ACTA CHEMICA SCANDINAVICA 22 (1968) 1307–1316

Reaction of Sugar Esters with Hydrogen Fluoride

VII. Ribofuranose and Arabinofuranose Derivatives

NIELS GREGERSEN and CHRISTIAN PEDERSEN

Organisk-Kemisk Laboratorium, Polyteknisk Læreanstalt, Bygning 201, Lyngby, Denmark

Acetylated and benzoylated derivatives of D-ribofuranose, when dissolved in anhydrous hydrogen fluoride, form 1,2-acetoxonium or benzoxonium ions (IIa and b). On further reaction with hydrogen fluoride these ions rearrange to 2,3-acetoxonium or benzoxonium ions (IVa and b). Acetylated or benzoylated D-arabinofuranose derivatives also yield 1,2-acetoxonium or benzoxonium ions (XIa and b) on brief treatment with hydrogen fluoride. On more prolonged reaction with hydrogen fluoride Walden inversion takes place at C-2 with formation of the 2,3-acetoxonium and benzoxonium ions (IVa and b) derived from β-D-ribofuranosyl fluoride. When the hydrogen fluoride solution is treated with water the 1,2-benzoxonium ions yield tri-*O*-benzoyl-D-furanosyl fluorides, whereas the 2,3-benzoxonium ion gives di-*O*-benzoyl-β-D-ribofuranosyl fluorides.

Brief treatment of 1-*O*-acetyl-tri-*O*-benzoyl-β-D-ribofuranose (XV) with anhydrous hydrogen fluoride has been shown to give tri-*O*-benzoyl-β-D-ribofuranosyl fluoride (IIIb).[1,2] By the same treatment methyl tri-*O*-benzoyl-α-D-arabinofuranoside (Xb) gave tri-*O*-benzoyl-α-D-arabinofuranosyl fluoride (XII).[2] Prolonged treatment of derivatives of ribofuranose and arabinofuranose with hydrogen fluoride, which has not been studied previously, is the subject of the present paper. The reactions with hydrogen fluoride have been studied by NMR spectroscopy as previously described.[3,4]

When tetra-*O*-acetyl-β-D-ribofuranose (Ia) was dissolved in anhydrous hydrogen fluoride at room temperature and an NMR spectrum taken after 10 min the result shown in Fig. 1 or Table 1 was obtained. The 3 proton signal at 3.02 ppm indicates that a 2-methyl-1,3-dioxolenium ion has been formed.[3,5] In agreement with this a 3 proton signal corresponding to acetic acid is found at 2.52 ppm.[3] Besides two acetoxy groups are present as seen from the 3 proton signals at 2.43 and 2.47. The low field doublet at 7.38 must arise from the anomeric proton and the coupling to H_2 (4.5 cps) shows that H_1 and H_2 are *cis* [6,7] and it furthermore shows that no glycosyl fluoride is present since the large coupling between H_1 and fluorine [8,9] is not observed. On this basis

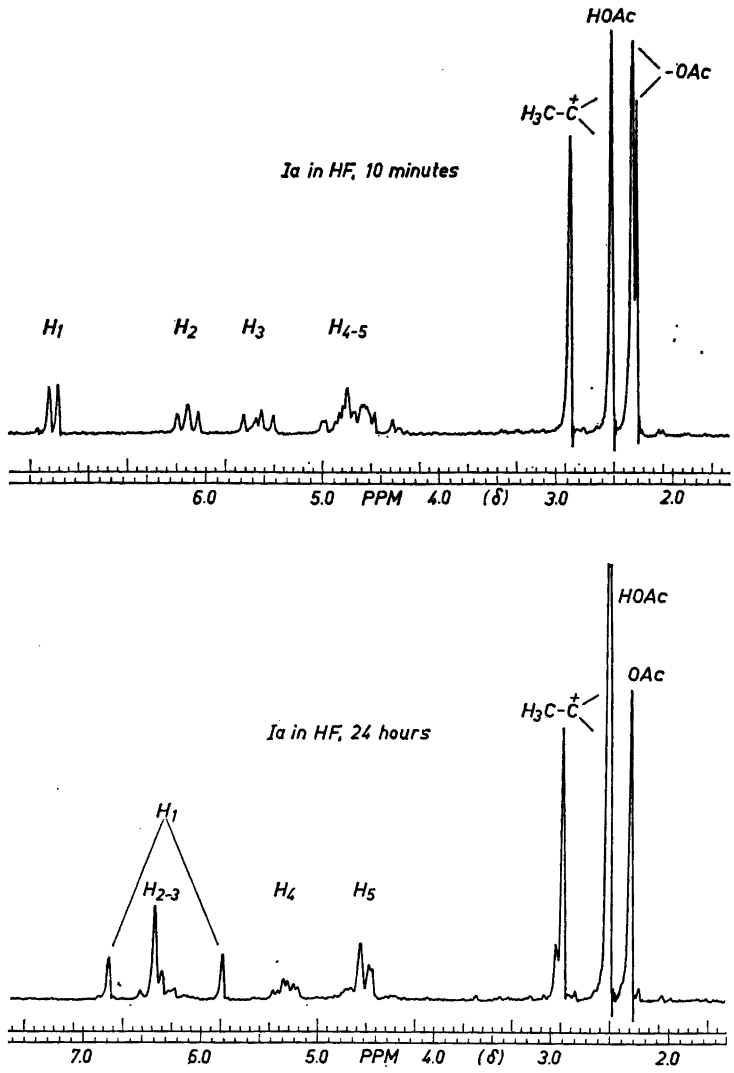


Fig. 1.

it must be assumed that tetra-*O*-acetyl-β-D-ribofuranose (Ia) forms the 1,2-acetoxonium ion (IIa), when dissolved in anhydrous hydrogen fluoride.

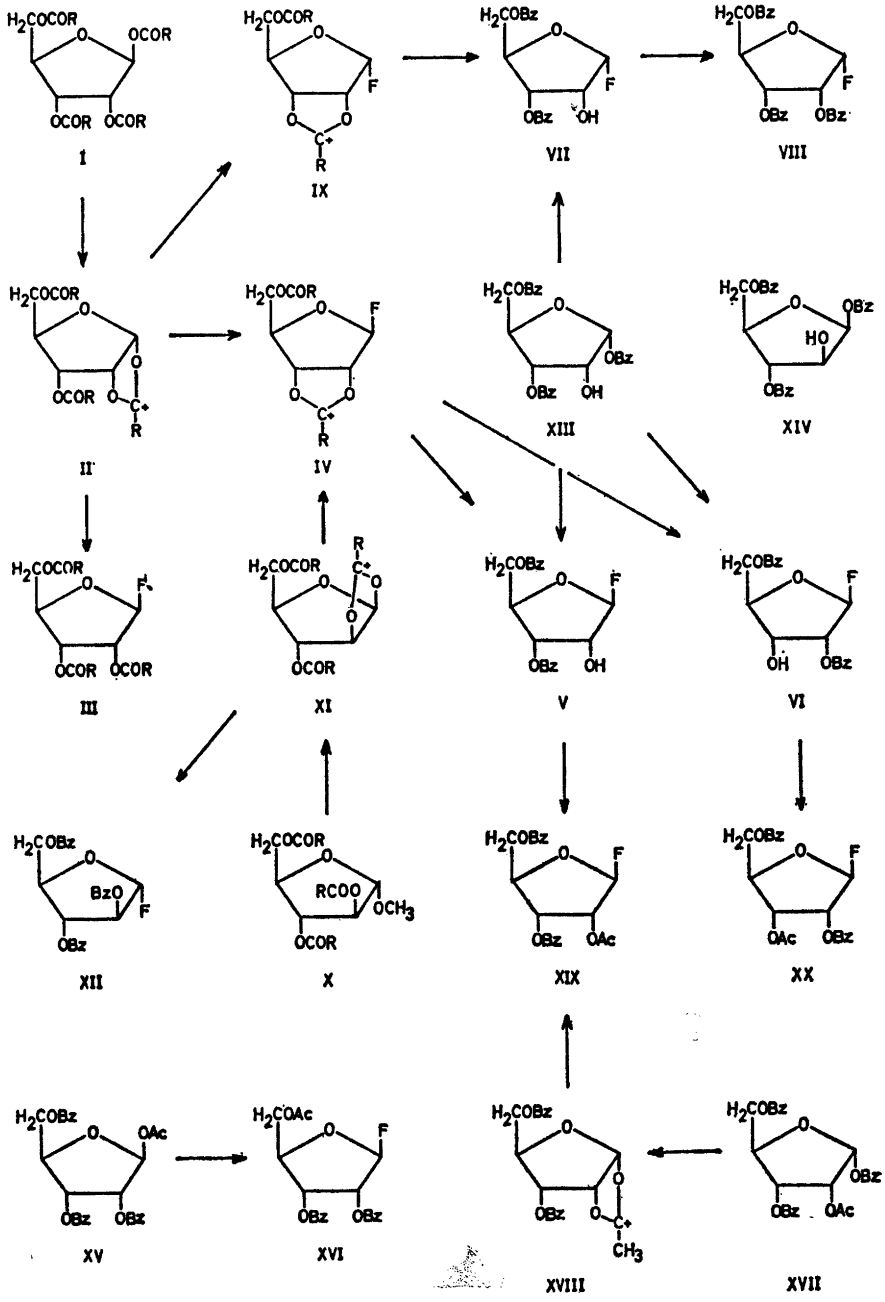
Tetra-*O*-benzoyl-β-D-ribofuranose (Ib) gave an analogous ion (IIb) when dissolved in hydrogen fluoride as seen from the NMR spectrum (Table 1). The tetrabenzoate is less suited for NMR studies because the aromatic protons give a complex group of signals which hide the signal of the anomeric proton. However, the signals from H_2, H_3, and H_{4-5} are very similar to those of the

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

Compound in HF	H_1	H_2	H_3	H_4	H_5	$H_3C-\overset{+}{C}<$	HOAc	—OAc
Ia, 10 min	7.38(d) $J_{12} = 4.5$	6.26(t) $J_{23} = 4-5$	5.6(q)	4.4—5.0(m)		3.02(s)	2.52(s)	2.43(s) 2.47(s)
Ia, 24 h	6.35(d) $J_{H_1F} = 58$ $J_{12} = 0$	6.2—6.6(m)		5.1—5.4(m)	4.6—4.8(m)	2.96(s)	2.52(s)	2.36(s)
Ib, 10 min	$J_{12} = 4.2$	6.60(q) $J_{23} = 5.9$	6.08(q) $J_{34} = 8.5$	4.6—5.3(m)				
Ib, 100 h	6.57(d) $J_{H_1F} = 57$ $J_{12} = 0$	6.3—6.9(m)		5.5—5.8(m)	4.8—5.1(m)			
Xa, 10 min	7.12(d) $J_{12} = 5.1$	6.04(q) $J_{23} = 1.0$	5.51(q) $J_{34} = 3.5$	4.4—5.1(m)		2.90(s)		2.32(s)
Xa, 24 h	identical with Ia, 24 hours							
Xb, 10 min	$J_{12} = 5$	6.66(q) $J_{23} = 1$	6.38(q) $J_{34} = 2.5$	4.9—5.5(m)				
Xb, 24 h	identical with Ib, 100 h							

(s) singlet; (d) doublet; (t) triplet; (m) multiplet.

a: R= CH_3 b: R= C_6H_5



acetate. When a solution of the tetrabenzoate (Ib) in hydrogen fluoride was worked up after it had been kept at room temperature for 10 min it gave a 70 % yield of tri-*O*-benzoyl-β-D-ribofuranosyl fluoride (IIIb). This fluoride must be formed from the ion (IIb) during the isolation procedure since no fluoride is present in the hydrogen fluoride solution. The tetraacetate (Ia) similarly gave tri-*O*-acetyl-β-D-ribofuranosyl fluoride (IIIa) as seen from the NMR spectrum of the crude product. Since (IIIa) was rather unstable it was not isolated in a pure state.

When a solution of the tetraacetate (Ia) in hydrogen fluoride was kept at room temperature NMR spectra, run at intervals, showed that the initially formed ion (IIa) disappeared while a new product was formed. After 24 h the NMR spectrum showed that the only products present in the solution were the 2,3-acetoxonium ion (IVa) and 2 equivalents of acetic acid. When the solution was kept for a week no further changes took place in the spectrum. That (IVa) is a fluoride is seen from the spectrum (Fig. 1 and Table 1) which shows H_1 as a doublet with the typical hydrogen-fluorine coupling of 58 cps;[8] since H_1 does not couple with H_2 it is a β-fluoride. The spectrum also shows that two equivalents of acetic acid have been liberated and that one acetoxonium ion and one *O*-acetyl group is present.

The tetrabenzoate (Ib), when kept in hydrogen fluoride at room temperature, underwent changes for *ca.* 100 h. After that time it gave a spectrum which indicated that the only product present was the benzoxonium ion (IVb), the NMR spectrum being quite similar to that of the corresponding acetate (IVa) (Table 1). Reaction of the ion (IVb) with water would be expected to give a mixture of the two di-*O*-benzoyl-β-D-ribofuranosyl fluorides (V) and (VI) and indeed this was found to be the case. When the tetrabenzoate (Ib) was kept in hydrogen fluoride for 150 h isolation by washing with water gave a 42 % yield of a mixture of 3,5- and 2,5-di-*O*-benzoyl-β-D-ribofuranosyl fluoride (V and VI). This mixture may be separated into the pure components. Besides, a 15 % yield of 3,5-di-*O*-benzoyl-α-D-ribofuranosyl fluoride (VII) was obtained. This product probably arises from the ion (IX) although this ion could not be detected in the NMR spectrum of the hydrogen fluoride solution. A low yield (8 %) of tri-*O*-benzoyl-β-D-ribofuranosyl fluoride (IIIb) was also obtained.

A solution of 1,3,5-tri-*O*-benzoyl-α-D-ribofuranose (XIII) in anhydrous hydrogen fluoride gave a very complicated NMR spectrum immediately after the solution was made. The spectrum changed rapidly and after a few hours at room temperature it became identical with the spectrum which the tetrabenzoate (Ib) gave after several days. Thus the tribenzoate (XIII) gives the benzoxonium ion (IV) much more rapidly than the tetrabenzoate (Ib), when treated with hydrogen fluoride. This was confirmed by working up a solution of (XIII) which had been kept in hydrogen fluoride for 20 h. The same products were obtained as those isolated from (Ib) which had been kept for 150 h in hydrogen fluoride. When (XIII) was kept in hydrogen fluoride for 15 min at −10° and then worked up, a mixture of di-*O*-benzoyl fluorides was obtained. Chromatography gave a 44 % yield of crude 3,5-di-*O*-benzoyl-α-D-ribofuranosyl fluoride (VII) and smaller amounts of (V) and (VI). Benzoylation of the α-fluoride (VII) gave tri-*O*-benzoyl-α-D-ribofuranosyl

fluoride (VIII). The tribenzoate (XIII) would not be expected to give the 1,2-benzoxonium ion (IIb), on reaction with hydrogen fluoride, and the experiment above indicates that the first products formed are a mixture of the fluorides (V, VI, and VII) with the α-fluoride (VII) predominating. On further reaction with hydrogen fluoride these fluorides are then converted into the 2,3-benzoxonium ions (IVb) and (IXb) with the β-anomer (IVb) predominating.

The behaviour of methyl α-D-arabinofuranoside triacetate (Xa) and the corresponding tribenzoate (Xb) towards hydrogen fluoride was also studied. NMR spectra taken immediately after the two compounds were dissolved in hydrogen fluoride showed that the dioxolenium ions (XIa and b) were formed. The NMR spectrum of the acetate (Table 1) shows H_1 as a doublet split by 5 cps due to coupling with H_2. This indicates that H_1 and H_2 are *cis* [6,7] and that a fluoride is not formed since no fluorine-hydrogen coupling is observed. On further standing in hydrogen fluoride solution the two compounds (Xa and b) underwent changes and after 24 h they gave NMR spectra which showed that the ions (IVa) and (IVb), respectively, had been formed. The spectra were completely identical with those obtained from the ribose derivatives (Ia) and (Ib). Brief treatment of (Xb) with hydrogen fluoride gave tri-*O*-benzoyl-α-D-arabinofuranosyl fluoride (XII), in agreement with earlier results.[2] The α-configuration was confirmed by NMR spectroscopy which shows that H_1 is not coupled to H_2 and that they are therefore in a *trans* position (Table 2). Reaction of (Xb) with hydrogen fluoride for 24 h gave the same products as those obtained from tetra-*O*-benzoyl-β-D-ribofuranose (Ib).

1,3,5-Tri-*O*-benzoyl-β-D-arabinofuranose [10] (XIV), when dissolved in hydrogen fluoride, gave a complicated NMR spectrum at first; but on standing for 24 h it was transformed into the ion (IVb).

When tri-*O*-benzoyl-β-D-ribofuranosyl fluoride (IIIb) was dissolved in hydrogen fluoride it immediately gave the 1,2-benzoxonium ion (IIb) and, on further standing, the ion (IVb) was formed. Thus the fluoride (IIIb) cannot exist in hydrogen fluoride solution. Analogously, the arabinosyl fluoride (XII) gave the 1,2-benzoxonium ion (XIb) when dissolved in hydrogen fluoride.

Brief treatment of 1-*O*-acetyl-tri-*O*-benzoyl-β-D-ribofuranose (XV) with hydrogen fluoride gives the β-fluoride (IIIb).[1,2] When (XV) was dissolved in hydrogen fluoride and an NMR spectrum taken at once it was found that the ion (IIb) was formed together with one equivalent of acetic acid. An NMR spectrum taken after this solution had been kept at room temperature for 1 h showed that the signal of acetic acid at 2.58 ppm had decreased and a new signal at 2.40 ppm had appeared, corresponding to the conversion of *ca.* 25 % of the acetic acid into an acetoxy group. This ratio did not change appreciably when the solution was kept for several days until the ion (IV) was formed. Thus, exchange of a benzoyl group with acetic acid must take place in hydrogen fluoride solution and since the formation of the 2,3-benzoxonium ion (IV) takes place without disappearance of the acetoxy signal the exchange must take place at C-5. Treatment of (XV) with hydrogen fluoride for 1 h gave a 51 % yield of (IIIb) and 18 % of a mono-*O*-acetyl-di-*O*-benzoyl-β-D-ribofuranosyl fluoride, presumably the 5-*O*-acetyl derivative (XVI). The NMR spectrum of (XVI) is of course quite similar to that of (IIIb); however,

the pattern of the signal of the two protons at C-5 is different from that of (IIIb), confirming that the acetoxy group is at C-5.

A solution of 2-*O*-acetyl-tri-*O*-benzoyl-α-D-ribofuranose[11] (XVII) in hydrogen fluoride gave an NMR spectrum which showed that the ion (XVIII) had been formed. The spectrum of (XVIII) was very similar to that of (IIb) except that the signal of an acetoxonium ion was present at 3.0 ppm. On standing in hydrogen fluoride the ion (IVb) was formed together with acetic acid, seen as a sharp signal at 2.54 ppm. At this stage, however, an acetoxy signal was also present at 2.37 ppm, corresponding to *ca.* 25 % of the total amount of acetate. Thus, as described above, a benzoyl group must exchange with an acetyl group and this can only involve the benzoyl group at C-5. Brief treatment of (XVII) with hydrogen fluoride gave a high yield of 2-*O*-acetyl-di-*O*-benzoyl-β-D-ribofuranosyl fluoride (XIX), formed from the ion (XVIII) when the hydrogen fluoride solution is washed with water.

The structures of the two di-*O*-benzoyl-β-D-ribofuranosyl fluorides (V) and (VI) were determined by acetylation. Thus, the 3,5-isomer (V) afforded (XIX), identical with the product described above. Acetylation of the 2,5-isomer (VI) gave the 3-*O*-acetate (XX), the structure of which appears from

Table 2. Chemical shifts (δ-values) and coupling constants (cps) of furanosyl fluorides in deuteriochloroform at 60 MHz.

Compound	H_1	H_2	H_3	H_4	H_5	OH or OAc
IIIb	5.98(d) $J_{H_1F} = 61.2$	5.8—6.0(m) $J_{12} = 0$		4.5—5.0(m)		
VIII	6.07(q) $J_{H_1F} = 63$	5.42(m) $J_{H_2F} = 20.5$	5.80(q) $J_{12} = 3.1$	4.5—5.0(m) $J_{23} = 6.4$ $J_{34} = 2.0$		
V	5.70(d) $J_{H_1F} = 61$	*ca.* 4.8 $J_{12} = 0$	5.3—5.6	4.3—4.8(m)		OH 2.6
VI	5.87(d) $J_{H_1F} = 61.7$	5.56(t) $J_{12} = 0$	*ca.* 4.8	4.3—4.9(m)		OH 3.1
VII	5.8(q) $J_{H_1F} = 64$	*ca.* 4.7 $J_{12} = 3.2$	5.4(q) $J_{23} = 6.5$	4.1—4.8(m) $J_{34} = 1.6$		OH 2.9
XVI	5.95(d) $J_{H_1F} = 61.3$	5.6—5.9(m) $J_{12} = 0$		4.0—4.8(m)		OAc 2.08(s)
XIX	5.83(d) $J_{H_1F} = 60.5$	5.5—5.9(m) $J_{12} = 0$		4.5—4.9(m)		OAc 2.10(s)
XX	5.89(d) $J_{H_1F} = 61$	5.5—5.9(m) $J_{12} = 0$		4.4—4.9(m)		OAc 1.97(s)
XII	5.95(d) $J_{H_1F} = 57.5$	5.5—5.7(m) $J_{12} = 0$		4.5—4.9(m)		

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

the fact that it is different from both the 5-*O*-acetate (XVI) and the 2-*O*-acetate (XIX). The NMR spectra of (XVI), (XIX), and (XX) are of course closely related (Table 2); they are, on the other hand sufficiently different to permit distinction between the three compounds. (V), m.p. 131—133°, is identical with the product described previously,[1] but at that time assumed to possess the α-configuration. That (V) is the β-anomer is seen from its NMR spectrum (Table 2) which shows that $J_{12} \simeq 0$, in agreement with the *trans* orientation of H_1 and H_2. The same coupling constant is found for all the fluorides to which the β-configuration is assigned (Table 2). Tetra-*O*-benzoyl-β-D-ribofuranose (Ib), the corresponding tetraacetate (Ia), and the 1-*O*-acetyl derivative (XV) also show $J_{12} \simeq 0$.

Although 3,5-di-*O*-benzoyl-α-D-ribofuranosyl fluoride (VII) was not obtained in a pure state it gave a well-resolved NMR spectrum (Table 2). That this product is the 3,5-dibenzoate and not the 2,5-isomer is seen from the quartet at 5.8δ. This low field quartet must represent a proton at a carbon atom which carries an *O*-benzoyl group and the coupling constants of 6.5 cps (J_{23}) and 1.6 cps (J_{34}) show that this proton is not adjacent to H_1 ($J_{12} = 3.2$ cps). The quartet must therefore represent H_3, and the product is the 3,5-di-*O*-benzoate. The anomeric structure of (VII) and of tri-*O*-benzoyl-α-D-ribofuranosyl fluoride (VIII) appears from the coupling between H_1 and H_2 which is similar to that found in other α-D-ribofuranose derivatives such as 1,3,5-tri-*O*-benzoyl-α-D-ribofuranose (XIII).[7] Thus, on the basis of NMR spectra, the anomeric structure of the two tribenzoates (IIIb) and (VIII) is well established. On the other hand, the relationship between the rotations of the two anomers is not in agreement with Hudson's rule [2] since the β-anomer is more dextrorotary than the α-anomer.

EXPERIMENTAL

Melting points are uncorrected. For details of thin layer chromatography and NMR spectra see Ref. 4.

*Reaction of tetra-*O*-benzoyl-β-*D*-ribofuranose (Ib) with hydrogen fluoride. (a) For 10 min.* A solution of (Ib) (500 mg) was kept in anhydrous hydrogen fluoride (1 ml) 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. The crude syrup (382 mg) was crystallized from ether-pentane giving 284 mg (69 %) of tri-*O*-benzoyl-β-D-ribofuranosyl fluoride (IIIb), m.p. 79—81°. Recrystallization from ether-pentane gave the pure product as colourless crystals, m.p. 81—83°, $[\alpha]_D^{22} = +120.3°$ (*c* 4, $CHCl_3$), identical with the product described previously.[1]

(b) For 150 h. In an analogous experiment (Ib) (500 mg) was kept in hydrogen fluoride (1 ml) for 150 h during which time the solution became dark coloured. The crude product (312 mg) was separated into three fractions by preparative thin layer chromatography eluting 3 times with ether-pentane (1:1). The fast running fraction gave 39 mg (8.6 %) of tri-*O*-benzoyl-β-D-ribofuranosyl fluoride (IIIb), identified by its NMR spectrum. The next fraction consisted of 133 mg (42 %) of a mixture of 2,5- and 3,5-di-*O*-benzoyl-β-D-ribofuranosyl fluorides (V) and (VI) (see below). The slowest running fraction gave 47 mg (15 %) of di-*O*-benzoyl-α-D-ribofuranosyl fluoride (VII). This product was not quite pure, but an NMR spectrum showed that it was identical with the material described below.

*Reaction of 1,3,5-tri-*O*-benzoyl-α-*D*-ribofuranose (XIII) with hydrogen fluoride. a) 15 min at −10°.* The tribenzoate (XIII) (500 mg) was dissolved in 1 ml of hydrogen fluoride which was cooled to −10° and the solution was kept at that temperature for 15 min.

Work up as described above gave 385 mg of a colourless syrup. Preparative thin layer chromatography with ether-pentane (1:1) as eluent separated this product into two main fractions. The fastest running fraction gave 65 mg (17 %) of a mixture of 2,5- and 3,5-di-*O*-benzoyl-β-D-ribofuranosyl fluorides (V) and (VI). The slower moving fraction gave 171 mg (44 %) of crude 3,5-di-*O*-benzoyl-α-D-ribofuranosyl fluoride (VII). This product contained an impurity, as seen from its NMR spectrum, and it could not be purified further by chromatography. It was benzoylated with benzoyl chloride in pyridine and the resulting tribenzoate (210 mg) was purified by preparative thin layer chromatography using ether-pentane (1:2) as eluent. The pure tri-*O*-benzoyl-α-D-ribofuranosyl fluoride (174 mg, 35 %) was obtained as a colourless syrup, $[\alpha]_D^{22} = +44.8°$ (*c* 1.1, $CHCl_3$). (Found: C 67.15; H 4.94. Calc. for $C_{26}H_{21}FO_7$: C 67.24; H 4.76).

b) 20 h at room temperature. A solution of (XIII) (500 mg) in hydrogen fluoride was kept at room temperature for 20 h. The crude product (353 mg) was separated into 3 fractions by preparative thin layer chromatography using ether-pentane (1:1) as eluent. The first fraction consisted of 26 mg (5 %) of tri-*O*-benzoyl-β-D-ribofuranosyl fluoride (IIIb). The second fraction gave 178 mg (45 %) of a mixture of the dibenzoates (V) and (VI). The third fraction gave 59 mg (15 %) of 3,5-di-*O*-benzoyl-α-D-ribofuranosyl fluoride (VII).

*Reaction of methyl tri-*O*-benzoyl-α-D-arabinofuranoside (Xb) with hydrogen fluoride.* The methyl glycoside (Xb) (500 mg) was dissolved in hydrogen fluoride (1 ml) and kept for 24 h at room temperature. The crude product (392 mg) was fractionated as described above yielding 44 mg (12 %) of (VII) and 150 mg (40 %) of a mixture of (V) and (VI). Besides, 73 mg (50 %) of methyl benzoate was isolated as the fastest moving fraction and identified through infrared and NMR spectra.

*Reaction of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (XV) with hydrogen fluoride for 1 h.* A solution of (500 mg) in hydrogen fluoride (1 ml) was kept for 1 h at room temperature. Work up as described above gave 420 mg of product which was separated into two fractions by preparative thin layer chromatography using ether-pentane (1:2) as eluent. The fast running fraction gave 236 mg (51 %) of material which was shown by NMR to be pure tri-*O*-benzoyl-β-D-ribofuranosyl fluoride. Crystallization from ether-pentane gave 180 mg, m.p. 80—82°. The slow running fraction gave 67 mg (18 %) of 5-*O*-acetyl-2,3-di-*O*-benzoyl-β-D-ribofuranosyl fluoride (XVI) as a colourless syrup which was pure as seen from its NMR spectrum. For analysis it was further purified by preparative thin layer chromatography with benzene as eluent. $[\alpha]_D^{22} = +93.6°$ (*c* 0.5, $CHCl_3$). Found: C 62.89; H 4.90. Calc. for $C_{21}H_{19}FO_7$: C 62.69; H 4.76).

*Reaction of 2-*O*-acetyl-1,3,5-tri-*O*-benzoyl-α-D-ribofuranose (XVII) with hydrogen fluoride.* A solution of (XVII) [11] (300 mg) in hydrogen fluoride (1 ml) was kept for 10 min at room temperature. The product (222 mg (93 %)) was essentially pure as seen from its NMR spectrum. For analysis it was further purified by preparative thin layer chromatography using ether-pentane (1:1) as eluent. The pure 2-*O*-acetyl-di-*O*-benzoyl-β-D-ribofuranosyl fluoride (XIX) was a colourless syrup, $[\alpha]_D^{22} = +50.1°$ (*c* 1.4, $CHCl_3$). (Found: C 62.53; H 4.74).

*2,5- and 3,5-Di-*O*-benzoyl-β-D-ribofuranosyl fluoride.* A mixture of the dibenzoates (V) and (VI) (178 mg), obtained as described above, was dissolved in ether (3 ml) and an equal volume of pentane was added. On standing over night prismatic crystals came out, yield 40 mg. This product was recrystallized twice from methylene chloride-pentane to give pure 2,5-di-*O*-benzoyl-β-D-ribofuranosyl fluoride (VI), m.p. 131—133°, $[\alpha]_D^{22} = +50.5°$ (*c* 0.2, $CHCl_3$), identical with the product described previously.[1]

The ether-pentane mother liquor was diluted with *ca.* 10 ml of pentane and kept over night during which time a second compound crystallized as small needles, yield 40 mg. This compound was recrystallized twice from ether-pentane to give pure 3,5-di-*O*-benzoyl-β-D-ribofuranosyl fluoride (V) with m.p. 102—105°, $[\alpha]_D^{22} = +98°$ (*c* 0.4, $CHCl_3$). (Found: C 63.48; H 4.86. Calc. for $C_{19}H_{17}FO_6$: C 63.33; H 4.76).

The mother liquor from these two products was shown by NMR spectroscopy to consist of a mixture of the two compounds. This was confirmed by benzoylation which gave tri-*O*-benzoyl-β-D-ribofuranosyl fluoride as the only detectable product.

*Acetylation of 3,5-di-*O*-benzoyl-β-D-ribofuranosyl fluoride (V).* To a mixture of pyridine (1 ml) and acetic anhydride (0.3 ml) was added 50 mg of (V) and the mixture was kept over night. Methylene chloride was then added and the solution was washed with 3 N sulphuric acid and saturated aqueous sodium hydrogen carbonate and dried. Evapora-

tion of the solvent left 47 mg (84 %) of 2-*O*-acetyl-3,5-di-*O*-benzoyl-β-D-ribofuranosyl fluoride (XIX) as a colourless syrup, $[\alpha]_D^{22} = +52.7°$ (*c* 0.9, $CHCl_3$). The NMR spectrum was identical with that of the product described above.

*Acetylation of 2,5-di-*O*-benzoyl-β-D-ribofuranosyl fluoride (VI).* Acetylation of (VI) (53 mg), as described above, gave 46 mg (78 %) of 3-*O*-acetyl-2,5-di-*O*-benzoyl-β-D-ribofuranosyl fluoride (XX). An NMR spectrum showed that the product was practically pure. For analysis it was further purified by preparative thin layer chromatography using benzene as eluent. $[\alpha]_D^{22} = +103°$ (*c* 0.4, $CHCl_3$). (Found: C 62.82; H 4.86. Calc. for $C_{21}H_{19}FO_7$: C 62.69; H 4.76).

The authors are indebted to civilingeniør S. Refn for the infrared spectra. Microanalyses were performed by Dr. A. Bernhardt.

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Received December 1, 1967.