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Reaction of Sugar Esters with Hydrogen Fluoride

VIII. Ribopyranose and Arabinopyranose Derivatives

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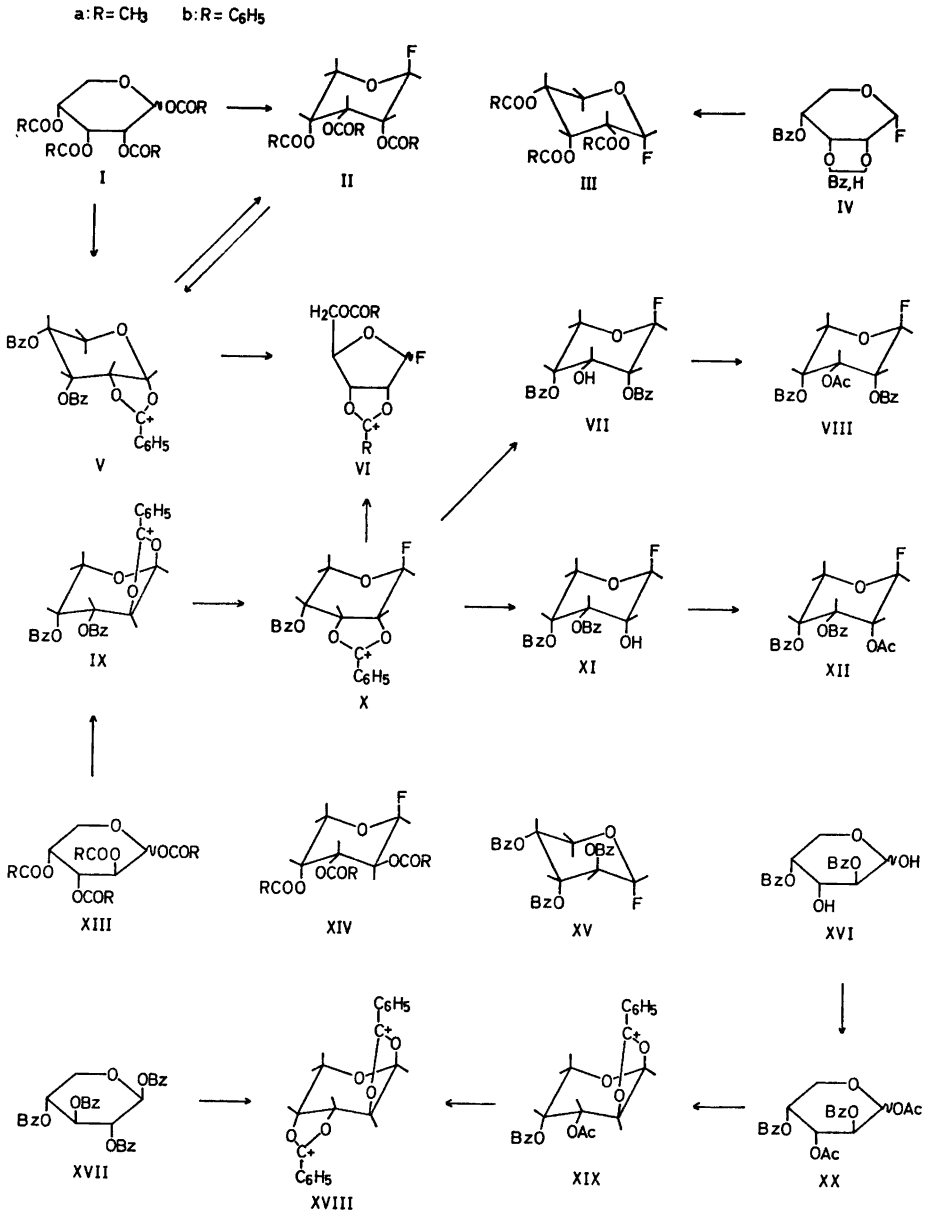
When tetra-*O*-acetyl-D-arabinopyranose or tetra-*O*-acetyl-D-ribopyranose are dissolved in hydrogen fluoride they form the corresponding acetylated β-D-pyranosyl fluorides, as seen from the NMR spectra of the hydrogen fluoride solutions. Both compounds, when kept for several days in hydrogen fluoride, rearrange and give a 2,3-acetoxonium ion derived from D-ribofuranosyl fluoride. The tetrabenzoates of D-arabinopyranose or D-ribopyranose do not form fluorides, when dissolved in hydrogen fluoride, but give 1,2-benzoxonium ions. On further reaction with hydrogen fluoride D-arabinopyranose tetrabenzoate rearranges to a 2,3-benzoxonium ion derived from ribopyranosyl fluoride and this ion, finally, undergoes ring contraction with formation of a ribofuranose derivative. The latter product is also formed when D-ribopyranose tetrabenzoate is kept in hydrogen fluoride for several days. 1,3-Di-*O*-acetyl-2,4-di-*O*-benzoyl-D-arabinopyranose does not form a ribopyranose derivative in hydrogen fluoride solution, but gives a 1,2—3,4-dibenzoxonium ion derived from arabinopyranose. The latter ion is also formed from tetra-*O*-benzoyl-D-xylopyranose.

Brief treatment of tetra-*O*-benzoyl-L-arabinopyranose with hydrogen fluoride has previously been found to give tri-*O*-benzoyl-α-L-arabinopyranosyl fluoride in 38 % yield.[1,2] When the reaction with hydrogen fluoride was allowed to proceed for 6 h a di-*O*-benzoyl-β-L-ribopyranosyl fluoride was obtained in 36 % yield.[1] Reaction of tetra-*O*-benzoyl-D-ribopyranose (Ib) with hydrogen fluoride for a few minutes gave a mixture of the anomeric tri-*O*-benzoyl-D-ribopyranosyl fluorides (IIb) and (IIIb), whereas a reaction time of 24 h gave a mixture from which only small amounts of di-*O*-benzoyl-β-D-ribopyranosyl fluoride and di-*O*-benzoyl-β-D-ribofuranosyl fluoride could be isolated.[3] Since it has been found that the reaction of sugar esters with anhydrous hydrogen fluoride can be followed conveniently by NMR spectroscopy[4] it was decided to reinvestigate the reaction of arabinopyranose and ribopyranose derivatives with hydrogen fluoride.



When tetra-*O*-acetyl-α-D-arabinopyranose (XIIIa) was dissolved in anhydrous hydrogen fluoride and an NMR spectrum taken after a few minutes it was found that tri-*O*-acetyl-β-D-arabinopyranosyl fluoride (XIVa) was formed, together with acetic acid, as the only detectable product. The spectrum

(Table 1) was completely identical with that of the fluoride (XIVa) in deuteriochloroform (Table 2), apart from the signal of acetic acid. In agreement with this, work up at this stage gives the β-fluoride (XIVa).[5,6] On further standing the spectrum changed and after *ca.* 80 h at room temperature it was found that the ion (VIa) had been formed, the spectrum being essentially identical with the spectra obtained, under the same conditions, from the tetraacetates of D-ribofuranose or D-arabinofuranose.[4] However, besides the signals of the ion (VIa), another set of signals was present indicating that another product must have been formed.

Tetra-*O*-acetyl-β-D-ribopyranose (Ia), when dissolved in hydrogen fluoride and kept for a few minutes, gave a spectrum which indicated that the only products present were tri-*O*-acetyl-β-D-ribopyranosyl fluoride (IIa) and acetic acid (Table 1). At this stage the β-fluoride can be obtained by working up the solution.[6] When the hydrogen fluoride solution was kept at room temperature it underwent further reaction as seen from the spectra and after *ca.* 5 days the ion (VIa) was formed as the final product together with an unidentified compound. The spectrum was completely identical with that obtained from arabinopyranose tetraacetate. The immediate formation of glycosyl fluorides in hydrogen fluoride solution is in contrast to the behaviour of the corresponding furanose derivatives which give 1,2-acetoxonium ions when dissolved in hydrogen fluoride.[4]

The two tetrabenzoates (Ib) and (XIIIb) would be expected to behave analogous to the tetraacetates and they should therefore both give the β-fluorides (IIb) and (XIVb) as the initial products, when dissolved in hydrogen fluoride. The spectrum, obtained a few minutes after tetra-*O*-benzoyl-β-D-arabinopyranose (XIIIb) was dissolved in hydrogen fluoride, was not well resolved (Table 1). The signal of the anomeric proton was hidden under the signals of the aromatic protons and could therefore not be seen. The spectrum is obviously different from those of the anomeric tri-*O*-benzoyl-D-arabinopyranosyl fluorides (XIVb) and (XV) (Table 2) and it is assumed that the product formed from (XIIIb) in hydrogen fluoride is the 1,2-benzoxonium ion (IX). Since the NMR signal of the two H-5 protons is rather narrow (Table 1) H-4 is probably equatorial and (IX) is therefore in the *1C* conformation. In analogy to the behaviour of the 1,2-benzoxonium ions observed in the furanose series [4] the ion (IX) would be expected to give the α-fluoride (XV) when the hydrogen fluoride solution is worked up. Previous experiments [1,2] have shown that a 38 % yield of the α-fluoride is obtained on brief treatment of arabinopyranose tetrabenzoate with hydrogen fluoride. In addition a 16 % yield of the β-fluoride (XIVb) has now been isolated by chromatography of the material in the mother liquor.

When tetra-*O*-benzoyl-β-D-ribopyranose (Ib) was dissolved in hydrogen fluoride and an NMR spectrum taken within a few minutes it was seen from the appearance of the signals of the two H-5 protons that a ribopyranose derivative in the *C1* conformation was formed (Table 1).[7,8] A doublet at 7.22 ppm, very close to the signals of the aromatic protons, is tentatively assigned to the anomeric proton. The product formed from (Ib) in hydrogen fluoride is not a glycosyl fluoride and is most likely to be the 1,2-benzoxonium ion (V). This is confirmed by the fact that work up at this stage gives pre-

Table 1. Chemical shifts (ppm) and coupling constants (cps) of pyranose derivatives in hydrogen fluoride.

Compound in HF, product formed, conformation	H_1	H_2	H_3	H_4	H_5	—OAc	HOAc
XIIIa, 10 min XIVa *1C*	6.1(q) $J_{H_1F} \simeq 50$	$J_{12} \simeq 1.5$	5.4—5.8(m)		4.0—4.6(m)	2.28(s) 2.34(s) 2.41(s)	2.62(s)
Ia, 10 min IIa *1C*	5.9(q) $J_{H_1F} = 47$	$J_{12} \simeq 1$	5.4—5.7(m)		4.05—4.6(m)	2.25(3H)(s) 2.39(6H)(s)	2.54(s)
XIIIb, 10 min IX *1C*			5.9—6.2(m)		4.65—4.8		
Ib, 10 min V *C1*	7.22(d) $J_{12} = 6.5$		5.9—6.4(m) $J_{45e} = 2.0$,	$J_{45a} = 6.1$	$H_{5a} = 5.06$, $H_{5e} = 4.70$ $J_{55} = 14$		
XIIIb, 24 h at 0° X *1C*	6.56(d) $J_{H_1F} = 47$ $J_{H_2F} \simeq 3$	5.96(q) $J_{12} \simeq 0$	6.63(q) $J_{23} = 7$	6.02(q) $J_{34} = 5.2$	4.4—4.5		
XIIIa, 24 h at 0° XVIIIa	7.32(d) $J_{12} = 7.5$	6.0(d) $J_{23} \simeq 0.5$	6.38(d) $J_{34} = 10$	6.0(d) $J_{45} \simeq 0.5$ and 1.3	4.3 and 4.8 $J_{55} = 16.5$	acetoxonium-signal 2.95	2.54(s)
XX, 10 min XIX *1C*			5.8—6.1(m)		4.55—4.7(m)	2.39(s)	2.63(s)
XX, 24 h at 0° XVIII	7.42(d) $J_{12} = 7.2$	6.25(d) $J_{23} \simeq 0.5$	6.68 $J_{34} \simeq 10$	6.25(d) $J_{45} \simeq 0.5$ and 1—2	4.36 and 4.94 $J_{55} = 16.4$		2.61(s)
XVII, 24 h at 0° XVIII	7.47(d) $J_{12} = 7.2$	6.30(d) $J_{23} \simeq 0.5$	6.73(d) $J_{34} \cong 10$	6.30(d) $J_{45} \simeq 0.5$ and 1—2	4.40 and 5.99 $J_{55} = 16.4$		

(s) singlet; (d) doublet; (q) quartet; (m) multiplet.

dominantly tri-*O*-benzoyl-β-D-ribopyranosyl fluoride (IIb).[3] When (IIb) was dissolved in hydrogen fluoride it gave a spectrum which was completely identical with that obtained from the tetrabenzoate (Ib).

When the tetrabenzoates of ribopyranose or arabinopyranose were kept in hydrogen fluoride solution at room temperature further reactions took place and after 6—8 days they both gave spectra which were identical with those obtained from the tetrabenzoates of ribofuranose or arabinofuranose[4] showing that the ion (VIb) had been formed. In agreement herewith work up at this stage gave the same mixture of di-*O*-benzoyl-α- and β-D-ribofuranosyl fluorides as that obtained from the corresponding furanose derivatives. The yields were somewhat lower, presumably due to decomposition because of the long reaction time required.

The isolation of di-*O*-benzoyl-β-D-ribopyranosyl fluoride (VII) or (XI) in 36 % yield from the reaction of arabinopyranose tetrabenzoate with hydrogen fluoride for 6 h[1] indicates that the 2,3-benzoxonium ion (X) was present in the hydrogen fluoride solution at this stage and that this ion is an intermediate in the reaction leading to ring contraction with formation of the furanose derivative (VIb). When a solution of arabinopyranose tetrabenzoate (XIIIb) in hydrogen fluoride was kept at room temperature it was found that the product first formed (see above) disappeared rather rapidly and after *ca.* 1 h the NMR spectrum was very complicated and remained complicated until the final product (VIb) was formed. It was not possible to detect with certainty the 2,3-benzoxonium ion (X) in the spectra at any time. When the same reaction was followed at 0° a less complex spectrum was obtained in the course of 12 h and this spectrum did not change much during the following 24 h. The spectrum probably represents the ion (X) (Table 1). When a solution of (XIIIb) in hydrogen fluoride was worked up after 20 h at 0° it gave a 35 % yield of the di-*O*-benzoyl-β-D-ribopyranosyl fluoride obtained previously.[1] In addition a second, crystalline, di-*O*-benzoyl-β-D-ribopyranosyl fluoride was isolated in 22 % yield. The latter product, by benzoylation, gave the tri-*O*-benzoylated β-fluoride (IIb). Since the ion (X) would give the two isomeric dibenzoates (VII) and (XI) by reaction with water, as done in the work up precedure, this ion must have been present to at least 57 % in the hydrogen fluoride solution. Besides, two isomeric di-*O*-benzoyl-α-D-ribopyranosyl fluorides (IV) were obtained in low yield from this experiment, one as an impure syrup, the other as a pure, crystalline, compound. Both these products gave tri-*O*-benzoyl-α-D-ribopyranosyl fluoride (IIIb) on benzoylation, thus establishing their structure except for the relative position of the benzoyl groups.

The behaviour of 1,3-di-*O*-acetyl-2,4-di-*O*-benzoyl-D-arabinose (XX) towards hydrogen fluoride was also studied. When (XX) was dissolved in hydrogen fluoride it at once liberated one equivalent of acetic acid and gave, presumably, the 1,2-benzoxonium ion (XIX). The NMR spectrum of the latter is identical with that of the product formed from arabinopyranose tetrabenzoate, except for the presence of an acetoxy signal (Table 1). When (XX) was kept in hydrogen fluoride for 24 h at 0° it was expected to form the acetoxonium analogue of (X). However, the spectrum obtained at this stage showed that two equivalents of acetic acid had been liberated and that no

signals corresponding to acetoxonium ions or acetoxy groups were present. An analysis of the spectrum (Table 1) indicated that the hydrogen fluoride solution contained, as the major product, the dibenzoxonium ion (XVIII) derived from arabinose. In accord with this work up of the hydrogen fluoride solution gave 2,4-di-*O*-benzoyl-D-arabinose (XVI), identical with the product described previously.[9]

When tetra-*O*-benzoyl-D-xylopyranose (XVII) is treated with hydrogen fluoride 2,4-di-*O*-benzoyl-D-arabinose is also obtained [9] and it was assumed that the dibenzoxonium ion (XVIII) is formed in hydrogen fluoride solution. This has now been confirmed by NMR spectroscopy. When (XVII) was kept in hydrogen fluoride for 24 h at 0° it gave an NMR spectrum which was identical with that obtained from 1,3-di-*O*-acetyl-2,4-di-*O*-benzoyl-D-arabinose (XX) except for the signal of acetic acid. The spectrum obtained from (XVII) (Table 1) indicated that the ion (XVIII) was the only product formed after 24 h reaction with hydrogen fluoride.

When tetra-*O*-acetyl-D-arabinopyranose (XIIIa) was kept in hydrogen fluoride for 24 h at 0° it gave a rather complicated NMR spectrum which indicated that several products were present at this stage. However, signals due to the diacetoxonium analogue of (XVIII) could be seen in the spectrum (Table 1). Since the tetraacetate (XIIIa) is converted into the ribofuranose derivative (VIa) on further reaction with hydrogen fluoride (see above) it might be expected that the dibenzoxonium ion (XVIII) would also give the corresponding ribofuranose derivative (VIb) when kept in hydrogen fluoride. This has however not been established with certainty yet, but will be discussed more extensively in a forthcoming paper which will describe the behaviour of xylose derivatives towards hydrogen fluoride.

Attempts to find which intermediates are involved in the conversion of ribopyranose tetrabenzoate (Ib) into the ribofuranose derivative (VIb) were not successful since the NMR spectra of (Ib) in hydrogen fluoride were very complicated, indicating a mixture of products, until the furanose derivative (VIb) was formed. When (Ib) was kept in hydrogen fluoride for 24 h at 0° and then worked up the main product was tri-*O*-benzoyl-β-D-ribopyranosyl fluoride (IIb). When the same reaction was performed at room temperature a complicated mixture of ribopyranose and ribofuranose derivatives was obtained in accord with previous findings.[3]

In Table 2 the NMR spectra of some of the compounds described in the present paper are given. Spectra of tri-*O*-benzoyl-α- and β-D-ribopyranosyl fluoride (IIIb) and (IIb) have been studied by Coxon,[7] whereas ^{19}F-spectra of some of the fluorides reported here have been investigated by Hall and Manville.[10] All δ-values and coupling constants were derived by a first order analysis. A detailed conformational analysis is not justified on the basis of the results given here. However, as seen from the signals of the H-5 protons,[7,8,11] all the pyranosyl fluorides apparently adopt the chair conformation in which the fluorine atom is axially oriented in agreement with the findings of Hall,[11] Coxon,[7] and Horton.[8]

The structure of the two di-*O*-benzoyl-β-D-ribopyranosyl fluorides (VII) and (XI) could not be decided on the basis of their NMR spectra. That both compounds are in the *1C* conformation is seen from the signals of the two H-5

Table 2. Chemical shifts (δ-values) and coupling constants (cps) of pyranose derivatives in deuteriochloroform.

Compound, conformation	H_1	H_2	H_3	H_4	H_5	−OAc −OH
XIVa, *1C*	5.8(q) $J_{H_1F} \simeq 50$	$J_{12} \simeq 1$	5.0−5.5(m) J_{45}=1 and 1.7		3.90 and 4.17 J_{55}=13.0	2.02(s) 2.12(s) 2.16(s)
XIVb, *1C*	6.09(q) $J_{H_1F} \simeq 52$	$J_{12} \simeq 1$	5.5−6.1(m) $J_{45} \simeq 1$ and 1.3		4.19 and 4.42 J_{55}=13.0	
XV, *C1*	5.71(q) J_{H_1F}=49	J_{12}=1.7	5.5−6.0(m)		3.9−4.7(m)	
IIa, *1C*	5.5(q) J_{H_1F}=48	J_{12}=2.2	5.15−5.50(m) J_{45}=1.8 and 2.6		4.0 and 4.21 J_{55}=13.6	2.05(3H)(s) 2.16(3H)(s)
VII, *1C*	5.8(q) $J_{H_1F} \simeq 50$	5.3−5.6(m) J_{12}=1.7	4.3−4.6	5.3−5.6(m)	4.15−4.25	3.1(d) J_{H_3OH}=7.7
XI, *1C*	5.78(q) J_{H_1F}=49.7	4.0−4.5 J_{12}=2.1	5.4−5.8(m)		4.0−4.5	3.09(d) J_{H_2OH}=9.8
VIII, *1C*	5.96(q) J_{H_1F}=48.0	$J_{12} \simeq 1$	5.5−5.7 $J_{45} \simeq 1$ and 1		4.22 and 4.40 J_{55}=13.0	2.02(s)
XII, *1C*	5.77(q) J_{H_1F}=49.0	J_{12}=2.0	5.4−5.8(m) J_{45}=2.0 and 1		4.20 and 4.39 J_{55}=13.3	2.13(s)
XX, *1C* α-anomer	5.3−6.1(m) J_{45}=1.8 and 2.9				4.28 and 4.02 J_{55}=12.8	1.97(s) 2.09(s)
XX, *1C* β-anomer	6.62(d) J_{12} 1−2	5.65−5.80(m) $J_{45} \simeq 1$ and 1.5			4.04 and 4.23 J_{55}=13.0	1.96(s) 2.16(s)

(s) singlet; (d) doublet; (q) quartet; (m) multiplet.

protons which occur within a narrow range indicating that the coupling to H-4 is small and, consequently, that H-4 must be equatorially oriented (Table 2). Acetylation of (VII) and (XI) gave (VIII) and (XII), respectively. The latter two compounds also have the *1C* conformation. The NMR spectra of (VIII) and (XII) are quite similar, however, (VIII) has its acetoxy signal at 2.02 δ whereas (XII) gives the corresponding signal at 2.13 δ. Since axial acetoxy groups generally give signals at lower field than equatorial acetoxy groups [8,11,12] then the compound which has its signal at 2.02 δ is probably the 3-*O*-acetyl isomer (VIII) and the corresponding dibenzoate must be the 2,4-isomer (VII) with m.p. 150−151°. This compound was previously assumed to be the 3,4-isomer (XI).[1] The di-*O*-benzoyl-β-D-ribopyranosyl fluoride with m.p. 111−113° must be the 3,4-isomer (XI) since, on acetylation, it gives

(XII) which has an NMR spectrum with an acetoxy signal at 2.13 δ, typical of axial acetoxy groups.

Acetylation of 2,4-di-*O*-benzoyl-D-arabinose [9] (XVI) gave a mixture of the anomeric 1,3-di-*O*-acetyl-2,4-di-*O*-benzoyl-D-arabinopyranoses (XX). The α-anomer crystallized and was obtained in 20 % yield. The material in the mother liquor consisted of almost pure β-anomer as seen from the NMR spectrum (Table 2). The two anomers behaved identical when treated with hydrogen fluoride.

EXPERIMENTAL

Melting points are uncorrected. For details of thin layer chromatography and NMR spectra see Ref. 13.

*Reaction of tetra-*O*-benzoyl-β-*D*-arabinopyranose (XIIIb) with hydrogen fluoride for 10 min.* The tetrabenzoate (XIIIb) (2 g) was dissolved in hydrogen fluoride (4 ml) and the solution was kept for 10 min at room temperature. Methylene chloride was then added and the mixture was poured into water. The organic layer was washed with aqueous sodium hydrogen carbonate and dried. Evaporation of the solvent gave 1.55 g of a syrup which crystallized from ether-pentane to give 380 mg of tri-*O*-benzoyl-α-D-arabinopyranosyl fluoride (XVb), m.p. 155—158°, identical with the product described previously.[1,2] The material in the mother liquor was separated into four fractions by preparative thin layer chromatography eluting twice with benzene. The slowest running fraction (165 mg) was a mixture of products. The second fraction gave 104 mg of 2,4-di-*O*-benzoyl-β-D-ribopyranosyl fluoride (VII), m.p. 145°. The third fraction gave 155 mg of tri-*O*-benzoyl-α-D-arabinopyranosyl fluoride, m.p. 156—158°, bringing the total yield of this product to 535 mg (32 %). The fastest running fraction gave 263 mg (16 %) of tri-*O*-benzoyl-β-D-arabinopyranosyl fluoride (XIVb) as a colourless syrup. $[\alpha]_D^{22} = -285°$ (*c* 0.9, $CHCl_3$). (Found: C 67.40; H 4.66. Calc. for $C_{26}H_{21}O_7F$: C 67.24; H 4.56).

*Reaction of tetra-*O*-benzoyl-β-*D*-arabinopyranose (XIIIb) with hydrogen fluoride for 6 days.* The tetrabenzoate (XIIIb) (500 mg) was kept in hydrogen fluoride (1 ml) for 6 days at room temperature. The dark coloured solution was worked up as described above giving 273 mg of a brown syrup. Preparative thin layer chromatography as described previously [4] gave 54 mg (17 %) of crude 3,5-di-*O*-benzoyl-α-D-ribofuranosyl fluoride. On benzoylation followed by preparative thin layer chromatography pure tri-*O*-benzoyl-α-D-ribofuranosyl fluoride was obtained. A second fraction consisted of 103 mg (32 %) of a mixture of 2,5- and 3,5-di-*O*-benzoyl-β-D-ribofuranosyl fluoride which was separated into the pure 2,5- and 3,5-isomer as described previously.[4] Besides the products described above, several other compounds were present in the crude product in small amounts as seen from thin layer chromatography.

*Reaction of tetra-*O*-benzoyl-β-*D*-ribopyranose (Ib) with hydrogen fluoride for 8 days.* Treatment of (Ib) with hydrogen fluoride for 8 days at room temperature gave, by the procedure described above, 12 % of 3,5-di-*O*-benzoyl-α-D-ribofuranosyl fluoride, 32 % of the mixture of 2,5- and 3,5-di-*O*-benzoyl-β-D-ribofuranosyl fluorides, and 8 % of tri-*O*-benzoyl-β-D-ribofuranosyl fluoride. The products were identified through their NMR spectra.

*Reaction of tetra-*O*-benzoyl-β-*D*-arabinopyranose (XIIIb) with hydrogen fluoride for 20 h at +5°.* A solution of (XIIIb) (4 g) was kept in hydrogen fluoride (8 ml) for 20 h at +5°. The mixture was then worked up as described above yielding 2.50 g of crude material which crystallized from ether-pentane to give 894 mg (35 %) of 2,4-di-*O*-benzoyl-β-D-ribopyranosyl fluoride (VII) with m.p. 145°, identified through its NMR spectrum. The remaining product was put on a column of silica gel (200 g) and, by elution with benzene-ether (8:2), it was separated into five fractions.

The first fraction to come off the column consisted of 228 mg (7 %) of a mixture of tri-*O*-benzoyl-α- and β-D-arabinopyranosyl fluoride (XVb) and (XIVb). Crystallization from ether-pentane gave 63 mg of the α-fluoride, m.p. 155—157°. Fraction 2 gave 570 mg (22 %) of 3,4-di-*O*-benzoyl-β-D-ribopyranosyl fluoride (XI) which was pure as seen from its NMR spectrum. Crystallization from ether-pentane gave 511 mg of colourless crystals,

m.p. 113—115°. Two additional recrystallizations did not change the m.p. $[\alpha]_D^{23} = -152°$ (*c* 0.8, $CHCl_3$). (Found: C 63.57; H 4.99. Calc. for $C_{19}H_{17}O_6F$: C 63.33; H 4.76). A sample of this product, by benzoylation with benzoyl chloride in pyridine, gave an almost quantitative yield of tri-*O*-benzoyl-β-D-ribopyranosyl fluoride (IIb), m.p. 137—139°, identified through mixed m.p. and NMR.

Further elution of the column gave, after a mixed fraction (133 mg) had been collected, a third fraction (89 mg) which consisted of 2,5- and 3,5-di-*O*-benzoyl-β-D-ribofuranosyl fluoride. Fraction 4 (125 mg), by crystallization from ether-pentane, gave 50 mg of 2,4-di-*O*-benzoyl-β-D-ribopyranosyl fluoride (VII), m.p. 146—148°. An NMR spectrum of the material in the mother liquor indicated that the main part of this product was a dibenzoylated α-D-ribopyranosyl fluoride (IV). Benzoylation and crystallization from ether-pentane gave 35 mg of tri-*O*-benzoyl-α-D-ribopyranosyl fluoride (IIIb), m.p. 198—200°, identified by mixed m.p. and NMR spectroscopy.[7]

Fraction 5 (136 mg) gave crystals from ether-pentane. One recrystallization gave 30 mg of a pure di-*O*-benzoyl-α-D-ribopyranosyl fluoride (IV), m.p. 125—126°, $[\alpha]_D^{23} = +84.4°$ (*c* 0.65, $CHCl_3$). (Found: C 63.48; H 4.96. Calc. for $C_{19}H_{17}O_6F$: C 63.33; H 4.76). Benzoylation of this product gave tri-*O*-benzoyl-α-D-ribopyranosyl fluoride, m.p. 198—200°, undepressed in admixture with an authentic sample.

Reaction of tetra-O-benzoyl-β-D-ribopyranose (Ib) with hydrogen fluoride for 20 h. A solution of (Ib) (500 mg) was kept in hydrogen fluoride (1 ml) for 20 h at room temperature. The crude product (291 mg) was a complicated mixture as seen from thin layer chromatography. By preparative thin layer chromatography using ether-pentane (1:1) as eluent it was separated into three main fractions. The fast running fraction (69 mg) consisted of impure tri-*O*-benzoyl-β-D-ribofuranosyl fluoride. The next fraction (43 mg) was shown by NMR to be a mixture of 2,5- and 3,5-di-*O*-benzoyl-β-D-ribofuranosyl fluoride. The slowest running fraction (71 mg) consisted mainly of 2,4-di-*O*-benzoyl-β-D-ribopyranosyl fluoride.

Acetylation of 2,4-di-O-benzoyl-β-D-ribopyranosyl fluoride (VII). To a mixture of pyridine (2 ml) and acetic anhydride (0.5 ml) was added 400 mg of (VII) and the mixture was kept over night at room temperature. Methylene chloride was then added and the solution was washed with 3 N sulphuric acid and saturated aqueous sodium hydrogen carbonate and dried. Evaporation of the solvent left 458 mg of a crystalline residue which was recrystallized from ether-pentane to give 338 mg (76 %) of 3-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-ribopyranosyl fluoride (VIII), m.p. 139—141°, $[\alpha]_D^{23} = -57.4°$ (*c* 1.3, $CHCl_3$). (Found: C 62.82; H 4.80. Calc. for $C_{21}H_{19}O_7F$: C 62.70; H 4.76).

Acetylation of 3,4-di-O-benzoyl-β-D-ribopyranosyl fluoride (XI). By the same procedure 120 mg of (XI) was acetylated and the crude product (112 mg) recrystallized from ether-pentane to give 91 mg (68 %) of 2-*O*-acetyl-3,4-di-*O*-benzoyl-β-D-ribopyranosyl fluoride (XII), m.p. 108—109°, $[\alpha]_D^{23} = -191°$ (c0.6, $CHCl_3$). (Found: C 62.71; H 4.74).

Acetylation of 2,4-di-O-benzoyl-D-arabinopyranose (XVI). Acetylation of 1.0 g of (XVI) as described above gave 1.225 g (99 %) of a syrupy product which was crystallized from ether-pentane to give 250 mg (20 %) of 1,3-di-*O*-acetyl-2,4-di-*O*-benzoyl-α-D-arabinose (XX), m.p. 148—149°, $[\alpha]_D^{23} = -153°$ (*c* 0.6, $CHCl_3$). (Found: C 62.42; H 5.15. Calc. for $C_{23}H_{22}O_9$: C 62.44; H 5.01). An NMR spectrum of the material in the mother liquor indicated that this was almost pure β-anomer containing a small amount of the α-anomer. This product was not purified further, but was used as such for the reaction with hydrogen fluoride.

Reaction of 1,3-di-O-acetyl-2,4-di-O-benzoyl-D-arabinopyranose (XX) with hydrogen fluoride. A solution of (XX) (220 mg) in hydrogen fluoride (0.5 ml) was kept at 0° for 36 h. The crude product (164 mg) was crystallized from ether-pentane to give 53 mg (30 %) of 2,4-di-*O*-benzoyl-D-arabinose (XVI), m.p. 164—166°, identical with the product described previously.[9]

Microanalyses were performed by Dr. A. Bernhardt.

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