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Preparation of Acetylated 1-Fluoroglycopyranosyl Cyanides

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Abstract

Reactions of acetylated 1-bromo-1-deoxy-glycopyranosyl cyanides of β-D-*galacto* (**2**) and α-D-*arabino* (**12**) configurations with silver fluoride in acetonitrile at room temperature gave the corresponding 1-deoxy-1-fluoro-glycopyranosyl cyanides (**5** and **13**, respectively) with inversion of the anomeric centre. Under similar conditions the β-D-*gluco* (**1**) and β-D-*xylo* (**3**) compounds resulted in the corresponding inverted 1-fluoroglycosyl cyanides (**4** and **6**, respectively) together with significant amounts of 1-cyano-2-hydroxy-glycals (**9** and **10**, respectively). Silver tetrafluoroborate in toluene at room temperature converted **2** and **3** into the 1-fluoroglycosyl cyanides (**7** and **8**, respectively) of retained anomeric configuration. 1-Chloro-1-deoxy-α-D-galactopyranosyl cyanide (**11**) also gave **7** with silver fluoride in acetonitrile at reflux temperature. Conformational equilibria of the 1-deoxy-1-fluoro-pentopyranosyl cyanides **6**, **8**, and **13** reflect counteraction of the anomeric effects exerted by the fluorine and the cyano group. 1-Deoxy-1-fluoro-α-D-galactopyranosyl cyanide proved to be a weak competitive inhibitor of *E. coli* β-D-galactosidase (K_i = 2 mM).

Keywords: carbohydrates; cyano compounds; fluorine compounds; enzyme inhibitors.

1. Introduction

Retaining glycosidases [1] are known to hydrolyse glycosidic bonds with the appearance on the mechanistic pathway of covalent glycosyl-enzyme intermediates [2] which are formed and decomposed via transition states of substantial oxocarbenium ion character. Destabilization of

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the transition state of decomposition may result in a so-called mechanism based inactivation of the enzyme [3,4] by suitably designed molecules. Such a destabilization can be achieved by introducing an electron-withdrawing group (EWG) in the vicinity of the positively charged atoms of the oxocarbenium ion-like intermediate i.e. in any position marked in Figure 1. To this end several 2-deoxy-2-fluoro mono- [4-6] and disaccharide derivatives [7] (EWG2 = F) were synthesised and tested against various glycosidases to validate the concept. The 2-fluoro substituents, however, disrupt the most important binding [8] between the enzyme and the 2-OH group. This was overcome by the introduction of a fluorine into the C-5 position [9] (EWG5 = F).

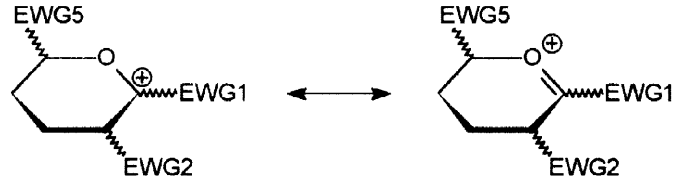


Figure 1

Destabilization of an oxocarbenium ion with the preservation of each binding interaction between the enzyme and the OH-groups of the saccharide can also be achieved by placing an electron-withdrawing group at the anomeric position in addition to a good leaving group. To the best of our knowledge 1-fluoroglycopyranosyl fluorides [10] (EWG1 = F) are the only compounds of this type which have been subjected to enzymatic evaluation [11,12]. Therefore, as part of an ongoing program to synthesise new inhibitors of glycosidases [13], we have set out to prepare 1-fluoroglycopyranosyl cyanides (EWG1 = CN).

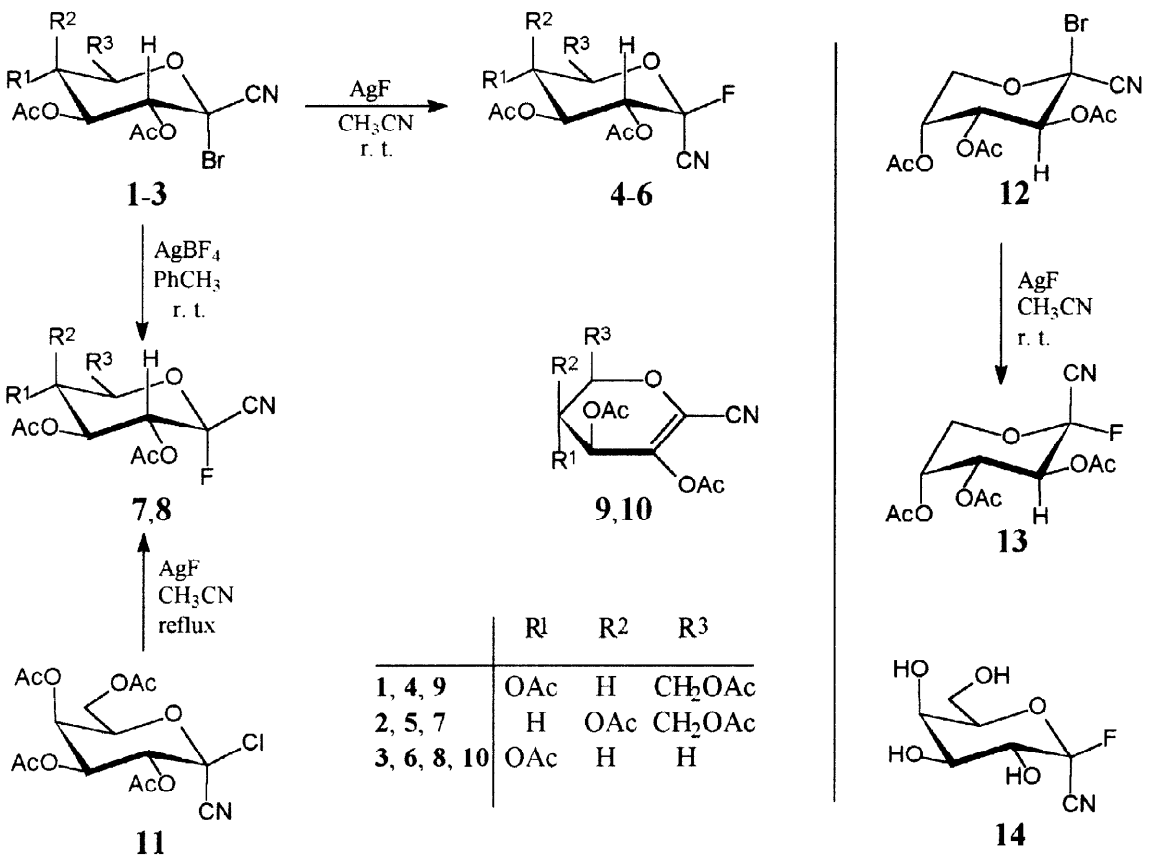
2. Results

The most commonly used reagent for the preparation of glycosyl fluorides [14-16] from the corresponding bromides or chlorides is silver fluoride in acetonitrile [17,18]. In these reactions the stereochemistry is governed by the participating substituent at C-2 resulting in 1,2-*trans* fluorides, while with non-participating groups at C-2 inversion takes place at the anomeric centre [16].

Following the above protocol the easily available 1-bromoglycopyranosyl cyanides [19] **1** [20], **2**, **3**, and **12** [21] were reacted with two equivalents of silver fluoride in dry acetonitrile at room temperature. The reactions needed more than two days for completion with the D-*galacto* (**2**) and D-*arabino* (**12**) configurated compounds and gave high yields of the corresponding fluorides **5** (90 %) and **13** (79 %), respectively, of inverted anomeric configuration in essentially pure state (TLC and ^{1}H NMR spectroscopy). On the contrary, the D-*gluco* (**1**) and D-*xylo* (**3**)

configurated bromides reacted faster, requiring less than 1 hour for complete transformation of the starting materials. Apart from the expected fluorides **4** and **6** the hydrogen bromide elimination products **9** and **10** [22], respectively, appeared in considerable amounts in the reaction mixtures (**4** : **9** = 1 : 1; **6** : **10** = 3 : 1 by ^{1}H NMR spectroscopy).

In order to obtain the fluorides of opposite anomeric configuration bromides **2** and **3** were reacted with two equivalents of silver tetrafluoroborate in toluene [23,24] at room temperature to give the 1-fluoroglycopyranosyl cyanides **7** (36 %) and **8** (38%), respectively. Fluoride **7** was also formed in more than 85 % ratio (^{1}H NMR spectroscopy of the crude mixture also showed the presence of an unidentified by product) from the 1-chlorogalactopyranosyl cyanide **11** [25] with four equivalents of silver fluoride in acetonitrile. This transformation, however, required prolonged refluxing of the reaction mixture because there was no change at room temperature after several days.



Scheme

Looking for less expensive substitutes for the silver based reagents, application of zinc fluoride with or without α,α'-bipyridyl [26] was tried but no reaction occurred. In a phase transfer catalyzed system consisting of a benzene solution of **12**, 50 % aqueous potassium

fluoride solution, and tetrabutylammonium-hydrogensulfate, only slow decomposition was observed.

Deprotection of **5** was performed using methanolic ammonia to give 1-deoxy-1-fluoro-α-D-galactopyranosyl cyanide (**14**) in order to carry out preliminary enzymatic studies.[1]

The new fluorides exhibited characteristic ^{1}H-^{19}F couplings in their ^{1}H NMR spectra (Table 2). Those with H-2 were ~10 Hz for **4-6** and **13**, and in keeping with literature values [27] indicated the *axial* H–*equatorial* F arrangement. For **7** and **8** these couplings (~20 Hz) agreed well with the *trans diaxial* positions of the nuclei involved. Proton coupled ^{13}C NMR spectra (Table 3) corroborated the above findings by showing larger couplings with H-2 in the CN resonance for **4-6** and **13** (4-6 Hz) than for **7** and **8** (<2 Hz) [cf 25]. For the pentose derivatives **6**, **8** and **13** composition of conformational equilibria (Table 1) was calculated by using $J_{4a,5a}$ = 11.6 Hz and $J_{4e,5e}$ = 1.5 Hz as limiting values for the $^{4}C_{1}$ and $^{1}C_{4}$ conformers, respectively [28].

3. Discussion

The described methods constitute simple ways for the preparation of the target compounds.

Each transformation with silver fluoride in acetonitrile resulted in inversion of the anomeric centre. This indicates that the directing effect of the participating 2-OAc substituent does not manifest itself here clearly shown by the reaction of **11** giving **7** as the main product. This finding suggests that an oxocarbenium ion can hardly develop during these processes that can be ascribed to the presence of the cyano group which would destabilize such intermediates. This is also in keeping with the fact that hydrogen bromide elimination was observed only in two cases. If the reactions proceeded through carbocationic intermediates the unsaturated compounds of type **9** and **10** should have appeared in each instance, since it had been shown that silver triflate catalyzed elimination of hydrogen bromide could be achieved from each investigated 1-bromoglycosyl cyanide [22].

All these facts suggest an S_N2 like mechanism which also requires the presence of silver ions as indicated by the failure of attempted transformations without silver. Therefore, we propose, that the reactions proceed through transition states in which the C-1–halogen bonds are weakened but not broken by complexation with a silver ion and more or less synchronously a backside attack of the fluoride ion takes place.

The basic fluoride ion can induce E2 elimination of HBr from **1** and **3** having an unhindered H-2, contrary to **2** and **12** in which H-2 is less accessible due to steric hindrance by the axial 4-OAc

[1] Compound **14** proved to be a weak competitive inhibitor of *E. coli* β-D-galactosidase (K_i = 2 mM) in an assay carried out as described before [13]. No inactivation was observed, probably because the leaving ability of fluorine was so strongly decreased by the presence of the cyano group that formation of a glycosyl-enzyme intermediate became impossible (see also Discussion).

(see Scheme). Expectedly, bimolecular substitution of the equatorial chlorine in **11** requires forcing conditions.

The outcome of experiments with silver tetrafluoroborate producing *axial* fluorides is in agreement with literature experiences [23, 24].

Appearance of $^5J_{F,H\text{-}4}$ couplings of ~2-3 Hz (Table 2) in **5**, **13**, and **14** but not in **4** and **6-8** is in keeping with literature experiences [27, 32-34] indicating that the fluorine and H-4 are in *trans coplanar* relationship to the bond which is the midpoint of the coupling pathway. This is a further indirect proof of the anomeric configuration of these 1-fluoroglycopyranosyl cyanides.

Conformational equilibria (Table 1) of the 1-fluoropentopyranosyl cyanides **6**, **8**, and **13** lie between those of the corresponding pentopyranosyl fluorides and cyanides. This is in accord with the estimated anomeric effect of the cyano group [29].

4. Conclusion

Reactions of 1-chloro- or 1-bromoglycopyranosyl cyanides with silver fluoride or silver tetrafluoroborate represent simple methods for the preparation of both anomers of 1-fluoroglycopyranosyl cyanides. All reactions with silver fluoride proceeded with inversion of the anomeric carbon thereby suggesting an S_N2 type substitution supported by electrophilic assistance of silver ions. Conformational equilibria of 1-fluoropentopyranosyl cyanides reflect a balance between anomeric effects exerted by the fluorine and the cyano group.

5. Experimental

Melting points were measured on a Kofler hot-stage and are uncorrected. Optical rotations were determined with a Perkin-Elmer 241 polarimeter at room temperature. NMR spectra were recorded with a Bruker WP 200 SY spectrometer (^{1}H, 200 MHz; ^{13}C, 50.3 MHz). TLC was performed on DC-Alurolle, Kieselgel 60 F_{254} (Merck), (eluent: ethyl acetate–hexanes 1 : 1); the plates were visualised by gentle heating. For column chromatography Kieselgel 60 (Merck) was used (eluent: ethyl acetate–hexanes 1 : 3). Organic solutions were dried over anhydrous $MgSO_4$ and concentrated in vacuo at 40-50°C (water bath).

General procedure A for the reaction of 1-chloro- (**11**) and 1-bromoglycopyranosyl cyanides (**1-3** and **12**) with silver fluoride: To a solution of a halo-cyanide (1 mmol) in dry acetonitrile (16 ml) dry silver fluoride (2 mmol) was added (the addition of the same amount of AgF was repeated in the case of **11** after 5 h) and the suspension was stirred at room temperature (heated at reflux for 10 h in the case of **11**) in the dark. After the reaction had reached completion (TLC) the mixture was diluted with chloroform (100 ml), filtered through Celite and concentrated.

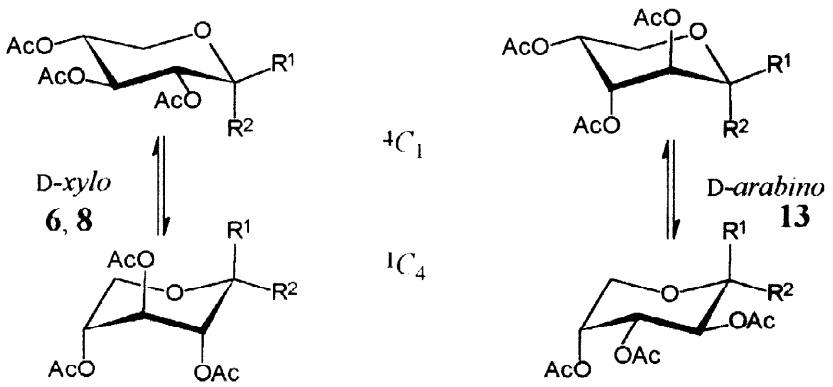


Table 1

Conformational equilibria of 1-fluoropentopyranosyl cyanides[a] and the related pentopyranosyl fluorides and cyanides

Compound	R^1	R^2	$^4C_1$	$^1C_4$	Solvent	Reference
D-*xylo*	F	H	28	72	$CDCl_3$	[27]
	H	CN	76 (85	24 15)[b]	C_6D_6	[30]
6	F	CN	33	67	C_6D_6	this work
D-*xylo*	H	F	~100		$CDCl_3$	[27]
	CN	H	55 (54	45 46)[c]	$CDCl_3$	[31]
8	CN	F	94	6	C_6D_6	this work
D-*arabino*	H	F	65	35	$CDCl_3$	[27]
	CN	H	13 (19	87 81)[b]	C_6D_6	[30]
13	CN	F	37	63	$CDCl_3$	this work

[a] Calculated on the basis of $J_{4,5}$ couplings using $J_{4a,5a}$ = 11.6 Hz and $J_{4e,5e}$ = 1.5 Hz as limiting values for the $^4C_1$ and $^1C_4$ conformers, respectively, taken from reference [28].

[b] Calculated on the basis of $J_{1,2}$ couplings using $J_{1a,2e}$ = 1.4 Hz and $J_{1e,2a}$ = 6.2 Hz as limiting values for the corresponding conformers taken from reference [31].

[c] Values taken from reference [31] calculated on the basis of $J_{1,2}$ couplings.

Table 2
^{1}H NMR spectroscopic data for the 1-fluoroglycopyranosyl cyanides measured at 200 MHz (δ [ppm], *J* [Hz])

Compound (solvent)	H-2 $J_{2,3}$ $J_{F,2}$	H-3 $J_{3,4}$ $J_{F,3}$	H-4 $J_{4,5}$ ($J_{4,5'}$[a]) $J_{F,4}$	H-5 $J_{5,6}$ /$J_{5,6'}$ $J_{F,5}$	H-6/H-6' (H-5/H-5'[a]) $J_{6,6'}$ ($J_{5,5'}$[a])	CH_3
4 (C_6D_6)	5.42 *9.0* *10.8*	5.26 *8.5* *~1*	5.51 *10.0*	**3.88** *4.0/2.0*	4.11/3.78 *12.8*	1.47 1.58 1.58 1.61
5[c] ($CDCl_3$)	5.50 *10.9* *12.1*	5.17 *3.2* *0.7*	5.52 *1.2* *3.0*	4.39 *5.9/6.8* *0.8*	4.27/4.21 *11.5*	2.01 2.09 2.19 2.20
6 (C_6D_6)	5.35 *5.4* *6.9*	5.26 *5.2*	4.64 *3.3 4.5*	—	3.74/3.45 *13.0*	1.53 1.54 1.56
7 ($CDCl_3$)	5.66 *10.6* *20.9*	5.25 *3.2*	5.54 *1.3*	4.46 *7.0/5.9*	4.20/4.15 *12.4*	2.00 2.08 2.20 2.21
8 (C_6D_6)	5.29 *9.7* *20.7*	5.44 *8.6*	4.78 *6.2 11.0*	—	3.42/3.13 *11.3*	1.46 1.56 1.59
13[b] ($CDCl_3$)	5.44 *8.3* *8.5*	5.21 *3.3*	5.34 *5.2 2.7* *2.2*	—	4.23/4.06 *12.9*	2.06 2.12 2.20
14[c] (D_2O)	3.95 *10.4* *14.7*	3.85 *3.1*	4.07 *0.8* *3.3*	4.12 *4.6/7.2* *1.0*	3.86 *n.d.*[d] *n.d.*[d]	—

[a] Applies for the pentose derivatives **6**, **8**, **13**. [b] 500 MHz. [c] 360 MHz. [d] Cannot be determined.

General procedure B for the reaction of 1-bromoglycopyranosyl cyanides (**2** and **3**) with silver tetrafluoroborate: To a solution of freshly dried silver tetrafluoroborate (2 mmol) in dry toluene (15 ml) a bromo-cyanide (1 mmol) dissolved in the same solvent (5 ml) was added at once when a white tar precipitated. The mixture was stirred at room temperature in the dark until the reactant had disappeared by TLC. The suspension was diluted with chloroform (50 ml), then filtered through Celite and the filtrate extracted with 1 M aq $Na_2S_2O_3$ solution (3 x 15 ml) and water (3 x 5 ml). The crude product was obtained by concentration of the dried organic layer.

Table 3
^{13}C NMR spectroscopic data for the 1-fluoroglycopyranosyl cyanides measured in $CDCl_3$ at 50.3 MHz (δ [ppm], *J* [Hz])

Compound	C-1 $J_{C,F}$	C-2 $J_{C,F}$	C-3 $J_{C,F}$	C-4	C-5	C-6	CN $J_{C,F}$ $J_{CN,H-2}$	CO	CH_3
4[a]	103.35 *221*	70.67 *31*	66.27 70.58 73.47			60.52	111.16 *45* *5.1*	168.27 169.00 169.31 170.16	20.25 20.31 20.44
5	104.10 *220*	68.07 *26*	68.84 *8.5*	65.63 72.98		60.43	111.23 *46* *6.1*	168.52 169.32 169.60 170.01	20.22 20.34
6	102.96 *225*	67.19 *33*	65.47 66.86		62.49	—	111.83 *42* *n.d.*[c]	168.22 168.78 169.48	20.38 20.46 20.63
7	102.00 *235*	67.18 *23*	66.46 66.95 71.64			60.48	111.66 *42* *<2*	168.69 169.38 169.58 169.99	20.36
8	102.27 *237*	70.41 *26*	67.00 68.78		62.08	—	111.75 *43* *<2*	168.64 169.36 169.46	20.35 20.09
13[a]	103.71 *224*	67.95 *30*	67.52 *5*	64.90	63.57	—	111.56 *44* *3.9*	168.32 169.29 169.59	20.34 20.36 20.54
14[b]	110.20 *212*	73.50 *23*	70.17 73.37 80.43			63.18	115.37 *47* *n.d.*[c]	—	—

[a] Measured at 125 MHz. [b] Measured in D_2O at 90 MHz. [c] Not determined.

2,3,4,6-Tetra-O-acetyl-1-deoxy-1-fluoro-α-D-glucopyranosyl cyanide **4**.—Prepared from **1** (1.46 g, 3.35 mmol) according to general procedure **A**: reaction time 1 h. Crude product: 1.11 g, identified as a mixture of **4** and **9** in ~1:1 ratio by ^1H NMR spectroscopy. Column chromatography afforded pure **4** (266 mg, 21 %) as a colourless syrup. $[\alpha]_D$ +57 (c=1.5, $CHCl_3$). Anal.: Calcd for $C_{15}H_{18}NO_9F$ (375.31): C, 48.01; H, 4.83; N, 3.73; F, 5.06. Found: C, 49.18; H, 5.11; N, 3.36; F, 5.49.

2,3,4,6-Tetra-O-acetyl-1-deoxy-1-fluoro-α-D-galactopyranosyl cyanide **5**.—Prepared from **2** (1.81 g, 4.15 mmol) according to general procedure **A**: reaction time 2 d. Crude product: practically pure **5** (1.40 g, 90 %) which was crystallized from EtOH. Mp 87-88 °C; $[\alpha]_D$ +80 (c=1.2, $CHCl_3$). Anal.: Calcd for $C_{15}H_{18}NO_9F$ (375.31): C, 48.01; H, 4.83; N, 3.73; F, 5.06. Found: C, 48.58; H, 4.99; N, 3.51; F, 5.21.

2,3,4-Tri-O-acetyl-1-deoxy-1-fluoro-α-D-xylopyranosyl cyanide **6**.—Prepared from **3** (0.50 g, 1.37 mmol) according to general procedure **A**: reaction time 1 h. Crude product: 220 mg, identified as a mixture of **6** and **10** in ~3:1 ratio by ^{1}H NMR spectroscopy. Column chromatography afforded pure **6** (47 mg, 11 %) which was crystallized from Et_2O-hexanes. Mp 119-121 °C; $[\alpha]_D$ -23 (c=1.5, $CHCl_3$). Anal.: Calcd for $C_{12}H_{14}NO_7F$ (303.24): C, 47.53; H, 4.65; N, 4.62; F, 6.26. Found: C, 47.78; H, 4.57; N, 4.59; F, 6.15.

2,3,4,6-Tetra-O-acetyl-1-deoxy-1-fluoro-β-D-galactopyranosyl cyanide **7**.—Prepared from **2** (0.32 g, 0.73 mmol) according to general procedure **B**: reaction time 1 week. Crude product: 164 mg. Column chromatography afforded pure **7** (99 mg, 36 %) as a colourless syrup. $[\alpha]_D$ +71 (c=1.1, $CHCl_3$). Anal.: Calcd for $C_{15}H_{18}NO_9F$ (375.31): C, 48.01; H, 4.83; N, 3.73; F, 5.06. Found: C, 47.88; H, 4.71; N, 3.59; F, 5.15.

2,3,4-Tri-O-acetyl-1-deoxy-1-fluoro-β-D-xylopyranosyl cyanide **8**.—Prepared from **3** (0.32 g, 0.88 mmol) according to general procedure **B**: reaction time 1 week. Crude product: 240 mg. Column chromatography afforded pure **8** (101 mg, 38 %) as a colourless syrup, which was crystallized from CH_2Cl_2-Et_2O. Mp 164-165 °C; $[\alpha]_D$ +23 (c=1.1, $CHCl_3$). Anal.: Calcd for $C_{12}H_{14}NO_7F$ (303.24): C, 47.53; H, 4.65; N, 4.62; F, 6.26. Found: C, 47.78; H, 4.78; N, 4.49; F, 6.39.

2,3,4-Tri-O-acetyl-1-deoxy-1-fluoro-β-D-arabinopyranosyl cyanide **13**.—Prepared from **12** (2.32 g, 6.37 mmol) according to general procedure **A**: reaction time 2 d. Crude product: practically pure **13** (1.52 g, 79 %) which was crystallized from EtOH. Mp 156-157 °C; $[\alpha]_D$ +63 (c=1.2, $CHCl_3$). Anal.: Calcd for $C_{12}H_{14}NO_7F$ (303.24): C, 47.53; H, 4.65; N, 4.62; F, 6.26. Found: C, 48.08; H, 4.80; N, 4.47; F, 6.28.

1-Deoxy-1-fluoro-β-D-galactopyranosyl cyanide **14**.—Prepared from **5** (375 mg, 1.00 mmol) with saturated methanolic ammonia (10 ml) at 0 °C. After 30 min the solution was concentrated, and subjected to column chromatography (eluent: chloroform-methanol 9 : 1) to give pure **14** (59 mg, 28 %) as a colourless syrup. $[\alpha]_D$ +97 (c=0.3, H_2O). Anal.: Calcd for $C_7H_{10}NO_5F$ (207.16): C, 40.59; H, 4.87; N, 6.76. Found: C, 40.38; H, 4.75; N, 6.57.

6. Acknowledgement

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