideallylated with palladium-on-charcoal in water, as previously reported[7]. *N*,*N*-Diallyl derivatives were synthesised from the epoxides **5**α and **5**β, and **6**α and **6**β (Scheme 3), obtained through benzylation[4] of methyl 2,3-anhydro-α(or β)-D-lyxofuranoside[8] and methyl 2,3-

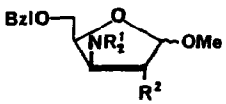


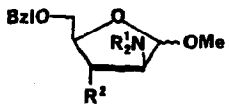
Scheme 3.

anhydro-α(or β)-D-ribofuranoside[9], respectively. Epoxides **5α** and **6α** reacted with diallylamine to furnish, after subsequent mesylation[10], the 3-diallylamino-α-D-*arabino* (**11α**) and 2-diallylamino-α-D-*arabino* (**10α**) derivatives, respectively. In contrast, **5β** gave a 3:1 mixture of 3-diallylamino-β-D-*arabino* (**12β**) and 2-diallylamino-β-D-*xylo* (**13β**) compounds, which were mesylated to give a mixture of **11β** + **14β**. Because of steric hindrance, the epoxide **6β** was unreactive towards diallylamine, and so it was necessary to work in two steps. Epoxide opening with ammonia gave a 9:1 mixture of the 3-amino-β-D-*xylo* (**7β**) and 2-amino-β-D-*arabino* (**8β**) isomers, which were *N*,*N*-diallylated by allyl bromide and then mesylated to give the mixed mesylates **9β** + **10β**. The results of fluorination of the dimeth-

TABLE I

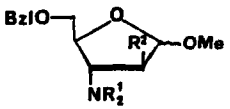
Fluorination [a] of the dimethyl (or diallyl) aminomesylates; yields and regioselectivity

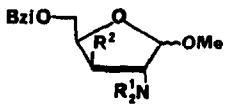




1 : R^1=Me, R^2=OMs
7[b]: R^1=H, R^2=OH
9[b]: R^1=All, R^2=OMs
15[b]: R^1=Me, R^2=F
19[b]: R^1=All, R^2=F

2: R^1=Me, R^2=OMs
8[b]: R^1=H, R^2=OH
10: R^1=All, R^2=OMs
16: R^1=Me, R^2=F
20: R^1=All, R^2=F





3 : R^1=Me, R^2=OMs
11 : R^1=All, R^2=OMs
12 : R^1=All, R^2=OH
17 : R^1=Me, R^2=F
21[c] : R^1=All, R^2=F

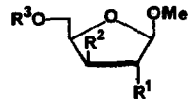
4[b] : R^1=Me, R^2=OMs
13[b] : R^1=All, R^2=OH
14[b] : R^1=All, R^2=OMs
18 : R^1=Me, R^2=F
22 : R^1=All, R^2=F

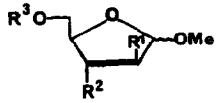
R^1 = Me			R^1 = All		
Starting compounds [d]	Products [e] yield (%)		Starting compounds	Products yield (%)	
	2-Fluoro	3-Fluoro		2-Fluoro	3-Fluoro
1α + **2α**		**16α** (80)	**10α**		**20α** (72)
1β + **2β**	**15β** (16)	**16β** (64)	**9β** + **10β**	**19β** (18)	**20β** (56)
3α	**17α** (85)	**18α** (11)	**11α**	**21α** (77)	**22α** (8)
3β + **4β**	**17β** (3)	**18β** (87)	**11β** + **14β**		**22β** (75)

[a] MeCN, $Et_3N \cdot 2HF$, 75°C. [b] Obtained only as β anomers. [c] Obtained only as the α anomer. [d] For the preparation of these, see ref 4. [e] For the formation of **16α** and **15β** + **16β**, see refs 14 and 4, respectively.

TABLE II

^{19}F NMR data and specific rotations of methyl amino- and dimethylamino-fluoropentofuranosides [a]





23β: R^1=F, R^2=NH_2, R^3=Bzl
25β : R^1=NH_2, R^2=F, R^3=Bzl
27β : R^1=F, R^2=NH_2, R^3=H
29β : R^1=NH_2, R^2=F, R^3=H
31β : R^1=F, R^2=NMe_2, R^3=H
33β : R^1=NMe_2, R^2=F, R^3=H

24 (α and β) : R^1=NH_2, R^2=F, R^3=Bzl
26α : R^1=F, R^2=NH_2, R^3=Bzl
28 (α and β) : R^1=NH_2, R^2=F, R^3=H
30α : R^1=F, R^2=NH_2, R^3=H
32 (α and β) : R^1=NMe_2, R^2=F, R^3=H
34α : R^1=F, R^2=NMe_2, R^3=H

	δF	$J_{1,F}$	$J_{2,F}$	$J_{3,F}$	$J_{4,F}$	$[\alpha]_D^{25}$	($CHCl_3$)
23β	−189.6	12.7	50.5	17.3		−65	(*c* 1.2)
24α	−179.7		18.3	54.5	26.6	+66	(*c* 1)
24β	−196.3		23.3	57.4	21.8	−69	(*c* 1.1)
25β	−195.6		15.7	52.5	26.8	−67.5	(*c* 1.2)
26α	−185.0	10.3	51.4	25.5		+97	(*c* 1.1)
27β	−188.2	12.5	51.3	20.0		−127	(*c* 1)
28α	−180.8		16.4	53.7	27.1	+115	(*c* 1)
28β	−194.4		22.4	56.8	23.0	−93	(*c* 1)
29β	−195.4		16.5	53.0	24.6	−83	(*c* 1)
30α	−185.2	10.2	51.3	24.8		+145	(*c* 1)
31β	−189.3	15.4	55.0	28.5		−60.5	(*c* 0.7)
32α	−194.9		21.1	54.6	15.3	+89	(*c* 0.3)
32β	−185.4		25.8	57.6	24.0	−97	(*c* 0.7)
33β	−198.9		23.8	53.7	16.1	−47	(*c* 1.4)
34α	−184.7	12.1	52.2	31.7		+148	(*c* 0.9)

[a] Compounds **31β**, **32α**, and **32β** have been previously described[14].

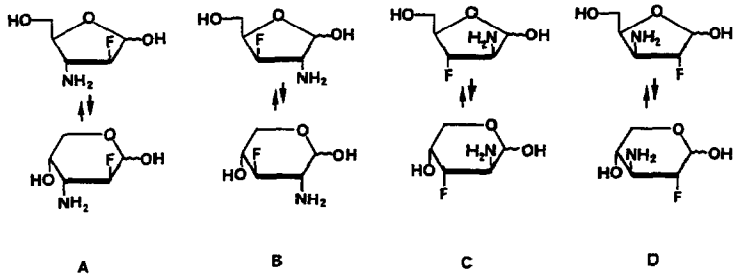
ylaminomesylates (**1–4**) and the diallylaminomesylates (**9–11** and **14**) are given in Table I. The structures of fluorinated compounds were established by ^1H NMR: the value of $J_{1,2}$*cis* is always greater than $J_{1,2}$*trans*[11] and there is a characteristic $^3J_{1,F}$ coupling constant for C-2 fluorinated products (see Table II); ^{13}C NMR shows two characteristic coupling constants ($^2J_{C\text{-}1,F}$ or $^2J_{C\text{-}4,F}$) depending on the position of fluorine. Methyl dimethylaminofluorofuranosides (**31–34**) were then obtained by C-5 debenzylation in acidic medium[12]. Diallylated compounds **19–22** were deallylated (Pd–C) giving **23–26**, but yields were always ~ 40%; this may be due to the presence of the *O*-benzyl group, and it might be better to use allyl as the protecting group because it is possible to remove the three allyl groups at the same time[13]. A final debenzylation proceeded with good yield (71–87%) to give the aminofluorofuranosides **27–30** (minor products **17β**, **18β**, and **22α** had not been deprotected). ^{19}F NMR and $[\alpha]_D$ data are shown in Table II.

From the results reported in Table 1 (R^1=All), it appears that, depending on which of the four *trans*-2(or 3)-amino-2,3-dideoxy-3(or 2)-fluoropentoses **A–D** is

TABLE III

Synthetic pathways to the four aminofluoro sugar A–D

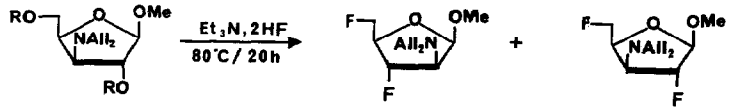
$5\alpha \rightarrow \rightarrow \rightarrow 21\alpha \rightarrow 26\alpha \rightarrow 30\alpha \cdots > A$	$5\beta \rightarrow \rightarrow \rightarrow 22\beta \rightarrow 25\beta \rightarrow 29\beta \cdots > B$
$6\alpha \rightarrow \rightarrow \rightarrow 20\alpha \rightarrow 24\alpha \rightarrow 28\alpha \cdots > C$	$6\beta \rightarrow \rightarrow \rightarrow 19\beta \rightarrow 23\beta \rightarrow 27\beta \cdots > D$



A B C D

wanted, suitable epoxides may be used as starting material; the four synthetic pathways are summarized in Table III.

Fluorination attempts at C-5.—Fluorination in the ring having given good results, we also tried to obtain 2,5- or 3,5-difluorinated furanosides starting from dimesylates, as previously described[14] for pyranoside derivatives. When the dialkylamino group is on the β face, fluorination does not occur because of the formation of stable azetidinium or pyrrolidinium ions, as recently reported[15]. One exception must be noted: starting from methyl 3-deoxy-3-diallylamino-2,5-di-*O*-methylsulfonyl-β-D-xylofuranoside (**36β**), the difluorinated derivatives **37β** and **38β** were obtained in moderate yields (Scheme 4). In this case, the first intermediate was an azetidinium ion (as previously observed for the dimethylamino analogue[15]) which underwent opening perhaps because of the great steric hindrance between one of the allyl groups and the anomeric methoxyl group. Fluoride ion attacks this azetidinium ion at C-5 rather than at C-3 because of the bulkiness of the C-2 mesyloxy group. The same regioselectivity was recently reported for an activated oxetane complex of a furanoside[16]. The 5-fluoro derivative analogue of **36β** is thus formed and then the assisted fluorination previously observed takes place, giving a mixture of the difluorinated compounds **37β** and **38β**. When the dialkylamino group is on the α face, heterocyclisation cannot occur, but fluorination at C-5 was nevertheless very difficult, as shown in Table IV. $Et_3N \cdot 2HF$ was not nucleophilic



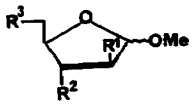
35β R=H
36β R=Ms

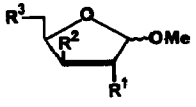
37β(44%) 38β(9%)

Scheme 4.

TABLE IV

Attempted C-5 fluorination of methyl furanosides having a dimethylamino group at the α face





39 (α and β) : R^1=R^3=OH, R^2=NMe_2
40 (α and β) : R^1=R^3=OMs, R^2=NMe_2
43α : R^1=F, R^2=NMe_2, R^3=OMs
45α : R^1=R^3=F, R^2=NMe_2

41β : R^1=NMe_2, R^2=R^3=OH
42β : R^1=NMe_2, R^2=R^3=OMs
44 (α and β) : R^1=NMe_2, R^2=F, R^3=OMs
46β : R^1=NMe_2, R^2=R^3=F

Mesylates	Products	Yield (%)	
		$Et_3N \cdot 2HF$	$Et_4N^+HF_2^-$
40α	**43**α	62	[a]
	44α	14	
43α	**45**α	0	21
40β + **42**β	**44**β		11
	46β		11

[a] Complex mixture.

enough to substitute the mesyloxy group at C-5. When the more efficient fluorinating agent $Et_4N^+HF_2^-$ was used, the difluorinated compounds **45**α or **46**β were obtained, but in poor yields probably because the strong basicity of the reagent leads to decomposition products.

In conclusion, assisted fluorination of diallylaminomesylates may lead to the four *trans*-2(or 3)-amino-2,3-dideoxy-3(or 2)-fluoropentoses (after deprotection and hydrolysis), but access to difluorinated derivatives seems very difficult or impossible starting from dimesylates. A strategy based on C-5 fluorination of starting epoxides, followed by the four steps just described (ring opening, mesylation, fluorination, and deprotection) might lead to 2,5- or 3,5-difluorinated derivatives. This work is currently in progress.

EXPERIMENTAL

General methods.—Melting points were determined with a Kofler apparatus and are uncorrected. Specific rotations were determined with a Perkin–Elmer 141 polarimeter. NMR spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si). ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker AM 300 instrument. Chemical shifts (δ) were recorded downfield from internal Me_4Si; ^{19}F NMR spectra were recorded with a Bruker AC 200 instrument with internal $CFCl_3$ and coupling constants (J in Hz) are first order; * indicates that δ values may have to be interchanged. TLC was performed on Kieselgel 60 F_{254} (Merck) and flash chromatography on Kieselgel 60 H (Merck).

General procedure for epoxide opening (method A).—A mixture of epoxide (1

mmol), DMF (1.5 mL), water (0.6 mL), and diallylamine (1.3 mL) was heated under reflux. When the reaction was complete (TLC), the solution was concentrated in vacuo and poured into ether (3 mL). The organic layer was washed with 2M HCl (0.7 mL) followed by satd aq K_2CO_3 (1 mL), and water. After concentration, the residual amino alcohols were purified by flash chromatography.

General procedure for mesylations (method B).—Amino alcohols were dissolved in CH_2Cl_2 and Et_3N (1.5 equiv). After cooling (−30°C), mesyl chloride (1.1 equiv) was added dropwise; when the reaction was complete (TLC), the mixture was poured into satd aq $NaHCO_3$, then extracted three times with CH_2Cl_2, and the organic layer was dried (Na_2SO_4), filtered, and concentrated in vacuo. Mesylates were generally not purified (unstable).

General procedure for fluorinations with $Et_3N \cdot 2HF$ (method C).—To a solution of the mesylate in MeCN (10%) were added Et_3N (1 equiv) and $Et_3N \cdot 3HF$ (2.1 equiv). The mixture was heated at 80°C and poured slowly into a stirred mixture of CH_2Cl_2 and aq $NaHCO_3$ when TLC indicated the reaction to be complete. The organic layer was washed, dried, filtered, and concentrated. The fluorinated compounds were purified by flash chromatography.

General procedure for debenzylations (method D).—To benzylated compound (1 g) dissolved in EtOH (0.6 mL), was added 2M HCl (3 equiv) and 10% Pd–C (230 mg), and the mixture was stirred under H_2 at 100 kPa. When debenzylation was complete (TLC), the catalyst was filtered off and the filtrate was made neutral by the addition of aq NaOH. After evaporation of EtOH, the mixture was saturated with NaCl and extracted with CH_2Cl_2. Conventional work-up including flash chromatography gave the purified compounds.

General procedure for dideallylation (method E).—The *N,N*-diallylated compound (1 g) was dissolved in water (3 mL), AcOH (3 mL), and EtOH (6 mL), then 10% Pd–C (170 mg) was added. The mixture was heated at 85°C under N_2 with a condenser maintained at 55°C to strip off the propanal. After completion of the reaction (TLC), the mixture was filtered, the filtrate was concentrated in vacuo, and primary amines were purified by flash chromatography.

Methyl 3-amino-5-O-benzyl-3-deoxy-β-D-xylofuranoside (**7β**) *and methyl 2-amino-5-O-benzyl-2-deoxy-β-D-arabinofuranoside* (**8β**).—A mixture of epoxide[4] **6β** (0.25 g) and NH_4OH (2 mL, 30 equiv) was heated at 100°C in a stainless-steel apparatus. The reaction was complete after 90 h (TLC, 10:1 CH_2Cl_2–MeOH). Ammonia was allowed to evaporate in vacuo, and flash chromatography (15:1 CH_2Cl_2–MeOH) of the product gave **7β** and **8β** (not separable) in a 9:1 ratio (determined by ^{13}C NMR) as a yellow syrup (0.254 g, 95%).

Compound **7β**: NMR, ^1H: δ 4.76 (s, 1 H, H-1), 4.55 and 4.54 (2d, 2 H, CH_2Ph, *J* 12.0), 4.44 (m, 1 H, H-4, Σ *J* 18.0), 4.05 (s, 1 H, H-2), 3.95 (3 H, OH, NH_2), 3.67–3.65 (m, 2 H, H-5,5′), 3.30 (s, 3 H, OMe), 3.30 (s, 1 H, H-3). ^{13}C: δ 109.1 (C-1), 80.5* (C-4), 79.9* (C-2), 73.5 (CH_2Ph), 69.3 (C-5), 58.8 (C-3), 55.1 (OMe).

Compound **8β**: NMR, ^{13}C: δ 102.9 (C-1), 81.9* (C-4), 76.2* (C-3), 73.3 (CH_2Ph), 72.2 (C-5), 61.0 (C-2), 54.9 (OMe).

Methyl 5-O-benzyl-3-deoxy-3-diallylamino-2-O-methylsulfonyl-β-D-xylofuranoside (**9β**) *and methyl 5-O-benzyl-2-deoxy-2-diallylamino-3-O-methylsulfonyl-β-D-arabinofuranoside* (**10β**).—A mixture of crude amino alcohols **7β** + **8β** (2.34 g), DMF (60 mL), diisopropylethylamine (3 equiv), and allyl bromide (8 equiv) was heated at 80°C. When the reaction was complete (0.5 h, TLC, 10:1 CH_2Cl_2–MeOH), the mixture was poured into satd aq $NaHCO_3$ and then extracted with EtOAc, and the organic layer was dried (Na_2SO_4), filtered, and concentrated. After flash chromatography (30:1 CH_2Cl_2–MeOH), an unseparable mixture was obtained as a yellow syrup (2.54 g, 82%). The mixture was mesylated according to method B (reaction time, 0.5 h; TLC, 2:1 ether–light petroleum), to give the mesylate mixture **9β** + **10β** as a yellow syrup (3.13 g, 100%).

Methyl 5-O-benzyl-2-deoxy-2-diallylamino-3-O-methylsulfonyl-α-D-arabinofuranoside (**10α**).—Method A starting from epoxide[4] **6α** (2.26 g; reaction time, 5 days; TLC, 30:1 CH_2Cl_2–MeOH). Flash chromatography (50:1 CH_2Cl_2–MeOH) gave methyl 5-O-benzyl-2-deoxy-2-dialkylamino-α-D-arabinofuranoside as a white solid (1.91 g, 60%); mp < 40°C; $[\alpha]_D^{24}$ + 49.1° (c 0.94, $CHCl_3$). NMR, ^1H: δ 5.78 (m, 2 H, 2 × CH=), 5.19 (m, 4 H, 2 × CH_2=), 4.85 (d, 1 H, H-1, $J_{1,2}$ 2.3), 4.58 (s, 2 H, CH_2Ph), 4.09–3.99 (m, 2 H, H-3,4), 3.69–3.68 (m, 2 H, H-5,5′), 3.36 (s, 3 H, OMe), 3.26 (dd, 1 H, H-2, $J_{2,3}$ 5.3), 3.22 and 3.16 (2dd, 4 H, 2 × CH_2N, J_{gem} 14.7, $J_{CH_2 \cdot Hvic}$ 6.4), 3.16 (1 H, OH). ^{13}C: δ 135.5 (2 C, 2 × CH=), 117.7 (2 C, 2 × CH_2=), 105.5 (C-1), 80.4 (C-4), 75.0* (C-3), 74.5* (C-2), 73.5 (CH_2Ph), 69.9* (C-5), 55.1 (OMe), 54.0 (2 C, 2 × CH_2N). Anal. Calcd for $C_{19}H_{27}NO_4$: C, 68.47; H, 8.11; N, 4.20. Found: C, 68.19; H, 8.01; N, 4.20.

The mesylate **10α** was obtained from the preceding compound (1.91 g) as a yellow liquid (2.36 g, 100%) by method B (reaction time, 1.5 h; TLC, 30:1 CH_2Cl_2–MeOH).

Methyl-5-O-benzyl-3-deoxy-3-diallylamino-2-O-methylsulfonyl-α-D-arabinofuranoside (**11α**).—Method A starting from epoxide[4] **5α** (2.9 g; reaction time, 66 h; TLC, 4:1 ether–light petroleum). Flash chromatography (1:1 ether–light petroleum) gave methyl 5-O-benzyl-3-deoxy-3-dialkylamino-α-D-arabinofuranoside as a yellow liquid (3.8 g, 93%), $[\alpha]_D^{30}$ + 6.8° (c 1.09, $CHCl_3$). NMR ^1H: δ 5.83–5.65 (m, 2 H, 2 × CH=), 5.27–5.08 (m, 4 H, 2 × CH_2=), 4.82 (s, 1 H, H-1), 4.62–4.60 (m, 2 H, CH_2Ph), 4.11 (d, 1 H, H-2, $J_{2,3}$ 2.9), 4.03 (ddd, 1 H, H-4, $J_{3,4}$ 7.1, $J_{4,5}$ 2.0, $J_{4,5'}$ 4.6), 3.71 (dd, 1 H, H-5, $J_{5,5'}$ 10.7), 3.59 (dd, 1 H, H-5′), 3.35 (s, 3 H, OMe), 3.23 (dd, 1 H, H-3), 3.24 and 3.08 (2dd, 4 H, 2 × CH_2N, J_{gem} 14.6, $J_{CH_2 \cdot Hvic}$ 3.4 and 7.1), 2.84 (s, 1 H, OH). ^{13}C: δ 136.4 (2 C, 2 × CH=), 117.2 (2 C, 2 × CH_2=), 110.2 (C-1), 79.3* (C-4), 76.8* (C-2), 70.8 (C-5). 70.3 (C-3), 54.7 (OMe), 54.2 (2 C, 2 × CH_2N). Anal. Calcd for $C_{19}H_{27}NO_4$: C, 68.47; H, 8.11; N, 4.20. Found: C, 68.27; H, 8.26; N, 4.57.

The mesylate **11α** was obtained from the preceding compound (1.05 g) as a yellow liquid (1.29 g, 100%) by method B (reaction time, 1 h; TLC, ether).

Methyl-5-O-benzyl-3-deoxy-3-diallylamino-β-D-arabinofuranoside (**12β**) *and methyl-5-O-benzyl-2-deoxy-2-diallylamino-β-D-xylofuranoside* (**13β**).—Method A starting from epoxide[4] **5β** (2.1 g; reaction time, 7 days; TLC, 4:1 ether–light

petroleum). After flash chromatography (1:1 ether–light petroleum), **12β** and **13β** were obtained (not separable) in a 75:25 ratio (determined by ^{1}H NMR) as a yellow liquid (2.7 g, 93%) which was used without purification for the next step. For ^{1}H NMR of **13β**, only separated signals are reported.

Compound **12β**: NMR, ^{1}H: δ 5.90–5.64 (m, 2 H, 2 × CH=), 5.25–5.08 (m, 4 H, 2 × CH_2=), 4.76 (d, 1 H, H-1, $J_{1,2}$ 4.8), 4.58 (s, 2 H, CH_2Ph), 4.22 (dd, 1 H, H-2, $J_{2,3}$ 7.7), 4.03 (td, 1 H, H-4, $J_{3,4}$ 7.4), 3.56 (dd, 1 H, H-5, $J_{4,5}$ 3.3, $J_{5,5'}$ 10.3), 3.48 (dd, 1 H, H-5', $J_{4,5'}$ 7.4), 3.37 (s, 3 H, OMe), 3.16 (t, 1 H, H-3), 2.44 (1 H, OH). ^{13}C: δ 136.3 (2 C, 2 × CH=), 117.2 (2 C, 2 × CH_2=), 102.6 (C-1), 78.5* (C-2), 73.7 (CH_2Ph), 73.3* (C-4), 73.3 (C-5), 67.0 (C-3), 55.0 (OMe), 53.8 (2 C, 2 × CH_2N).

Compound **13β**: NMR, ^{1}H: δ 4.91 (s, 1 H, H-1), 3.34 (s, 3 H, OMe). ^{13}C: δ 135.3 (2 C, 2 × CH=), 117.8 (2 C, 2 × CH_2=), 107.0 (C-1), 93.6 (C-3), 80.4 (C-4), 73.6 (CH_2Ph), 72.8 (C-2), 69.1 (C-5), 55.6 (OMe), 54.0 (2 C, 2 × CH_2N).

Methyl 5-O-benzyl-3-deoxy-3-diallylamino-2-O-methylsulfonyl-β-D-arabinofuranoside (**11β**) *and methyl 5-O-benzyl-2-deoxy-2-diallylamino-3-O-methylsulfonyl-β-D-xylofuranoside* (**14β**).—The mesylates **11β** and **14β** were obtained (not separable) from the preceding mixture (2.7 g) as a yellow liquid (3.2 g, 96%) by method B (reaction time, 2 h; TLC, ether).

Methyl 5-O-benzyl-2,3-dideoxy-3-dimethylamino-2-fluoro-α-D-arabinofuranoside (**17α**) *and methyl 5-O-benzyl-2,3-dideoxy-2-dimethylamino-3-fluoro-α-D-xylofuranoside* (**18α**).—Method C starting from mesylate[4] **3α** (1 g; reaction time, 5 h; TLC, ether). The two compounds were isolated by flash chromatography (1:1 ether–light petroleum), giving successively **17α** (0.67 g, 85%) and **18α** (0.09 g, 11%) as yellow liquids.

Compound **17α**: $[\alpha]_D^{28}$ + 102.0° (*c* 1.1, $CHCl_3$). NMR, ^{1}H: δ 5.05 (d, 1 H, H-1, $J_{1,F}$ 12.0), 4.95 (dd, 1 H, H-2, $J_{2,3}$ 2.2, $J_{2,F}$ 52.0), 4.62 (s, 2 H, CH_2Ph), 4.15 (ddd, 1 H, H-4, $J_{3,4}$ 8.0, $J_{4,5}$ 2.4, $J_{4,5'}$ 5.9), 3.73 (dd, 1 H, H-5, $J_{5,5'}$ 11.0), 3.63 (dd, 1 H, H-5'), 3.38 (s, 3 H, OMe), 2.96 (ddd, 1 H, H-3, $J_{3,F}$ 37.5), 2.29 (s, 6 H, NMe_2). ^{13}C: δ 106.7 (d, 1 C, C-1, $J_{1,F}$ 36.1), 95.9 (d, 1 C, C-2, $J_{2,F}$ 179.5), 79.2 (d, 1 C, C-4, $J_{4,F}$ 4.0), 73.8 (CH_2Ph), 72.7 (d, 1 C, C-3, $J_{3,F}$ 23.4), 71.2 (C-5), 54.9 (OMe), 43.4 (s, 2 C, NMe_2). ^{19}F: δ −184.4. Anal. Calcd for $C_{15}H_{22}FNO_3$: C, 63.60; H, 7.77; F, 6.71; N, 4.95. Found: C, 63.61; H, 7.88; F, 6.52; N, 4.95.

Compound **18α**: $[\alpha]_D^{28}$ + 56.8° (*c* 0.66, $CHCl_3$). NMR, ^{1}H: δ 5.21 (ddd, 1 H, H-3, $J_{2,3}$ 4.6, $J_{3,4}$ 5.5, $J_{3,F}$ 56.0), 4.95 (d, 1 H, H-1, $J_{1,2}$ 4.4), 4.63 (s, 2 H, CH_2Ph), 4.47 (m, 1 H, H-4, Σ *J* 37.0, $J_{4,F}$ 21.0), 3.78–3.59 (m, 2 H, H-5,5'), 3.41 (s, 3 H, OMe), 2.77 (ddd, 1 H, H-2, $J_{2,F}$ 31.0), 2.36 (s, 6 H, NMe_2). ^{19}F: δ −196.0 (insufficient material for elemental analysis and ^{13}C NMR).

Methyl 5-O-benzyl-2,3-dideoxy-3-dimethylamino-2-fluoro-β-D-arabinofuranoside (**17β**) *and methyl 5-O-benzyl-2,3-dideoxy-2-dimethylamino-3-fluoro-β-D-xylofuranoside* (**18β**).—Method C starting from the mesylate mixture **3β** + **4β** (0.5 g; reaction time, 3 days; TLC, 1:2 light petroleum–AcOEt). After flash chromatography (1:1 light petroleum–AcOEt), **17β** and **18β** were obtained (not separable) in a 4:96 ratio (determined by ^{1}H NMR) as a yellow liquid (0.35 g, 90%), **17β** + **18β**:

$[\alpha]_D^{22}$ −44.8° (*c* 1.36, $CHCl_3$). Anal. Calcd for $C_{15}H_{22}FNO_3$: C, 63.60; H, 7.77; F, 6.71; N, 4.95. Found: C, 63.84; H, 7.91; F, 6.43; N, 5.15.

Compound **17β**: NMR, ^{19}F: δ −199.5, $J_{1,F}$ or $J_{3,F}$ 20.0, $J_{2,F}$ 51.0.

Compound **18β**: NMR, ^1H: δ 5.08 (ddd, 1 H, H-3, $J_{2,3}$ 2.3, $J_{3,4}$ 5.3, $J_{3,F}$ 53.2), 4.86 (d, 1 H, H-1, $J_{1,2}$ 2.8), 4.61 (s, 2 H, CH_2Ph), 4.35 (m, 1 H, H-4, Σ *J* 39.0, $J_{4,F}$ 21.0), 3.81–3.65 (m, 2 H, H-5,5′, $J_{5,F}$ 1.7, $J_{5',F}$ 1.7), 3.43 (s, 3 H, OMe), 2.98 (ddd, 1 H, H-2, $J_{2,F}$ 24.7), 2.32 (s, 6 H, NMe_2). ^{13}C: δ 106.8 (d, 1 C, C-1, $J_{1,F}$ 4.1), 93.3 (d, 1 C, C-3, $J_{3,F}$ 187.8), 79.6 (d, 1 C, C-4, $J_{4,F}$ 20.4), 76.8 (d, 1 C, C-2, $J_{2,F}$ 23.4), 73.5 (CH_2Ph), 68.7 (d, 1 C, C-5, $J_{5,F}$ 12.4), 55.9 (OMe), 43.3 (NMe_2). ^{19}F: δ −195.6.

*Methyl 5-O-benzyl-3-diallylamino-2,3-dideoxy-2-fluoro-β-*D*-xylofuranoside* (**19β**) *and methyl 5-O-benzyl-2-diallylamino-2,3-dideoxy-3-fluoro-β-*D*-arabinofuranoside* (**20β**).—Method C starting from the mesylate mixture **9β** + **10β** (5.3 g; reaction time, 1.5 h; TLC, 2:1 ether–light petroleum). The two compounds were isolated by flash chromatography (1:8 ether–light petroleum) giving successively **19β** (0.8 g, 18%) and **20β** (2.4 g, 56%) as yellow syrups.

Compound **19β**: $[\alpha]_D^{28}$ −34.2° (*c* 0.84, $CHCl_3$). NMR, ^1H: δ 5.83–5.70 (m, 2 H, 2 × CH=), 5.19–5.12 (m, 4 H, 2 × CH_2=), 5.04 (dd, 1 H, H-1, $J_{1,2}$ 1.9, $J_{1,F}$ 16.2), 5.00 (ddd, 1 H, H-2, $J_{2,3}$ 5.8, $J_{2,F}$ 53.6), 4.59 (s, 2 H, CH_2Ph), 4.44 (ddd, 1 H, H-4, $J_{3,4}$ 8.0, $J_{4,5}$ 3.2, $J_{4,5'}$ 8.0), 3.70 (dd, 1 H, H-5, $J_{4,5}$ 3.2, $J_{5,5'}$ 10.9), 3.62 (dd, 1 H, H-5′), 3.54 (ddd, 1 H, H-3, $J_{3,F}$ 27.3), 3.41 (s, 3 H, OMe), 3.19–3.11 (m, 4 H, 2 × CH_2N). ^{13}C: δ 134.4 (s, 2 C, 2 × CH=), 117.9 (s, 2 C, 2 × CH_2=), 108.2 (d, 1 C, C-1, $J_{1,F}$ 36.5), 99.0 (d, 1 C, C-2, $J_{2,F}$ 182.1), 81.3 (d, 1 C, C-4, $J_{4,F}$ 7.2), 73.5 (CH_2Ph), 70.2 (C-5), 66.9 (d, 1 C, C-3, $J_{3,F}$ 20.9), 55.8 (OMe), 54.4 (s, 2 C, 2 × NCH_2). ^{19}F: δ −189.9. Anal. Calcd for $C_{19}H_{26}FNO_3$: C, 68.06; H, 7.76; F, 5.67; N, 4.18. Found: C, 67.92; H, 7.79; F. 5.68; N, 4.02.

Compound **20β**: $[\alpha]_D^{26}$ −29.6° (*c* 0.97, $CHCl_3$). NMR, ^1H: δ 5.97–5.84 (m, 2 H, 2 × CH=), 5.22–5.15 (m, 4 H, 2 × CH_2=), 5.11 (ddd, 1 H, H-3, $J_{2,3}$ 7.1, $J_{3,4}$ 4.4, $J_{3,F}$ 57.4), 4.87 (d, 1 H, H-1, $J_{1,2}$ 4.5), 4.57 (s, 2 H, CH_2Ph), 4.31 (dddd, 1 H, H-4, $J_{4,5}$ 6.6, $J_{4,5'}$ 6.6, $J_{4,F}$ 23.9), 3.60 (dd, 1 H, H-5, $J_{5,5'}$ 11.0), 3.58 (dd, 1 H, H-5′), 3.41 (ddd, 1 H, H-2, $J_{2,F}$ 24.8), 3.34–3.27 (m, 4 H, 2 × CH_2N), 3.30 (s, 3 H, OMe). ^{13}C: δ 134.1 (s, 2 C, 2 × CH=), 118.4 (s, 2 C, 2 × CH_2=), 104.0 (d, 1 C, C-1, $J_{1,F}$ 10.7), 97.1 (d, 1 C, C-3, $J_{3,F}$ 182.8), 80.8 (d, 1 C, C-4, $J_{4,F}$ 27.2), 73.4 (CH_2Ph), 71.8 (d, 1 C, C-5, $J_{5,F}$ 5.2), 69.0 (d, 1 C, C-2, $J_{2,F}$ 19.3), 54.8 (OMe), 54.1 (s, 2 C, 2 × NCH_2). ^{19}F: δ −186.7. Anal. Calcd for $C_{19}H_{26}FNO_3$: C, 68.06; H, 7.76; F, 5.67; N, 4.18. Found: C, 68.32; H, 7.64; F, 5.53; N, 4.11.

*Methyl 5-O-benzyl-2-diallylamino-2,3-dideoxy-3-fluoro-α-*D*-arabinofuranoside* (**20α**).—Method C starting from the mesylate **10α** (2.28 g; reaction time, 5 h; TLC, 1:2 ether–light petroleum). Flash chromatography (ether) gave **20α** as a yellow syrup (1.34 g, 72%), $[\alpha]_D^{29}$ +53.4° (*c* 0.8, $CHCl_3$). NMR, ^1H: δ 5.86–5.72 (m, 2 H, 2 × CH=), 5.22–5.12 (m, 4 H, 2 × CH_2=), 4.99 (ddd, 1 H, H-3, $J_{2,3}$ 4.5, $J_{3,4}$ 7.0, $J_{3,F}$ 55.3), 4.87 (d, 1 H, H-1, $J_{1,2}$ 2.1), 4.60 (s, 2 H, CH_2Ph), 4.25 (dddd, 1 H, H-4, $J_{4,5}$ 3.0, $J_{4,5'}$ 4.3, $J_{4,F}$ 16.8), 3.74 (dd, 1 H, H-5, $J_{5,5'}$ 11.0), 3.68 (dd, 1 H, H-5′), 3.54 (ddd, 1 H, H-2, $J_{2,F}$ 23.9), 3.38 (s, 3 H, OMe), 3.18–3.14 (m, 4 H, 2 × CH_2N).

^{13}C: δ 135.1 (s, 2 C, 2 × CH=), 117.9 (s, 2 C, 2 × CH_2=), 106.1 (d, 1 C, C-1, $J_{1,F}$ 9.1), 93.4 (d, 1 C, C-3, $J_{3,F}$ 184.7), 79.1 (d, 1 C, C-4, $J_{4,F}$ 26.9), 73.6 (CH_2Ph), 72.6 (d, 1 C, C-2, $J_{2,F}$ 21.0), 68.6 (C-5), 55.1 (OMe), 53.9 (s, 2 C, 2 × NCH_2). ^{19}F: δ −194.0. Anal. Calcd for $C_{19}H_{26}FNO_3$: C, 68.06; H, 7.76; F, 5.67; N, 4.18. Found: C, 68.02; H, 7.81; F, 5.69; N, 4.10.

Methyl 5-O-benzyl-3-diallylamino-2,3-dideoxy-2-fluoro-α-D-arabinofuranoside (**21α**) *and methyl 5-O-benzyl-2-diallylamino-2,3-dideoxy-3-fluoro-α-D-xylofuranoside* (**22α**).—Method C starting from the mesylate **11α** (5.7 g; reaction time, 10 h; TLC, 1:1 ether–light petroleum). The two compounds were isolated by flash chromatography (1:8 ether–light petroleum) giving successively **21α** (3.5 g, 77%) and **22α** (0.37 g, 8%) as yellow syrups.

Compound **21α**: $[\alpha]_D^{28}$ + 96.6° (*c* 1.1, $CHCl_3$). NMR, ^1H: δ 5.78–5.65 (m, 2 H, 2 × CH=), 5.19–4.99 (m, 4 H, 2 × CH_2=), 5.01 (d, 1 H, H-1, $J_{1,F}$ 12.1), 4.93 (dd, 1 H, H-2, $J_{2,3}$ 2.4, $J_{2,F}$ 52.8), 4.61 (s, 2 H, CH_2Ph), 3.99 (ddd, 1 H, H-4, $J_{3,4}$ 8.8, $J_{4,5}$ 1.8, $J_{4,5'}$ 5.8), 3.73 (dd, 1 H, H-5, $J_{5,5'}$ 11.0), 3.62 (dd, 1 H, H-5'), 3.42 (ddd, 1 H, H-3, $J_{3,F}$ 32.7), 3.36 (s, 3 H, OMe), 3.27–3.00 (m, 4 H, 2 × CH_2N). ^{13}C: δ 135.8 (s, 2 C, 2 × CH=), 117.4 (s, 2 C, 2 × CH_2=), 106.8 (d, 1 C, C-1, $J_{1,F}$ 36.5), 95.7 (d, 1 C, C-2, $J_{2,F}$ 182.1), 78.9 (d, 1 C, C-4, $J_{4,F}$ 5.1), 73.5 (CH_2Ph), 70.4 (C-5), 68.0 (d, 1 C, C-3, $J_{3,F}$ 23.5), 54.4 (s, 2 C, 2 × CH_2N), 54.3 (OMe). ^{19}F: δ −184.0. Anal. Calcd for $C_{19}H_{26}FNO_3$: C, 68.06; H, 7.76; F, 5.67; N, 4.18. Found: C, 67.67; H, 7.77; F, 5.61; N, 4.13.

Compound **22α**: $[\alpha]_D^{22}$ + 48.2° (*c* 0.86, $CHCl_3$). NMR, ^1H: δ 5.97–5.84 (m, 2 H, 2 × CH=), 5.24–5.15 (m, 4 H, 2 × CH_2=), 5.24 (ddd, 1 H, H-3, $J_{2,3}$ 5.1, $J_{3,4}$ 5.8, $J_{3,F}$ 57.3), 4.96 (d, 1 H, H-1, $J_{1,2}$ 4.6), 4.60 (s, 2 H, CH_2Ph), 4.41 (dddd, 1 H, H-4, $J_{4,5}$ 4.2, $J_{4,5'}$ 7.0, $J_{4,F}$ 20.8), 3.73 (ddd, 1 H, H-5, $J_{5,5'}$ 10.7, $J_{5,F}$ 1.7), 3.64 (ddd, 1 H, H-5', $J_{5',F}$ 1.6), 3.41 (ddd, 1 H, H-2, $J_{2,F}$ 31.0), 3.38 (s, 3 H, OMe), 3.33–3.25 (m, 4 H, 2 × CH_2N). ^{13}C: δ 134.3 (s, 2 C, 2 × CH=), 118.4 (s, 2 C, 2 × CH_2=), 102.6 (d, 1 C, C-1, $J_{1,F}$ 9.9), 95.2 (d, 1 C, C-3, $J_{3,F}$ 185.5), 76.8 (d, 1 C, C-4, $J_{4,F}$ 20.1), 73.6 (CH_2Ph), 70.6 (d, 1 C, C-2, $J_{2,F}$ 22.3), 68.1 (d, 1 C, C-5, $J_{5,F}$ 15.2), 55.0 (OMe), 54.4 (s, 2 C, 2 × CH_2N). ^{19}F: δ −195.3. Anal. Calcd for $C_{19}H_{26}FNO_3$: C, 68.06; H, 7.76; F, 5.67; N, 4.18. Found: C, 67.86; H, 7.75; F, 5.34; N, 3.89.

Methyl 5-O-benzyl-3-diallylamino-2,3-dideoxy-3-fluoro-β-D-xylofuranoside (**22β**).—Method C starting from the mesylate mixture **11β** + **14β** (1.7 g; reaction time, 66 h; TLC, 1:1 ether–light petroleum). Flash chromatography (1:4 ether–light petroleum) gave **22β** as a yellow syrup (1.04 g, 75%), $[\alpha]_D^{29}$ −38.9° (*c* 1.1, $CHCl_3$). NMR, ^1H: δ 5.85–5.72 (m, 2 H, 2 × CH=), 5.25–5.13 (m, 4 H, 2 × CH_2=), 5.11 (ddd, 1 H, H-3, $J_{2,3}$ 1.9, $J_{3,4}$ 5.4, $J_{3,F}$ 53.2), 4.88 (d, 1 H, H-1, $J_{1,2}$ 2.3), 4.57 (s, 2 H, CH_2Ph), 4.35 (dddd, 1 H, H-4, $J_{4,5}$ 5.0, $J_{4,5'}$ 7.3, $J_{4,F}$ 21.5), 3.74 (ddd, 1 H, H-5, $J_{5,5'}$ 10.2, $J_{5,F}$ 1.5), 3.68 (ddd, 1 H, H-5', $J_{5',F}$ 1.7), 3.50 (ddd, 1 H, H-2, $J_{2,F}$ 24.9), 3.38 (s, 3 H, OMe), 3.22–3.08 (m, 4 H, 2 × CH_2N). ^{13}C: δ 135.0 (s, 2 C, 2 × CH=), 118.0 (s, 2 C, 2 × CH_2=), 106.9 (d, 1 C, C-1, $J_{1,F}$ 4.1), 93.5 (d, 1 C, C-3, $J_{3,F}$ 187.2), 80.3 (d, 1 C, C-4, $J_{4,F}$ 20.4), 73.5 (s, 1 C, CH_2Ph), 72.6 (d, 1 C, C-2, $J_{2,F}$ 23.7), 69.0 (d, 1 C, C-5, $J_{5,F}$ 13.2), 55.6 (OMe), 53.9 (s, 2 C, 2 × CH_2N). ^{19}F: δ −196.0. Anal.

Calcd for $C_{19}H_{26}FNO_3$: C, 68.06; H, 7.76; F, 5.67; N, 4.18. Found: C, 68.42; H, 8.08; F, 5.48; N, 4.24.

Methyl 3-amino-5-O-benzyl-2,3-dideoxy-2-fluoro-β-D-xylofuranoside (**23β**).— Method E starting from the *N,N*-diallylamine **19β** (0.25 g; reaction time, 23 h; TLC, 2:1 ether–light petroleum). Flash chromatography (light petroleum) gave **23β** as a yellow syrup (0.075 g, 40%), $[\alpha]_D^{23}$ −65.3° (*c* 1.22, $CHCl_3$). NMR, ^{1}H: δ 4.97 (d, 1 H, H-1), 4.74 (d, 1 H, H-2), 4.59 (s, 2 H, CH_2Ph), 4.45 (q, 1 H, H-4, $J_{3,4} = J_{4,5} = J_{4,5'}$ 5.9), 3.71 (dd, 1 H, H-5, $J_{5,5'}$ 10.0), 3.67 (dd, 1 H, H-5'), 3.54 (dd, 1 H, H-3), 3.36 (s, 3 H, OMe), 1.47 (s, 2 H, NH_2). ^{13}C: δ 106.5 (d, 1 C, C-1, $J_{1,F}$ 33.5), 99.9 (d, 1 C, C-2, $J_{2,F}$ 181.0), 80.9 (C-4), 73.5 (CH_2Ph), 69.3 (C-5), 56.3 (d, 1 C, C-3, $J_{3,F}$ 23.2), 55.3 (OMe). ^{19}F: see Table II. Because of the small quantity obtained, elemental analysis was performed at the next step (see **27β**).

Methyl 2-amino-5-O-benzyl-2,3-dideoxy-3-fluoro-α-D-arabinofuranoside (**24α**).— Method E starting from the *N,N*-diallylamine **20α** (1 g; reaction time, 28 h: TLC, 1:1 ether–light petroleum). Flash chromatography (ether) gave **24α** as a yellow syrup (0.29 g, 38%), $[\alpha]_D^{27}$ +66.4° (*c* 1.13, $CHCl_3$). NMR, ^{1}H: δ 4.80 (s, 1 H, H-1), 4.75 (dd, 1 H, H-3, $J_{3,4}$ 2.4), 4.60 (s, 2 H, CH_2Ph), 4.34 (m, 1 H, H-4), 3.73–3.64 (m, 2 H, H-5,5'), 3.48 (d, 1 H, H-2), 3.40 (s, 3 H, OMe), 1.58 (s, 2 H, NH_2). ^{13}C: δ 110.9 (C-1), 99.1 (d, 1 C, C-3, $J_{3,F}$ 184.8), 82.8 (d, 1 C, C-4, $J_{4,F}$ 27.6), 73.6 (CH_2Ph), 69.1 (d, 1 C, C-5, $J_{5,F}$ 7.6), 62.2 (d, 1 C, C-2, $J_{2,F}$ 22.5), 55.0 (OMe). ^{19}F: see Table II. Anal. Calcd for $C_{13}H_{18}FNO_3$: C, 61.18; H, 7.06; F, 7.45; N, 5.49. Found: C, 61.56; H, 7.03; F, 6.73; N, 5.71.

Methyl 2-amino-5-O-benzyl-2,3-dideoxy-3-fluoro-β-D-arabinofuranoside (**24β**).— Method E starting from the *N,N*-diallylamine **20β** (2.76 g; reaction time, 23 h; TLC, 2:1 ether–light petroleum). Flash chromatography (ether) gave **24β** as a yellow syrup (0.86 g, 41%), $[\alpha]_D^{29}$ −69.0° (*c* 1.14, $CHCl_3$). NMR, ^{1}H: δ 4.75 (d, 1 H, H-1, $J_{1,2}$ 4.6), 4.67 (ddd, 1 H, H-3, $J_{2,3}$ 6.7, $J_{3,4}$ 5.3), 4.57 (s, 2 H, CH_2Ph), 4.21 (m, 1 H, H-4), 3.56 (m, 1 H, H-5), 3.55 (m, 1 H, H-5'), 3.51 (ddd, 1 H, H-2), 3.32 (s, 3 H, OMe), 1.92 (s, 2 H, NH_2). ^{13}C: δ 103.6 (d, 1 C, C-1, $J_{1,F}$ 10.3), 99.6 (d, 1 C, C-3, $J_{3,F}$ 183.9), 79.7 (d, 1 C, C-4, $J_{4,F}$ 25.2), 73.2 (CH_2Ph), 71.4 (d, 1 C, C-5, $J_{5,F}$ 4.3), 60.3 (d, 1 C, C-2, $J_{2,F}$ 21.1), 55.1 (OMe). ^{19}F: see Table II. Anal. Calcd for $C_{13}H_{18}FNO_3$: C, 61.18; H, 7.06; F, 7.45; N, 5.49. Found: C, 61.15; H, 7.13; F, 7.06; N, 5.59.

Methyl 2-amino-5-O-benzyl-2,3-dideoxy-3-fluoro-β-D-xylofuranoside (**25β**).— Method E starting from the *N,N*-diallylamine **22β** (0.2 g; reaction time, 26 h; TLC, 2:1 ether–light petroleum). Flash chromatography (15:1 CH_2Cl_2–MeOH) gave **25β** as a pale yellow liquid (0.072 g, 46%), $[\alpha]_D^{31}$ −67.5° (*c* 1.16, $CHCl_3$). NMR, ^{1}H: δ 4.75 (dd, 1 H, H-3, $J_{3,4}$ 4.2), 4.72 (s, 1 H, H-1), 4.60 (s, 2 H, CH_2Ph), 4.51 (dddd, 1 H, H-4, $J_{4,F}$ 26.8, $J_{4,5}$ 5.3, $J_{4,5'}$ 2.0), 3.77 (dd, 1 H, H-5, $J_{5,5'}$ 9.8), 3.72 (dd, 1 H, H-5'), 3.57 (d, 1 H, H-2), 3.36 (s, 3 H, OMe), 1.43 (s, 2 H, NH_2). ^{13}C: δ 110.4 (C-1), 96.9 (d, 1 C, C-3, $J_{3,F}$ 187.3), 80.4 (d, 1 C, C-4, $J_{4,F}$ 19.4), 73.4 (CH_2Ph), 68.8 (d, 1 C, C-5, $J_{5,F}$ 13.6), 62.1 (d, 1 C, C-2, $J_{2,F}$ 23.9), 55.3 (OMe). ^{13}F: see Table II. Because of the small quantity obtained, elemental analysis was performed at the next step (see **29β**).

Methyl 3-amino-5-O-benzyl-2,3-dideoxy-2-fluoro-α-D-arabinofuranoside (**26α**).—Method E starting from the *N,N*-diallylamine **21α** (0.3 g; reaction time, 41 h; TLC, 1:1 ether—light petroleum). Flash chromatography (1:1 ether–light petroleum) gave **26α** as a pale yellow liquid (0.097 g, 43%), $[\alpha]_D^{26}$ +96.6° (*c* 1.0, $CHCl_3$). NMR, ^1H: δ 5.04 (d, 1 H, H-1), 4.65 (dd, 1 H, H-2, $J_{2,3}$ 1.6), 4.60 (s, 2 H, CH_2Ph), 3.96 (m, 1 H, H-4, Σ *J* 16.2, $J_{3,4}$ 5.4), 3.68–3.59 (m, 2 H, H-5,5′), 3.37 (s, 3 H, OMe), 3.27 (ddd, 1 H, H-3), 1.53 (s, 2 H, NH_2). ^{12}C: δ 106.5 (d, 1 C, C-1, $J_{1,F}$ 34.2), 101.5 (d, 1 C, C-2, $J_{2,F}$ 182.2), 84.9 (d, 1 C, C-4, $J_{4,F}$ 1.7), 73.5 (CH_2Ph), 70.7 (C-5), 59.0 (d, 1 C, C-3, $J_{3,F}$ 23.5), 54.8 (OMe). ^{19}F: see Table II. Because of the small quantity obtained, elemental analysis was performed at the next step (see **30α**).

Methyl 3-amino-2,3-dideoxy-2-fluoro-β-D-xylofuranoside (**27β**).—Method D starting from the *O*-benzyl **23β** (0.3 g; reaction time, 17 h; TLC, 10:1 CH_2Cl_2–MeOH). Flash chromatography (10:1 CH_2Cl_2–MeOH) gave **27β** as a pale yellow liquid (0.2 g, 87%). NMR, ^1H: δ 4.91 (d, 1 H, H-1), 4.69 (d, 1 H, H-2), 4.28 (q, 1 H, H-4, $J_{3,4} = J_{4,5} = J_{4,5'}$ 5.1), 3.72 (t, 1 H, H-5, $J_{5,5'}$ 12.0), 3.69 (t, 1 H, H-5′), 3.53 (dd, 1 H, H-3), 3.32 (s, 3 H, OMe), 2.53 (s, 3 H, OH, NH_2). ^{13}C: δ 106.6 (d, 1 C, C-1, $J_{1,F}$ 33.7), 100.7 (d, 1 C, C-2, $J_{2,F}$ 183.1), 81.7 (C-4), 61.6 (C-5), 56.7 (d, 1 C, C-3, $J_{3,F}$ 22.8), 55.3 (OMe). For $[\alpha]_D$ and ^{19}F: see Table II. Anal. Calcd for $C_6H_{12}FNO_3$: C, 43.64; H, 7.27; N, 8.48; F, 11.52. Found: C, 43.57; H, 7.49; N, 8.28; F, 11.11.

Methyl 2-amino-2,3-dideoxy-3-fluoro-α-D-arabinofuranoside (**28α**).—Method D starting from the *O*-benzyl **24α** (0.34 g; reaction time, 17 h; TLC, 10:1 CH_2Cl_2–MeOH). Flash chromatography (12:1 CH_2Cl_2–MeOH) gave **28α** as a white solid (0.20 g, 77%), mp 80°C. NMR, ^1H: δ 4.80 (s, 1 H, H-1), 4.75 (dd, 1 H, H-3, $J_{3,4}$ 2.3), 4.36 (qd, 1 H, H-4, $J_{4,5} = J_{4,5'}$ 2.3), 3.83 (dd, 1 H, H-5, $J_{5,5'}$ 12.2), 3.75 (dd, 1 H, H-5′), 3.56 (d, 1 H, H-2), 3.40 (s, 3 H, OMe), 2.85 (s, 3 H, OH, NH_2). ^{13}C: δ 110.2 (C-1); 98.2 (d, 1 C, C-3, $J_{3,F}$ 184.0), 84.6 (d, 1 C, C-4, $J_{4,F}$ 26.2), 61.4 (d, 1 C, C-2, $J_{2,F}$ 23.5), 60.0 (d, 1 C, C-5, $J_{5,F}$ 8.4), 55.0 (OMe). For $[\alpha]_D$ and ^{19}F: see Table II. Anal. Calcd for $C_6H_{12}FNO_3$: C, 43.64; H, 7.27; N, 8.48; F, 11.52. Found: C, 43.44; H, 7.47; N, 8.41; F, 11.33.

Methyl 2-amino-2,3-dideoxy-3-fluoro-β-D-arabinofuranoside (**28β**).—Method D starting from the *O*-benzyl **24β** (0.86 g; reaction time, 16 h; TLC, 10:1 CH_2Cl_2–MeOH). Flash chromatography (8:1 CH_2Cl_2–MeOH) gave **28β** as a colourless liquid (0.44 g, 68%). NMR , ^1H: δ 4.85 (d, 1 H, H-1, $J_{1,2}$ 4.7), 4.78 (ddd, 1 H, H-3, $J_{2,3}$ 6.0, $J_{3,4}$ 4.5), 4.17 (qd, 1 H, H-4, $J_{4,5} = J_{4,5'}$ 4.5); 3.72 (dd, 1 H, H-5, $J_{5,5'}$ 11.8), 3.68 (dd, 1 H, H-5′), 3.58 (ddd, 1 H, H-2), 3.45 (s, 3 H, OMe), 2.46 (s, 3 H, OH, NH_2). ^{13}C: δ 103.9 (d, 1 C, C-1, $J_{1,F}$ 9.0), 98.7 (d, 1 C, C-3, $J_{3,F}$ 182.9), 82.1 (d, 1 C, C-4, $J_{4,F}$ 24.9), 63.0 (d, 1 C, C-5, $J_{5,F}$ 5.3), 60.0 (d, 1 C, C-2, $J_{2,F}$ 22.0), 56.0 (OMe). For $[\alpha]_D$ and ^{19}F: see Table II. Anal. Calcd for $C_6H_{12}FNO_3$: C, 43.64; H, 7.27; N, 8.48; F, 11.52. Found: C, 43.97; H, 7.11; F, 11.36; N, 8.71.

Methyl 2-amino-2,3-dideoxy-3-fluoro-β-D-xylofuranoside (**29β**).—Method D starting from the *O*-benzyl **25β** (0.26 g; reaction time, 16 h; TLC, 6:1 CH_2Cl_2–MeOH). Flash chromatography (6:1 CH_2Cl_2–MeOH) gave **29β** as a yellow solid

(0.14 g, 71%), mp 96°C. NMR, ^{1}H: δ 4.78 (ddd, 1 H, H-3, $J_{2,3}$ 1.0, $J_{3,4}$ 4.7), 4.68 (s, 1 H, H-1), 4.39 (m, 1 H, H-4, ΣJ 41.2), 3.85–3.70 (m, 2 H, H-5,5′), 3.56 (dd, 1 H, H-2), 3.34 (s, 3 H, OMe), 2.10 (s, 3 H, OH, NH_2). ^{13}C: δ 110.7 (C-1), 97.7 (d, 1 C, C-3, $J_{3,F}$ 187.8), 82.2 (d, 1 C, C-4, $J_{4,F}$ 19.8), 62.8 (d, 1 C, C-2, $J_{2,F}$ 23.9), 61.8 (d, 1 C, C-5, $J_{5,F}$ 13.4), 56.1 (OMe). For $[\alpha]_D$ and ^{19}F: see Table II. Anal. Calcd for $C_6H_{12}FNO_3$: C, 43.64; H, 7.27; F, 11.52; N, 8.48. Found: C, 43.87; H, 7.53; F, 11.95; N, 8.70.

*Methyl 3-amino-2,3-dideoxy-2-fluoro-α-*D*-arabinofuranoside* (**30α**).—Method D starting from the *O*-benzyl **26α** (0.43 g; reaction time, 18 h; TLC, 10:1 CH_2Cl_2–MeOH). Flash chromatography (10:1 CH_2Cl_2–MeOH) gave **30α** as a colourless liquid (0.25 g, 77%). NMR, ^{1}H: δ 5.03 (d, 1 H, H-1), 4.68 (dd, 1 H, H-2, $J_{2,3}$ 1.2), 3.87 (m, 1 H, H-4, ΣJ 14.4), 3.82–3.69 (m, 2 H, H-5,5′), 3.38 (s, 3 H, OMe), 3.32 (ddd, 1 H, H-3, $J_{3,4}$ 5.1), 2.53 (s, 3 H, OH, NH_2). ^{13}C: δ 106.4 (d, 1 C, C-1, $J_{1,F}$ 34.0), 101.5 (d, 1 C, C-2, $J_{2,F}$ 182.3), 86.2 (d, 1 C, C-4, $J_{4,F}$ 1.8), 62.4 (C-5), 57.7 (d, 1 C, C-3, $J_{3,F}$ 23.5), 54.7 (OMe). For $[\alpha]_D$ and ^{19}F: see Table II. Anal. Calcd for $C_6H_{12}FNO_3$: C, 43.64; H, 7.27; N, 8.48. Found: C, 43.67; H, 7.27; N, 8.20.

*Methyl 2,3-dideoxy-2-dimethylamino-3-fluoro-β-*D*-xylofuranoside* (**33β**) *and methyl 2,3-dideoxy-3-dimethylamino-2-fluoro-β-*D*-arabinofuranoside* (**34β**).—Method D starting from the *O*-benzyl mixture **17β** + **18β** (0.24 g; reaction time, 19 h; TLC, 6:1 CH_2Cl_2–MeOH). After chromatography (6:1 CH_2Cl_2–MeOH), **33β** and **34β** were obtained (not separable) in a 96:4 ratio (determined by ^{19}F NMR) as a yellow liquid (0.15 g, 79%).

Compound **33β**: NMR, ^{1}H: δ 5.13 (ddd, 1 H, H-3, $J_{2,3}$ 3.9, $J_{3,4}$ 6.2), 4.84 (d, 1 H, H-1, $J_{1,2}$ 3.1), 4.29 (m, 1 H, H-4, ΣJ 30.8), 3.87–3.76 (m, 2 H, H-5,5′), 3.46 (s, 3 H, OMe), 3.26 (s, 1 H, OH), 3.00 (ddd, 1 H, H-2), 2.32 (s, 6 H, NMe_2). ^{13}C: δ 106.9 (d, 1 C, C-1, $J_{1,F}$ 6.4), 93.5 (d, 1 C, C-3, $J_{3,F}$ 187.0), 80.6 (d, 1 C, C-4, $J_{4,F}$ 21.0), 76.5 (d, 1 C, C-2, $J_{2,F}$ 21.9), 61.2 (d, 1 C, C-5, $J_{5,F}$ 10.2), 56.0 (OMe), 43.5 (s, 2 C, NMe_2). For $[\alpha]_D$ and ^{19}F: see Table II.

Compound **34β**: NMR ^{19}F: δ −200.3 ($J_{1,F}$ or $J_{3,F}$ 20.6, $J_{2,F}$ 56.6). Surprisingly this mixture seems to be unstable: three attempts to obtain elemental analysis after purification always gave unsatisfactory results.

*Methyl 2,3-dideoxy-3-dimethylamino-2-fluoro-α-*D*-arabinofuranoside* (**34α**).—Method D starting from the *O*-benzyl **17α** (0.3 g; reaction time, 19 h; TLC, 6:1 CH_2Cl_2–MeOH). Flash chromatography (8:1 CH_2Cl_2–MeOH) gave **34α** as a yellow syrup (0.15 g, 64%). NMR, ^{1}H: δ 5.02 (d, 1 H, H-1), 5.00 (dd, 1 H, H-2, $J_{2,3}$ 2.4), 4.08 (ddd, 1 H, H-4, $J_{3,4}$ 7.9, $J_{4,5}$ 3.0, $J_{4,5'}$ 4.5), 3.90 (dd, 1 H, H-5, $J_{5,5'}$ 12.0), 3.76 (dd, 1 H, H-5′), 3.38 (s, 3 H, OMe), 3.09 (ddd, 1 H, H-3), 2.59 (s, 1 H, OH), 2.35 (s, 6 H, NMe_2). ^{13}C: δ 106.4 (d, 1 C, C-1, $J_{1,F}$ 36.1), 95.7 (d, 1 C, C-2, $J_{2,F}$ 179.6), 79.6 (d, 1 C, C-4, $J_{4,F}$ 4.0), 71.6 (d, 1 C, C-3, $J_{3,F}$ 23.5), 62.8 (C-5), 54.5 (OMe), 43.1 (s, 2 C, NMe_2). For $[\alpha]_D$ and ^{19}F: see Table II. Anal. Calcd for $C_8H_{16}FNO_3$: C, 49.74; H, 8.29; F, 9.84; N, 7.25. Found: C, 49.47; H, 8.37; F, 9.73; N, 7.52.

*Methyl 3-deoxy-3-diallylamino-β-*D*-xylofuranoside* (**35β**).—A mixture of methyl

2,3-anhydro-β-D-ribofuranoside[9] (0.96 g) and NH_4OH (8 mL, 30 equiv) was heated at 100°C in a stainless-steel apparatus. When the reaction was complete (16 h, TLC, 3:1 CH_2Cl_2–MeOH), the solution was concentrated in vacuo. After flash chromatography (10:1 CH_2Cl_2–MeOH), methyl 3-amino-3-deoxy-β-D-xylofuranoside[17] was obtained as a yellow syrup (1.07 g, 100%). A mixture of the preceding aminoalcohol (1.07 g), DMF (60 mL), diisopropylethylamine (3 equiv), and allyl bromide (8 equiv) was heated at 80°C. When the reaction was complete (0.5 h, TLC, 10:1 CH_2Cl_2–MeOH), the mixture was poured into a satd aq $NaHCO_3$, then extracted with EtOAc, and the organic layer was dried (Na_2SO_4), filtered, and concentrated in vacuo. After flash chromatography (15:1 CH_2Cl_2–MeOH), **35β** (1.12 g, 70%) was obtained as a yellow syrup which was used without purification for the next step. NMR, ^1H: δ 5.94–5.81 (m, 2 H, 2 × CH=), 5.24–5.16 (m, 4 H, 2 × CH_2=), 4.82 (d, 1 H, H-1, $J_{1,2}$ 3.2), 4.34 (dd, 1 H, H-2, $J_{2,3}$ 7.6), 4.26 (td, 1 H, H-4, $J_{3,4}$ 7.2, $J_{4,5} = J_{4,5'}$ 5.2), 3.74 (dd, 1 H, H-5, $J_{5,5'}$ 12.3), 3.72 (dd, 1 H, H-5'), 3.43 (t, 1 H, H-3), 3.43 (s, 3 H, OMe), 3.31 and 3.25 (2dd, 4 H, 2 × CH_2N, J_{gem} 14.6, $J_{H,Hvic}$ 6.4 and 6.2), 3.31 (m, 2 H, OH). ^{13}C: δ 135 (2 C, 2 × CH=), 118.4 (2 C, 2 × CH_2=), 110.9 (C-1), 80.4* (C-2), 77.4* (C-4), 68.4 (C-3), 63.0 (C-5), 56.2 (OMe), 54.8 (2 C, 2 × CH_2N).

Methyl 3-deoxy-3-diallylamino-2,5-di-O-methylsulfonyl-β-D-xylofuranoside (**36β**). —Method B starting from the *N,N*-diallylamine **35β** (3.22 g; reaction time, 0.5 h; TLC, 4:1 ether–light petroleum); **36β** was isolated as a very unstable white solid (4.49 g, 85%). NMR (C_6D_6), ^1H: δ 5.69–5.56 (m, 2 H, 2 × CH=), 5.15–5.00 (m, 5 H, 2 × CH_2=, H-2), 4.86 (d, 1 H, H-1, $J_{1,2}$ 2.2), 4.44–4.20 (m, 3 H, H-4,5,5'), 3.16 (dd, 1 H, H-3, $J_{2,3}$ 4.0, $J_{3,4}$ 13.2), 3.14 (s, 3 H, OMe), 3.18 and 3.04 (2dd, 4 H, 2 × CH_2N), 2.34 (s, 3 H, OMs), 2.30 (s, 3 H, OMs). ^{13}C: δ 134.6 (2 C, 2 × CH=), 118.2 (2 C, 2 × CH_2=), 108.6 (C-1), 84.4* (C-2), 79.3* (C-4), 69.7 (C-5), 66.2 (C-3), 56.1 (OMe), 54.4 (2 C, 2 × CH_2N), 37.9 (OMs), 36.9 (OMs).

Methyl 2-diallylamino-3,5-difluoro-2,3,5-trideoxy-β-D-arabinofuranoside (**37β**) *and methyl 3-diallylamino-2,5,-difluoro-2,3,5-trideoxy-β-D-xylofuranoside* (**38β**).— Method C starting from the dimesylate **36β** (2 g; reaction time, 10 h 30; TLC, 4:1 ether–light petroleum). The mixture was purified by flash chromatography (1:5 ether–light petroleum) giving successively **38β** (0.11 g, 9%), and **37β** (0.54 g, 44%) as yellow syrups.

Compound **37β**: $[\alpha]_D^{21}$ −78.3° (*c* 1.0, $CHCl_3$). NMR, ^1H: δ 5.99–5.85 (m, 2 H, 2 × CH=), 5.23–5.16 (m, 4 H, 2 × CH_2=), 5.17 (ddd, 1 H, H-3, $J_{2,3}$ 7.2, $J_{3,4}$ 4.7, $J_{3,F3}$ 57.3), 4.92 (dd, 1 H, H-1, $J_{1,2}$ 4.4, $J_{1,F3}$ 1.5), 4.59 (ddd, 1 H, H-5, $J_{4,5}$ 5.6, $J_{5,5'}$ 9.7, $J_{5,F5}$ 48.0), 4.56 (ddd, 1 H, H-5', $J_{4,5'}$ 6.1, $J_{5',F5}$ 48.0), 4.35 (tddd, 1 H, H-4, $J_{4,F3}$ 23.5, $J_{4,F5}$ 16.0), 3.46 (ddd, 1 H, H-2, $J_{2,F3}$ 24.2), 3.38 (s, 3 H, OMe), 3.36 and 3.29 (2dd, 4 H, 2 × CH_2N). ^{13}C: δ 134.1 (2 C, 2 × CH=), 118.5 (2 C, 2 × CH_2=), 104.1 (d, C-1, $J_{1,F3}$ 10.9), 95.4 (dd, C-3, $J_{3,F3}$ 183.8, $J_{3,F5}$ 6.0), 83.3 (dd, C-5, $J_{5,F3}$ 5.0, $J_{5,F5}$ 173.4), 80.2 (dd, C-4, $J_{4,F3}$ 28.0*, $J_{4,F5}$ 21.4*), 68.8 (d, C-2, $J_{2,F3}$ 18.8), 55.0 (OMe), 54.2 (2 C, 2 × CH_2N). ^{19}F: δ −227.1 (F-5), −189,0 (F-3). Anal. Calcd for $C_{12}H_{19}F_2NO_2$: C, 58.29; H, 7.69; F, 15.38; N, 5.67. Found: C, 58.22; H, 7.84; F, 15.06; N, 5.63.

Compound **38β**: $[\alpha]_D^{21}$ −96°8 (*c* 1.0, $CHCl_3$). NMR, ^1H: δ 5.87–5.74 (m, 2 H, 2 × CH=), 5.23–5.16 (m, 4 H, 2 × CH_2=), 5.07 (dd, 1 H, H-1, $J_{1,2}$ 2.0, $J_{1,F2}$ 15.7), 5.02 (ddd, 1 H, H-2, $J_{2,3}$ 6.0, $J_{2,F2}$ 53.4), 4.60 (ddd, 1 H, H-5, $J_{4,5}$ 3.6, $J_{5,5'}$ 10.3, $J_{5,F5}$ 47.8), 4.55 (ddd, 1 H, H-5′, $J_{4,5'}$ 7.0, $J_{5',F5}$ 47.8), 4.50 (dddd, 1 H, H-4, $J_{3,4}$ 6.0, $J_{4,F5}$ 18.0), 3.62 (td, 1 H, H-3, $J_{3,F2}$ 27.2), 3.44 (s, 3 H, OMe), 3.22 and 3.15 (2dd, 4 H, 2 × CH_2N). ^{13}C: δ 134.2 (2 C, 2 × CH=), 118.1 (2 C, 2 × CH_2=), 108.2 (d, C-1, $J_{1,F2}$ 36.5), 98.5 (d, C-2, $J_{2,F2}$ 182.2), 83.6 (d, C-5, $J_{5,F5}$ 169.8), 80.4 (dd, C-4, $J_{4,F2}$ 7.5, $J_{4,F5}$ 19.2), 67.0 (dd, C-3, $J_{3,F2}$ 21.3, $J_{3,F5}$ 6.2), 55.8 (OMe), 54.6 (2 C, 2 × CH_2N). ^{19}F: δ −227.1 (F-5), −189.5 (F-2). Anal. Calcd for $C_{12}H_{19}F_2NO_2$: C, 58.29; H, 7.69; F, 15.38; N, 5.67. Found: C, 58.01; H, 7.81; F, 15.22; N, 5.52.

Methyl 3-deoxy-3-dimethylamino-α-D-arabinofuranoside (**39α**).—A mixture of methyl 2,3-anhydro-α-D-lyxofuranoside[8] (3 g) and 80 mL of a 40% aq solution of dimethylamine (50 equiv) was heated at 50°C. When the reaction was complete (7 h, TLC, 3:1 CH_2Cl_2–MeOH), the solution was concentrated in vacuo. After flash chromatography (4:1 CH_2Cl_2–MeOH), **39α** was obtained as a yellow syrup (3.8 g, 98%), $[\alpha]_D^{31}$ +105° (*c* 0.86, $CHCl_3$). NMR, ^1H: δ 4.80 (s, 1 H, H-1), 4.18 (d, 1 H, H-2, $J_{2,3}$ 2.5), 4.11 (dt, 1 H, H-4, $J_{3,4}$ 7.0, $J_{4,5} = J_{4,5'}$ 3.6), 3.91 (dd, 1 H, H-5, $J_{5,5'}$ 12.0), 3.69 (dd, 1 H, H-5′), 3.75 (s, 1 H, OH), 3.36 (s, 3 H, OMe), 2.87 (dd, 1 H, H-3), 2.34 (s, 6 H, NMe_2). ^{13}C: δ 109.7. (C-1), 79.5* (C-2), 76.6* (C-4), 74.0 (C-3), 63.0 (C-5), 54.8 (OMe), 43.2 (2 C, NMe_2). Anal. Calcd for $C_8H_{17}NO_4$: C, 50.20; H, 8.90; N, 7.33. Found: C, 50.36; H, 9.15; N, 7.30.

Methyl 3-deoxy-3-dimethylamino-2,5-di-O-methylsulfonyl-α-D-arabinofuranoside (**40α**).—Method B starting from the dimethylamino derivative **39α** (1.19 g; reaction time, 2.5 h; TLC, 30:1 CH_2Cl_2–MeOH), **40α** was isolated as a white solid (1.77 g, 82%), mp 77°C, $[\alpha]_D^{22}$ +44.9° (*c* 1.13, $CHCl_3$). NMR, ^1H: δ 5.08 (s, 1 H, H-1), 5.05 (d, 1 H, H-2, $J_{2,3}$ 3.1), 4.54 (dd, 1 H, H-5, $J_{4,5}$ 2.1, $J_{5,5'}$ 11.7), 4.35 (dd, 1 H, H-5′, $J_{4,5'}$ 5.1), 4.17 (ddd, 1 H, H-4, $J_{3,4}$ 8.3), 3.40 (s, 3 H, OMe), 3.18 (dd, 1 H, H-3), 3.10 (s, 6 H, 2 × OMs), 2.38 (s, 6 H, NMe_2). ^{13}C: δ 106.2 (C-1), 80.7* (C-2), 75.4* (C-4), 71.4 (C-3), 69.2 (C-5), 55.0 (OMe), 42.5 (2 C, NMe_2), 38.6 (OMs), 37.7 (OMs). Anal. Calcd for $C_{10}H_{21}NO_8S_2$: C, 34.58; H, 6.05; N, 4.03; S, 18.44. Found: C, 35.00; H, 6.15; N, 3.96; S, 18.11.

Methyl 3-deoxy-3-dimethylamino-β-D-arabinofuranoside (**39β**) *and methyl 2-deoxy-2-dimethylamino-β-D-xylofuranoside* (**41β**).—A mixture of methyl 2,3-anhydro-β-D-lyxofuranoside[8] (4 g) and 40% aq dimethylamine (100 mL, 50 equiv) was heated at 50°C. When the reaction was complete (8 h, TLC, 1:2 light petroleum–acetone) the solution was concentrated in vacuo. After flash chromatography (2:1 light petroleum–acetone)., **39β** and **41β** were obtained (not separable) in a 75:25 ratio (determined by ^1H NMR) as a yellow liquid (3.77 g, 72%).

Compound **39β**: NMR, ^1H: δ 4.79 (d, 1 H, H-1, $J_{1,2}$ 4.6), 4.20 (dd, 1 H, H-2, $J_{2,3}$ 7.2), 4.10 (s, 1 H, OH), 4.05 (ddd, 1 H, H-4, $J_{3,4}$ 6.4, $J_{4,5}$ 3.5, $J_{4,5'}$ 6.2), 3.70 (dd, 1 H, H-5, $J_{5,5'}$ 11.5), 3.60 (dd, 1 H, H-5′), 3.47 (s, 3 H, OMe), 2.65 (dd, 1 H, H-3), 2.35 (s, 6 H, NMe_2). ^{13}C: δ 103.0 (C-1), 81.1* (C-2), 74.7* (C-4), 70.7 (C-3), 65.7 (C-5), 55.4 (OMe), 43.2 (2 C, NMe_2).

Compound **41β**: NMR, ^{1}H: δ 4.83 (d, 1 H, H-1, $J_{1,2}$ 2.6), 4.37 (dd, 1 H, H-3, $J_{2,3}$ 5.0, $J_{3,4}$ 6.6), 4.20–4.10 (dt, 1 H, H-4, $J_{4,5}$ 4.7, $J_{4,5'}$ 4.4), 3.87 (dd, 1 H, H-5, $J_{5,5'}$ 12.0), 3.76 (dd, 1 H, H-5′), 3.42 (s, 3 H, OMe), 2.76 (dd, 1 H, H-2), 2.35 (s, 6 H, NMe_2). ^{13}C: δ 106.2 (C-1), 81.1* (C-3), 78.5* (C-4), 73.8 (C-2), 62.1 (C-5), 55.3 (OMe), 43.2 (2 C, NMe_2). Anal. Calcd for $C_8H_{17}NO_4$: C, 50.20; H, 8.90; N, 7.33. Found: C, 50.56; H, 8.72; N, 7.18.

*Methyl 3-deoxy-3-dimethylamino-2,5-di-*O*-methylsulfonyl-β-*D*-arabinofuranoside* (**40β**) *and methyl 2-deoxy-2-dimethylamino-3,5-di-*O*-methylsulfonyl-β-*D*-xylofuranoside* (**42β**).—Method B starting from the preceding mixture (3.0 g; reaction time, 2.5 h; TLC, 6:1 CH_2Cl_2–MeOH). The two compounds **40β** and **42β** were obtained (not separable) in a 75:25 ratio as a red solid (5.45 g, 100%). After crystallisation in toluene, **40β** was obtained as a white solid, mp 100°C.

Compound **40β**: NMR, ^{1}H: δ 5.04–4.99 (m, 2 H, H-1, 2), 4.18 (m, 1 H, H-4, Σ J 17.8), 4.31–4.29 (m, 2 H, H-5,5′), 3.47 (s, 3 H, OMe), 3.28 (m, 1 H, H-3), 3.12 (s, 3 H, OMs), 3.09 (s, 3 H, OMs), 2.38 (s, 6 H, NMe_2). ^{13}C: δ 101.3 (C-1), 76.9* (C-2), 74.6* (C-4), 71.5 (C-5), 67.6 (C-3), 55.5 (OMe), 42.0 (2 C, NMe_2), 39.0 (OMs) 37.7 (OMs). Anal. Calcd for $C_{10}H_{21}NO_8S_2$: C, 34.58; H, 6.05 N, 4.03; S, 18.44. Found: C, 34.52; H, 6.06; N, 4.17; S. 18.60.

Compound **42β**: NMR, ^{1}H: δ 5.24 (dd, 1 H, H-3, $J_{2,3}$ 4.1, $J_{3,4}$ 6.6), 4.92 (d, 1 H, H-1, $J_{1,2}$ 2.2), 4.58 (m, 1 H, H-4, Σ J 18.5), 4.41–4.38 (m, 2 H, H-5,5′), 3.44 (s, 3 H, OMe), 3.22 (dd, 1 H, H-2), 3.14 (s, 3 H, OMs) 3.02 (s, 3 H, OMs), 2.35 (s, 6 H, NMe_2). ^{13}C: δ 106.2 (C-1), 77.9* (C-3), 77.2* (C-4), 75.9 (C-2), 68.1 (C-5), 55.7 (OMe), 42.6 (2 C, NMe_2), 38.6 (OMs), 37.4 (OMs).

*Methyl 2,3-dideoxy-3-dimethylamino-2-fluoro-5-*O*-methylsulfonyl-α-*D*-arabinofuranoside* (**43α**) *and methyl 2,3-dideoxy-2-dimethylamino-3-fluoro-5-*O*-methylsulfonyl-α-*D*-xylofuranoside* (**44α**).—Method C starting from the dimesylate **40α** (0.47 g; reaction time, 24 h; TLC, 1:1 light petroleum–acetone). Flash chromatography (4:1 light petroleum–acetone) gave **43α** as a yellow solid (0.23 g, 62%, mp 48°C), and **44α** as a yellow liquid (0.05 g, 14%).

Compound **43α**: $[\alpha]_D^{25}$ +106.8° (*c* 0.98, $CHCl_3$). NMR, ^{1}H: δ 5.03 (d, 1 H, H-1, $J_{1,F}$ 11.9), 4.98 (dd, 1 H, H-2, $J_{2,3}$ 2.1, $J_{2,F}$ 52.1), 4.55 (dd, 1 H, H-5, $J_{4,5}$ 2.1, $J_{5,5'}$ 11.8), 4.35 (dd, 1 H, H-5′, $J_{4,5'}$ 5.5), 4.18 (ddd, 1 H, H-4, $J_{3,4}$ 7.9), 3.39 (s, 3 H, OMe), 3.09 (s, 3 H, OMs), 3.02 (ddd, 1 H, H-3, $J_{3,F}$ 31.6), 2.32 (s, 6 H, NMe_2). ^{13}C: δ 106.5 (d, C-1, $J_{1,F}$ 36.2), 95.7 (d, C-2, $J_{2,F}$ 180.4). 77.0 (d, C-4, $J_{4,F}$ 4.1), 71.9 (d, C-3, $J_{3,F}$ 24.0), 69.7 (C-5), 54.7 (OMe), 42.9 (2 C, NMe_2), 37.7 (OMs). ^{19}F: δ −184.0. Anal. Calcd for $C_9H_{18}FNO_5S$: C, 39.85; H, 6.64; F, 7.01; N, 5.17. Found: C, 39.93; H, 6.69; F, 6.83; N, 4.89.

Compound **44α**: $[\alpha]_D^{28}$ +52.5° (*c* 0.4, $CHCl_3$). NMR, ^{1}H: δ 5.34 (td, 1 H, H-3, $J_{2,3} = J_{3,4}$ 6.0, $J_{3,F}$ 56.3), 5.04 (d, 1 H, H-1, $J_{1,2}$ 4.3), 4.70–4.30 (m, 3 H, H-4,5,5′), 3.50 (s, 3 H, OMe), 3.12 (s, 3 H, OMs), 2.86 (td, 1 H, H-2, $J_{1,2} = J_{2,3}$ 4.8, $J_{2,F}$ 30.0), 2.40 (s, 6 H, NMe_2). ^{13}C: δ 102.5 (d, C-1, $J_{1,F}$ 10.2), 95.5 (d, C-3, $J_{3,F}$ 186.0): 75.4* (d, C-2, $J_{2,F}$ 21.1), 75.2* (d, C-4, $J_{4,F}$ 19.7), 67.3 (d, C-5, $J_{5,F}$ 17.2), 55.3 (OMe), 44.5 (2 C, NMe_2), 37.6 (OMs). ^{19}F: δ −196.0 ($J_{4,F}$ 19.6). Anal. Calcd for

$C_9H_{18}FNO_5S$: C, 39.85; H, 6.64; F, 7.01; N, 5.17; S, 11.81. Found: C, 39.99; H, 6.83; F, 7.20; N, 5.23; S, 11.97.

Methyl 3-dimethylamino-2,5-difluoro-2,3,5-trideoxy-α-D-arabinofuranoside (**45α**). —A solution of 0.16 g of the mesylate **43α** was dissolved in 2 mL of MeCN, then poured into a flask containing $Et_4N^+HF_2^-$ obtained from 0.88 g of commercially available $Et_4N^+F^- \cdot 2H_2O$ dried at 120°C in vacuo during 0.5 h[18]; after heating at 60°C for 16 h (TLC, 2:1 light petroleum–acetone), processing was the same as in the mesylation procedure (method B). The product was purified by flash chromatography (2:1 light petroleum–acetone) giving **45α** as a yellow syrup (0.03 g, 21%). NMR, ^1H: δ 5.08–5.00 (m, 2 H, H-1, H-2, $J_{1,F2}$ 12.3, $J_{2,F2}$ 51.6), 4.67 (ddd, 1 H, H-5, $J_{4,5}$ 2.3, $J_{5,F5}$ 47.6), 4.52 (ddd, 1 H, H-5′, $J_{4,5'}$ 5.1, $J_{5',F5}$ 47.4), 4.17 (dddd, 1 H, H-4, $J_{3,4}$ 8.4, $J_{4,F5}$ 22.6), 3.38 (s, 3 H, OMe), 3.00 (ddd, 1 H, H-3, $J_{2,3}$ 2.7, $J_{3,F2}$ 31.6), 2.34 (s, 6 H, NMe_2). ^{13}C: δ 106.6 (d, C-1, $J_{1,F2}$ 36.1), 95.1 (dd, C-2, $J_{2,F2}$ 180.1, $J_{2,F5}$ 1.6), 82.9 (d, C-5, $J_{5,F5}$ 174), 78.0 (dd, C-4, $J_{4,F2}$ 4.1, $J_{4,F5}$ 18.3), 71.3 (dd, C-3, $J_{3,F2}$ 23.7, $J_{3,F5}$ 7.2), 54.7 (OMe), 43.1 (2 C, NMe_2). ^{19}F: δ −228.0 (F-5), −184.7 (F-2). Because of the small quantity obtained, an elemental analysis was not made.

Methyl 2,3-dideoxy-2-dimethylamino-3-fluoro-5-O-methylsulfonyl-β-D-xylofuranoside (**44β**) *and methyl 2-dimethylamino-3,5-difluoro-2,3,5-trideoxy-β-D-xylofuranoside* (**46β**).—The mixture of the dimesylates **40β** and **42β** (0.5 g) was submitted to fluorination as described for **43α** (reaction time, 0.5 h; TLC, 1:1 light petroleum–acetone). Flash chromatography (4:1 light petroleum–acetone) gave successively **44β** and **46β** as yellow liquids (0.04 g; 11% each).

Compound **44β**: NMR, ^1H: δ 5.18 (ddd, 1 H, H-3, $J_{3,F}$ 53.0, $J_{2,3}$ 3.6, $J_{3,4}$ 5.7), 4.90 (d, 1 H, H-1, $J_{1,2}$ 2.4), 4.55–4.30 (m, 3 H, H-4,5,5′), 3.57 (s, 3 H, OMe), 3.10 (s, 3 H, OMe), 3.06 (m, 1 H, H-2), 2.43 (s, 6 H, NMe_2). ^{13}C: δ 107.0 (C-1), 93.0 (d, C-3, $J_{3,F}$ 187.0), 78.0* (d, C-4, $J_{4,F}$ 32.4), 76.4* (d, C-2, $J_{2,F}$ 19.8), 68.3 (C-5), 55.8 (OMe), 43.1 (2 C, NMe_2), 37.2 (OMe). ^{19}F: δ −197.7 (ddd, $J_{F,H2}$ 21.0).

Compound **46β**: NMR, ^1H: δ 5.12 (ddd, 1 H, H-3, $J_{3,F3}$ 53.0, $J_{2,3}$ 2.7, $J_{3,4}$ 5.5), 4.88 (d, 1 H, H-1, $J_{1,2}$ 2.5), 4.82–4.55 (m, 2 H, H-5,5′), 4.41–4.31 (m, 1 H, H-4), 3.43 (s, 3 H, OMs), 3.01 (ddd, 1 H, H-2, $J_{2,F3}$ 23.0), 2.30 (s, 6 H, NMe_2). ^{13}C: δ 107.2 (C-1), 93.0 (d, C-3, $J_{3,F3}$ 188.0), 83.1 (d, C-5, $J_{5,F5}$ 170.0), 80.1* (d, C-2, $J_{2,F3}$ 20.0), 76.3* (d, C-4, $J_{4,F}$ 22.1), 56.4 (OMs), 43.1 (2 C, NMe_2). ^{19}F: δ −195 (F-3, $J_{F,H4}$ 16.0), −225 (F-5, $J_{F,H5}$ 64.0). Because of the small quantities obtained, elemental analysis were not made.

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